OPTICAL STUDIES OF OFF-CENTRE IONS
IN STRONTIUM OXIDE

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A thesis submitted for the degree of
DOCTOR OF PHILOSOPHY
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by
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S T A T E M E N T

The studies detailed in this dissertation were carried out during my stay as a full-time Research Scholar in the Department of Solid State Physics, Research School of Physical Sciences, at the Australian National University, Canberra.

The research described in this volume is my own except where otherwise stated.

This thesis has never in any form been submitted to another institution for the award of a higher degree.

Ian H. Brunskill

Canberra, July 1979
ACKNOWLEDGEMENTS

This investigation has been carried out under the supervision of Dr N.B. Manson with whom it has been a privilege to work.

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Last, but not least, I thank the Australian National University for the award of a PhD Scholarship enabling me to study in Canberra.
Experimental and theoretical investigations of strontium oxide doped with nickel and strontium oxide doped with cobalt are described in this thesis.

The principal experimental technique is that of recording the absorption spectrum. This is completed over a wide range of wavelengths (0.4μ to 2.0μ) and of temperature (2 K to 300 K). The effect of magnetic fields of up to 5 T are investigated and for sharp lines the Zeeman, or for broad bands the MCD, spectra are recorded. Large electric fields of up to 50 kV/cm are also used and Stark and pseudo-Stark effects recorded.

The absorption bands of SrO: Ni\(^{2+}\) and SrO: Co\(^{2+}\) show very large oscillator strengths and this suggests that the impurity does not sit at a site of inversion symmetry. The Zeeman measurements confirm that the transitions are electric dipole allowed and a group theoretical analysis of the polarization proves that the local site symmetry is C\(^{3v}\). It is proposed that this arises from a static off-centre ion displacement; calculations suggest the impurity is more stable when displaced along the trigonal axis and support a model where the transition-metal ion sits at a non-centrosymmetric site along a \(< 111 >\)-type direction.

Electric field experiments provide support for this model and dipole re-alignment is observed.

Other sites, particularly those of C\(^{2v}\) or C\(^{s}\) symmetry in the case of SrO: Ni\(^{2+}\), appear after heat-treatment in air and possible explanations incorporating associated lattice defects are proposed.
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CHAPTER 1

INTRODUCTION
CHAPTER 1

INTRODUCTION

The physics and chemistry of the solid state very often involves impurities or defects in crystals and a large class of phenomena and devices depends on their presence. The control and understanding of defect properties is, therefore, very important.

The alkaline earth oxides MgO, CaO, SrO and BaO are the divalent relatives of the alkali-halides. They are isostructural with rocksalt and their binding is mainly ionic. Their simplicity in structure makes them particularly attractive for both the experimentalist and theoretician to study. They have lagged behind the alkali-halides in fundamental research because they present awkward materials' problems. Their high melting points, MgO (2800°C), CaO (2580°C), SrO (2430°C), BaO (1923°C) [1], make it impractical to try the commonly used techniques of crystal growth (Kyropoulos, Stockbarger methods) and purification (zone-refining). The melting points of the commonly used crucibles, platinum (1772°C) and iridium (2410°C) are in general lower than these melting temperatures.

As often happens, one of the alkaline earth oxides has received more attention than the others. In this case, MgO has been favoured followed by CaO, SrO and BaO [2]. Good quality MgO single crystals have been available for some time but the other three present problems as they are hygroscopic in varying degrees.

The alkaline earth oxides being formed from divalent impurities will readily accommodate divalent ions of similar size. Divalent
with incompletely filled d-electron shells (see Table 1.1) can be incorporated into the lattice and can then be studied by a range of spectroscopic techniques not available in the case of closed shell systems. The transition-metal ion acts as a probe and its electronic structure mirrors the symmetry of the local crystal field including nearby crystal defects such as vacancies and interstitials. The structure of the paramagnetic ion can be investigated by spectroscopic methods including the application of magnetic [5] and electric field perturbations [6]. Such external fields lower the site symmetry of the impurity and sometimes split degenerate energy levels. The splitting patterns and their polarizations allow one to determine the transformation properties of the related ground- and excited-state wavefunctions. A parameterization of the observed energy levels can be made using the well-established crystal field model which has been fairly successful for transition-metal and rare-earth ions in solids. Where there is poor resolution of the Zeeman or Stark split components, then a modulation approach [7] is the more practical. In Zeeman studies the polarization is modulated and measurements are made of magnetic circular or linear dichroism (MCD, MLD). Electric fields have proved a little more versatile in that, in addition to modulating the radiation, they can be modulated in the range of -100 Hz, and this technique has been given some emphasis in this thesis.

Using optical techniques, primarily visible absorption measurements, the only divalent systems previously studied are:
Table 1.1. Atomic and ionic configurations of the transition-metal ions and alkali-earths. Ionic radii are shown on the right.

(The spectroscopy of 3d complexes is described in a review article by J. Ferguson [4]).
BaO crystals with impurities are not available in good optical quality and have not been studied. Several of the other SrO and CaO systems, the blanks in the above chart, have been investigated in this Department but only SrO:Ni$^{2+}$ and SrO:Co$^{2+}$ showed well-established prominent absorption bands; in the latter case the absorption was different and more structured than that previously reported [15]. These particular systems were of especial interest as they are the end members of a series for which fairly complete information was available on the first two and in the case of one of these, nickel, an "interesting effect" had been established for the central member CaO:Ni$^{2+}$. In CaO:Ni$^{2+}$ there is a strong electron-vibration interaction and if this were larger it could have the effect of displacing the ion away from the substitutional site ("off-centre ion"). This can also be effected by electrostatic forces where a small ion replaces a larger one, as is the case for KCl:Li$^+$ [16,17]. SrO:Ni$^{2+}$ and SrO:Co$^{2+}$ were, therefore, considered ideal systems with which to investigate the possibility of such effects.

A large number of these divalent impurity systems have been studied by EPR [18]. In MgO and CaO the impurity predominantly substitutes directly for the metal ion and occupies an octahedral site. In comparison little attention has been focussed on doped-SrO and even less on

| d$^2$ | ................. |
| d$^3$ | MgO:V$^{2+}$ [8] |
| d$^4$ | ................. |
| d$^5$ | MgO:Mn$^{2+}$ [9] |
| d$^6$ | MgO:Fe$^{2+}$ [10] |
| d$^7$ | MgO:Co$^{2+}$ [11], CaO:Co$^{2+}$ [13], SrO:Co$^{2+}$ [15] |
| d$^8$ | MgO:Ni$^{2+}$ [12], CaO:Ni$^{2+}$ [14], |
doped-BaO - the mis-match in ionic radii between the impurities and strontium and barium presents difficulties for crystal growth.

EPR work on BaO:Mn$^{2+}$ has been reported by Weightman et al. [19] and Sochava et al. [20]; they found a trigonal impurity site and suggested the presence of an off-centre system. More recently SrO:Cu$^{2+}$ was the subject of a study by Russian workers [21] who succeeded in re-aligning the dipoles arising from off-centre ions.

The aim of the present study is:

(1) to establish the site symmetry of the impurities cobalt and nickel in strontium oxide,

(2) to describe the energy levels observed and to compare them with the predictions of crystal field theory,

(3) to establish a model for the impurity site with special emphasis on an off-centre ion model, and

(4) to provide evidence of a dipole system.

In addition, optical absorption measurements have been used to monitor the effect of heat-treatments in both oxidising and reducing atmospheres and it is intended that the nature of these be established.

In parallel with this work, Edgar and Haider have studied the EPR of the SrO:Co$^{2+}$ and SrO:Ni$^{2+}$ systems and reference to their work will be made where appropriate.
References


CHAPTER TWO

EXPERIMENTAL TECHNIQUES

2.1 Crystals
2.2 Equipment
2.3 Sample environment
2.1 Crystals

Strontium oxide is the divalent equivalent of and has the same space group ($O_h^5$) as the alkali-halides. The metal and oxygen ions sit at sites of $O_h$ symmetry. Below are some simple physical properties of this alkaline-earth oxide:

- Melting point: $2420^\circ C$ [1]
- Boiling point: ~$3000^\circ C$ [2]
- Refractive index: 1.810 [2]
- Density: 4.7 gm/cc [2]
- Lattice constant: 5.160 $\AA$ [3]

In addition, strontium oxide is hygroscopic.

The transition-metal ion-doped SrO was grown to our specification by W. & C. Spicer Ltd. A mixture of fine powders of SrO and transition-metal oxides were melted using the alternating current carbon arc method, the arc being run for about two hours using approximately 14 kw of power. For both nickel- and cobalt-doped SrO crystalline masses were obtained from which small single crystal pieces up to 5 mm$^3$ were cleaved for optical work.

By quickly scanning the optical absorption, it was observed that the dopant level varied for crystals taken from the same growth. A more accurate analysis by atomic absorption showed this to be the case, with levels varying from 90 ppm to 1200 ppm.

The untreated Ni- and Co-doped crystals were dark brown to opaque and were sometimes not transparent enough for optical work but
after a few hours heat-treatment in a vacuum at \(-1350^\circ\text{C}\) they cleared
due, it is assumed, to the removal of a colour centre. The nickel
samples became pink, whereas the cobalt became light blue. Crystals
were then cleaved down (100) faces or cut along symmetry axes with a
Capco Q35 (Caplin Engineering Co.) precision cutting machine; they
were polished on 45\(\mu\) and 15\(\mu\) diamond mats using oil and diamond grains
as abrasives.

Samples required for polarization experiments were tested
for anomalous birefringence under a polariscope. If strained (e.g.
from cutting) the crystals were further annealed in vacuum for a few
hours. This resulted in optically isotropic samples. Heat-treatments
in air, nitrogen, and oxygen were carried out in a Gallenkamp muffler
furnace \((0 - 1350^\circ\text{C})\) and in an EMI radio frequency furnace \((0 - 1800^\circ\text{C})\).

2.2 Equipment

Some measurements were carried out on a Cary 17 spectrophotometer,
a double beam instrument capable of measuring absorption in the
wavelength region between 186 nm \((53,763 \text{ cm}^{-1})\) and 2,650 nm \((3,774 \text{ cm}^{-1})\).
The instrument, however, only gave satisfactory signal-to-noise when
operated at low resolution and was unsatisfactory for resolving the
structure in the SrO:Ni\(^{2+}\) and SrO:Co\(^{2+}\) spectra. The vast majority of
the data was, therefore, taken on an assembled instrument which did
not have these shortcomings. The system was flexible and many of the
components could be interchanged to look at different spectral regions
and to use different measuring techniques. The components of the single
beam system are described on the next page.
Two types of experiment using this system are portrayed in Figure 2.1 - electric field modulation and magnetic circular dichroism. With very minor adjustments direct Zeeman, DC field Stark, and electric field dichroism studies can be attempted. The essential components of the unit are: a light source, glass or quartz lenses, polarizing optics, a detector, and a monochromator.

White light from a tungsten lamp is focussed onto the entrance slits of the monochromator which dispersed the light into its component wavelengths. The resulting monochromatic radiation is then focussed onto the crystal sample and the attenuated beam is focussed onto the detector. The signal is fed either to a Keithley micro-voltmeter (direct absorption) or to a PAR 129A lock-in amplifier (differential absorption) and the amplified transmission signal is plotted on a chart-recorder - Hewlett-Packard, Honeywell, National (2-pen) and Rika Denki (2-pen) recorders were all available. The tungsten lamp was powered by a Hewlett-Packard 6267B stabilised DC power supply. The drift of the light intensity was ~0.5%, thus absorption as low as ~2% could be readily monitored.

The configuration in Figure 2.1 can be reversed with white light incident upon the sample and the detector bolted onto the monochromator exit slit. In this case a light-tight box is not necessary. Heat-filters were available to prevent sample warming by the incident radiation. Figure 2.2 shows an example of this configuration.

Two monochromators were used to record the data in this thesis, a Jarrell-Ash and a Spex. The Jarrell-Ash instrument is a 1.0 m Czerny-Turner scanning spectrometer with f/8.7 optics. For the spectral region 22,500 cm$^{-1}$ (444 nm) to 11,000 cm$^{-1}$ (909 nm) a grating with
Figure 2.1. Schematic diagram of the high-resolution single beam unit.
1180 lines/mm and blazed at 750 nm was used. The effective resolution was $<1 \text{ cm}^{-1}$. Infra-red ($1\mu - 3\mu$) measurements were possible using a grating with 300 lines/mm and blazed at $2.4\mu$ (germanium and silicon filters were available for infra-red work). The effective resolution in the infra-red was $\sim 2 \text{ cm}^{-1}$. The grating is driven with a precision sine bar drive which gives a spectral sweep linear in energy. In addition, a 0.75 m Czerny-Turner Spex model 1700 monochromator with f/6.8 optics was used. The grating had 600 lines/mm and was blazed at 1.3 $\mu$m; the sweep was linear in wavelength.

For measurements in the visible EMI photomultiplier tubes 9558B and 9659B were used. The cathode is of the S-20 (trialkali) type which provides a very high quantum efficiency (23% at 380 nm) in the blue as well as an extremely good response in the red. The spectral region for the 9558B is 165 nm ($60,606 \text{ cm}^{-1}$) to 850 nm ($11,765 \text{ cm}^{-1}$), while for the 9659B it is down towards 900 nm ($11,110 \text{ cm}^{-1}$). Infra-red studies were accomplished with PbS and InAs photoconductive detectors.

The optics system included a Glan-Thomson linear polarizer and for experiments involving circular polarization (axial Zeeman, MCD) a Fresnel rhomb was oriented to act as a $\lambda/4$ plate. This was used in conjunction with another Fresnel rhomb which redirects the beam along its original path. This could then be used to replace the linear polarizer in Figure 2.1.

For MCD studies a photo-elastic modulator was used to chop between right- and left-circularly polarized light. This operates on the principle of the piezo-optical effect [4]. An oscillating strain is sustained in a quartz crystal, modulating its birefringence periodically, so the quartz behaves as an oscillating wave plate.
2.3 Sample Environment

For absorption and most temperature-dependence studies the sample was mounted on a sample holder in a quartz glass flow-tube which sat in a liquid helium dewar - the configuration is represented in Figure 2.2. Helium liquid is boiled off through the flow-tube and so cools the crystal - the rate at which this boiling occurs determines the crystal temperature, monitored by a carbon resistor (270 Ω at room temperature) located above the sample. Spectra from 300K to ~8K were

Figure 2.2. Measurement of absorption using a quartz glass flow-tube.
recorded with temperature stability, below 50K, of approximately ±1 K -
this was somewhat worse at elevated temperatures. The flow-tube was
also used in conjunction with the Cary 17 instrument. The flow-tube
facilitated reasonably quick and easy measurements and it was possible
to change samples easily.

An Oxford Instruments superconducting magnet designed according
to our specifications was used for the Zeeman work. The magnet has a
split-coil and enables transverse and longitudinal data to be accumulated;
a schematic diagram of the cryostat is shown in Figure 2.3. The sample
sits in exchange gas at 4.2 K and a field of 5 Tesla; pumping on the
helium bath affords the possibility of operation at 1.8 K and 6 T, if
necessary. Running in persistent mode the field exhibits a homogeneity
of 1.3% over a 2 cm³ volume; this has the consequence of producing
line-broadening for a g of 2 an order of magnitude below the resolution
used in these studies, about 1 cm⁻¹. The sample holder was equipped
with a heater and 270 Ω carbon resistor for temperature control and
monitoring respectively. A range of temperatures between 5 K and 100 K
was attained by adjusting the quantity of exchange gas and the resistance
heating. The sample could be changed without having to warm up the
cryostat.

For electric field perturbations two systems were used, the one
where the crystal sat in a vacuum of 10⁻⁶ torr, next to a heat exchanger,
and the other where it sat in exchange gas in a cryostat similar to that
in Figure 2.3.

The former arrangement entailed a modification of an AIR
Products and Chemicals LT-3-110 Heli-Tran Liquid Helium Transfer
Refrigerator (Figure 2.4). The helium flows at a constant rate from a
pressurized dewar (~3 psi) through a pliable high efficiency transfer
Figure 2.3. The superconducting magnet used for the Zeeman studies.
Figure 2.4. (a) The experimental configuration for electric field studies, using a continuous flow cryostat.

(b) A schematic of the sample mounting.
line to the sample interface where, via a copper block, it cools the sample mounted between rigid copper electrodes, one of which is at earth potential (Figure 2.4(b)). A thermocouple, chromel vs gold (0.07% atomic % iron), indicates the temperature of the cold block. The advantage of this system, apart from its inherent flexibility, over that of the other lies chiefly in the size of breakdown voltage, which is significantly lower in helium exchange gas. Using the continuous flow cryostat, fields of up to ~50 kV/cm were obtained, whereas values about half this strength were possible in the conventional cryostat. This reduction in field strength reduces the size of an AC modulated signal not by two, but by four! (see Chapter 3). If low temperature studies are desirable, then there lies in the Heli-Tran system a disadvantage because the cold finger construction imposes a lower limit on temperature of ~15K.
References


CHAPTER THREE

EXPERIMENTAL RESULTS

Part A: SrO:Ni$^{2+}$

3.1 Introduction
3.2 The $C_{3v}$ Absorption
3.3 The Sidebands of the Zero-phonon Lines
3.4 The Absorption Between 13520 cm$^{-1}$ and 13000 cm$^{-1}$

Part B: SrO:Co$^{2+}$

3.5 Introduction
3.6 The Optical Absorption
PART A: \textit{SrO:Ni}^{2+}

3.1 Introduction

The as-grown crystals were dark brown to black but it was possible to measure the transmission using thin crystal slices about 0.5 to 1 mm thick. There were various absorption bands apparent which were not present in undoped SrO and these are attributed to the nickel impurities. Heating the dark crystals at \(-1400^\circ\text{C}\) in vacuum for a few hours removed the strong absorption and the crystals were quite transparent with a light pink colour. The impurity absorption bands were changed but this change could, without the return of the dark colour, be reversed by alternating heat treatments (to be described in a later chapter). The dark colour was, therefore, not due to nickel centres.

The as-grown Co-doped crystals were similarly dark in colour and behaved similarly to heat-treatments. The dark colour is, therefore, considered to arise from some form of intrinsic colour centre or precipitate but this has not been studied in detail.

The Ni-doped samples have been subject to numerous heat-treatments at various temperatures and various atmospheres (this is dealt with in detail in Chapter 7). In this way it was established that there were two sets of independent intensity-correlating bands. With heat-treatments, it is possible to obtain either set alone. The strengths of the bands were found to be directly proportional to Ni concentrations, which were in the range of 100 to 1200 ppm, measured using chemical absorption analysis. The one set gives absorption at \(-4300\ \text{cm}^{-1}\) (2326 nm), 6000 cm\(^{-1}\) (1667 nm), 13500 cm\(^{-1}\) (741 nm), 15800 cm\(^{-1}\) (633 nm), and 19000 cm\(^{-1}\) (526 nm). It is concluded that these absorptions arise
from single ion transitions at the one centre and the Zeeman measurements presented in the next chapter show that the symmetry of the centre is $C_{3v}$. It is convenient to adopt the description of the centre at this stage. The $C_{3v}$ centre is responsible for the absorption spectrum shown in Figures 3.1 and 3.2; in Figure 3.3 we see a representative sample of absorption spectra in the visible from six "as-grown" crystals.

The second set of intensity correlated absorption gives a strong band at $14500 \text{ cm}^{-1}$ (690 nm) with other weaker features in the visible, another at $19000 \text{ cm}^{-1}$ (526 nm), and at $8000 \text{ cm}^{-1}$ (1250 nm) in the infra-red. This absorption is likewise concluded to arise from one centre and the symmetries suggested by the observations are $C_{2v}$ or $C_s$. Consequently the centre is labelled $C_{2v s}$. Also to assist the presentation, the data and discussion for this centre are found in Chapter 7. The present chapter is restricted to the absorption of the $C_{3v}$ centre.

3.2 The $C_{3v}$ Absorption

The features of the absorption bands are immediately taken as highly significant:

(i) the very large strength of the bands compared with other $d^n \leftrightarrow d^n$ transitions in cubic crystals, and

(ii) the presence of what appears to be zero-phonon transitions.

The strength of the $C_{3v}$ bands is best judged by comparing them with the visible spectrum shown by nickel of similar concentration in an MgO host. In Figure 3.4(a) the spin-allowed absorption bands corresponding to transitions from the $^3A_{2g}(e^2)$ ground state to the $^3T_{1g}^a$ and $^3T_{1g}^b$ crystal field terms (each an admixture of $^3T_{1g}(t^2)$ and $^3T_{1g}(t^2)$)
Figure 3.1. The optical absorption of SrO:Ni$^{2+}$ taken at ~20K.

Figure 3.2. A continuation of the spectrum. The dashed line is an absorption due to the quartz flow tube.
Figures 3.3 (a) to (f). The absorption spectra of six untreated crystals of SrO:Ni$^{2+}$, taken at ~20K.
Figures 3.4 (a) and (b). In (a) the absorption of MgO:Ni$^{2+}$ in the visible is reproduced from reference [1]; (b) shows the absorption of SrO:Ni$^{2+}$ in the same spectral region. In both cases transitions occur from a $^3A_{2g}$ ground state.
are reproduced from reference [1]. The absorption in Figure 3.4(b) corresponds to transitions from the ground state to a component of the $^3T_{1g}^b$ level for SrO:Ni$^{2+}$. Pappalardo et al [1] calculated the oscillator strengths for nickel in MgO and an estimate of the same parameter is made here for nickel in SrO, assuming the strengths quoted in [1] and using the relationships,

$$f_{\text{MgO:Ni}^{2+}} = \text{constant} \times \frac{\text{band intensity (MgO:Ni}^{2+})}{\text{concentration (MgO:Ni}^{2+})}$$  \hspace{1cm} (3.2-1)

$$f_{\text{SrO:Ni}^{2+}} = \text{constant} \times \frac{\text{band intensity (SrO:Ni}^{2+})}{\text{concentration (SrO:Ni}^{2+})}$$  \hspace{1cm} (3.2-2)

where the f's are the oscillator strengths. Combining these and including a term allowing for differences in sample thickness, the oscillator strength for nickel in SrO can be written,

$$f_{\text{SrO:Ni}^{2+}} = \frac{\text{band intensity (SrO:Ni}^{2+})}{\text{band intensity (MgO:Ni}^{2+})} \times \frac{\text{concentration (MgO:Ni}^{2+})}{\text{concentration (SrO:Ni}^{2+})} \times \frac{\text{crystal thickness (MgO:Ni}^{2+})}{\text{crystal thickness (SrO:Ni}^{2+})} \times f_{\text{MgO:Ni}^{2+}}.$$  \hspace{1cm} (3.2-3)

The integrated band intensities, concentrations and crystal dimensions are measured experimentally and so an estimate of the oscillator strengths for SrO:Ni$^{2+}$ can be found:

$$f_{\text{SrO:Ni}^{2+}} \approx 1.6 \times 10^{-3}.$$  

This value is about two orders of magnitude larger than that for the
nickel ion occupying a centrosymmetric site in MgO, given in reference [1] as \(1.6 \times 10^{-5}\).

In MgO the nickel impurity substitutes directly for the magnesium and retains local octahedral symmetry. It is generally recognised that the absorption intensity for \(3d^n \leftrightarrow 3d^n\) transitions in an ion at a site with inversion symmetry arises from either a magnetic dipole mechanism or an electric dipole one induced by odd parity vibrations. The \(^3T_{1g}(t^2_2, t^2_e)\) bands in MgO:Ni\(^{2+}\) are considered to be phonon-induced [2] as they increase substantially with temperature according to \(\text{Coth}(\hbar\omega/2kT)\). The \(^3A_{2g} \leftrightarrow ^3T_{2g}\) transition is, on the other hand, of the magnetic dipole type and is temperature independent [3]. This is the normal behaviour for single ion absorption: phonon-induced transitions increase with temperature whereas allowed transitions are temperature independent.

In contrast to this behaviour, the corresponding bands in SrO:Ni\(^{2+}\) show no such dependence. In Figures 3.5(a)-(f) and 3.6(a)-(c) the bands drop in intensity as the sample temperature increases and their intensity at room temperature is only about 10%-20% of the low temperature intensity. The temperature dependence is plotted for the 13500 cm\(^{-1}\) band and the 14500 cm\(^{-1}\) band in Figure 3.7. This indicates that the bands are not vibrationally-induced. It would appear that the transitions are allowed at low temperatures (indicated by their large oscillator strengths) but the intensity mechanism is strongly temperature dependent. A possible way in which this could happen will be discussed later.

To substantiate the claim that the sharp lines at the onset of the bands are zero-phonon lines and the following structure is vibronic in nature, it should be shown that, at higher temperatures,
Figures 3.5 (a)-(f). The temperature dependence of the absorption for SrO:Ni$^{2+}$ in the visible. At 200K (see (f)) there are only hints of the bands remaining.
(e) $T=120K$

(f) $T=200K$

WAVELENGTH (nm) →
Figures 3.6 (a)–(c). The temperature dependence of the infra-red band of SrO:Ni$^{2+}$. The band has completely disappeared at room temperature (c).
Figure 3.7. The decrease in intensity for the two bands, at 13500 cm\(^{-1}\) and at 14500 cm\(^{-1}\). Normalisation is against the low temperature band strength.
vibronic features (modified by a Boltzmann factor) also appear to the lower energy side of the supposed zero-phonon lines. Fortunately the overall band intensity does not drop significantly before positive identification of such structure is lost. The half-widths of the sharp lines increase from about 5-10 cm\(^{-1}\) at ~5K to about ~30 cm\(^{-1}\) at 100K, at which temperature the sideband structure is still reasonably well resolved. The temperature dependence of the halfwidth of the 13520 cm\(^{-1}\) (739.6 nm) line is shown in Figure 3.8. A close inspection of the band at 13500 cm\(^{-1}\) (740 nm) in Figure 3.9 reveals a line appearing, at sufficiently high temperatures, about 65 cm\(^{-1}\) lower in energy than the main sharp line. A temperature dependence plot in Figure 3.10, assuming the following Boltzmann thermal population of states above the ground level,

\[
I = I_0 e^{-\Delta E/kT}
\]

shows that the hot feature does have its origin ~65 cm\(^{-1}\) above the ground state and is, therefore, vibronic in origin, as are the broader transitions lying to the high energy side of the 13520 cm\(^{-1}\) line. A similar symmetry is clearly observed in Figure 3.6(b) about each of the three lines in the infra-red, at 6024 cm\(^{-1}\) (1660 nm), 6368 cm\(^{-1}\) (1506.5 nm), and 7000 cm\(^{-1}\) (1428.6 nm), about the line at 4317 cm\(^{-1}\)
Figure 3.8. The temperature dependence of the 13520 cm$^{-1}$ line halfwidth.
Figure 3.9. Vibrational sideband appearing to the lower energy side of the 13520 cm⁻¹ (739.6 nm) line.

Figure 3.10. A logarithmic plot of the intensity of the low energy Anti-Stokes' band, I, relative to the intensity of the one phonon Stokes' line, I₁, against 1/kT. The gradient gives E ≈ 65 cm⁻¹.
(2316.4 nm) in Figure 3.16 in Section 3.3, and about the 15820 cm$^{-1}$ (632.1 nm) line - see Figure 3.17 in the same section. These sharp lines are, therefore, all taken as electronic origins ("zero-phonon" lines).

In addition, in the infra-red band a 'hot line' appears at 40 cm$^{-1}$ to the lower energy side of the 6368 cm$^{-1}$ line, shown in Figure 3.11(a)-(b). This line steals intensity from the main line and its sideband. A temperature dependence analysis (Figure 3.12) indicates the origin of the transition is located at ~17 ± 3 cm$^{-1}$ above the ground state: as there are no vibrational bands appearing anywhere close to this frequency, it is concluded that it is an electronic origin. This result is supported by the EPR work of Haider [4] who, likewise, claims that there is an energy level about 18 cm$^{-1}$ above the ground state.

It will be shown later that the crystal field calculations suggest that there should be absorption bands further into the infra-red. These were anticipated to be above 2500 cm$^{-1}$ and, therefore, in the range within which quartz windows could be used. CsI windows were used but the signal-to-noise was significantly poorer and less satisfactory for detection of weak absorption bands (no strong bands were observed!).

Satisfactory spectra were obtained with quartz windows except for the fact that in the region of 3500 cm$^{-1}$ there was a strong absorption due to OH$^-$ in the windows. In these investigations only one weakly absorbing band was observed at 3000 cm$^{-1}$, shown in Figures 3.13(a)-(b). The absorption could still, however, result from an OH$^-$ impurity in the SrO itself. Although the main OH$^-$ absorption is likely to be within the same 3500 cm$^{-1}$ band, it is possible for the OH$^-$ to be associated with other impurities to give weak absorption shifted slightly in energy. The observed band at 3000 cm$^{-1}$ was not repeated in other
Figure 3.11 (a). The infrared band of SrO:Ni, between 6000 and 7000 cm$^{-1}$.

(b) At higher temperatures a line (B) appears about 40 cm$^{-1}$ to the high energy side of line (A). A plot of this temperature dependence is shown overleaf.
Figure 3.12. The logarithmic plot of the relative intensities of lines A and B, IA/IB, against 1/kT. The gradient gives $E \approx 17 \text{ cm}^{-1}$. 
Figure 3.13.

(a) The SrO:Ni$^{2+}$ absorption between 4000 and 2500 cm$^{-1}$, taken with a Perkin-Elmer 180 spectrophotometer. The strong absorption at $\approx$3500 cm$^{-1}$ is probably due to a combination of OH$^{-}$ in the system and strontium hydroxide in the sample, whilst that at $\approx$2800 cm$^{-1}$ is due to the quartz cryostat windows.

(b) The weak absorption at $\approx$3150 cm$^{-1}$ is amplified. Its possible origin is discussed in the text.
smaller crystals and so the evidence for a Ni$^{2+}$ absorption is too tenuous to be used at this stage.

3.3 The Sidebands of the Zero-phonon Lines

The creation of phonons accompanying the absorption process creates vibrational sidebands displaced, at low temperatures, to the high energy side of the zero-phonon line in absorption (it's the reverse for emission!). At high enough temperatures the vibrational states will be populated and equivalent peaks observed to the low energy side of the zero-phonon origin, as has already been shown in Section 3.2. The low energy sideband will reflect the vibrational modes of the ion in the ground state and these may not be exactly equal to those in the excited state - this explains the lack of complete mirror symmetry. The electron-vibration interaction gives rise to the schematic energy level structure:

\[ \begin{align*}
\text{vibronic n} = &\ 2 \\
\text{vibronic n} = &\ 1 \\
\text{electronic origin n} = &\ 0 \\
\text{vibronic n} = &\ 2 \\
\text{vibronic n} = &\ 1 \\
\text{electronic origin n} = &\ 0
\end{align*} \]

For a given progression the intensity ($I_n$) of each vibrational
quantum (n) relative to that of the first \( (I_0) \) is given by the Poisson distribution \[5\]

\[
\frac{I_n}{I_0} = \frac{S^n}{n!} \tag{3.3-1}
\]

where \( S \) is a parameter included to generate the bandshape.

The zero-phonon origins with their sidebands are shown in detail in Figures 3.14, 3.15, 3.16 and 3.17 where the phonon frequencies in wavenumbers are indicated. These are summarised in the following table:

<table>
<thead>
<tr>
<th>Band ((\text{cm}^{-1}))</th>
<th>Low (high energy side)</th>
<th>Intermediate</th>
<th>High (low energy side)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4300</td>
<td>80</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6000</td>
<td>90</td>
<td>210</td>
<td>470</td>
</tr>
<tr>
<td>13500</td>
<td>100</td>
<td>120,280</td>
<td>470</td>
</tr>
<tr>
<td>15800</td>
<td>60</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3.1. Analysis of the sidebands in SrO:Ni\(^{2+}\). The frequencies are in wavenumbers.

The impurity ion, then, can be used as a probe to obtain detailed information on the vibrational spectrum of the crystal environment, and constitutes one method of observing the phonon density of states. Rieder et al. [6] have calculated the phonon density of states in SrO with a shell-model using inelastic neutron scattering and this
Figure 3.14. Part of the 6000 cm\(^{-1}\) band for SrO:Ni\(^{2+}\), showing the vibrational structure. The modes coupling onto the zero-phonon origins (truncated) are indicated - figures are in wavenumbers.
Figure 3.15. The vibrational sideband of the 13520 cm\(^{-1}\) line (frequencies in wavenumbers).
Figure 3.16. SrO:Ni\textsuperscript{2+} - The temperature behaviour of the 4317 cm\textsuperscript{-1} line. The vibrational structure is indicated.

is reproduced in Figure 3.18. It shows acoustical phonon branches at ~130 cm\textsuperscript{-1} and at ~200 cm\textsuperscript{-1} and an optical branch maximum at ~280 cm\textsuperscript{-1}. Similar frequencies are observed in the vibrational sidebands for SrO:Ni\textsuperscript{2+}. It is concluded that the intermediate frequencies in Table 3.1 arise from essentially lattice modes which are, perhaps, only slightly perturbed due to the impurity. There are, however, additional modes appearing at about 80-100 cm\textsuperscript{-1} (60 cm\textsuperscript{-1} in the 15800 cm\textsuperscript{-1} band) and at ~470 cm\textsuperscript{-1}. Both modes lie on the extreme edges of the density of states function. They are relatively sharp and are considered to be a low and
Figure 3.17. Vibronic structure around the 15820 cm\(^{-1}\) transition. The 60 cm\(^{-1}\) mode coupling onto the zero-phonon origin is lower in frequency than is found elsewhere in the spectrum.

Figure 3.18. The phonon density of states from reference [6].
a high frequency resonance mode. Consideration is now given as to how they arise.

Nickel (atomic weight 59) is considerably lighter (as is cobalt (59)) than strontium (88) and so one may expect a local mode of higher frequency appearing due to the mass defect (see the review article by Barker et al. [7]) - this could explain the vibration at ~470 cm\(^{-1}\). This argument does not explain the low frequency progression - rather we must anticipate our later conclusion that the impurity has lost its inversion symmetry through a static odd-parity displacement - so that the impurity lies off-centre along a \(<111>-direction; systems such as RbCl:Ag\(^+\) [8] and RbBr:Ag\(^+\) [9] exhibit similar off-centre motion. The displacement results in a change of force constants between the impurity and ligands. In Figure 3.19 the impurity space is shown for an ion displaced along a 3-fold axis. This model would produce high (due to force constant \(k\)) and low frequency (due to force constant \(k'\)) local modes of \(A_1g\) symmetry and this may explain the 80-100 cm\(^{-1}\) and 470 cm\(^{-1}\) energies. The frequency of the local mode varies considerably from state to state. This suggests there is a change in the force constant \(k\) and \(k'\) and probably the off-centre location varies from state to state.

![Impurity space diagram](image)

Figure 3.19. The impurity space for an impurity off-centre along a \(<111>-direction. The spring constant \(k > k'\).
3.4 The Absorption Between 13520 cm$^{-1}$ and 13000 cm$^{-1}$

In most of the spectra in the visible region there has appeared to the low energy side of the 13520 cm$^{-1}$ zero-phonon line considerable structure composed of sharp but mainly weak lines (apart from the vibronic line discussed earlier). The spectral region is shown in Figure 3.20 with the stronger features being labelled numerically.

The lines do not intensity correlate with the C$_{3v}$ band, nor do they all intensity correlate with one another. This is revealed in Figure 3.22(a)-(e). Correlating the intensities taken with a range of untreated and heat-treated crystals, there seems to be at least two families of absorption lines grouped in the following manner:

\[
\begin{align*}
\text{Group I} & : \quad 4,5,6 \\
\text{Group II} & : \quad 1,2,3
\end{align*}
\]

Evidence for the behaviour of the other lines is meagre owing to their low intensities or broader absorptions; they may well form groups on their own.

The transitions presumably arise from centres of low symmetry and certainly a magnetic field produces no change (apart from a shift) in the lines. Under application of alternating electric fields (reported in Chapter 8) the centres are shown to have no inversion symmetry.

The absorption lines always appear at the same energy, indicating they are not a result of random strains in the crystal but rather of a regular lattice defect. Similar features have been observed
Figure 3.20. The structure to the lower energy side of the 13520 cm$^{-1}$ line. Positions of lines are given in wavenumbers (cm$^{-1}$).
in MgO:Cr\(^{3+}\) where Schawlow et al [10], Imbusch et al [11], and Glass [12] have postulated the existence of cation vacancies near to the chromium ion to conserve charge neutrality. The vacancies produce a small non-random perturbation on the crystalline field and so the impurity senses a superposition of the two (and a lower symmetry field) - this causes the transition to be displaced slightly in energy. The nearer the vacancy the stronger the perturbation (and the more removed will be the transition from the original).

Doubly charged impurity ions in the alkaline earth oxides can be incorporated into the lattice with no charge compensation and so in SrO:Ni\(^{2+}\) one would not expect vacancy formation; to produce vacancies in the alkaline earth-oxides it is necessary to use particle radiation (neutrons, electrons, or protons) [13]. The lines are present when the C\(_{3v}\) band is strong but are considerably weaker (sometimes completely disappearing) when the trigonal band becomes less intense. The C\(_{3v}\) band reflects the concentration of nickel in the host lattice as its intensity increases linearly with the nickel impurity content. The above observations show that the intensity of the lines to the lower energy side of the trigonal band increases more rapidly than the linear increase of the C\(_{3v}\) band. This suggests the centre responsible for the absorption in this region is likely to be nickel pairs (and triads etc.). In these centres the Ni\(^{2+}\) environment will experience a further perturbation due to the associated Ni\(^{2+}\) ion and the position of the zero-phonon line subsequently changes. The model we are discussing is drawn in Figure 3.21, where it is shown that several different configurations of off-centre displacements can arise. The crystallographically inequivalent centres and their relative occupation could account for the pattern of lines observed. In this diagram it is
Figure 3.21. The formation of nickel aggregates may be responsible for the structure below 13520 cm$^{-1}$. The single ion site is perturbed by other nearby nickel ions.

assumed that each ion is still displaced off-centre along the $<111>$-type directions. This need not be the case as the symmetry of the site is low and has not been established. Other off-centre or, in principle, on-centre sites could be present but it should be noted that the energy levels of the centres being discussed are not substantially different from single ion energy levels (largest shift <400 cm$^{-1}$). Therefore the modification of the crystal field must be small, suggesting that there are only small changes to the trigonal field, i.e. small perturbations to the $<111>$ off-centre displacement.
Crystals were heat-treated in vacuum and air to see what effect this had on the 'pair' lines in question. Some results are displayed in Figures 3.22(a)-(e). After heat-treatment in vacuum the C\textsubscript{3v} band and the pair lines are always strong (the C\textsubscript{2vs} band disappeared altogether after a long enough heat-treatment in a reducing atmosphere, as will be discussed in Chapter 7) - this is shown in (a). In a typical experimental cycle crystals were heat-treated in air at various temperatures and quenched by dropping them into oil; the concentration of reaction components (in this case, the nickel ions) at room temperature is then equal to the equilibrium concentration of reaction components at the temperature from which the sample is quenched. (b) shows the absorption spectrum after the crystal has undergone heat-treatments at 600°C for 6 hours and at 700°C for 13 hours - the pair lines have lost intensity and so has the C\textsubscript{3v} band. After two further treatments at 800°C (6 hrs) and 900°C (13 hrs) the pair lines have disappeared and the C\textsubscript{3v} band has become weaker - portrayed in (c). The intensity appears to have gone into a broad band on the lower energy side of the zero-phonon line. The complete cycle is represented in Figure 3.23, where the fall in intensities of the C\textsubscript{3v} band and two of the pair lines has been plotted. Further treatments in air at more elevated temperatures (T \textgreater 1000°C) brought back the sharper pair line structure and additionally strengthened the C\textsubscript{3v} band shown in (d). Finally, when the crystal was heat-treated again at ~1100°C for 5 hours the C\textsubscript{2vs} band started to appear, but the pair line structure remained about the same strength. It is worth noting that x-irradiation did not affect any of the spectra and this eliminates any suggestion of valence state changes (UV-irradiation also provided a negative result).

The temperature dependence of the pair lines is shown in Figure 3.24(a)-(c). Apart from line broadening and the anti-Stokes'
SrO: Ni$^{2+}$ heat-treated in vacuum at 1350 °C (15h)

Further heat-treatments in air at 500 °C (15h), 600 °C (6h), and 700 °C (13h)

Figure 3.22 (a)-(e). A cycle of heat-treatments on a SrO: Ni$^{2+}$ sample. After each treatment the crystal was quenched so that the equilibrium concentration of impurities (or defects) at the high temperature could be observed at helium temperatures.
Further heat-treatments in air at 800 °C (6h) and 900 °C (13h)

Further heat-treatment in air at 1000 °C (3h)

Further heat-treatment in air at 1130 °C (5h) and 1230 °C (16h)

Figure 3.22 (a) - (e) continued.
Figure 3.23. The variation of intensity with treatment temperature for line 2, line 6 and the $C_{3v}$ band (see Figure 3.20). Note these lines are all affected differently by the heat treatments and must therefore be associated with separate centres.
Figure 3.24 (a)-(c). The temperature dependence of the 'pair' lines. The intense transition (arrowed) is the vibronic line discussed in Section 3.2.
Figure 3.25. The three transitions at ~13230 cm$^{-1}$. The high energy line loses all intensity to the central one at ~15 K.
transitions appearing no change occurs.

The one exception to the above is a very unusual temperature variation of two lines at ~755 nm. One of the lines at 13240 cm$^{-1}$ is present at low temperatures but loses its intensity at about 15K to the adjacent line at 13233 cm$^{-1}$. The absorption is shown in Figure 3.25. The transitions have approximately 3 to 4 cm$^{-1}$ halfwidths and are 7.5 cm$^{-1}$ apart. In addition, a hot feature appears at 13223 cm$^{-1}$, 10 cm$^{-1}$ lower in energy from the central line and these are all indicated in Figure 3.25. This latter hot feature can be understood if there is a level about ~17 cm$^{-1}$ above the ground state but the complete disappearance of the high energy line at 13240 cm$^{-1}$ is not understood. It is considered that the present behaviour must arise from some thermal rearrangement of one of these centres but no quantitative treatment of these has proved successful.

Summing up, the evidence suggests that the nickel tends to aggregate at temperatures below or around 900°C but at temperatures above this the equilibrium concentration of larger nickel aggregates seems to diminish, although smaller aggregates, presumably pairs, still remain strongly evident.
PART B: SrO:Co$^{2+}$

3.5 Introduction

The concentrations of cobalt in SrO were similar to those found for nickel. The crystals as received were a dark brown colour and almost opaque but after treatment in vacuum at ~1400°C for a few hours, the broad background absorption in the visible region giving rise to the brown colouration was removed leaving the samples a light blue colour. Crystal slices of desired crystallographic orientation were prepared and the optical absorption between 4.2K and 300K was monitored using the same techniques as previously described.

Many of the observations of the SrO:Co$^{2+}$ crystals were similar to those observed for SrO:Ni$^{2+}$. In particular more than one centre was present in the as-grown crystal but after heating it in vacuum at 1400°C just one centre, as in the SrO:Ni$^{2+}$ case, with $C_{3v}$ symmetry remained [14]. This centre was, as will be shown, concluded to be due to an off-centre Co$^{2+}$ ion and was considered to be the most interesting subject to study.

The $C_{3v}$ centre is not the centre reported in the literature by Sochava et al. [15]. Their crystals were heat-treated in oxygen which has the effect of removing the $C_{3v}$ band. In its place centres of $C_{2v}$ and $C_s$ symmetry are created. These give different optical absorption although the band positions are at the same energy - the absorption measured by Sochava et al. is reproduced in Figure 3.26. The bands show little structure in marked contrast with those associated with the $C_{3v}$ site (Fig. 3.27). EPR measurements of Haider support the observations but no systematic analysis of the effect of heat-treatments has been undertaken as yet and these bands will not be discussed further.
The absorption shown in the lower halves of Figures 3.27(a) and (b) comprises three strong bands centred at \( -8000 \text{ cm}^{-1} \) (1250 nm), \( 14000 \text{ cm}^{-1} \) (714 nm), and \( 18000 \text{ cm}^{-1} \) (1555 nm), together with a weak band at \( -16000 \text{ cm}^{-1} \) (625 nm). The bands at \( 18000 \text{ cm}^{-1} \) and \( 16000 \text{ cm}^{-1} \) show only broad features whereas the other two contain sharp, well-resolved lines with vibrational sidebands.

The strengths of the absorptions are, paralleling the SrO:Ni\(^{2+}\) case, exceptionally large and this is emphasised by making comparison with the MgO:Co\(^{2+}\) absorption. Pappalardo et al. [16] studied the optical absorption of MgO:Co\(^{2+}\) and found the paramagnetic ion to have octahedral coordination. The optical absorption of MgO:Co\(^{2+}\) has been recorded and is shown in the upper portions of Figure 3.27(a) and (b) with the spectrum.
Figure 3.27(a). The infra-red absorptions of MgO:Co$^{2+}$ and SrO:Co$^{2+}$. The concentration of cobalt in the MgO host was ~6000 ppm as against ~220 ppm in SrO.
Figure 3.27(b). The absorption of MgO:Co$^{2+}$ and SrO:Co$^{2+}$ in the visible.
of SrO:Co\(^{2+}\) below, for the same wavelength region. The energy level assignments (due to Pappalardo) are included for the MgO:Co\(^{2+}\). Both crystals were of comparable thickness but chemical analysis showed the concentration of cobalt in MgO was 6000 ppm, whereas the concentration in SrO was only 220 ppm. The oscillator strengths for MgO:Co\(^{2+}\) have been taken from reference [1] and the relations (3.2-1) and (3.2-2) used with the appropriate integrated intensities and concentrations. For this purpose the \(^{4}T_{1}(e\text{t}^2)\) bands have been used as an example:

\[
 f_{\text{MgO:Co}^{2+}} = 1.6 \times 10^{-5} \text{ (from [16])} \quad \text{and} \quad f_{\text{SrO:Co}^{2+}} = 2.6 \times 10^{-3} \text{.}
\]

The oscillator strength for cobalt in SrO is seen to be more than two orders of magnitude greater than for the same ion in MgO, indicating that the transitions in SrO are allowed rather than vibrationally induced.

The overall band intensity behaves the same way as the nickel bands - it does not increase with temperature, rather it drops in intensity and by room temperature it is only ~20% of its low temperature value (see Figure 3.28).

Following the same arguments we adopted in Part A for nickel, the sharp lines at 13538 cm\(^{-1}\) (738.7 nm), 13584 cm\(^{-1}\) (736.2 nm), and at 7657 cm\(^{-1}\) (1306 nm) are shown to be zero-phonon transitions. At higher temperatures vibronic structure is observed on the low energy as well as on the high energy side of the electronic origins - the temperature dependence of the visible band at \(-14000\) cm\(^{-1}\) in Figure 3.28 clearly shows this. Approximately 20 cm\(^{-1}\) to the lower frequency side of the 13538 cm\(^{-1}\) line, a transition grows in intensity with increasing temperature - it is labelled V in Figure 3.29(a). Its temperature dependence in Figure 3.29(b) reveals it has a vibronic origin \(-65\) cm\(^{-1}\)
Figure 3.28. The behaviour of the 14000 cm$^{-1}$ band at three different temperatures.
Figure 3.29 (a)-(b). In (a) the appearance of a transition at higher temperatures, about 65 cm$^{-1}$ from the 13584 cm$^{-1}$ line; (b) shows it is a vibronic transition from a level about 65 cm$^{-1}$ above the electronic origin.
above the ground level and \( V \) is then seen to be a vibronic transition accompanying the second zero-phonon line at \( 13584 \text{ cm}^{-1} \). The hot vibronic line in the infra-red band likewise established the presence of a \( 65 \text{ cm}^{-1} \) vibronic level associated with the ground state.

The vibrational sidebands of the zero-phonon lines are very much the same as those found for \( \text{SrO:Ni}^{2+} \). A low frequency \( 90 \text{ cm}^{-1} \) mode couples onto each of the electronic origins and higher frequencies of \( \sim 210 \text{ cm}^{-1} \) and \( 470 \text{ cm}^{-1} \) are observed coupling onto the infra-red line. Their origin is believed to be the same as for \( \text{SrO:Ni}^{2+} \). Figure 3.30(a) shows the vibrational structure for the infra-red and Figure 3.30(b) for the visible.
Figure 3.30 (a)-(b). The vibrational structure in the infra-red (a) and visible (b) for SrO:Co$^{2+}$. Frequencies of the modes are indicated in wavenumbers.
References

CHAPTER FOUR

THE ZEEMAN EFFECT

PART A: SrO:Ni$^{2+}$

4.1 Introduction
4.2 Theoretical Background
4.3 Experimental Results

PART B: SrO:Co$^{2+}$

4.4 Experimental Results
4.5 Analysis
PART A

SrO: Ni$^{2+}$

4.1 Introduction

Interpretation of an absorption or emission spectrum depends on determining (i) the impurity or defect centre responsible and (ii) the degeneracies of the electronic states involved in the observed transitions. There are two types of degeneracy, electronic and orientational. The latter will occur in the case of non-cubic sites in optically isotropic (i.e. cubic) crystals; it is then necessary to consider the number of geometrically equivalent sites. The presence of degenerate energy levels may be established by investigating the effect of external perturbations such as stress [1], magnetic [2], and electric fields [3] on the optical spectrum. The electronic degeneracy may be partially or completely removed by the perturbation and this will be reflected by the splitting of the absorption line.

The sample material can restrict the type of experiment one is able to perform. An unstrained sample is a pre-requisite for each experiment and for stress it must withstand the perturbation without cracking and be of an adequate dimension to suit the geometry of the experiment. Electric field studies (Stark spectroscopy) are naturally restricted to insulating solids and the fields limited by the dielectric strength of the material in question and the breakdown characteristics of the medium in which the sample is located (e.g. vacuum or exchange gas etc.). Zeeman experiments, on the other hand, encounter few of these problems and with the intense magnetic fields now available, it is a very flexible and powerful technique.
Before presenting the experimental results it is useful to briefly recapitulate the evidence gathered so far:

(i) the sharp absorption peaks discussed in the previous chapter are believed to be zero-phonon lines. They are very intense and must surely be electric dipole in origin, implying the local symmetry of the centre is a sub-group of $O_h$ without an inversion operator, and

(ii) the separation of the intense spin-allowed bands in the visible at 19000 and 13500 cm$^{-1}$ and in the infra-red at 6000 and 4300 cm$^{-1}$ must result from a low-symmetry field.

In the next section it will be shown by utilising the Zeeman selection rules that the Ni$^{2+}$ centre can be proved to be at a site of $C_{3v}$ symmetry.

4.2 Theoretical Background

The first ever account of the Zeeman effect in crystals was given in 1930 by Bethe [4], who gave a quantum mechanical treatment of the effect for tetragonal crystals. A more recent review article by Runciman [2] adopting a group-theoretical approach provides the background for this section. Extensive use is made of the point group tables of Koster et al. [5]; the $C_{3v}$ point-group table accompanied by the tables of coupling coefficients is reproduced from this reference and appears in Appendix I.
In the $C_{3v}$ point group and an even electron system $g_\perp = 0$ and the electronic degeneracy is lifted solely by the projection of the magnetic field along the axis of the centre, i.e. $g = g_\parallel \cos \theta$.

The doubly degenerate $\Gamma_3$ states can be chosen to transform as $\frac{1}{\sqrt{2}}(x+iy)$ and $\frac{1}{\sqrt{2}}(x-iy)$ where the trigonal coordinate system is used with $z \parallel <111>$, $y \parallel <1\overline{1}0>$, and $x$ orthogonal to these two. The size of the splitting observed for the case where $H \parallel <111>$ is

$$< \frac{1}{\sqrt{2}}(x+iy) | \beta (L_z + 2S_z) H_z | \frac{1}{\sqrt{2}}(x+iy) > = - < \frac{1}{\sqrt{2}}(x-iy) | \beta (L_z + 2S_z) H_z | \frac{1}{\sqrt{2}}(x-iy) > = g\beta H_z$$

(4.2-1)

where $\beta$ is the Bohr magneton. The separation of the states will be twice this amount. The splitting will be less for those centres not along the field direction. These are four optically equivalent directions for trigonal centres in cubic crystals. A summary of the geometries of the centres for three major field directions is given in Table 4.1.

<table>
<thead>
<tr>
<th>Direction of field</th>
<th>$\cos \theta$ (number of sites)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt;100&gt;$</td>
<td>$\frac{1}{\sqrt{3}}$ (4)</td>
</tr>
<tr>
<td>$&lt;1\overline{1}0&gt;$</td>
<td>$0(2); \sqrt{2}/3$ (2)</td>
</tr>
<tr>
<td>$&lt;111&gt;$</td>
<td>$1(1); \frac{1}{3}$ (3)</td>
</tr>
</tbody>
</table>

Table 4.1. Values of $\cos \theta$ for each of the four trigonal orientations when the magnetic field is along the 3 axes of symmetry of a cubic crystal
To establish the intensities appearing in the Zeeman pattern, the perturbation operator is the electric dipole operator which transforms as x, y and z. In the $C_{3v}$ group the electric dipole operator spans the space $\Gamma_1 + \Gamma_3$; $\pi$-polarized light transforms as $\Gamma_1$ and $\sigma$-polarized light as $\Gamma_3$. Further, left-circularly polarized light ($a^+$) transforms as $\frac{1}{\sqrt{2}} (x+iy)$ and right-circularly polarized light ($a^-$) as $\frac{1}{\sqrt{2}} (x-iy)$. The experimental configuration for Zeeman polarization measurements is found in Figure 4.1.

Figure 4.1. The transverse and axial Zeeman experiments. The polarized light is directed along the dashed axis.
To find out whether a transition matrix element \(< \Gamma_1 | \Gamma_d | \Gamma_j >\) is non-zero, it must be determined whether the product between the representations of the initial and final states and the electric dipole operator, \(\Gamma_1 \times \Gamma_d \times \Gamma_j\), contains the identity representation. If it includes the identity representation once only the transition is allowed and uniquely defined. If \(\Gamma_1\) is included more than once the transition is allowed but not uniquely defined; if the triple product does not include \(\Gamma_1\) the transition is forbidden. Using these arguments it is possible to calculate the relative intensities and splittings of the Zeeman pattern for trigonal \(\Gamma_{1,2} \rightarrow \Gamma_3\) transitions. The selection rules for a \(\Gamma_3 \rightarrow \Gamma_{1,2}\) transition (\(C_{3v}\) point group) are:

For the \(\Gamma_3 \rightarrow \Gamma_3\) transition, the transition matrix element

\(< \Gamma_3 | \Gamma_3 | \Gamma_3 >\) and \(< \Gamma_3 | \Gamma_1 | \Gamma_3 >\)

each contain the identity \(\Gamma_1\) representation. Thus the transitions are group theoretically allowed in both \(\sigma\) and \(\pi\) polarizations but there is no symmetry imposed relationship between their intensities.

Utilising Koster it can be shown that intensity distributions for these transitions for a field along the axis are:
It should be noted that when the circularly polarized transitions are present the transition from the lowest Zeeman component is of the opposite circular polarization to that involved in the case of a $\Gamma_1(\Gamma_2)$ excited state, i.e. in the low temperature limit transitions to $\Gamma_1(\Gamma_2)$ and $\Gamma_3$ excited states will be oppositely polarized.

When the field and (the light vector) is inclined at an angle $\theta$, the splitting is reduced by $\cos \theta$. To determine the selection rules imposed by the $C_{3v}$ site symmetry (neglecting field mixing) the light vectors must be redescribed with respect to the axis of the $C_{3v}$ centre, e.g. for a rotation $\theta$ about the $y$-axis.
From this it can be deduced that allowed circularly polarized transitions reduce in intensity by \( (\frac{1}{2} + \frac{1}{2} \cos \theta)^2 \) and become observed in the opposite circular polarization as \( (-\sin \theta)^2 \). Transitions which are \( z \)-polarized for the field along the axis reduce in \( \pi \) intensity by \( \cos^2 \theta \) and become observed in right and left circular polarization as \( \frac{1}{2} \sin^2 \theta \).

To obtain the observed patterns one must also sum the individual intensities for the centres in geometrically inequivalent sites. In the case of the \( \Gamma_{1,2} \rightarrow \Gamma_3 \) transition these have been calculated, in part by Runciman [2] (transverse pattern) and in part by Manson et al. [6] (axial patterns) - these are shown in Figure 4.2. A fully resolved \( \Gamma_3 \rightarrow \Gamma_3 \) transition has not been observed and consequently the complex theoretical...
Figure 4.2. The calculated electric dipole Zeeman patterns for an $\Gamma_1 (\Gamma_2) \rightarrow \Gamma_3$ transition for a trigonal centre in a cubic crystal.
4.3 Experimental Results

The Zeeman patterns for the 15820 cm⁻¹ line are shown in Figures 4.3, 4.4 and 4.5 for the field along the three main crystallo­graphic directions: <100>, <110>, and <111>. The calculated intensity patterns (not scaled to the measured absorption) for a $\Gamma_3 \rightarrow \Gamma_{1,2}$ transition are alongside the experimental data - the intensities are calculated from Figure 4.2 and assume a Boltzmann distribution of the ground Zeeman components.

The experimental and calculated patterns are in good agreement and show the transition is from a $\Gamma_3$ ground state to an upper singly degenerate state. In addition, the $\sigma$-polarized transitions equal the $\alpha = \frac{1}{2} (\alpha^+ + \alpha^-)$ intensities, proving the original assumption that the transitions are electric dipole in origin ($\alpha = \pi$ for magnetic dipole transitions).

In Figures 4.6, 4.7, 4.8 and 4.9 a selection of Zeeman data is presented for the two infra-red lines at 6024 and 6368 cm⁻¹, along with Boltzmann-modified intensity calculations. The patterns for each line are very similar and support the $\Gamma_3 \rightarrow \Gamma_{1,2}$ assignment. Accepting that the theoretical model is only exact for the case of the field along the trigonal axes and that there is depolarization due to the optics, agreement is good.

The line at 7000 cm⁻¹ is significantly broader than the other infra-red lines and the Zeeman data is consequently less informative (Figure 4.10(a)). Nevertheless, the transition at low temperatures is very clearly of opposite circular polarization to the 6024 and 6368 cm⁻¹ pattern is omitted.
Fig. 4.3. SrO:Ni$^{2+}$: Zeeman pattern for the 15820 cm$^{-1}$ line. The dotted line indicates the zero field position.
Fig. 4.4. SrO:Ni$^{2+}$: Zeeman pattern for the 15820 cm$^{-1}$ line.
Fig. 4.5. SrO:Ni$^{2+}$: Zeeman pattern for the 15820 cm$^{-1}$ line.
Fig. 4.6. SrO:Ni$^{2+}$: Transverse Zeeman patterns for the 6024 and 6368 cm$^{-1}$ lines.
Fig. 4.7. SrO:Ni$^{2+}$: Zeeman patterns (circular polarization) for the 6024 and 6368 cm$^{-1}$ lines.
Fig. 4.8. SrO:Ni$^{2+}$: Transverse Zeeman patterns for the 6024 and 6368 cm$^{-1}$ lines.
Fig. 4.9. SrO:Ni$^{2+}$: Axial Zeeman patterns for the 6024 and 6368 cm$^{-1}$ lines.
Fig. 4.10 (a) The 7000 cm$^{-1}$ line exhibits the opposite circular polarization to that of the 6024 and 6368 cm$^{-1}$ lines, as does the 6408 cm$^{-1}$ line in (b). This shows the absorption is due to a $\Gamma_3 \rightarrow \Gamma_3$ transition.
lines. This is a clear indication that the excited state is of $\Gamma_3$ symmetry, as noted in the previous section. The rest of the Zeeman observations of this line are consistent with the assignment and, as will be shown elsewhere, consistent with crystal field calculations which suggest the infra-red lines are associated with the spin-orbit components $\Gamma_1 + \Gamma_2 + 2\Gamma_3$ of the $3^3E$ crystal field term. The 'hot' zero-phonon line at 6408 cm$^{-1}$ according to the crystal field calculation arises from a $\Gamma_1 \rightarrow \Gamma_3$ transition but no Zeeman polarization or shifts were observed (implying that the excited state splitting has not been resolved), as seen in Figure 4.10(b).

There remain two lines, the very strong zero-phonon line at 13520 cm$^{-1}$ and the weaker one in the infra-red at 4317 cm$^{-1}$. These behave similarly in field, showing very little sign of any polarization and only small shifts in the field (Figure 4.11(b)). This is only consistent with $\Gamma_3 \rightarrow \Gamma_3$ transitions which are predominantly $\pi$-allowed and the g-values of ground and excited states are only slightly different (to account for small shifts). These seem rather severe restrictions but it would appear that these conditions could arise as the crystal field analysis implies that the transition is associated with a $3^3A \rightarrow 3^3A$ transition and is likely to be only $\pi$-allowed. Furthermore, being orbital singlets the g-values will be both largely spin splitting and, hence, similar in magnitude. This will be discussed more fully later.

From the studies it is possible to evaluate the g-value of the ground state from the size of the field splitting. The patterns for the 15820 cm$^{-1}$ line are the most clearly resolved and these give $g \approx 2.3 \pm 0.1$. 
Fig. 4.11. SrO: Ni²⁺: Zeeman studies on the 13520 cm⁻¹ line.
4.4 Experimental Results

Co$^{2+}$ in SrO has been shown by EPR measurements to be in a site of trigonal symmetry [7]. Zeeman measurements on the 1353 cm$^{-1}$ line are shown in Figures 4.12, 4.13, 4.14 and 4.15 for two high symmetry field directions; it is observed that the $<100>$ field pattern appears the most simple (smallest number of lines) to analyse. This likewise implies trigonal symmetry as all centres are equivalent; for all other directions there are at least two groups of inequivalent orientations of the centres.

For field directions other than $<001>$ the separate lines are not fully resolved. In particular, no identification has been made of the lines with the field along the axis of the centre (i.e. the trigonal axis), for which group-theoretical selection rules could be used directly. The most straightforward case to analyze is that of the $<001>$ data.

4.5 Analysis

The symmetry of the centre is trigonal and assuming that the transitions are electric-dipole allowed it must also lack a centre of inversion. The only sub-groups of $O_h$ satisfying these conditions are $D_3$ and $C_{3v}$ for which the transformation properties are the same. We must, therefore, calculate the selection rules within these groups for transitions from a $\Gamma_4$ ground state to $\Gamma_4$ and $\Gamma_{5,6}$ excited states and treat the case where the field is not along the axes of the centre.

Consider one centre aligned along $<111>$:
Figure 4.12. SrO:Co$^{2+}$: transverse and axial Zeeman data ($H \parallel <100>$) for the 13538 cm$^{-1}$ line. Note that $\alpha \approx \sigma$ indicating the transition is electric dipole ($\alpha$: axial geometry without polarisation).
Figure 4.13. SrO:Co$^{2+}$: transverse and axial Zeeman data ($H \parallel <111>$) for the 13538 cm$^{-1}$ line. Again, $\alpha \approx \sigma$. 

---

For the 13538 cm$^{-1}$ line, the transverse and axial Zeeman data are shown with different symbols and directions. The graph illustrates the absorption spectrum in zero field and under an axial field ($H \parallel <111>$). The absorption peaks are labeled with different symbols ($\pi$, $\sigma$, $\alpha$, $\alpha^+$) to distinguish between the transverse and axial components. The axial field strength is indicated as 5 TESLA. The figure highlights the comparison between transverse and axial Zeeman effects, showing how the transitions are affected by the magnetic field orientation.
Figure 4.14. SrO:Co$^{2+}$: transverse and axial Zeeman data ($H \parallel <100>$) for the 13584 cm$^{-1}$ line. Note that $\alpha \approx \sigma$. 
Figure 4.15. SrO:Co$^{2+}$: transverse and axial Zeeman data ($H \parallel <111>$) for the 13584 cm$^{-1}$ line; $a \approx \sigma$, showing the transition is electric dipole.
The light vectors for a field along the centre transform as:

\[ \alpha^+: \Gamma_3^+ \left( \frac{1}{\sqrt{2}} (x+iy) \right) \]
\[ \alpha^-: \Gamma_3^- \left( \frac{1}{\sqrt{2}} (x-iy) \right) \]
and \( z \) or \( \pi: \Gamma_1 \)

and the selection rules are:

When the field is at an angle \( \theta \) to the \( <111> \) axis (a rotation \( \theta \) about \( y \)), the light vector can be re-expressed with respect to the field axis in terms of the vectors for \( H \parallel <111> \):
\[
\alpha^+ = (\frac{1}{2} + \frac{1}{2}\cos\theta)\alpha^+ - (\frac{1}{2} - \frac{1}{2}\cos\theta)\alpha^- - \frac{\sin\theta}{\sqrt{2}} z \tag{4.5-1}
\]

\[
\alpha^- = -(\frac{1}{2} - \frac{1}{2}\cos\theta)\alpha^+ + (\frac{1}{2} + \frac{1}{2}\cos\theta)\alpha^- - \frac{\sin\theta}{\sqrt{2}} z \tag{4.5-2}
\]

\[
z' = \frac{\sin\theta}{\sqrt{2}} \alpha^+ + \frac{\sin\theta}{\sqrt{2}} \alpha^- + \cos\theta z \tag{4.5-3}
\]

For ease of manipulation define:

\[
P = (\frac{1}{2} + \frac{1}{2}\cos\theta)
\]

\[
Q = (\frac{1}{2} - \frac{1}{2}\cos\theta)
\]

\[
R = \frac{1}{\sqrt{2}} \sin\theta
\]

\[
N = \cos\theta .
\]

With such a field direction the eigenstates are dependent on the \( g \) values, \( g_{||} \) and \( g_l \), of the state. The field along the \( z' \) axis transforms as

\[
S'_z = \frac{\sin\theta}{\sqrt{2}} S_+ + \frac{\sin\theta}{\sqrt{2}} S_- + \cos\theta S_z . \tag{4.5-4}
\]

The eigenstates are given by diagonalizing

\[
\begin{pmatrix}
\Gamma^+_4 \\
\Gamma^-_4 \\
\end{pmatrix}
\begin{pmatrix}
\Gamma^+_4 \\
\Gamma^-_4 \\
\end{pmatrix}
= \begin{pmatrix}
g_{||}\cos\theta & g_l\sin\theta \\
g_l\sin\theta & -g_{||}\cos\theta
\end{pmatrix} \tag{4.5-5}
\]

The eigenvalues are:

\[
\lambda = \pm \sqrt{g_{||}^2\cos^2\theta + g_l^2\sin^2\theta} \tag{4.5-6}
\]

and the eigenstates,
The eigenstates and eigenvalues of the ground $\Gamma_4$ and the excited $\Gamma_4$ states are, therefore, given in terms of the $g_\parallel$ and $g_\perp$ of the ground and excited states, respectively, where $C_1$ and $C_2$ are used for the ground state. The equivalent excited states are now labelled $d_1$ and $d_2$ for convenience.

The absorption of $\pi$-polarized, $\alpha^+$ (left-circularly polarized), and $\alpha^-$ (right-circularly polarized) light defined with respect to the $C_{3v}$ axis (the same result is obtained for a rotation about $x$ or $y$ and, hence, the system is axial about the trigonal centre) associated with the four transitions between the components of the $\Gamma_4$ states are given by the square of the following values.

\[
\begin{align*}
\Gamma_4^+ & \to \Gamma_4^+ \\
\alpha^+ & = -(P c_1 + Q c_2) A + R(c_1 + c_2) B \\
\alpha^- & = (Q c_1 - P c_2) A + R(c_1 + c_2) B \\
\pi^+ & = -(R c_1 - R c_2) A + N(c_1 + c_2) B \\
\end{align*}
\]
\( \pi' = -(Rc_1d_1 + Rc_2d_2)A + N(-c_1d_2 + c_2d_1)B \)  \hspace{1cm} (4.5-14)

where \( A = 1 \) for \( \sigma \)-transitions and \( B = 1 \) for \( \pi \)-transitions.

\( \Gamma_4^- \rightarrow \Gamma_4' \) or \( \Gamma_4^+ \) transitions are obtained from the above by the interchange of \( \alpha^+ \) and \( \alpha^- \), but for the consideration of low temperature Zeeman measurements it is simpler to restrict attention to transitions from \( \Gamma_4^+ \).

The intensity pattern is, therefore, given for any field direction in the \((1\overline{1}0)\) plane. Calculation can be made for \( \theta = 0^\circ \) (\( H \parallel <111> \)), \( \theta = -54^\circ \) (\( H \parallel <001> \)), \( \theta = 36^\circ \) (\( H \parallel <110> \)), and \( \theta = 72^\circ \) (\( H \parallel <11\overline{1}> \)). The outstanding field direction is the case of a field along \(<1\overline{1}0>\) which is not obtained for a rotation about the \( y \)-axis. Consideration is now given to \( H \parallel <001> \) for which good data is available. The value of \( P = 0.79, Q = 0.21, R = -0.58, N = 0.58, c_1 = 0.80 \) and \( c_2 = 0.60 \). The \( g \)-values of the ground state are taken from reference [7]: \( g_\parallel = 2.17 \) and \( g_\perp = 5.48 \).

Hence,

\[ \Gamma_4^+ \rightarrow \Gamma_4^+ \]

\[ \alpha^+ = -(0.5d_2 + 0.12d_1)A - (0.46d_1 + 0.34d_2)B \]  \hspace{1cm} (4.5-15)

\[ \alpha^- = (0.17d_2 + 0.47d_1)A - (0.46d_1 + 0.34d_2)B \]  \hspace{1cm} (4.5-16)

\[ \pi' = -(0.46d_2 - 0.35d_1)A + (0.46d_1 + 0.34d_2)B \]  \hspace{1cm} (4.5-17)

\[ \Gamma_4^+ \rightarrow \Gamma_4^- \]

\[ \alpha^+ = -(0.5d_1 - 0.12d_2)A + (0.46d_2 - 0.34d_1)B \]  \hspace{1cm} (4.5-18)

\[ \alpha^- = (0.17d_1 - 0.47d_2)A + (0.46d_2 - 0.34d_1)B \]  \hspace{1cm} (4.5-19)

\[ \pi' = -(0.46d_1 + 0.35d_2)A - (0.46d_2 - 0.34d_1)B \]  \hspace{1cm} (4.5-20)
It is noted that transitions polarized along the axis of the centre B ≠ 0 cannot by themselves give rise to polarized transitions at this angle (or preferentially circularly polarized transitions at any angle - not a surprising result). Consider, therefore, the case where A ≠ 0 (setting B = 0) – the strong circular polarization of the 13538 cm⁻¹ line indicates this is so. The values of d₁ and d₂ are determined by the g-values of the excited state. g <001> is known but not the individual components (analysis of other field directions should be able to be used to establish this but this has not been possible). Two extremes can arise – where g₁ = 0, then d₁ = 1 and d₂ = 0. When g₁ >> g∥, d₁ = \( \frac{1}{\sqrt{2}} \) and d₂ = \( \frac{1}{\sqrt{2}} \). The intensities are then:

\[
\begin{align*}
\Gamma_4^+ & \rightarrow \Gamma_4^+ \\
& \quad \text{ experiment (arb. units)} \\
& \text{d₁} >> \text{d₂} \
\end{align*}
\]

\[
\begin{align*}
\alpha^+ &= 0.06 & 0.77 & 0.3 \\
\alpha^- &= 0.88 & 0.82 & 1.1 \\
\pi' &= 0.49 & 0.02 & 0.6 \\
\end{align*}
\]

\[
\begin{align*}
\Gamma_4^+ & \rightarrow \Gamma_6^+ \\
& \quad \text{ experiment (arb. units)} \\
& \text{d₁} >> \text{d₂} \\
\end{align*}
\]

\[
\begin{align*}
\alpha^+ &= 1.00 & 0.29 & 1.0 \\
\alpha^- &= 0.12 & 0.18 & 0.01 \\
\pi' &= 0.84 & 1.30 & 1.4 \\
\end{align*}
\]

The \( \Gamma_4^+ \rightarrow \Gamma_4^+ \) prediction gives moderate agreement with the experimental intensity pattern. A small value for the d₁/d₂ ratio could improve the agreement. It should be noted, however, that a very similar
comparison could be made for a $\Gamma_4 + \Gamma_{5,6}$ transition (the analysis is similar to the case for $d_2 = 0$ as $g_\perp = 0$ exactly).

So if one starts off at $\theta = 0^\circ$ with only one circularly polarized transition allowed, by $\theta = 54^\circ$ all transitions are allowed. Moreover, because the sign of the g-value of the excited state is unknown, the polarity (left or right) of the parent electronic transition for $\theta = 0^\circ$ cannot be established. The interpretation of the $<001>$ data is, therefore, too flexible. True consistency for splitting (i.e. g-values) and polarizations must be obtained for the other field directions but the lack of resolution (not instrumental) has prohibited a satisfactory analysis.

The evidence supports the assignment of the 13538 cm\(^{-1}\) line as one zero-phonon line, probably associated with a $\Gamma_4$ excited state. Manson and Edgar previously claimed because of the presence of strong left- and right-circular polarization that at least two states, a $\Gamma_4$ and a $\Gamma_{5,6}$, must lie at this position. This, as seen from the calculation, need not be the case.

The line at 13584 cm\(^{-1}\) is significantly more complicated and more than the two components are seen for a field along $<001>$. This is taken to indicate the presence of more than one electronic origin but no more detailed analysis is possible. This appears plausible in terms of crystal field theory. The spin-orbit splitting of the lowest components of the $^4T_1$ crystal field term is of the order of ~100 cm\(^{-1}\) (see the next Chapter). No degenerate levels are predicted but this is not out of the question. There are insufficient energy levels to make a detailed fit. Degeneracies arising from other mechanisms such as a Jahn-Teller interaction may have to be considered but the presence of an off-centre distortion together with a Jahn-Teller distortion can
provide a very complex situation.

The above analysis is not considered entirely satisfactory and efforts to improve the fits are unwarranted without improving the \( <111> \) and \( <110> \) field data. This is further emphasized by Manson and Edgar who made MCD/EPR double resonance measurements. They showed that for a \( <100> \) field saturating the EPR line affected only the lower energy Zeeman component of the 13538 cm\(^{-1}\) line. The signal expected with the present model would be that the upper Zeeman component would be only a factor 2 smaller. In further work [8], they have shown that the MCD signal and the EPR modulated MCD signal do not correlate (see Fig. 4.16). Correlation would have been expected for any band arising from a single ground state irrespective of the excited state levels. The crystal had apparently only the \( C_{3v} \) centre and the overlap of other Co\(^{2+}\) lines seems unlikely. These measurements are not understood and remain an outstanding difficulty.

Zeeman measurements of the infra-red band are only partially complete. They give lines that are only weakly circularly polarized and this indicates the transitions are predominantly \( \pi \)-polarized (\( B \rightharpoonup A \)). This would be consistent with the trigonal crystal field model for a \( ^4\text{II} \rightarrow ^4\text{II} \) transition which would be likely to be \( \pi \)-polarized.
Figure 4.16. The upper figure is reproduced from reference [7]. The same authors have recently obtained the lower experimental traces. One trace is the MCD as in (c) above (except the line CD is totally absorbing and hence distorted). The second trace (noisier signal) is the change in the MCD when the trigonal EPR signal is saturated. The MCD band itself is of C-type, temperature dependent, and should be equivalent to the latter if associated with the same ground state.
References

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CHAPTER FIVE

CRYSTAL FIELD THEORY

PART A: SrO: Ni$^{2+}$

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5.3 Electronic Degeneracies in a Crystalline Environment
5.4 Terms and Configurations
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PART A: SrO: \( \text{Ni}^{2+} \)

5.1 Introduction

It has been shown in Chapter 4 that divalent nickel substitutes for strontium in SrO at a site of trigonal symmetry. The electronic configuration of \( \text{Ni}^{2+} \) is \( ls^22s^22p^63s^23p^64s^23d^8 \) and so there is an open shell of 8 3d-electrons. In this chapter conventional crystal field theory is adopted to evaluate the energy levels and corresponding eigenstates of the \( d^8 \) system in a trigonal environment.

The crystal field concept was first introduced in the early 1930's by Bethe [1], Van Vleck [2] and Schlapp and Penney [3,4]. In this original theory the open shell ion interacts with an electrostatic field arising from the neighbouring ligands represented by point charges. Any overlap between the ligand and impurity orbitals is neglected. Modern crystal field theory has developed considerably since then although the form the interaction with the lattice takes is not very different. The important point is that, provided the form of the interaction takes into account the symmetry of the problem and the strength of the interaction is handled using semi-empirical adjustable parameters, an accurate description of the energy levels and basis states can be obtained.

In this chapter a strong field approach is advantageous as the eigenstates, as will be seen, are very close to the strong field bases.
5.2 The Hamiltonian

The Hamiltonian for the \( N \) electrons of the impurity ion can be written as

\[
H = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} - \sum_{i=1}^{N} \frac{e^2}{|r_i|} + \frac{1}{2} \sum_{i,j=1}^{N} \frac{e^2}{|r_{ij}|} + \sum_{i=1}^{N} \xi(\mathbf{r}_i) \hat{L}_i \cdot \hat{S}_i + V(\mathbf{r}_i) .
\]

The first four terms in the Hamiltonian yield the usual atomic Hamiltonian operator: the first term represents the kinetic energy of the electrons, the second their potential energy due to the nucleus, the third is the two-electron operator, describing the exchange and Coulomb interaction, and the fourth describes the spin-orbit interaction. The last term, \( V(\mathbf{r}_i) \), expresses the effects of the superimposed non-spherical potential field produced by the ligands surrounding the impurity in question. Only electrons in the unfilled 3d-shell need be considered as the inner closed-shell electrons provide only a constant shift to the energy levels which are to be calculated.

5.3 Electronic Degeneracies in a Crystalline Environment

When an ion enters a crystal the degeneracies of the electronic terms of the free ion are lifted because of the crystalline symmetry. It can be an advantage to consider this in two steps. Initially the crystalline environment can be considered cubic and some degeneracy is removed; further degeneracies are lifted if the symmetry of the crystal field is lowered, in the present case to \( C_{3v} \) symmetry. Such reductions for the 0 and \( C_{3v} \) symmetries are shown in Table 5.1.
Table 5.1. Splitting of the free-ion terms in cubic and trigonal crystal fields. Trigonal representations are distinguished from the cubic by a caret.

For the $3d^N$ ions the splitting of the free-ion term is a consequence of the removal of the fivefold spatial degeneracy of the $d$-orbitals through interaction with a crystal field; remaining are the triply degenerate $t_2$-orbital and doubly degenerate $e$-orbital. Qualitatively, then, one may deduce the pattern of the energy levels from symmetry arguments alone. To arrive at a quantitative description of the system, however, a full quantum mechanical calculation using the appropriate crystal field model must be attempted.

### Table 5.1. Splitting of the free-ion terms in cubic and trigonal crystal fields. Trigonal representations are distinguished from the cubic by a caret.

<table>
<thead>
<tr>
<th>L</th>
<th>Symbol</th>
<th>$O$-representation</th>
<th>$C_{3v}$-representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>S</td>
<td>$A_1$</td>
<td>$\hat{A}_1$</td>
</tr>
<tr>
<td>1</td>
<td>P</td>
<td>$T_1$</td>
<td>$\hat{A}_2 + E$</td>
</tr>
<tr>
<td>2</td>
<td>D</td>
<td>$E + T_2$</td>
<td>$E + \hat{A}_1 + \hat{E}$</td>
</tr>
<tr>
<td>3</td>
<td>F</td>
<td>$A_2 + T_1 + T_2$</td>
<td>$\hat{A}_2 + \hat{A}_2 + \hat{E} + \hat{A}_1 + \hat{E}$</td>
</tr>
<tr>
<td>4</td>
<td>G</td>
<td>$A_1 + E + T_1 + T_2$</td>
<td>$\hat{A}_1 + \hat{E} + \hat{A}_2 + \hat{E} + \hat{A}_1 + \hat{E}$</td>
</tr>
</tbody>
</table>

5.4 **Terms and Configurations**

In an octahedral crystal field an electron can occupy either a triply degenerate level $t_2$, energy $-4Dq$, or a doubly degenerate $e$ level, energy $6Dq$, where $Dq$ is a measure of the octahedral field strength. The particular way the $N$ electrons are placed in the $e$ and
t_2 orbitals (with due respect to the Pauli principle!) is called a configuration.

In principle the energy levels of any N-electron system can be calculated but for larger N use can be made of the simple relationship between the matrix elements of operators in the states of the t_2^n e^(n+m=N) configuration and those in the complementary states of t_2^6-n e^(4-m) [5]. With this adjustment we can now discuss holes instead of electrons.

5.5 Construction of the Basis States

The best way to solve the Schrödinger equation is to firstly solve the following equation involving only one-electron operators:

\[ H_0 \psi(r_1 \sigma_1, r_2 \sigma_2, \ldots, r_N \sigma_N) = E_0 \psi(r_1 \sigma_1, r_2 \sigma_2, \ldots, r_N \sigma_N) \]  

(5.5-1)

where \( r \) is a spatial coordinate and \( \sigma \) a spin coordinate. The electron exchange/Coulomb term is then considered as a small perturbation.

The state function can be represented by a Slater determinant, which takes into account the anti-symmetrical nature of the electronic wavefunction,

\[
\psi(r_1 \sigma_1, r_2 \sigma_2, \ldots, r_N \sigma_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\phi_k(r_1 \sigma_1) & \phi_k(r_1 \sigma_1) & \ldots & \phi_k(r_1 \sigma_1) \\
\phi_k(r_2 \sigma_2) & \sigma_k(r_2 \sigma_2) & \ldots & \ldots \\
\ldots & \ldots & \ldots & \ldots \\
\phi_k(r_N \sigma_N) & \ldots & \ldots & \phi_k(r_N \sigma_N)
\end{vmatrix} \equiv |\phi_k \phi_k \ldots \phi_k| 
\]

(5.5-2)

The \( \phi \)'s are products of an orbital and a spin function and are called
spin-orbitals. Their construction is described in the following three sub-sections.

5.5.1 Two-spin functions

The spin eigenfunctions, \( \Phi \) (SM), are written as a linear combination of the product of two spin functions in the following manner:

\[
\Phi \text{(SM)} = \sum_{m_1 m_2} \theta(s_1 m_1) \theta(s_2 m_2) \langle s_1 m_1 s_2 m_2 | SM \rangle . \tag{5.5-3}
\]

\( \Phi \) (SM) is an eigenfunction of \( \hat{S}^2 \) and \( S_z \) and \( \theta(s_1 m_1) \) is an eigenfunction of \( \hat{s}^2 \) and \( s_{1z} \). The coefficients, \( \langle s_1 m_1 s_2 m_2 | SM \rangle \), in the summation are called Wigner coefficients. For the two-hole problem, \( s_1 = s_2 = \frac{1}{2} \) and the necessary coefficients appear in Table 5.2. The four spin functions are found in Table 5.3.

\[
s_2 = \frac{1}{2}
\]

<table>
<thead>
<tr>
<th>s = ( s_1 + \frac{1}{2} )</th>
<th>( m_2 = \frac{1}{2} )</th>
<th>( m_2 = -\frac{1}{2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sqrt{\frac{s_1 + m + \frac{1}{2}}{2s_1 + 1}} )</td>
<td>( \sqrt{\frac{s_1 - m + \frac{1}{2}}{2s_1 + 1}} )</td>
<td>( \sqrt{\frac{s_1 - m - \frac{1}{2}}{2s_1 + 1}} )</td>
</tr>
<tr>
<td>( \sqrt{\frac{s_1 - m + \frac{1}{2}}{2s_1 + 1}} )</td>
<td>( \sqrt{\frac{s_1 + m + \frac{1}{2}}{2s_1 + 1}} )</td>
<td>( \sqrt{\frac{s_1 - m - \frac{1}{2}}{2s_1 + 1}} )</td>
</tr>
</tbody>
</table>

Table 5.2. Wigner coefficients \( \langle s_1 m_1 s_2 m_2 | SM \rangle \).
Table 5.3. The spin eigenfunctions for the $d^{2,8}$ problem
($\uparrow: m = \frac{1}{2}$ and $\downarrow: m = -\frac{1}{2}$).

5.5.2 Two-orbital functions

The orbital functions are constructed in a similar way as the spin functions and are eigenfunctions of $L^2$ and $L_z$ written as linear combinations of product wave functions:

$$\psi(\Gamma_Y) = \sum_{\Gamma_1\Gamma_2} \phi(\Gamma_1\Gamma_1)\phi(\Gamma_2\Gamma_2) <\Gamma_1\Gamma_1\Gamma_2\Gamma_2|\Gamma_Y>$$  

(5.5-4)

where the Clebsch-Gordan (C-G) coefficients, $<\Gamma_1\Gamma_1\Gamma_2\Gamma_2|\Gamma_Y>$, form a unitary matrix. As the impurity has a local site symmetry of $C_3v$, use will be made of the C-G coefficients with trigonal bases, $<\Gamma_1\Gamma_1\Gamma_2\Gamma_2|\Gamma_M>$, which are expressible in terms of the cubic coefficients:

$$<\Gamma_1\Gamma_1\Gamma_2\Gamma_2|\Gamma_M> = \sum_{\Gamma_1\Gamma_1\Gamma_2\Gamma_2} <\Gamma_1\Gamma_1\Gamma_1\Gamma_1|\Gamma_M> <\Gamma_2\Gamma_2\Gamma_2\Gamma_2|\Gamma_M> <\Gamma_1\Gamma_1\Gamma_2\Gamma_2|\Gamma_M> <\Gamma_Y|\Gamma_M>$$  

(5.5-5)

The numerical coefficients $<\Gamma_Y|\Gamma_M>$ are:
\[ u = \begin{bmatrix} -1 & 1 \\ -i & -i \end{bmatrix} \times \frac{1}{\sqrt{2}} \]  

\[ \xi = \begin{bmatrix} -\bar{\omega} & \bar{\omega} & 1 \\ -\bar{\omega} & \omega & 1 \end{bmatrix} \times \frac{1}{\sqrt{3}} \]  

where \( \omega = e^{2\pi i/3} \) and \( \bar{\omega} = \omega^2 = e^{-2\pi i/3}. \)

The coefficients arise from the choice of the trigonal axes \((X,Y,Z)\), where \(Z\) and \(Y\) are chosen along the \(<111>-\) and \(<\overline{1}0\>\)-type directions respectively. The relation between the \(x, y\) and \(z\) cubic axes and the \(X, Y, Z\) axes is

\[ x = -\frac{1}{\sqrt{6}} X + \frac{1}{\sqrt{2}} Y + \frac{1}{\sqrt{3}} Z \]

\[ y = -\frac{1}{\sqrt{6}} X - \frac{1}{\sqrt{2}} Y + \frac{1}{\sqrt{3}} Z \]  

\[ z = \frac{\sqrt{2}}{\sqrt{3}} X + \frac{1}{\sqrt{3}} Z \]  

(5.5-8)

The components of the trigonal bases are listed in Table 5.4.
Irreducible representation | Component | Base $\phi(\Gamma M)$
--- | --- | ---
$T_1$ | $a_+$ | $Y_{11}(\theta\phi)$
 | $a_-$ | $Y_{1-1}(\theta\phi)$
 | $a_0$ | $Y_{10}(\theta\phi)$

$E$ | $u_+$ | $-[Y_{2-2}(\theta\phi) - \sqrt{2} Y_{21}(\theta\phi)]/\sqrt{3}$
 | $u_-$ | $[Y_{22}(\theta\phi) + \sqrt{2} Y_{2-1}(\theta\phi)]/\sqrt{3}$

$T_2$ | $x_+$ | $[-\sqrt{2} Y_{2-2}(\theta\phi) + Y_{21}(\theta\phi)]/\sqrt{3}$
 | $x_-$ | $[\sqrt{2} Y_{22}(\theta\phi) - Y_{2-1}(\theta\phi)]/\sqrt{3}$
 | $x_0$ | $Y_{20}(\theta\phi)$

Table 5.4. Components of the trigonal basis states. The spherical harmonics, $Y_{\ell m}$, are referred to the $X,Y,Z$ coordinate system.

5.5.3 The two-hole (electron) spin-orbital functions

We are now in a position to construct the 45 spin-orbital basis states. As an example, the state $|e_1^T a_0^0\rangle$ will be constructed here. Use is made of the $E \times T_2$ table of C-G coefficients in Table 5.5. A complete set of tables of the C-G coefficients with trigonal bases is given in Appendix I. The orbital component of the state function is $\frac{1}{\sqrt{2}} |u_+ x_-| - \frac{1}{\sqrt{2}} |u_- x_+|$. As the state is a singlet, the spin function is $\frac{1}{\sqrt{2}} (|\uparrow\downarrow> - |\downarrow\uparrow>)$ - see Table 5.3. Making use of the anti-symmetry of the determinantal functions,
\[ |e^{-\frac{i}{2}T_1 a_0} \rangle = \frac{1}{2} \left[ |u_- x_+ \rangle - |u_+ x_- \rangle - |x_- u_+ \rangle + |x_+ u_- \rangle \right] \] (S.5-9)

where the unbarred characters represent \( m = \frac{1}{2} \), the barred \( m = -\frac{1}{2} \).

\[
\begin{array}{c|c|c|c|c|c|c}
E \times T_2 & \Gamma & T_1 & T_2 \\
M_1 & M & a_+ & a_- & a_0 & x_+ & x_- & x_0 \\
\hline
x_+ & 0 & -\frac{i}{\sqrt{2}} & 0 & 0 & \frac{1}{\sqrt{2}} & 0 \\
u_+ x_- & 0 & 0 & \frac{i}{\sqrt{2}} & 0 & 0 & -\frac{1}{\sqrt{2}} \\
x_0 & -\frac{1}{\sqrt{2}} & 0 & 0 & \frac{1}{\sqrt{2}} & 0 & 0 \\
\hline
x_+ & 0 & 0 & \frac{i}{\sqrt{2}} & 0 & 0 & -\frac{1}{\sqrt{2}} \\
u_- & 0 & 0 & -\frac{i}{\sqrt{2}} & 0 & 0 & 0 \\
x_0 & 0 & \frac{i}{\sqrt{2}} & 0 & 0 & \frac{1}{\sqrt{2}} & 0 \\
\end{array}
\]

Table 5.5. Clebsch-Gordan coefficients, \( < \Gamma_{1} M_{1} \Gamma_{2} M_{2} | \Gamma M > \) with trigonal bases. The coefficients for \( |e^{-\frac{i}{2}T_1 a_0} \rangle \) are circled.

The full set of basis states are given in Table 5.6.

5.6 The Matrix Elements

5.6.1 The exchange and Coulomb matrix elements

The exchange and Coulomb terms are evaluated between the basis states by evaluating integrals of the form
Table 5.6. The basis states (written in the form of $|t_{2e}^{M}S\alpha M\rangle$) for the $3d^{2,3}$ system using trigonal coordinate geometry. They are listed in the order that the trigonal crystal field and spin-orbit matrix elements are given in Table 4.8.

1. $|t_{2}^{2}3T_{1a0}^{+}\rangle = -i|x_{+}x_{-}|$
2. $|t_{2}^{2}3T_{1a0}^{0}\rangle = -\frac{i}{\sqrt{2}} [|x_{+}x_{-}| - |x_{-}x_{+}|]$
3. $|t_{2}^{2}3T_{1a0}^{-}\rangle = -i|x_{+}x_{-}|$
4. $|t_{2e}^{3}3T_{1a0}^{+}\rangle = -\frac{i}{\sqrt{2}} [|u_{+}x_{-}| - |u_{-}x_{+}|]$
5. $|t_{2e}^{3}3T_{1a0}^{0}\rangle = -\frac{i}{2} [|u_{+}x_{+}| - |u_{+}x_{-}| + |x_{+}u_{+}| - |x_{-}u_{+}|]$
6. $|t_{2e}^{3}3T_{1a0}^{-}\rangle = -\frac{i}{\sqrt{2}} [|\bar{u}_{-}x_{+}| - |\bar{u}_{+}x_{-}|]$
7. $|e_{2}^{2}3A_{2e}^{2}^{+}\rangle = -i|u_{+}u_{-}|$
8. $|e_{2}^{2}3A_{2e}^{2}^{0}\rangle = -\frac{i}{\sqrt{2}} [|u_{+}\bar{u}_{-}| - |u_{-}\bar{u}_{+}|]$
9. $|e_{2}^{2}3A_{2e}^{2}^{-}\rangle = -i|\bar{u}_{+}\bar{u}_{-}|$
10. $|t_{2}^{2}3T_{1a}^{+}\rangle = -i|x_{+}x_{0}|$
11. $|t_{2}^{2}3T_{1a}^{+}\rangle = -\frac{i}{\sqrt{2}} [|x_{+}x_{0}| - |x_{0}x_{+}|]$
12. $|t_{2}^{2}3T_{1a}^{-}\rangle = -i|x_{+}x_{0}|$
13. $|t_{2}^{2}3T_{1a}^{-}\rangle = i|x_{-}x_{0}|$
14. $|t_{2}^{2}3T_{1a}^{-}\rangle = -\frac{i}{\sqrt{2}} [|x_{0}x_{-}| - |x_{-}x_{0}|]$
15. $|t_{2}^{2}3T_{1a}^{-}\rangle = i|x_{-}x_{0}|$
16. $|t_{2e}^{3}3T_{2x}^{+}\rangle = -\frac{1}{\sqrt{2}} [|u_{+}x_{-}| - |u_{-}x_{0}|]$
17. $|t_{2e}^{3}3T_{2x}^{0}\rangle = -\frac{1}{2} [|u_{+}x_{-}| - |u_{-}x_{0}| + |x_{0}u_{+}| - |x_{-}u_{+}|]$
18. $|t_{2e}^{3}3T_{2x}^{-}\rangle = -\frac{1}{\sqrt{2}} [|\bar{u}_{-}x_{+}| - |\bar{u}_{+}x_{0}|]$
19. $|t_{2e}^{3}3T_{2x}^{-}\rangle = -\frac{1}{\sqrt{2}} [-|u_{+}x_{+}| - |u_{-}x_{0}|]$
20. $|t_{2e}^{3}3T_{2x}^{-}\rangle = -\frac{1}{2} [-|u_{+}x_{+}| - |u_{-}x_{0}| + |x_{0}u_{+}| + |x_{-}u_{+}|]$
21. $|t_{2e}^{3}3T_{2x}^{-}\rangle = -\frac{1}{\sqrt{2}} [-|\bar{u}_{+}x_{+}| - |\bar{u}_{+}x_{0}|]$
22. $|t_{2e}^{3}3T_{1a}^{+}\rangle = -\frac{i}{\sqrt{2}} [|u_{+}x_{0}| + |u_{-}x_{-}|]$
23. $|t_{2e}^{3}3T_{1a}^{0}\rangle = -\frac{i}{2} [|u_{+}x_{0}| + |u_{-}x_{-}| - |x_{0}u_{+}| - |x_{-}u_{+}|]$
24. $|t_{2e}^{3}3T_{1a}^{-}\rangle = -\frac{i}{\sqrt{2}} [|\bar{u}_{+}x_{0}| + |\bar{u}_{-}x_{-}|]$

cont./...
Table 5.6. (cont’d)

| \[t_{2e}^3 T_{1a_+} > | & = & - \frac{1}{\sqrt{2}} \left[ |u_x^+| - |u_x^-| \right] \\
26. | \[t_{2e}^3 T_{1a_0} > | & = & - \frac{1}{2} \left[ |u_+ x^+| - |u_- x^-| - |x^+_+| + |x_0^-| \right] \\
27. | \[t_{2e}^3 T_{1a_-} > | & = & - \frac{1}{\sqrt{2}} \left[ |u^+_+| - |u^-^-| \right] \\
28. | \[t_{2e}^3 T_{2x_0} > | & = & - \frac{1}{\sqrt{3}} \left[ - \frac{1}{\sqrt{2}} |x^+ x^-| - \frac{1}{\sqrt{2}} |x^+_+| - \sqrt{2} |x_0 x^-| \right] \\
29. | \[t_{2e}^3 T_{1a_0} > | & = & - \frac{1}{\sqrt{2}} \left[ |u_+ x^-| + |u^- x^+| - |x^+_+| \right] \\
30. | \[t_{2e}^3 T_{1a_-} > | & = & - \frac{1}{\sqrt{2}} \left[ |u^+_+| + |u^-^-| \right] \\
31. | \[t_{2e}^3 T_{2x_0} > | & = & - \frac{1}{\sqrt{3}} \left[ - \frac{1}{\sqrt{2}} |x^+ x^-| + \frac{1}{\sqrt{2}} |x_0 x^-| \right] \\
32. | \[t_{2e}^3 T_{2x_+} > | & = & - \frac{1}{\sqrt{3}} \left[ \left( \frac{1}{\sqrt{2}} |x^+ x^-| + \sqrt{2} |x^- x^+| + \frac{1}{\sqrt{2}} |x_0 x^+| \right) \right] \\
33. | \[t_{2e}^3 T_{2x_0} > | & = & - \frac{1}{\sqrt{3}} \left[ - \sqrt{2} |x^+ x^-| + \frac{1}{\sqrt{2}} |x_0 x^-| + \frac{1}{\sqrt{2}} |x_0 x^+| \right] \\
34. | \[t_{2e}^3 T_{2x_0} > | & = & - \frac{1}{\sqrt{3}} \left[ |x^+ x^-| - |x_0 x^-| + |x_0 x^+| \right] \\
35. | \[t_{2e}^3 T_{2x_0} > | & = & - \frac{1}{\sqrt{3}} \left[ |x^+ x^-| - |x_- x^+| - |x_0 x^-| \right] \\
36. | \[t_{2e}^3 T_{2x_0} > | & = & - \frac{1}{2} \left[ |u^+_+| + |u^-^-| + |x^- x^+| + |x_0 x^-| \right] \\
37. | \[t_{2e}^3 T_{2x_0} > | & = & - \frac{1}{\sqrt{3}} \left[ |x^+ x^-| - |x_0 x^-| - |x_0 x^+| \right] \\
38. | \[t_{2e}^3 T_{2x_0} > | & = & - \frac{1}{\sqrt{3}} \left[ - |x^+ x^-| + |x_- x^+| + |x_0 x^-| \right] \\
39. | \[t_{2e}^3 T_{2x_0} > | & = & - \frac{1}{\sqrt{3}} \left[ - |x^+ x^-| + |x_0 x^-| + |x_0 x^+| \right] \\
40. | \[t_{2e}^3 T_{2x_0} > | & = & - \frac{1}{\sqrt{3}} \left[ - |x^+ x^-| - |x_0 x^-| - |x_0 x^+| \right] \\
41. | \[t_{2e}^3 T_{2x_0} > | & = & - \frac{1}{\sqrt{3}} \left[ - |x^- x^+| - |x_0 x^-| - |x_0 x^+| \right] \\
42. | \[t_{2e}^3 T_{2x_0} > | & = & - \frac{1}{\sqrt{3}} \left[ |x^+ x^-| + |x^- x^+| \right] \\
43. | \[t_{2e}^3 T_{2x_0} > | & = & - \frac{1}{\sqrt{3}} \left[ - |x^+ x^-| + |x_- x^+| - |x_0 x^-| \right] \\
44. | \[t_{2e}^3 T_{2x_0} > | & = & - \frac{1}{\sqrt{3}} \left[ - |x^+ x^-| + |x^- x^+| + |x_0 x^-| \right] \\
45. | \[t_{2e}^3 T_{2x_0} > | & = & - \frac{1}{\sqrt{3}} \left[ - |x^+ x^-| + |x_- x^+| + |x_0 x^-| \right] \\

\[ \sum dt_1 dt_2 \langle t_2^m e^n S_T \alpha M | g_{12} | t_2^{m'} e^{n'} S_T \alpha M \rangle \]  

(5.6-1)

where \( g_{12} \) is the two-electron operator in the Hamiltonian in (5.2-1). Evaluation is simplified as \( g_{12} \) is independent of spin coordinates and the spin-orbital can, as a consequence, be replaced by orbital functions. Results are expressible in terms of two-electron Coulomb and exchange integrals, which may be re-expressed by Racah parameters: A, B and C (the A term just shifts the energy levels by a constant amount and so, for convenience, will not appear in the matrix elements). These elements have been calculated by Tanabe and Sugano [6] and are found along with the octahedral field elements in Table 5.7.

<table>
<thead>
<tr>
<th>( ^1A_1 )</th>
<th>( ^3T_1 )</th>
<th>( ^1E )</th>
<th>( ^1T_2 )</th>
<th>( ^3A_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_2^2 )</td>
<td>( t_2^2 )</td>
<td>( t_2^2 )</td>
<td>( t_2^2 )</td>
<td>( t_2^2 )</td>
</tr>
<tr>
<td>( -8Dq + 10B )</td>
<td>( \sqrt{6}(2B+C) )</td>
<td>( -8Dq + B + 2C )</td>
<td>( -8Dq + B + 2C )</td>
<td>( 12Dq - 8B )</td>
</tr>
<tr>
<td>( e^2 )</td>
<td>( 12Dq + 8B + 4C )</td>
<td>( -2\sqrt{3}B )</td>
<td>( 2\sqrt{3}B )</td>
<td>( 12Dq - 8B )</td>
</tr>
<tr>
<td>( t_2^e )</td>
<td>( 2Dq + 4B )</td>
<td>( 2Dq + 2C )</td>
<td>( 2Dq + 2C )</td>
<td>( 2Dq - 8B )</td>
</tr>
</tbody>
</table>

Table 5.7. Matrix elements of the Coulomb/exchange and octahedral crystal field interactions. The matrices are symmetric.
5.6.2 The trigonal field interaction

The trigonal crystal field is a one-electron operator and transforms as $A_1 + T_2$ in the cubic group [7]. As $A_1$ is totally symmetric, its effect is to produce a uniform shift in all energy levels. The splitting of the cubic energy levels results solely from the part of the trigonal field transforming as $T_2, V_T^2$. Only the triply degenerate $T_1$ and $T_2$ states are split by $V_T^2$ as $T_1 \otimes T_1 \in T_2$ and $T_2 \otimes T_2 \in T_2$.

For an $N$-electron system the operator may be written as

$$V_T^2 = \sum_{i=1}^{N} V_{i}^T$$ (5.6-1)

and the strength of the crystal field can be defined by two parameters, $v$ and $v'$, originally defined by Pryce and Runciman [8]:

$$< x_\pm | v_T^2 | x_\pm > = -\frac{1}{3} v$$ (5.6-2)

$$< x_0 | v_T^2 | x_0 > = \frac{2}{3} v$$ (5.6-3)

and

$$< x_\pm | v_T^2 | u_\pm > = v'$$ (5.6-4)

Evaluation of $< t_2^1 T_1 a_+^0 | V_T^2 | t_2^2 T_2 x_+^0 >$ is given here as an example. From Table 5.6,

$$| t_2^1 T_1 a_+^0 > = -\frac{1}{2} \left[ | u_+ x_0 > + | u_- x_0 > + | x_0 u_+ > + | x_0 u_+ > \right]$$ (5.6-5)

and

$$| t_2^2 T_2 x_+^0 > = -\frac{1}{\sqrt{3}} \left[ \frac{1}{\sqrt{2}} | x_+ x_0 > + \sqrt{2} | x_- x_0 > + \frac{1}{\sqrt{2}} | x_0 x_+ > \right]$$ (5.6-6)

Using the orthonormality of the trigonal components, most of the terms in the matrix expansion are zero and we are left with
The trigonal crystal field matrix elements are included in Table 5.8.

5.6.3 The spin-orbit interaction

For a d^2 system the spin transforms as T_1 (or, in the reduced C_{3v} group, A_2 + E). Group theoretically we can predict the splitting pattern of the energy levels:

\[(A_2 + E) \otimes A_1 = A_2 + E\]  \hspace{1cm} (5.6-8)
\[(A_2 + E) \otimes A_2 = A_1 + E\]  \hspace{1cm} (5.6-9)
\[(A_2 + E) \otimes E = E + E + A_2 + A_1\]  \hspace{1cm} (5.6-10)

Quantitatively, evaluation of the matrix element

\[< a S T M | \Sigma \xi_1(r_1) \hat{l}_1 \cdot \hat{s}_1 | a' S' T' M' Y' >\] is required. With trigonal bases the matrix elements of the spin-orbit interaction are given as (see [5]),

\[< a S T M | H_{SO} | a S T M > = (-1)^{M_S - M'_S} ([2S+1](\Gamma))^{-\frac{1}{2}} < a S T \| V(T_1) \| a' S' T' > \times < S M | S' M' _1 M' _S - M' _S > < \Gamma M | \Gamma' T' _1 M' _S - M' _S >\]  \hspace{1cm} (5.6-11)

which is an expression for the Wigner-Eckart theorem for the matrix of
spin-orbit interaction. The M's represent the trigonal components, $x^\pm$, $x_0$, $a^\pm$, $a_0$ and $u^\pm$ (for $T_2$, $T_1$ and $E$ respectively) - they are zero for the components of $A_1$ and $A_2$. The a's represent the electron configuration. The double-barred matrices are reducible in terms of single electron functions:

$$< t^2 \text{em} \Gamma || V(1T_1) || t^2 \text{em}+1 \Gamma' > = C_0 < t^2 || v(1T_1) || e >$$ (5.6-12)

$$< t^2 \text{em} \Gamma || V(1T_1) || t^2 \text{em} \Gamma ' > = C_1 < t^2 || v(1T_1) || t_2 >$$ (5.6-13)

where $< t^2 || v(1T_1) || e > = -3\sqrt{2}i\xi$ and $< t^2 || v(1T_1) || t_2 > = 3i\xi$. The coefficients are found in the tables of reduced matrices of spin-orbit interaction reproduced from Sugano et al [5] in Appendix I.

As an example the matrix element $< t_2e^3T_2 x_+ + |H_{so}| e^2 \text{1E} u_0 >$ is calculated here:

Wigner coefficient: $< 11|0011 > = 1$ (see Appendix I)

Clebsch-Gordan coefficient: $< T_2 x_+ | Eu_{-1} t_1 a_2 > = -\frac{1}{\sqrt{2}}$ (see Appendix I)

$$(-1)^{M_S-M_S'} = -1$$

$$[(2S+1)(\Gamma)]^{1/2} = \frac{1}{3}$$

$$< t_2e^3T_2 || V(1T_1) || e^2 \text{1E} > = \frac{1}{\sqrt{2}} < t_2 || v(1T_1) || e >$$

$$= -3i\xi$$

$$< t_2e^3T_2 x_+ + |H_{so}| e^2 \text{1E} u_0 > = \frac{\xi}{\sqrt{2}}$$ (5.6-14)

A complete list of spin-orbit matrix elements appears in Table 5.8.
Table 5.8. The non-zero trigonal field and spin-orbit matrix elements

\[
A(i, j) = A^*(j, i).
\]

\[
\begin{align*}
A(1,1) & = -\frac{2}{3} \nu \\
A(2,2) & = -\frac{2}{3} \nu \\
A(3,3) & = -\frac{2}{3} \nu \\
A(1,4) & = \frac{\sqrt{2}}{2} \nu' \\
A(4,4) & = -\frac{1}{3} \nu \\
A(2,5) & = \frac{\sqrt{2}}{2} \nu' \\
A(5,5) & = -\frac{1}{3} \nu \\
A(3,6) & = \frac{\sqrt{2}}{2} \nu' \\
A(6,6) & = -\frac{1}{3} \nu \\
A(4,7) & = \frac{\sqrt{2}}{2} \nu' \\
A(5,8) & = \frac{\sqrt{2}}{2} \nu' \\
A(6,9) & = \frac{\sqrt{2}}{2} \nu' \\
A(10,10) & = -\frac{1}{3} \nu - \frac{1}{2} \zeta \\
A(1,11) & = -\frac{1}{2} \zeta \\
A(4,11) & = \frac{1}{2} \zeta \\
A(11,11) & = \frac{1}{3} \nu \\
A(2,12) & = -\frac{1}{2} \zeta \\
A(5,12) & = \frac{1}{2} \zeta \\
A(12,12) & = \frac{1}{3} \nu + \frac{1}{2} \zeta \\
A(2,13) & = -\frac{1}{2} \zeta \\
A(5,13) & = \frac{1}{2} \zeta \\
A(13,13) & = \frac{1}{3} \nu + \frac{1}{2} \zeta \\
A(3,14) & = -\frac{1}{2} \zeta \\
A(6,14) & = \frac{1}{2} \zeta \\
A(14,14) & = \frac{1}{3} \nu \\
A(15,15) & = \frac{1}{3} \nu - \frac{1}{2} \zeta \\
A(10,16) & = -\frac{i}{2} (\sqrt{2} \nu' - \zeta) \\
A(14,16) & = i \zeta \\
A(16,16) & = \frac{1}{6} \nu + \frac{1}{4} \zeta \\
A(1,17) & = -\frac{i}{2} \zeta \\
A(4,17) & = \frac{i}{4} \zeta \\
A(7,17) & = -i \zeta \\
A(11,17) & = -\frac{i}{\sqrt{2}} \nu' \\
A(15,17) & = i \zeta \\
A(17,17) & = \frac{1}{6} \nu \\
A(2,18) & = -\frac{i}{2} \zeta \\
A(5,18) & = \frac{i}{4} \zeta \\
A(8,18) & = -i \zeta \\
A(12,18) & = -\frac{i}{2} (\sqrt{2} \nu' + \zeta) \\
A(18,18) & = \frac{1}{6} \nu - \frac{1}{4} \zeta \\
A(2,19) & = \frac{i}{2} \zeta \\
A(5,19) & = -\frac{i}{4} \zeta \\
A(8,19) & = i \zeta \\
A(13,19) & = \frac{i}{2} (\sqrt{2} \nu' + \zeta) \\
A(19,19) & = \frac{1}{6} \nu - \frac{1}{4} \zeta \\
A(3,20) & = \frac{i}{2} \zeta \\
A(6,20) & = -\frac{i}{4} \zeta \\
A(9,20) & = i \zeta \\
A(10,20) & = i \zeta \\
A(14,20) & = \frac{i}{\sqrt{2}} \nu' \\
A(20,20) & = \frac{1}{6} \nu \\
A(11,21) & = i \zeta
\end{align*}
\]

cont./...
Table 5.8. (cont'd)

| A(15,21) | $\frac{i}{2} (\sqrt{2} \, v' - \zeta) $ |
| A(21,21) | $\frac{1}{6} v$ |
| A(10,22) | $-\frac{1}{2} (\sqrt{2} \, v' - \zeta) $ |
| A(16,22) | $-\frac{i}{4} (2v - \zeta) $ |
| A(20,22) | $\frac{i}{2} \zeta $ |
| A(22,22) | $\frac{1}{6} v + \frac{1}{4} \zeta $ |
| A(1,23) | $\frac{1}{2} \zeta $ |
| A(4,23) | $\frac{1}{4} \zeta $ |
| A(11,23) | $-\frac{1}{2} v' $ |
| A(17,23) | $-\frac{i}{2} v $ |
| A(21,23) | $\frac{i}{2} v $ |
| A(23,23) | $\frac{1}{6} v $ |
| A(2,24) | $\frac{1}{2} \zeta $ |
| A(5,24) | $\frac{1}{4} \zeta $ |
| A(12,24) | $-\frac{1}{2} (\sqrt{2} \, v' + \zeta) $ |
| A(18,24) | $-\frac{i}{4} (2v + \zeta) $ |
| A(24,24) | $\frac{1}{6} v - \frac{1}{4} \zeta $ |
| A(2,25) | $\frac{1}{2} \zeta $ |
| A(5,25) | $\frac{1}{4} \zeta $ |
| A(13,25) | $-\frac{1}{2} (\sqrt{2} \, v' + \zeta) $ |
| A(19,25) | $\frac{i}{2} (v + \zeta) $ |
| A(25,25) | $\frac{1}{6} v - \frac{1}{4} \zeta $ |
| A(3,26) | $\frac{1}{2} \zeta $ |
| A(6,26) | $\frac{1}{4} \zeta $ |
| A(14,26) | $-\frac{1}{2} v' $ |
| A(16,26) | $\frac{i}{2} \zeta $ |
| A(20,26) | $\frac{i}{2} v $ |

| A(26,26) | $\frac{1}{6} v $ |
| A(15,27) | $-\frac{1}{2} (\sqrt{2} \, v' - \zeta) $ |
| A(17,27) | $\frac{i}{2} \zeta $ |
| A(21,27) | $\frac{i}{4} (2v - \zeta) $ |
| A(27,27) | $\frac{1}{6} v + \frac{1}{4} \zeta $ |
| A(2,28) | $-\frac{i}{\sqrt{3}} \zeta $ |
| A(5,28) | $-\frac{i}{\sqrt{3}} \zeta $ |
| A(12,28) | $-\frac{i}{2\sqrt{3}} \zeta $ |
| A(13,28) | $-\frac{i}{2\sqrt{3}} \zeta $ |
| A(18,28) | $-\frac{\sqrt{3}}{2} \zeta $ |
| A(19,28) | $\frac{\sqrt{3}}{2} \zeta $ |
| A(24,28) | $-\frac{i}{2\sqrt{3}} \zeta $ |
| A(25,28) | $-\frac{i}{2\sqrt{3}} \zeta $ |
| A(2,29) | $\frac{2}{3} v $ |
| A(2,29) | $\frac{2}{3} v $ |
| A(5,29) | $\frac{i\sqrt{3}}{2} \zeta $ |
| A(12,29) | $-\frac{\sqrt{3}}{2} \zeta $ |
| A(13,29) | $-\frac{\sqrt{3}}{2} \zeta $ |
| A(24,29) | $-\frac{i\sqrt{3}}{2} \zeta $ |
| A(25,29) | $-\frac{i\sqrt{3}}{2} \zeta $ |
| A(28,29) | $\frac{2\sqrt{2}}{3} v $ |
| A(2,30) | $i\zeta $ |
| A(5,30) | $\frac{i}{2} \zeta $ |
| A(8,30) | $i\zeta $ |
| A(12,30) | $\frac{1}{2} \zeta $ |
| A(13,30) | $\frac{1}{2} \zeta $ |
| A(18,30) | $\frac{i}{4} \zeta $ |

cont./...
<table>
<thead>
<tr>
<th>Table 5.8. (cont'd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(19,30) = - $\frac{1}{4} \zeta$</td>
</tr>
<tr>
<td>A(24,30) = $\frac{i}{4} \zeta$</td>
</tr>
<tr>
<td>A(25,30) = $\frac{i}{4} \zeta$</td>
</tr>
<tr>
<td>A(28,30) = $-\frac{\sqrt{2}}{\sqrt{3}} v'$</td>
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<td>A(29,30) = $\frac{2}{\sqrt{3}} v'$</td>
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<td>A(30,30) = $-\frac{1}{3} v$</td>
</tr>
<tr>
<td>A(5,31) = $i\zeta$</td>
</tr>
<tr>
<td>A(24,31) = $-i\zeta$</td>
</tr>
<tr>
<td>A(25,31) = $-i\zeta$</td>
</tr>
<tr>
<td>A(30,31) = $\sqrt{2} v'$</td>
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</tr>
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</tr>
<tr>
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</tr>
<tr>
<td>A(6,33) = $\frac{i}{2\sqrt{3}} \zeta$</td>
</tr>
<tr>
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</tr>
<tr>
<td>A(22,33) = $-\frac{i}{\sqrt{3}} \zeta$</td>
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<tr>
<td>A(26,33) = $\frac{i}{2\sqrt{3}} \zeta$</td>
</tr>
<tr>
<td>A(33,33) = $-\frac{i}{3} v$</td>
</tr>
<tr>
<td>A(1,34) = $-\frac{i}{\sqrt{6}} \zeta$</td>
</tr>
<tr>
<td>A(4,34) = $\frac{i\sqrt{2}}{\sqrt{3}} \zeta$</td>
</tr>
</tbody>
</table>

cont./...
Table 5.8. (cont'd)

| A(20,37) | = | $-\frac{1}{4} \zeta$ | A(27,40) | = | $-\frac{i}{\sqrt{2}} \zeta$ |
| A(22,37) | = | $\frac{i}{2} \zeta$ | A(36,40) | = | $-v'$ |
| A(26,37) | = | $-\frac{i}{4} \zeta$ | A(38,40) | = | $iv'$ |
| A(33,37) | = | $\frac{1}{4\sqrt{2}} v'$ | A(6,41) | = | $\frac{i}{\sqrt{2}} \zeta$ |
| A(35,37) | = | $\frac{1}{\sqrt{3}} v'$ | A(16,41) | = | $\frac{1}{\sqrt{2}} \zeta$ |
| A(37,37) | = | $\frac{1}{6} v$ | A(20,41) | = | $\frac{1}{\sqrt{2}} \zeta$ |
| A(1,38) | = | $\frac{1}{2} \zeta$ | A(22,41) | = | $\frac{i}{\sqrt{2}} \zeta$ |
| A(4,38) | = | $-\frac{1}{4} \zeta$ | A(26,41) | = | $\frac{i}{\sqrt{2}} \zeta$ |
| A(11,38) | = | $-\frac{i}{2} \zeta$ | A(38,41) | = | $-v'$ |
| A(17,38) | = | $\frac{i}{4} \zeta$ | A(39,41) | = | $-iv'$ |
| A(21,38) | = | $\frac{1}{2} \zeta$ | A(1,42) | = | $-i\zeta$ |
| A(23,38) = | $\frac{1}{4} \zeta$ | A(4,42) | = | $\frac{i}{2} \zeta$ |
| A(32,38) | = | $\frac{i\sqrt{3}}{\sqrt{2}} v'$ | A(7,42) | = | $i\zeta$ |
| A(36,38) | = | $-\frac{i}{2} v$ | A(11,42) | = | $-\frac{i}{2} \zeta$ |
| A(38,38) | = | $\frac{1}{6} \zeta$ | A(17,42) | = | $\frac{1}{4} \zeta$ |
| A(3,39) | = | $-\frac{1}{2} \zeta$ | A(23,42) | = | $\frac{i}{4} \zeta$ |
| A(6,39) | = | $\frac{1}{4} \zeta$ | A(32,42) | = | $\frac{\sqrt{3}}{2} \zeta$ |
| A(14,39) | = | $\frac{1}{2} \zeta$ | A(36,42) | = | $-\frac{1}{4} \zeta$ |
| A(16,39) | = | $-\frac{i}{2} \zeta$ | A(38,42) | = | $-\frac{i}{4} \zeta$ |
| A(20,39) = | $\frac{i}{4} \zeta$ | A(40,42) | = | $-\frac{1}{\sqrt{2}} \zeta$ |
| A(26,39) = | $-\frac{1}{4} \zeta$ | A(42,42) | = | $-\frac{1}{3} v$ |
| A(33,39) | = | $-\frac{i\sqrt{3}}{\sqrt{2}} v'$ | A(12,43) | = | $-\frac{1}{2} \zeta$ |
| A(37,39) | = | $\frac{i}{2} v$ | A(13,43) | = | $\frac{i}{2} \zeta$ |
| A(39,39) = | $\frac{1}{6} \zeta$ | A(18,43) | = | $\frac{1}{4} \zeta$ |
| A(4,40) = | $\frac{i}{\sqrt{2}} \zeta$ | A(19,43) | = | $\frac{1}{4} \zeta$ |
| A(17,40) = | $-\frac{1}{\sqrt{2}} \zeta$ | A(24,43) | = | $\frac{i}{4} \zeta$ |
| A(21,40) = | $\frac{1}{\sqrt{2}} \zeta$ | A(25,43) | = | $-\frac{i}{4} \zeta$ |
| A(23,40) = | $\frac{i}{\sqrt{2}} \zeta$ | A(43,43) = | $-\frac{1}{3} v$ |

cont./...
Table 5.8. (cont'd)

\begin{align*}
A(4,44) & = i\zeta \\
A(6,44) & = -\frac{1}{2} \zeta \\
A(9,44) & = -i\zeta \\
A(14,44) & = \frac{1}{2} \zeta \\
A(20,44) & = \frac{1}{4} \zeta \\
A(26,44) & = -\frac{1}{4} \zeta \\
A(33,44) & = -\frac{\sqrt{3}}{2} \zeta \\
A(37,44) & = \frac{1}{4} \zeta \\
A(39,44) & = -\frac{1}{4} \zeta \\
A(41,44) & = \frac{1}{\sqrt{2}} \zeta \\
A(44,44) & = -\frac{1}{3} \nu \\
A(12,45) & = -\frac{1}{2} \zeta \\
A(13,45) & = \frac{1}{2} \zeta \\
A(18,45) & = -\frac{1}{4} \zeta \\
A(19,45) & = -\frac{i}{4} \zeta \\
A(24,45) & = \frac{1}{4} \zeta \\
A(25,45) & = -\frac{1}{4} \zeta \\
A(43,45) & = -\frac{1}{2} \zeta \\
A(45,45) & = -\frac{1}{3} \nu 
\end{align*}
Some of these matrix elements were checked against those calculated by Rahman and Runciman [9], who used the same trigonal bases; the authors, however, did not calculate all the spin-orbit elements and, as a consequence, the full calculation using the matrix elements in Tables 5.7 and 5.8 was compared with a weak field calculation performed by MacFarlane [10] using the following parameters:

\[
\begin{align*}
D_q &= 1800 \text{ cm}^{-1} \quad B = 610 \text{ cm}^{-1} \quad C = 2500 \text{ cm}^{-1} \quad v = 800 \text{ cm}^{-1} \\
v' &= 200 \text{ cm}^{-1} \quad \zeta = 155 \text{ cm}^{-1}.
\end{align*}
\]

The $45 \times 45$ matrix was machine diagonalised and exact agreement was obtained.

5.7 Discussion of the Crystal Field Parameters

The problem is to parameterize the four strong bands observed in the experiment at 19000, 15800, 13500 and 6000 cm$^{-1}$. The results of a $d^{2,8}$ cubic field calculation are reproduced in Figure 5.1 from reference [11]. For the present case spin-orbit, $B$, and $C$ have not been used as entirely free parameters, rather they have been given values slightly lower than the free ion values for Ni$^{2+}$.

Calculation of selection rules for $C_{3v}$ $^{3}A_2 \rightarrow ^{3}A_2$ and $^{3}A_2 \rightarrow ^{3}E$ electric dipole transitions have been made using the coupling coefficients of Koster [12](see Appendix I). The results are summarised for the infra-red band in Figure 5.2. It means that a $^{3}A_2 \rightarrow ^{3}A_2$ will only give one strong $\pi$ transition from the $\Gamma_3$ component of the ground state (the Greek script denotes the spin-orbit component of the trigonal term). This is the observed situation for the 13500 cm$^{-1}$ band and consequently the line is assigned to $^{3}A_2(\Gamma_3) \rightarrow ^{3}A_2(\Gamma_3)$ transition.
The calculation also suggests that transitions from the $\Gamma_3$ component of the ground state should give three lines with the symmetry of the excited state being $\Gamma_1$, $\Gamma_2$ and $\Gamma_3$ belonging to a $3E$ trigonal level. This is exactly what is observed in the 6000 cm$^{-1}$ band. Furthermore, the hot band possibly to an $\Gamma_3$ level is also produced in the model. So the components of the spin-orbit split $3E$ are all located.

With the above assignments it is possible to select two values of $D_q$, about $-600$ cm$^{-1}$ and $-320$ cm$^{-1}$, which give rise to spin-allowed bands at 6000 and 13500 cm$^{-1}$. In the first model (A) they would arise from trigonally split components of the $3T_1^a$ term, whereas in the second model (B) the infra-red band arises from this term and the strong bands in the visible would have their origin in the $3T_1^b$ term.

There are, however, a number of indications that model B with the lower cubic field parameter is actually the correct physical situation. The splitting of the $3T_1^b$ term into the $3E$ and $3A$ trigonal components varies as $-(v-v')$ and that of the $3T_1^a$ as $-(v+v')$. To achieve the observed energy level ordering with model A requires a large negative $v$ and positive $v'$. However, such parameter values do not give the $\Gamma_3$ component of $3A_2$ as the ground state. Model B with a positive $v$ gives the correct order of ground state components and increasing the magnitude of $-v'$ reduces the ground state splitting. In addition, this model gives the right ordering of the excited states.

The A level (at 15800 cm$^{-1}$) giving the rather weak band at 15800 cm$^{-1}$ is not predicted, however, and is an outstanding difficulty, and remained so even when attempting to adjust the crystal field parameters in both minor and major ways (see Appendix II). We have not been able in any of these attempts to obtain a triplet level ($S=1$) at this position while simultaneously fitting the other stronger bands (20000, 13500 and
Figure 5.1. Energy level curves for a $d^8$ electronic system immersed in a field of octahedral symmetry for $\zeta = -550 \text{ cm}^{-1}$, $B = 950 \text{ cm}^{-1}$ and $C = 3150 \text{ cm}^{-1}$ [11].
Figure 5.2. The selection rules for the infra-red band allowed transitions are indicated. All of the $^3\Sigma$ spin-orbit components are observed. The 'hot' line at 6408 cm$^{-1}$ is not observed at low temperatures because it violates the spin-conservation rule ($\Delta m_s = 0$). The line observed at 4317 cm$^{-1}$ might be due to the $^3\Pi_2(\Gamma_3) \rightarrow ^3\Sigma_2(\Gamma_3)$ transition. The spin-orbit functions are composed from the table of coupling coefficients in Appendix I.
6000) as triplets, i.e. spin allowed. The strength of the 15800 cm\(^{-1}\) indicates that it is more likely anyway to arise from a singlet level and hence to be associated with a spin-forbidden transition. Familiarity with Ni\(^{2+}\) spin-forbidden transitions in other systems would suggest that this could arise from \(^1E\) or the \(^1T_2\). However, of these the only \(\Gamma_1\) or \(\Gamma_2\) level is that associated with the \(^1T_2\). This state is split in similar fashion (order and magnitude) to the higher \(^3T_{1g}\) band and hence always appears below the \(^3A_2\) component of the \(^2T_{1g}\) which is claimed to lie at 13500 cm\(^{-1}\). The spin-orbit splitting of the \(^3A_2\) itself, even allowing for the interaction with this state, cannot displace by 2300 cm\(^{-1}\) from the \(^3A_2(\Gamma_3)\) component (see Fig. 5.3). Further experiments such as EPR/MCD double resonance seem desirable to conclusively establish that this band does indeed arise from the same centre.

An energy level diagram based on model B is shown in Figure 5.2 where \(Dq\), \(B\), \(C\) and \(\xi\) are fixed and the trigonal field components are varied in a fixed ratio \(\frac{v'}{v} = -\frac{1}{4}\) and we see that the spin-allowed bands are reasonably well predicted. It will be shown in the next section (Part B) that a similar value of \(Dq\) is used to fit the spectrum of SrO:Co\(^{2+}\) and so adds additional support to the present choice of model.
Figure 5.3. The energy levels of a $d^8$ system (SrO:Ni$^{2+}$) with $D_q = -320$ cm$^{-1}$, $B = 850$ cm$^{-1}$, $C = 3700$ cm$^{-1}$, $\zeta = -600$ cm$^{-1}$, and $v' = -v/4$. The $O_h$ terms are indicated on the left. The $\cdots$ are singly degenerate levels and $\ldots$ are doubly degenerate levels.
5.8 Introduction

Co$^{2+}$ has the electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$ and so represents a 3-hole system. The 3-hole problem is treated theoretically in much the same way as that for the 2-hole system, and only a very brief group theoretical description of the states will be given here, followed by an example of an energy level calculation. A more detailed account for finding the states appears in Chapter 3 of reference [5].

5.9 The Symmetry of the 3-hole state functions

The three holes (electrons) are placed, as in the $d^{2.8}$ case, into the $t_2$ and e orbitals to form configurations $e^3$, $t^2 e^2$, $t^2 e$ and $t^3$. There are 120 ways of placing the 3 holes into the ten 3d orbitals. The terms arising from the configurations can be found by taking each of the orbital terms arising from the two hole configurations ($e^2$, et$_2$, t$_2^2$) and combining each with a further $t_2$ or e orbital making sure not to violate Pauli's exclusion principle! Table 5.9 lists the terms for Co$^{2+}$.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Terms</th>
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<tbody>
<tr>
<td>$t^3_2$</td>
<td>$^u T_2$ $^2 E$ $^2 T_1$ $^2 T_2$</td>
</tr>
<tr>
<td>$t^2 e$</td>
<td>$^u T_1$ $^u T_2$ $^2 A_1$ $^2 A_2$ $^2 E$ $^2 T_1$ $^2 T_2$</td>
</tr>
<tr>
<td>te$^2$</td>
<td>$^u T_1$ $^2 T_1$ $^2 T_2$</td>
</tr>
</tbody>
</table>

Table 5.9. Terms arising for Co$^{2+}$ (d$^7$).
5.10 The Trigonal Field and Spin-Orbit Reductions

The cobalt ion has been shown through EPR studies to have local \( C_{3v} \) symmetry and so the orbitally triply degenerate cubic state functions undergo the following reductions in the low symmetry crystal field:

\[
T_1 \rightarrow \hat{A}_2 + \hat{E} \\
T_2 \rightarrow \hat{A}_1 + \hat{E}
\]

where the caret signifies we are working in the trigonal group.

Further degeneracies in the state functions are lifted by the spin-orbit interaction. Spin ± \( \frac{1}{2} \) transforms as \( \Gamma_4 \) and spin ± \( \frac{3}{2} \) transforms as \( \Gamma_4 + \Gamma_{5,6} \) under the group \( C_{3v} \). Spin-orbit components of the crystal field terms are found by forming the direct products \( \Gamma_{\text{spin}} \otimes \Gamma_{\text{orbit}} \). As an example, a \( ^4\hat{A}_2 \) state will split into two components under the spin-orbit interaction:

\[
\Gamma_{\text{spin}} \otimes \Gamma_{\text{orbit}} = (\Gamma_4 + \Gamma_{5,6}) \otimes (\hat{A}_2) = \Gamma_4 + \Gamma_{5,6}.
\]

The list of spin-orbit components for \( \text{Co}^{2+} \) is given in Table 4.11. \( \Gamma_4, \Gamma_5 \) and \( \Gamma_6 \) are particular irreducible representations of the \( C_{3v} \) double group; \( \Gamma_5 \) and \( \Gamma_6 \) irreducible representations are complex conjugates and are degenerate in the absence of a magnetic field - hence, the labelling \( \Gamma_{5,6} \). The components appearing in Table 5.11 are all Kramer doublets.
5.11 The Energy Level Calculation

The energy matrices of the octahedral crystal field, Coulomb, and exchange interactions (Dq, B and C) have been calculated in the strong field coupling scheme by Tanabe and Sugano [6]; spin-orbit (ξ) matrix elements have been published by Runciman and Schroeder [13]. The trigonal field interaction is represented, as in the previous chapter, by v and v'. The complete set of matrix elements for a full calculation were privately communicated [14] and the matrix was machine diagonalised; the calculation was checked by comparing the eigenvalues with the energy levels in reference [15] which used the same strong field scheme. There was exact agreement.

5.12 Discussion of Parameters

As with nickel, a low value of Dq was favoured (B and C were fixed) and a relatively large trigonal field parameter was required to separate the \( ^4\hat{E} \) and \( ^4\hat{A} \) components of the \( ^4T_{1} \) term in the visible.
The crystal field calculation with the following parameters:

\[ D_q = -320 \text{ cm}^{-1}, \quad B = 760 \text{ cm}^{-1}, \quad C = 3500 \text{ cm}^{-1}, \quad v = 816 \text{ cm}^{-1}, \]
\[ v' = -2333 \text{ cm}^{-1} \text{ and } \zeta = -450 \text{ cm}^{-1} \]

predicts spin-allowed bands at \( 17700 \text{ cm}^{-1} (^4\Delta) \), \( 14000 \text{ cm}^{-1} (^4\Sigma) \) and \( 7200 \text{ cm}^{-1} (^4\Sigma) \) with the correct trigonal ground term of \( ^4\Delta \) from the \( ^4T_1 \).

A rigorous fit of the energy levels was not attempted here because of the small number of energy levels observed plus the fact that these could not be exclusively identified. The spin-orbit interaction predicts a splitting of approximately 100 cm\(^{-1}\) between the spin-orbit components of the \( ^4\Sigma \) absorption at about 14000 cm\(^{-1}\) where the 13584 and 13538 cm\(^{-1}\) lines are found.

It is not quite understood why components of the \( ^4T_2 \) were not observed - it indicates the presence of strong selection rules, as seems to be the case for nickel.
References

CHAPTER 6

OFF-CENTRE INSTABILITIES

6.1 Introduction

6.2 Description of the Calculation

6.3 Results
6.1 Introduction

Over the last decade considerable attention has been given to systems exhibiting induced dipoles [1,2], such as KCl containing trace amounts of lithium. Experiments involving paraelectric cooling [3] and ultrasonic propagation [4] have provided evidence that the lithium ion substitutes for the potassium ion but does not sit at the regular lattice site, preferring equivalent 'off-centre' locations. Qualitatively one might expect a possible lattice distortion whenever there is a large mis-match in ionic radius between the substituent and replaced ion, as is the case with Li$^+$ (0.68 Å) and K$^+$ (1.33 Å). The attractive electrostatic interaction could then overcome the repulsive forces which normally stabilise the impurity ion at the regular lattice site. Mathew [5] was the first to demonstrate how this could occur and obtained a minimum in the potential energy away from the ideal lattice site. His work was quickly succeeded with calculations of a more fundamental nature by two groups: Wilson et al. [6], and Quigley and Das [7], both employing a polarizable point-ion model with repulsion between nearest neighbours given by Born-Mayer-type potentials. They were successful in showing that off-centre configurations for KCl:Li$^+$ along 4-, 3- and 2-fold axes had lower energies than the substitutional centrosymmetric site.

A similar situation may arise here as both the ions Ni$^{2+}$ (ionic radius 0.69 Å) and Co$^{2+}$ (ionic radius 0.74 Å) are substantially smaller than the displaced ion strontium (ionic radius 1.12 Å) and a calculation of the location of the energy minimum in these two cases has been undertaken.
6.2 Description of the Calculation

The approach adopted in the case of SrO:Ni and SrO:Co$^{2+}$ is similar to that of Quigley and Das [7]. A cubic lattice network of 125 point-charge ions was set up and the energy of the impurity-containing lattice was calculated with respect to the perfect lattice, where the strontium assumed a centrosymmetric site. The following interactions were considered:

a) a Coulomb point-charge interaction, including a crystal field interaction with the surrounding lattice ($\Delta E_e$),

b) a Born-Mayer-Verwey-type repulsive potential ($\Delta E_R$), and

c) a monopole-dipole interaction and a dipole-dipole interaction ($\Delta E_p$).

The paramagnetic defect is allowed to displace along three directions $<111>$, $<110>$, and $<100>$ and the nearest neighbour anions were allowed to relax with respect to the impurity under the constraint of maintaining $C_{3v}$, $C_{2v}$, and $C_{4v}$ symmetry respectively. The parameters describing the relaxation of the seven ions are defined in Fig. 6.1.

The electrostatic interaction is taken over the relaxed ions and, additionally, over virtual charge pairs ($\pm q$) created at regular lattice sites. This allows the use of a cubic potential arising from charges at normal lattice sites. So,

$$
\Delta E_e = \sum_{J=1}^{7} \sum_{K=1}^{7} q_J q_K \left( \frac{1}{r_{JK}^2} + \frac{1}{r_{JK}^2} - \frac{1}{r_{JK}^2} - \frac{1}{r_{JK}^2} \right) + \sum_{J=1}^{7} q_J V_L(x,y,z)
$$

(6.2-1)

where the primed notation refers to relaxed positions, and the unprimed
Figure 6.1. Definition of the displacement parameters for <111>, <110>, and <100> off-centre motion.
to normal lattice sites; $r_{J,K}$, for instance, is the distance between
relaxed ion J and an ion sitting at a lattice site (a virtual charge
in this case).

The cubic potential $V_L$ is expressed in Cartesian coordinates:

$$V_L = \frac{35}{4} (-1.0275) \left[ x^4 + y^4 + z^4 - \frac{3}{5} r^4 \right] - \frac{21}{2} (-1.3339)$$

$$\times \left\{ x^6 + y^6 + z^6 + \frac{15}{4} \left[ x^4 y^2 + x^2 y^4 + x^4 z^2 + x^2 z^4 + y^4 z^2 + y^2 z^4 \right] - \frac{15}{14} r^6 \right\}$$

(6.2-2)

where use has been made of expanding the crystal field potential in
terms of Legendre polynomials [8] and truncating the expression after
the first few even terms.

The repulsive potential was of the Born-Mayer-Verwey type:

$$R_{BMV}(r) = A \exp \left( -\frac{r}{\rho} \right) \quad r \geq r_0$$

(6.2-3)

$$= B + \frac{C}{r^{12}} \quad r \leq r_0$$

(6.2-4)

where $r$ is the interionic separation and $r_0$ the sum of the ionic radii.
A and $\rho$ are constants relevant to the particular interaction under scrutiny
(e.g. SrO, NiO, CoO), as are B and C which are evaluated by imposing
continuity conditions on the potential and its first derivative. Values
for A and $\rho$ were taken from Clendenen and Drickamer [9] and Das [10].

The repulsive energy change is obtained by taking the difference between
the pairwise sum of nearest neighbour repulsive energies in the distorted
SrO: Ni, Co lattice and the SrO lattice. The 7 central ions are allowed
to relax and we consider the change in repulsive energy for these ions
and their nearest neighbours:
<table>
<thead>
<tr>
<th>Crystal</th>
<th>Nearest-neighbour distance (Å)</th>
<th>Repulsive-force parameter, A (ergs)</th>
<th>Repulsive-force parameter, ρ(Å)</th>
<th>Positive ion polarizability (Å³)</th>
<th>Negative ion polarizability</th>
</tr>
</thead>
<tbody>
<tr>
<td>N10</td>
<td>2.09</td>
<td>$1.602 \times 10^{-9}$ [9]</td>
<td>0.324 [9]</td>
<td>0.39 [12]</td>
<td>2.0</td>
</tr>
<tr>
<td>CoO</td>
<td>2.13</td>
<td>$1.670 \times 10^{-9}$ [9]</td>
<td>0.324 [9]</td>
<td>0.42 [12]</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table 6.1. Constants used in the calculation. B and C are evaluated by imposing continuity conditions on the potential and its first derivative.
A difficulty arises in obtaining a reliable determination of these two parameters A and p associated with the Ni,Co $\leftrightarrow$ O repulsive interaction in the SrO lattice. A and p have been established for NiO and CoO [9] but the interionic distances in these crystals need not be the same as those in the doped SrO system. The quantitative aspects of this calculation may therefore be rather unreliable.

The dipole terms in (c) arise solely from the central ionic displacement which induces dipoles in the surrounding ligands through relaxation. The polarization energy involves:

(i) the interaction of each point dipole with the electric field arising from the other ions (dipole-monopole term), and

(ii) the interaction between the dipoles (dipole-dipole).

The polarization term may be formulated in the following way:

$$
\Delta E_p = -\frac{1}{2} \sum_{I=1}^{7} \alpha_I \sum_{J=1, K=1}^{125, 125} \frac{e_I e_J}{|r_{I,J}^*|^3} \frac{\hat{r}_{I,K}^*}{|r_{I,K}^*|^3} + \frac{1}{2} \sum_{I=1}^{7} \sum_{J=1, K=1}^{125, 125} \frac{E_{I,J}' E_{J,I}'}{|\hat{r}_{I,J}'|^3} \frac{3(\hat{r}_{I,J}'^*, \hat{E}_{I,J}^*) (\hat{r}_{I,J}'^*, \hat{E}_{J,I}^*)}{|r_{I,J}^*|^5}.
$$

Suffices have been primed to indicate that the seven ions allowed to displace are in their relaxed positions. $\alpha_I$ is the electronic polarizability.
of the ion in question and values for these were taken from Tessman et al. [11] and Fraga et al. [12]. These are included with the other input parameters in Table 6.1.

Minimum energy configurations were found using a principal axis method described in reference 13.

6.3 Results

The minimum energy configurations for both SrO:Ni\(^{2+}\) and SrO:Co\(^{2+}\) are shown in Table 6.2. The results of the calculations for the three symmetry directions are displayed in Figure 6.2 (nickel) and in Figure 6.3 (cobalt). In each case the impurity favours an off-centre site along a \(<111>\) -direction, displacing by about ~0.5 Å from the substitutional site. The potential well is slightly deeper for nickel than for cobalt by about ~0.08 eV, a result not surprising considering a simple hard sphere model; the cobalt radius of 0.74 Å is slightly larger than that of nickel's (0.69 Å).

In parallel to this work Edgar and Haider [14] have shown that Fe\(^{2+}\) undergoes a similar distortion in a SrO host; they included in the Hamiltonian additional terms arising from low symmetry crystal fields and covalency contributions which effectively reduce the charge of all ions by about 5%. A comprehensive study involving off-centre displacements of paramagnetic ions in SrO has been compiled by Haider [15] who used these extra terms in calculations involving a network of 343 ions of which 26 were allowed to relax. He found that the inclusion of the extra terms for both cases, cobalt and nickel, produced softer potentials but did not affect the size of off-centre displacement.
<table>
<thead>
<tr>
<th>Impurity displacement along</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
<th>P5</th>
<th>P6</th>
<th>P7</th>
<th>Off-centre by (Å)</th>
<th>Potential well depth (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 111 &gt;</td>
<td>12</td>
<td>7</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>0.53</td>
<td>-0.26</td>
</tr>
<tr>
<td>&lt; 110 &gt;</td>
<td>12</td>
<td>8</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>-3</td>
<td>1</td>
<td>0.43</td>
<td>-0.20</td>
</tr>
<tr>
<td>&lt; 100 &gt;</td>
<td>10</td>
<td>9</td>
<td>0</td>
<td>1</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>0.26</td>
<td>-0.11</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SrO :Co$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 111 &gt;</td>
</tr>
<tr>
<td>&lt; 110 &gt;</td>
</tr>
<tr>
<td>&lt; 100 &gt;</td>
</tr>
</tbody>
</table>

Table 6.2. Off-centre displacement parameters for SrO:Ni$^{2+}$ and SrO:Co$^{2+}$. The P parameters are given in percentage of the nearest-neighbour lattice distance. Potential well depths are given with respect to the minimum energy for the impurity sitting at the normal lattice site.
Figure 6.2. Predictions of the off-centre calculation for SrO: Ni$^{2+}$. 
Figure 6.3. The Co$^{2+}$ ion is also shown to prefer an off-centre site along the trigonal axis.
Whilst the quantitative aspects of these calculations are not entirely reliable, they do provide very substantial justification for 'off-centre' location for the nickel and cobalt ions in strontium oxide which has been proposed in Chapters 3 and 4. The experimentally determined barrier heights (see Chapter 8) are smaller (by a factor of about 5x) and suggest the consideration of a larger complex and other terms may provide more realistic quantities. However, the ratio between the barrier heights for nickel and cobalt is observed to lie close to that predicted by calculation.
References

CHAPTER 7

HEAT TREATMENTS

7.1 Introduction

7.2 Experimental Procedure

7.3 Experimental Results

7.3.1 Heat-treatments

7.3.2 Absorption

7.3.3 Magnetic Field Measurements

7.4 The Polarization of the Field-Induced Lines

7.5 Comparison with Experimental Polarizations

7.6 Discussion of the Centre

7.7 Heat-Treatments on SrO:Co$_{2}^{2+}$
7.1 Introduction

The absorption of SrO:Ni$^{2+}$ has its origin in two main centres. The trigonal centre has already been discussed at length and in this Chapter a description of the other centre, previously described as $C_{2v}$, will be presented. The aim is to gain some insight into the thermal generation and annihilation, and consequently the nature, of the centre.

7.2 Experimental Procedure

A Gallenkamp muffler furnace with a 3 cm internal diameter aluminium oxide tube inserted in the horizontal axial hole was used for heating the samples at 1350°C or below. For heat-treatments at higher temperatures an E.M.I. radio frequency furnace was available - temperatures in this case were estimated with an optical pyrometer. The samples could be heated in static air (no air flowing), flowing oxygen, and flowing nitrogen. Crystals were, in addition, heat-treated in a vacuum ($\sim 10^{-5}$ torr) molybdenum wire-wound furnace, capable of producing temperatures of up to 1400°C. Samples could be quenched by displacing them from the high temperature portion of the aluminium oxide tube into a beaker of oil at room temperature, or annealed (still in their respective atmospheres) by switching down the furnace.

Low temperature absorption measurements were made to monitor the effect of heating the crystals in the various atmospheres. Zeeman studies were again used to locate the site symmetry of the centre.

7.3 Experimental Results

7.3.1 Heat-treatments

A representative sample of absorption measurements in the visible on as-grown SrO:Ni$^{2+}$ crystals has appeared in Chapter 3,
Figures 3.3(a) to (f), and it is quite evident that two different centres are responsible for the strong bands at ~14500 cm\(^{-1}\) and 13500 cm\(^{-1}\) (the C\(_{3v}\) centre is held responsible for the 15800 cm\(^{-1}\) band too). There was no correlation between the appearance of any of the absorption bands and bulk strain, observed through crossed polars. Subsequent heating in oxygen and reducing atmospheres has the effect of altering the relative strengths of these absorption bands. Examples of this cycling on the absorption bands in the visible are shown in Figures 7.1 and 7.2. There was no measurable difference between quenching and annealing the crystals.

Heat-treating in air had the same effect as heating in oxygen - C\(_{2v}\) band intensity increases, whereas the C\(_{3v}\) band becomes weaker. The conversion, however, was slower in air. Heat-treatment in reducing atmospheres had the reverse effect on the spectrum - conversion was faster in vacuum than in nitrogen. The pair lines also increased in intensity, as well as the C\(_{3v}\) band. The rate of conversion was also faster with higher temperature and slower at lower temperature with no measurable conversion below ~1000°C. The effect of cumulative heat-treatments is displayed in Figure 7.3.

7.3.2 Absorption

The centre created by the oxidizing conditions gives absorption bands in the near infra-red at 8000 cm\(^{-1}\) (1250 nm) and the visible at 14500 (690 nm) and 20000 cm\(^{-1}\) (500 nm). The strength of the bands is similar to that of the C\(_{3v}\) absorptions. The temperature behaviour of the visible band has already been discussed in Chapter 3. Of primary interest is the very detailed vibronic band with its electronic origin at 14340 cm\(^{-1}\) (697.4 nm). Several other but weaker
Figure 7.1. SrO:Ni$^{2+}$: heating in flowing oxygen. The effect of cumulative heat-treatments in other atmospheres was studied - see Figure 7.3.
Figure 7.2. SrO:Ni$^{2+}$: heating in flowing nitrogen. The same effect was observed when using a vacuum environment.
Figure 7.3. SrO:Ni$^{2+}$: heat-treatments in reducing and oxidizing atmospheres. The intensity of the $C_{2vs}$ band has been normalised with respect to the total intensity of the 13500 and 14500 cm$^{-1}$ absorptions.
sharp lines were present at higher temperatures: 14270 cm\(^{-1}\) (753.6 nm) and 13675 cm\(^{-1}\). The vibrational sideband of the 14340 cm\(^{-1}\) line is found in Figure 7.4(a) and below in Figure 7.4(b) the vibrations coupling onto the 14270 cm\(^{-1}\) line are also shown. A temperature dependence plot of this transition (Figure 7.5) indicates it has an origin about 10 cm\(^{-1}\) above the ground state; the 13675 cm\(^{-1}\) line has the same origin. Figure 7.4(c) shows the sharp infra-red line associated with this centre.

The effect of various perturbations (as well as heat-treatments) on the optical absorption was investigated. Several measurements were made without positive results. The magnetic circular dichroism (MCD) was recorded but no signal was observed. This indicates that the centre is of a low symmetry where all (but accidental) degeneracies are lifted. Uniaxial stress measurements of the sharp lines were likewise unsuccessful in that the crystals fractured before any splitting pattern was resolved. Modulated electric field measurements were used and these did give meaningful signals. From the lineshapes it is concluded that the centre does not possess a centre of inversion. In addition, the high temperature modulated electric field lineshapes are different to those obtained for the C\(_{3v}\) bands and this reflects the different nature of the two centres. The electric field measurements are presented in the next chapter.

The magnetic field measurements are far from uninformative. Although neither splitting nor polarization of the zero-phonon lines is observed, additional lines appear in the presence of a magnetic field. They are polarized and their polarization imposes some restrictions on the symmetry of the centre.
Figure 7.4. (a) and (b) show the vibrational sideband structure of the two origins at 14340 and 14270 cm$^{-1}$.

(c) The line in the infra-red which intensity correlates with the visible band.
Figure 7.5. The line at 14270 cm\(^{-1}\) has its origin -10 cm\(^{-1}\) above the ground state, found from this temperature dependence analysis. \(I(697)\) is the intensity of the 14340 cm\(^{-1}\) line.
7.3.3 Magnetic Field Measurements

Two field-induced lines are observed. They appear 10 cm$^{-1}$ to the high energy side of the lines at 13675 and 14270 cm$^{-1}$ respectively, see Figure 7.6. The lines are not circularly polarized and so only the transverse patterns are shown in Figures 7.7 & 7.8 for the field directions $<100>$, $<111>$, and $<110>$.

The field-induced transitions originate from the true ground state; they are clearly forbidden (or exceedingly weak) in the absence of a field. The 'hot' lines at 13675 and 14270 cm$^{-1}$ decrease slightly in a field but this can be attributed to an increase in the separation of the two ground state components from ~10 cm$^{-1}$ to ~11 cm$^{-1}$ as a consequence of the field mixing. Such a change in energy would lead to a 30% decrease in intensity at 4.2K. At very high temperatures ~50K the population of the level at 10 cm$^{-1}$ will not be affected by small changes in energy. Correspondingly at these temperatures there is simply a direct transfer of intensity from one line to the other, amounting to, in the largest case, ~25% at 5 tesla.

It is possible that these lines are group theoretically forbidden and consideration is now given to the possible point group involved. The site group must be a subgroup of 0$_h$ without inversion symmetry where all the single group representations are non-degenerate. The only group satisfying these conditions and giving transitions forbidden by symmetry is C$_{2v}$. Given, however, a non-degenerate ground state $\Gamma_i$, transitions to only one other irreducible representation $\Gamma$ will be forbidden. Field mixing in the ground state with a neighbouring state $\Gamma_j$ may permit the initial transitions to be seen but on these symmetry arguments the polarization of the lines could be predicted and, therefore, all field-induced transitions would have the same
Figure 7.6 Under application of a magnetic field, two other transitions at 14280 and 13685 cm$^{-1}$ are induced.
Figure 7.7. Experimental polarizations of the field-induced line at 13685 cm\(^{-1}\). (—— \(\pi\), ----- \(\sigma\), ..... no field).
Figure 7.8. Experimental polarizations of the field-induced transition at 14280 cm\(^{-1}\). (----- \(\pi\), ----- \(\sigma\), .... no field).
polarization. This is not the case as the line at 13685 cm\(^{-1}\) is preferentially \(\sigma\), whereas the line at 14280 cm\(^{-1}\) is preferentially \(\pi\)-polarized. This situation cannot be reached on strictly group-theoretical arguments. Therefore, although one of these transitions in zero field may still be symmetry forbidden, the other must simply be 'accidentally' weak. Accordingly they may both be accidentally weak in which case the restriction to only the \(C_{2v}\) group is not justified.

In SrO:Co\(^{2+}\), as was mentioned in Chapter 3, Section 3.1, site symmetries of \(C_{2v}\) and \(C_s\) have been observed for crystals heated in oxygen. Considering the very similar behaviour of Ni\(^{2+}\) and Co\(^{2+}\) in SrO in many other aspects it seems a strong possibility that SrO:Ni\(^{2+}\) crystals will likewise produce centres of equivalent symmetry. Here only one centre is observed but it is likely to have either \(C_{2v}\) or \(C_s\) symmetry. As the 13500 and 14500 cm\(^{-1}\) bands are similar in oscillator strength it is likely that they have the same origin. The intense zero-phonon line at 13520 cm\(^{-1}\) is attributed to a \(\left(3\hat{A}\right)\Gamma_3 \rightarrow \left(3\hat{A}\right)\Gamma_3\) transition at the \(C_{3v}\) centre and the transitions at each site are polarized along the \(C_{3v}\) axis (summing the crystallographically equivalent \(C_{3v}\) centres results in an unpolarized line in a cubic crystal). If the symmetry is lowered to \(C_s\) then both ground and excited states will split and give only two transitions polarized along the \(z\) axis as in the following diagram:

![Diagram](image)
This could lead to a satisfactory account of the lines at 14270 and 14340 cm\(^{-1}\). For this to be correct the field mixing would be caused by the component of the field along the \(<111>\) axis, i.e. the polarization would be equivalent to a centre of \(C_{3v}\) symmetry. A calculation of the polarizations is made in the following section.

### 7.4 The Polarization of the Field-Induced Lines

A general case of \(C_s\) symmetry is considered and centres of \(C_{3v}\) and \(C_{2v}\) (and \(C_{4v}\)) symmetry become special cases which lie in a \((011)\) plane. For one centre the component of the field along a direction \(\theta\) to the \(<001>\) axis is considered to cause the mixing of the ground state wavefunctions and it is assumed that this results in a transition which is polarized along the same direction (\(\pi\)-polarized). (Later polarizations along directions at right angles to the field are also considered).

Each centre has an \(x\), \(y\) and \(z\)-axis, fixed with respect to the centre; \(x\) and \(z\) are in the reflection plane, the \((1\overline{1}0)\) plane and \(y\) is perpendicular to it. The component of the field along a direction \(\theta\) to the \(<001>\) axis will induce the transition and the transition will be polarized along this direction. This is taken as the \(z\)-axis of the centre. The problem is to calculate the observed polarization of the field induced lines for all angles \(\theta\) from 0° \(<001>\), through 54° \(<111>\) to 90° \(<110>\). In addition, for each centre at angle \(\theta\) there will be eleven other centres related to the first by symmetry. There is no splitting observed and consequently the intensity contribution from each has to be summed.

The axes for one centre are defined by the following diagram:
Consider a three-level system $i$, $j$, and $e$ where only the $j \rightarrow e$ transition is allowed. In particular,

$$< e | P_\alpha | j > = 1 \quad \text{and} \quad < e | P_\alpha | i > = 0$$  \hspace{1cm} (7.4-1)

where $P_\alpha$ is the operator involved in the transition. Assume it is the component of the field along the $z_1$-axis which causes the relevant field mixing. Then using first-order perturbation theory the ground state wavefunction becomes

$$| i > + a \hat{H} \cdot z_1 | j >.$$  \hspace{1cm} (7.4-2)
Hence, the transition matrix element between the ground state and state \( e \) becomes allowed and is equal to \( \alpha \hat{H} \cdot \hat{z}_1 I \) and polarized in the same sense as the transition \( e \rightarrow j \), i.e. \( P_\alpha \).

Consider firstly a transition which is polarized along the \( z_1 \) axis of the centre, i.e.

\[
\langle e | P_\alpha | j \rangle = \langle e | z_1 | j \rangle = I_z .
\]  

(7.4-3)

The allowed transition matrix element is given by \( \langle e | \hat{E} \cdot \hat{z}_1 | j \rangle \), where \( \hat{E} \) is the light vector, and the field induced matrix element is

\[
\alpha (\hat{H} \cdot \hat{z}_1) (\hat{E} \cdot \hat{z}_1) I_z .
\]  

(7.4-4)

When considering intensities this expression is squared.

Evaluation must be made of the vector product of the centre \( z_1 \) axis with the magnetic field and the electromagnetic field's electric vector. The latter two are related and the parallel case corresponds to \( \pi \)-polarization and the orthogonal to \( \sigma \)-polarization. For a \( <001> \) field direction

\[
\frac{\hat{H} \cdot \hat{z}_1}{|\hat{H} \cdot \hat{z}_1|} = \cos \theta \]  

(7.4-5a)

for \( \pi \):

\[
\frac{\hat{E} \cdot \hat{z}_1}{|\hat{E} \cdot \hat{z}_1|} = \cos \theta \]  

(7.4-5b)

for \( \sigma \):

\[
\frac{\hat{E} \cdot \hat{z}_1}{|\hat{E} \cdot \hat{z}_1|} = \frac{1}{\sqrt{2}} \sin \theta .
\]  

(7.4-5c)

This means for the one centre the contribution to the \( \pi \) intensity (neglecting a constant proportionality term) is \( \cos^4 \theta \) and to the \( \sigma \)
intensity, $\frac{1}{2}\sin^2\theta\cos^2\theta$. It is a trivial exercise to generate the direction cosines of the other 11 symmetry-related centres by rotation about the cubic 4- and 3-fold axes. They are listed in Table 7.1. By finding their projection on the $<001>$ and $<100>$ directions their contribution to the above measurement may also be found. This gives as the total intensity of a field induced line:

$$\pi\text{-polarization: } 4(\cos^4\theta + \frac{1}{2}\sin^4\theta)$$

and $\sigma\text{-polarization: } 4(\cos^2\theta\sin^2\theta + \frac{1}{2}\sin^4\theta)$. 

The analytic functions are shown in Figure 7.9 for the three high symmetry field directions. Equivalent expressions have been obtained for the $e \rightarrow j$ transition when polarized along the $x_1$- or $y_1$-directions by replacing $\hat{E} \cdot \hat{z}_1$ by $\hat{E} \cdot \hat{x}_1$ and $\hat{E} \cdot \hat{y}_1$ respectively. The intensities are likewise displayed in Figure 7.9. The analytic functions are summarised in Table 7.2.

7.5 Comparison with Experimental Polarizations

The observed intensities should correspond to the values calculated above (or some superposition of them) and used to determine the value of $\theta$ and consequently the symmetry of the centre.

The 13685 cm$^{-1}$ line is observed in $\sigma$ polarization for a magnetic field along the $<001>$ direction. This establishes that the angle $\theta$ must be $0^\circ$ or $90^\circ$ or close to those limits. The other line at 14280 cm$^{-1}$ is preferentially $\pi$-polarized but with the smallest $\pi/\sigma$ ratio in the case of a $<001>$ field direction. This is only consistent with $\theta = 90^\circ$ or close to it and this would restrict the 13685 cm$^{-1}$ line to $x$ polarization. The observed polarizations are consistent with a value $\theta \approx 70^\circ - 90^\circ$ if some allowance is made for depolarization. The
Table 7.1. Axes of the \((x_1, y_1, z_1)\) 12 equivalent \(C_s\) centres. The \(x_1\) and \(z_1\) axes lie in the \(C_s\) mirror-plane and \(y_1\) is perpendicular to it. 

\(\theta\) is the angle \(z_1\) makes with the <001> axis.

<table>
<thead>
<tr>
<th>(x_1)</th>
<th>(y_1)</th>
<th>(z_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((-\frac{1}{\sqrt{2}} \cos \theta \quad \frac{1}{\sqrt{2}} \cos \theta \quad -\sin \theta))</td>
<td>((-\frac{1}{\sqrt{2}} \cos \theta \quad \frac{1}{\sqrt{2}} \cos \theta \quad -\sin \theta))</td>
<td>((-\frac{1}{\sqrt{2}} \sin \theta \quad \frac{1}{\sqrt{2}} \sin \theta \quad \cos \theta))</td>
</tr>
<tr>
<td>((-\frac{1}{\sqrt{2}} \cos \theta \quad -\sin \theta \quad \frac{1}{\sqrt{2}} \cos \theta))</td>
<td>((-\frac{1}{\sqrt{2}} \cos \theta \quad -\sin \theta \quad \frac{1}{\sqrt{2}} \cos \theta))</td>
<td>((-\frac{1}{\sqrt{2}} \sin \theta \quad \frac{1}{\sqrt{2}} \sin \theta \quad \cos \theta))</td>
</tr>
<tr>
<td>((-\sin \theta \quad \frac{1}{\sqrt{2}} \cos \theta \quad \frac{1}{\sqrt{2}} \cos \theta))</td>
<td>((-\sin \theta \quad \frac{1}{\sqrt{2}} \cos \theta \quad \frac{1}{\sqrt{2}} \cos \theta))</td>
<td>((-\frac{1}{\sqrt{2}} \sin \theta \quad \frac{1}{\sqrt{2}} \sin \theta \quad \cos \theta))</td>
</tr>
<tr>
<td>((\frac{1}{\sqrt{2}} \cos \theta \quad \frac{1}{\sqrt{2}} \cos \theta \quad -\sin \theta)) ((\frac{1}{\sqrt{2}} \cos \theta \quad \frac{1}{\sqrt{2}} \cos \theta \quad -\sin \theta))</td>
<td>((\frac{1}{\sqrt{2}} \cos \theta \quad \frac{1}{\sqrt{2}} \cos \theta \quad -\sin \theta)) ((\frac{1}{\sqrt{2}} \cos \theta \quad \frac{1}{\sqrt{2}} \cos \theta \quad -\sin \theta))</td>
<td>((\frac{1}{\sqrt{2}} \sin \theta \quad \frac{1}{\sqrt{2}} \sin \theta \quad \cos \theta)) ((\frac{1}{\sqrt{2}} \sin \theta \quad \frac{1}{\sqrt{2}} \sin \theta \quad \cos \theta))</td>
</tr>
<tr>
<td>((-\sin \theta \quad \frac{1}{\sqrt{2}} \cos \theta \quad \frac{1}{\sqrt{2}} \cos \theta))</td>
<td>((-\sin \theta \quad \frac{1}{\sqrt{2}} \cos \theta \quad \frac{1}{\sqrt{2}} \cos \theta))</td>
<td>((-\frac{1}{\sqrt{2}} \sin \theta \quad \frac{1}{\sqrt{2}} \sin \theta \quad \cos \theta))</td>
</tr>
</tbody>
</table>
Figure 7.9. Calculated polarizations for the field-induced lines (— π, —— σ; for the <110>: ———— observe <110> and .... observe <001>).
Table 7.2. Analytic expressions for the intensity of field-induced lines.

\[(\sqrt{2}\sin\theta + \cos\theta) = A \quad (\sin\theta + \sqrt{2}\cos\theta) = C\]
\[(\sqrt{2}\sin\theta - \cos\theta) = B \quad (\sin\theta - \sqrt{2}\cos\theta) = D\]

Field along \(<001>\)

for \(z\) transitions
\[
\begin{align*}
\sigma_z & : 4(\cos^4\theta + \sin^4\theta) \\
\sigma_y & : 2\cos^4\theta + 2\sin^4\theta + \cos^2\theta \sin^2\theta
\end{align*}
\]

Field along \(<111>\)

\[
\begin{align*}
\pi_z & : \frac{1}{3} A^4 + \frac{1}{3} B^4 + \frac{2}{3} \cos^4\theta \\
\pi_x & : \frac{1}{3} A^2 B^2 + \frac{1}{3} B^2 C^2 + \frac{2}{3} \sin^2\theta \cos^2\theta \\
\pi_y & : \frac{4}{3} \cos^2\theta
\end{align*}
\]

Field along \(<110>\)

\[
\begin{align*}
\sigma_z <001> & : 2\sin^2\theta \cos^2\theta + \frac{1}{2} C^2 \sin^2\theta + \frac{1}{2} D^2 \sin^2\theta \\
\sigma_x <001> & : 2\sin^4\theta + \frac{1}{2} C^2 \cos^2\theta + \frac{1}{2} D^2 \cos^2\theta \\
\sigma_y <001> & : \frac{1}{4} C^2 + \frac{1}{2} D^2
\end{align*}
\]

\[
\begin{align*}
\sigma_x <110> & : 2\sin^4\theta + \frac{1}{2} C^2 \cos^2\theta + \frac{1}{2} D^2 \cos^2\theta \\
\sigma_y <110> & : \frac{1}{4} C^2 + \frac{1}{2} D^2 + 2 \sin^2\theta
\end{align*}
\]
\( \pi/\sigma \) ratio for \( \theta=90^\circ \) and the various field directions are given in Table 7.3 together with the observed ratio \( \pi/\sigma \):  

<table>
<thead>
<tr>
<th>Field direction</th>
<th>(&lt;001&gt;)</th>
<th>(&lt;111&gt;)</th>
<th>(&lt;110&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>z-polarized</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>predicted</td>
<td>2</td>
<td>4</td>
<td>5 (obs.&lt;001&gt;)</td>
</tr>
<tr>
<td>experimental (14280)</td>
<td>1.4±0.2</td>
<td>2.4±0.2</td>
<td>3.1±0.2</td>
</tr>
<tr>
<td><strong>x-polarized</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>predicted</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>experimental (13685)</td>
<td>0.1±0.1</td>
<td>1.0±0.2</td>
<td>0.7±0.2</td>
</tr>
</tbody>
</table>

Table 7.3. Comparison between experiment and calculation for the field-induced lines (indicated in brackets).

Allowing for \(-15\%\) depolarization of the light these values make reasonable comparison. Unfortunately the presence of any depolarization for these specific traces was not recorded. 15% depolarization is considered large but values as high as this have been recorded in some crystals.

It is noted that if \( \theta \) is less than 90° the theoretical \( \pi/\sigma \) ratio for the \(<111>\) and \(<110>\) field directions increases and consequently to give consistence with the experimental values there would have to be larger depolarization present. Significantly higher values are improbable and, therefore, this restricts \( \theta \) to 90° or close to 90°. It is concluded that the centre is likely to have \( C_{2v} \) symmetry although \( C_s \) symmetry has not been completely ruled out.

A summary of the transitions for the \( C_{2v} \) centre is shown in Figure 7.10.
Figure 7.10. Summary of the transitions for the C$_{2v}$s centre. The infra-red line was not studied in any detail. The dashed transitions are field-induced.
7.6 **Discussion of the Centre**

That we are dealing with divalent nickel in both centres is supported by both optical and EPR studies [1]. For the reduced centre both techniques give \( g_\perp = 0 \) and there is no sign of a Kramer's degeneracy (which would be the case for Ni\(^{3+}\)). The orthorhombic or monoclinic centre is not observed using EPR because the low symmetry splitting of 10 cm\(^{-1}\) is far too large for detection - in addition, there is again no sign of Kramer's doublets in optical or EPR spectra.

It is clear that this centre departs significantly from \( C_{3v} \) symmetry and the model suggested earlier is inappropriate. There are, however, certain features of the model which may still be relevant. The very large oscillator strength of the band and its significant decrease with increasing temperature must arise from a very large odd parity field which decreases with temperature. In the case of the \( C_{3v} \) centre the large odd parity field arises from the Ni\(^{2+}\) ion sitting off-centre and the change occurs because the off-centre location apparently moves slightly with temperature towards the on-centre location. This could also be the case here although the presence of another defect must have altered the direction of the off-centre displacement.

Although it no longer seems possible to directly link the excited state wavefunctions for this oxidized centre and the \( C_{3v} \) centre it is likely that both the bands may still arise from a component of the cubic \( ^3T_1 \) crystal field term. If the off-centre displacement is similar in magnitude (even though different in direction) and the wavefunctions are related it is not surprising that the bands have similar strengths.
There remains the problem of proposing some relevant models for the oxidized centre. Since centres of both $C_{2v}$ and $C_s$ symmetry appear in SrO:Co$^{2+}$ [1] it would be appropriate to have models for both symmetries, although only one would be present for SrO:Ni$^{2+}$. The fact that the conversion from the single Ni$^{2+}$ ion centre ($C_{3v}$) can be complete indicates that the other centre is unlikely to arise from being associated with a different impurity. It is more likely to be a vacancy, an additional oxygen, or strontium forming with the nickel an associate defect. No overall charge compensation is required for the substitutional Ni$^{2+}$ ion and so vacancies, additional Sr$^{2+}$, or OH$^-$ appear improbable. Oxygen could, however, be incorporated to form an $O_2^{2-}$ molecule. Formation of such a centre has been proposed for an orthorhombic centre in SrO:Cu$^{2+}$ [2]. The Cu$^{2+}$ or in this case Ni$^{2+}$ is significantly smaller than the Sr$^{2+}$ and so without substantial relaxation there would be unoccupied space in its neighbourhood. There is certainly then room in the lattice for $O_2^{2-}$ whose maximum size of 4.29 Å [3] is not much greater than the monatomic ion diameter of 2.80 Å. If incorporated in the nearest neighbour position and an off-centre displacement is allowed, $C_{2v}$ and $C_s$ centres can arise in several ways; depicted in Figure 7.11. The first of these models has $C_{2v}$ symmetry and is equivalent to setting $\theta = 0^\circ$ in the calculations. In view of the polarization measurements this centre seems unlikely, although it remains a possibility for SrO:Co$^{2+}$. Of the $C_s$ models the third looks the better possibility as the comparison between experimental data and calculation suggests $\theta$ is between 70$^\circ$ and 90$^\circ$. This model can be broken down into three different configurations as we see in Figure 7.12. Electric field studies in the final chapter suggest (i) and (ii) are the more plausible as it would be more difficult for the nickel to re-orient by thermal activation to an equivalent site (a 180$^\circ$ rotation) -
Figure 7.11. Incorporation of an $O_2^{2-}$ molecule into the complex to form $C_{2v}$ and $C_s$ centres.

Figure 7.12. Three different $C_s$ configurations. In the first two the impurity moves off-centre in the Y-Z plane, in the third it can displace in both the (100)- and (110)-type planes.
in (iii) the nickel will only have to rotate 90° about the Z axis to find an energetically equivalent site. No re-orientations are observed, so the nickel is locked in position by a harder potential and it is thought this is more likely to be the case in centres (i) and (ii).

7.7 Heat-Treatments on SrO:Co$^{2+}$

Two new centres appear after heating SrO:Co$^{2+}$ in air or oxygen, and these have been verified as having C${}_5$ and C${}_2$ symmetry by EPR studies in this department [1]. The C${}_3$ centre is restored upon heat-treatment in a reducing atmosphere at the expense of the other centres. Some results of these heat-treatments are shown in Figures 7.13 and 7.14. A systematic investigation, however, has not been undertaken and conclusions are tentative.
Figure 7.13. SrO:Co$^{2+}$: heating in air. EPR studies of Haider and Edgar show that the C$_{3v}$ site eventually is annihilated by this treatment and centres of C$_{2v}$ and C$_s$ symmetry are created.
Figure 7.14. SrO:Co$^{2+}$: heat-treatment in air at 1700°C.
References


CHAPTER 8

ELECTRIC FIELD STUDIES

8.1 Introduction
8.2 The Differential Modulation Technique
8.3 Experimental Results
8.4 Reorientation Effects
8.5 Conclusion
8.1 Introduction

Valuable information on the local symmetry of impurities in a crystal can be gained by observing changes in their optical properties under the influence of an external electric field. In particular a study of the Stark effect provides a unique opportunity to explain the nature of the inversion symmetry of centres which determine the fundamental aspects of the effect; if the local point group symmetry contains inversion the Stark effect is quadratic (splitting $\propto E^2$) but will be linear, and generally much larger, if the impurity centre sits in a non-centrosymmetric site (splitting $\propto E$) [1].

Observations on the Stark effect on broad bands (e.g. colour centres in the alkali halides), for which a very detailed theory has been developed [2], have proved fruitful. For the present studies, however, observations have been made of purely electronic lines, the theory for which has been expounded by Kaplyanskii [3,4].

Analysis of the splitting, intensity, and polarization patterns gives complementary information about the symmetry of the centre as obtained from Zeeman studies (although the electric field will not lift Kramer's degeneracies). Electric field studies, however, are invaluable for the study of off-centre and tunneling behaviour of impurity centres [5], and this is the primary task in this chapter, although any information on the symmetry of the centre will be used to substantiate the results of the Zeeman work (Chapter 4).

Upto the present time, linear Stark splitting of zero-phonon lines in very high static fields has been observed experimentally in the spectra of both impurity (N3 centre in diamond) [6] and defect centres
However, even with the most intense fields available, typically $10^5 \text{V cm}^{-1}$, the linear Stark splitting in the majority of cases is less than the width of the zero-phonon line and consequently the necessary spectral resolution is not present. The quadratic splitting is generally two orders of magnitude smaller than its linear counterpart and has not been observed at all.

The problem of small unresolved Stark splittings can be overcome by the use of differential modulation techniques which amplify small changes in the spectra [8]. The problem is transformed from one of a frequency shift into one of an amplitude measurement and the amplitudes are usually easier to measure than frequencies. No DC field splitting was observed with either SrO:Ni$^{2+}$ or SrO:Co$^{2+}$ and so electro-modulation measurements were used.

Two types of experiments were attempted. In one a DC field was applied and the polarization was modulated. However, no field induced signals were obtained even when the technique of Lucy et al [9] was used. In the second type of experiment a modulated field was applied and the modulation of the signal was detected using phase sensitive techniques. All the signals reported in this Chapter were obtained in this way.

### 8.2 The Differential Modulation Technique

Suppose an external field $E$ splits a line with profile $y$ where,

$$ y = A \text{N} F(v-v_0) $$

(8.2-1)

in which $N$ represents the number of centres contributing to the line, $A$ is the transition probability, $v_0$ is the absorption centre, and $F$ is the 'normalised' lineshape. For an applied electric field $A = A(E)$,
\[ y = y_0 + \frac{\partial y}{\partial E} \Delta E + \frac{1}{2} \frac{\partial^2 y}{\partial E^2} (\Delta E)^2 + \ldots \quad \text{(8.2-2)} \]

where the first and second derivatives may be re-expressed in the following manner:

\[
\frac{\partial y}{\partial E} = \left( \frac{\partial y}{\partial v} \frac{\partial v}{\partial E} + \frac{\partial y}{\partial N} \frac{\partial N}{\partial E} + \frac{\partial y}{\partial A} \frac{\partial A}{\partial E} \right) \quad \text{(8.2-3)}
\]

and
\[
\frac{\partial^2 y}{\partial E^2} = \frac{\partial}{\partial E} \left( \frac{\partial y}{\partial E} \right)
\]

\[
= \frac{\partial^2 y}{\partial v^2} \left( \frac{\partial v}{\partial E} \right)^2 + \frac{\partial y}{\partial v} \frac{\partial^2 v}{\partial E^2} + 2 \frac{\partial^2 y}{\partial v \partial N} \frac{\partial N}{\partial E} \frac{\partial v}{\partial E} + \frac{\partial^2 y}{\partial N^2} \left( \frac{\partial N}{\partial E} \right)^2 + \frac{\partial y}{\partial N} \frac{\partial^2 N}{\partial E^2} + 2 \frac{\partial^2 y}{\partial A \partial N} \frac{\partial N}{\partial E} \frac{\partial A}{\partial E} + \frac{\partial^2 y}{\partial A^2} \left( \frac{\partial A}{\partial E} \right)^2 + \frac{\partial y}{\partial A} \frac{\partial^2 A}{\partial E^2} + 2 \frac{\partial^2 y}{\partial A \partial v} \frac{\partial A}{\partial E} \frac{\partial v}{\partial E} \quad \text{(8.2-4)}
\]

Knowing the differential profile in the field \( \Delta y(v,E) \), \( (y-y_0) \), one can find the magnitude of the field-induced change of the line moments. By definition [8]

\[
\Delta M^{(1)} = S^{-1} \int v \Delta y(v,E) dv = \Sigma I_i \Delta_i \quad \text{(8.2-5)}
\]

and

\[
\Delta M^{(2)} = S^{-1} \int (v-v_0)^2 \Delta y(v,E) dv = \Sigma I_i \Delta_i^2 \quad \text{(8.2-6)}
\]

where \( \Delta M^{(1)} \) is the ith change of moment and \( I_i \) and \( \Delta_i \) are the component intensity and shift respectively.
In all cases measured there was no zeroth moment (erroneous zeroth moments appear in cases where the peak absorption was too large) and this implies that in all cases the absorption strength does not change with field $\frac{\partial A}{\partial E} = 0; \frac{\partial ^2 A}{\partial E^2} = 0$. 

In addition we wish to first consider centres which are not reoriented by the field and therefore $\frac{\partial N}{\partial E} = 0, \frac{\partial ^2 N}{\partial E^2} = 0$. The equation then simplifies to:

$$y = y_0 + \frac{\partial y}{\partial \nu} \frac{\partial}{\partial E} \Delta E \bigg( \frac{\partial y}{\partial E} \bigg) \Delta E^2 + \frac{1}{2} \frac{\partial ^2 y}{\partial \nu \partial E^2} \bigg( \frac{\partial y}{\partial E} \bigg) \Delta E^2 . \hspace{1cm} (8.2-7)$$

For a cubic crystal and the centres randomly distributed, there will be equal numbers aligned along the field and opposed to it. So for every centre 1 there will be an equivalent centre 2 such that $\frac{\partial y_1}{\partial E} = -\frac{\partial y_2}{\partial E}$. Thus the second term in row one of Equation (8.2-7) will be zero. For an oscillating field $\Delta E = E \cos \omega t$. The second row of Equation (8.2-7) gives two signals $\propto E^2$ and modulated at a frequency $2\omega$.

Linear Stark Effect

Where there is no centre of inversion $\frac{\partial y}{\partial E} \neq 0$ (need not be zero). Then there can be a signal with a second derivative line shape $\frac{\partial ^2 y}{\partial \nu ^2}$.

Quadratic Line Shape

If the symmetry group does possess an inversion operator, then $\frac{\partial y}{\partial E} = 0$ but $\frac{\partial ^2 y}{\partial E^2}$ need not be zero and the level of each centre will shift in the same direction (regardless of field polarity). This means that for defects with a centre of inversion the electro-modulated signal will have
a first derivative shape.

Setting $\Delta_1 = \delta_1 E \cos \omega t$ for a linear Stark effect and $\Delta_1 = \gamma_1 E^2 \cos^2 \omega t$ for the quadratic it is possible to extract the 'hidden' splitting pattern from the measured changes of moment and absorption:

$$\Delta M^{(1)} = \int \nu \frac{\Delta J(\nu, E)}{J_0 e^{-k(\nu)}} d\nu$$

experimentally measured

and

$$\Delta M^{(2)} = \int (\nu - \nu_0)^2 \frac{\Delta J(\nu, E)}{J_0 e^{-k(\nu)}} d\nu$$

(8.2-8)

(8.2-9)

where $\Delta J$ is the differential signal and $J_0 e^{-k(\nu)}$ the absorption. It follows that

$$\Sigma I_1 \delta_1 = \frac{2 \Delta M^{(1)}}{E^2 \int k(\nu) d\nu}$$

(8.2-10)

$$\Sigma I_1 \delta_1^2 = \frac{2 \Delta M^{(2)}}{E^2 \int k(\nu) d\nu}$$

(8.2-11)

The intensity of the components is calculated from geometrical and group theoretical considerations as in reference [4], and the right-hand side in (8.2-10) and (8.2-11) are experimental observations.

The experimental configuration has been essentially described in Chapter 2. The AC field at frequency $\omega$ is applied across the crystal perpendicular to the axis of radiation and a standard phase-sensitive detection technique is used to measure the corresponding differential signal. This, being proportional to $E^2$ (see Figure 8.6), is measured at the double frequency $2\omega$. 
8.3 Experimental Results

At low temperatures ($T \leq 20K$) the differential absorption for each of the zero-phonon lines in SrO:Ni$^{2+}$ and SrO:Co$^{2+}$ clearly manifests a second derivative shape indicating the impurities are residing at non-centrosymmetric sites. A selection of measurements is shown in Figures 8.1, 8.2, 8.3, 8.4 and 8.5. In accord with (8.2-7) the differential signal depends quadratically on the field - this is shown in Figure 8.6. At approximately 40 kV/cm deviation from the quadratic effect begins and this is apparently associated with the larger splitting making the expansion in (8.2-2) invalid. However, even at these larger fields the splitting was unable to be resolved (measurements were, however, taken at fields below 40 kV/cm so as to keep within the limits of the assumptions). Modulation studies of the 'pair' lines in SrO:Ni$^{2+}$ also indicate a linear nature of the Stark effect, as expected - the lineshapes are shown in Figure 8.7.

Results of the measurements are summarized in Table 8.1. The polarization measurements for the SrO:Co$^{2+}$ and SrO:Ni$^{2+}$ $C_{3v}$ transitions were inconclusive as both pseudo-Stark (arising from orientational degeneracy) and Stark splitting are involved and for a complete analysis more than one parameter is required [4] and this has not been attempted here. The transitions at the SrO:Ni$^{2+}$ $C_{2v}$ site, however, do not require consideration of the lifting of electronic degeneracy and so the experimental polarization may be compared with that predicted from the lifting of orientational degeneracy - see Figure 8.8. Considering the $\Gamma_1^{+} \Gamma_1$ transition for a centre of $C_{2v}$ symmetry, with field along $<110>$ (view down $<001>$), $\pi/\sigma = 5$ and the experimental ratio is ~3.5; for $\hat{E} \parallel <100>$, $\left(\frac{\pi}{\sigma}\right)_{calc} = 2$ and that observed is ~1.5. The departure could arise from depolarization of the light. The signals are therefore
Figure 8.1. SrO:Ni$^{2+}$: electromodulation of the 15800 cm$^{-1}$ band.

Figure 8.2. SrO:Ni$^{2+}$: the 13520 cm$^{-1}$ line.
Figure 8.3. Sr0:Ni$^{2+}$: the modulated lineshapes for the 6024 and 6368 cm$^{-1}$ lines.
Figure 8.4. SrO:Ni$^{2+}$: electromodulation of the 14340 cm$^{-1}$ line - the differential signal has been normalised against the absorption (necessary for evaluating line splitting).
Figure 8.5. SrO:Co²⁺: electromodulation studies of the band at 14000 cm⁻¹.
Figure 8.6. The quadratic field dependence of the differential signal measured on the 15820 cm$^{-1}$ line in SrO:Ni$^{2+}$. 
Figure 8.7. SrO:Ni$^{2+}$: electromodulation studies of the structure near the 13520 cm$^{-1}$ line. The weak feature at about 13530 cm$^{-1}$ is thought to have the same origin as the 'pair lines'.

Differential Signal

Absorption

13520 cm$^{-1}$

T=8K

T=22K

28 KV/CM ALONG <100>

WAVE LENGTH (nm)
Table 8.1. Summary of electromodulation studies in the visible for SrO:Ni$^{2+}$ and SrO:Co$^{2+}$.

| SrO:Ni$^{2+}$ |  |
|---------------|--|---|
| Line (cm$^{-1}$) | Field direction | Shape (1st or 2nd derivative) | $^a$Splitting (cm$^{-1}$ per V/cm.) | Polarization ($\pi/\sigma \pm 0.2$) |
| 15820 | $<100>$ | 2nd | 0.42 $10^{-5}$ | 1.0 |
| | $<110>$ | 2nd | 0.28 $10^{-5}$ | 1.5 |
| | | | 0.56 $10^{-5}$ | |
| 13520 | $<100>$ | 2nd | 0.41 $10^{-5}$ | 1.0 |
| | $<110>$ | 2nd | 1.1 |
| | $<111>$ | 2nd | -0.8 |
| 'Pair' lines | $<100>$ | 2nd | 1.0 |
| | $<110>$ | 2nd | 2.0 |
| 14340 | $<100>$ | 2nd | 0.25 $10^{-5}$ | 1.0 |
| | $<110>$ | 2nd | 0.20 $10^{-5}$ | 3.5 |
| | | | 0.40 $10^{-5}$ | |
| 14270 | $<100>$ | 2nd | 1.0 |
| | $<110>$ | 2nd | 3.5 |
| 13675 | $<100>$ | 2nd | 1.0 |
| | $<110>$ | 2nd | 3.5 |

| SrO:Co$^{2+}$ |  |
|--------------|--|---|
| 13538 | $<111>$ | 2nd | 0.5 |
| 13584 | $<111>$ | 2nd | |

* more than one value is given when there are more than two components in the splitting pattern.

1 view down $<1\bar{1}0>$
2 view down $<001>$
Figure 8.8. SrO:Ni$^{2+}$: the 14340 and 13675 cm$^{-1}$ lines arising from the lower symmetry centre (C$_{2v}$) show second derivative lineshapes. On the right are the calculated polarization patterns for a $\Gamma_1(\Gamma_2)\rightarrow\Gamma_1(\Gamma_2)$ transition for a C$_{2v}$ centre. Pseudo-Stark splitting need only be considered. The relative intensities of the components (=$I_i$) are shown as are the relative distances (=$A_i$) between symmetrically located splitting components.
consistent with a $C_{2v}$ centre but as in the magnetic field measurements the possibility that the centre is not of slightly lower symmetry cannot be ruled out.

8.4 Reorientation Effects

If the dipoles are not fixed but are aligned or partially aligned in the field, then we have $\frac{\partial N}{\partial E} \neq 0$ and extra terms in (8.2-2) must be considered.

The dipoles will follow the field but with a phase lag. This is assumed to be of the Debye form

$$N = N_0 \left(1 - \frac{\mu}{kT} \left(\frac{1}{1 + \omega^2 \tau^2} + \frac{i\omega \tau}{1 + \omega^2 \tau^2}\right)\right). \tag{8.4-1}$$

Thus,

$$\frac{\partial N}{\partial E} = N_0 \frac{\mu \hat{n}}{kT} \left(\frac{1}{1 + \omega^2 \tau^2} + \frac{i\omega \tau}{1 + \omega^2 \tau^2}\right). \tag{8.4-2}$$

where $\mu$ is the dipole moment and $\hat{n} = \frac{\hat{E}}{|\hat{E}|}$ a unit vector in the direction of the field.

Note $\frac{\partial^2 N}{\partial E^2} = 0$ and $\frac{\partial^2 N}{\partial n^2} = 0$, so the additional term to be considered is then $2 \frac{\partial^2 N}{\partial n \partial E} \left(\frac{\partial N}{\partial E}\right)$. This leads to two temperature dependent terms - both first derivatives and one in phase with the external field, the other out of phase (complex part):

(i) $\Delta y = \frac{\partial^2 N}{\partial n \partial E} \cdot \frac{\partial n}{\partial E} \cdot \frac{N_0 \mu \hat{n}}{kT} \left(\frac{1}{1 + \omega^2 \tau^2}\right)$ \tag{8.4-3}

and

(ii) $\Delta y = \frac{\partial^2 N}{\partial n \partial E} \cdot \frac{\partial n}{\partial E} \cdot \frac{N_0 \mu \hat{n}}{kT} \left(\frac{\omega \tau}{1 + \omega^2 \tau^2}\right) \tag{8.4-4}$

Both of these are in addition to the temperature independent second derivative lineshape given previously.
This treatment explains the nature of the differential lineshape observed for both SrO:Ni$^{2+}$ and SrO:Co$^{2+}$. At lower temperatures (~20K for SrO:Co$^{2+}$ and ~55K for SrO:Ni$^{2+}$) the temperature independent second derivative lineshape (taking into account line broadening) was present but above these temperatures the lineshape changed to first derivative. Both the low and high temperature lineshapes are shown for SrO:Co$^{2+}$ in Figures 8.5 and 8.9. Experimental cycles are displayed in Figures 8.10 (SrO:Co$^{2+}$, 13538 cm$^{-1}$ line), 8.11 (SrO:Ni$^{2+}$, 15820 cm$^{-1}$), and 8.12 (SrO:Ni$^{2+}$, 13520 cm$^{-1}$). In the case of the studies on SrO:Co$^{2+}$ the out-of-phase component (8.4-4) was also measured. The cycle from 2nd to 1st derivative signals was reversible. The experiments indicate, then, that dynamic behaviour is present in both systems, similar to that observed in Rb(Cl,Br):Ag$^+$ where $<110>$ dipoles are present [10]. The impurities at high temperature are able to reorient to equivalent sites. At low temperatures the orientation is frozen in position. The temperature at which they are just able to jump from one orientation to another gives an indication of the potential barrier heights. These are lower for the cobalt ion than for the nickel.

The lines arising from the $C_{2vs}$ centre were also studied but did not display any relaxation characteristics at elevated temperatures and support the conclusion of the model discussed for this centre in Chapter 7, where the impurity is locked in a deep well arising from the local nature of the nearby defects causing the lowering of symmetry.

With the available data it is possible to estimate approximately the activation energy $\epsilon$ using the usual form for the dielectric relaxation $\tau$,

$$\tau = \tau_0 \exp (\epsilon/kT)$$

(8.4-5)
Figure 8.9. SrO:Co$^{2+}$: the lines in the visible exhibit first derivative lineshapes for $T \geq 20K$. 
Figure 8.10. SrO:Co$^{2+}$: the electromodulated lineshape (unbroken line) changes from the low temperature 2nd to a 1st derivative lineshape around 20K. The phase signal (broken line) is also shown. The cycle was reversible.
Figure 8.11. Similar behaviour is exhibited by the $C_{3v}$ lines in SrO:Ni$^{2+}$ but the temperature at which the change in lineshape occurs is somewhat higher, around 55K.
Figure 8.12. SrO:Ni$^{2+}$: temperature dependence of the differential lineshape for the 13520 cm$^{-1}$ line. The same effect was not exhibited by the C$_{2v}$ lines indicating there were no reorientation effects for this lower symmetry centre in the particular temperature range under study.
where the pre-exponential factor may be estimated from the vibrational sideband, assuming the classical thermally activated reorientation is achieved by an $A_{lg}$ vibration (the 90 cm$^{-1}$ mode). In (8.4-5), $\tau$ is estimated from the reciprocal of the applied field frequency, $\omega$ (at reorientation $\omega t = 1$) and so $\omega \approx 8.3 \text{ ms}$. $\tau_0$ is calculated from

$$vibrational\ energy = \frac{\hbar \omega}{\tau_0} \quad \text{(8.4-6)}$$

and $\tau_0 \approx 7.3 \times 10^{-5} \text{ ms}$. The value of $T$ in (8.4-5) is estimated at about $20 \text{ K} \pm 5 \text{ K}$ for SrO:Co$^{2+}$ and for SrO:Ni$^{2+}$ $55 \text{ K} \pm 10 \text{ K}$. With these values, the barrier heights are:

$$\varepsilon_{Co} \approx (0.020 \pm 0.005) \text{eV} \quad \varepsilon_{Ni} \approx (0.055 \pm 0.011) \text{eV}.$$

These do not make very good comparison with the theoretical calculations which give the $<111>$ potential wells almost an order of magnitude larger (0.18 eV for cobalt and 0.26 eV for nickel). The ratio of the Nickel to Cobalt values is, however, in the correct order.

8.5 Conclusion

Research on off-centre systems is now well into its second decade with the major part of the work being done on the alkali-halides. Many techniques have evolved including ionic-thermal current monitoring [11] and electro-birefringence measurements [9] to substantiate claims by both theoretician and experimentalist of off-centre behaviour. Differential optical absorption methods have had limited use in the search so far as the systems do not generally exhibit sharp zero-phonon structure. The paramagnetic impurities nickel and cobalt in SrO offer just that
advantage. The symmetry of the centres has been found by the well-known technique of Zeeman spectroscopy (although the work reported here must be extended in the case of cobalt) and the model of an off-centre system has been substantiated by the electromodulation studies. Although the estimation of the activation energy on the basis of the present data is rather crude it does offer a means of comparison with the off-centre calculation which predicts a potential well for nickel to be a factor of 1.5 deeper than for cobalt; the experimental evaluation of this ratio is $2.7 \pm 0.5$ and the comparison is considered to be reasonable.

The measurements reported in this Chapter can be improved, but in addition it is hoped that PER, ITC, and electric field dichroism will be applied to these systems, in order that reliable and consistent measures of the dipole moments (estimated to be $-1.0 \text{ e}\AA$) and the activation energies can be obtained.
References

Table used in Chapter 5 (from "Multiplets of Transition Metal Ions in Crystals", Sugano et al., Academic Press, N.Y. (1970)

Wigner Coefficients $< j_1m_1j_2m_2|jm >$

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TABLES OF REDUCED MATRICES
OF SPIN-ORBIT INTERACTION

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\( d' \) \( \langle t_{\text{e}}S' \parallel V(1T_2) \parallel t_{\text{e}}S' \rangle \)

\[
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^3T_1 & \sqrt{2}/3 & -1 & -\sqrt{2}/3 & -1/\sqrt{2} \\
^1E & 1/\sqrt{3} & 1/\sqrt{2} \\
^1T_1 & 1/\sqrt{2} \\
\end{array}
\]

\( \langle t_{\text{e}}S' \parallel V(1T_2) \parallel t_{\text{e}}S' \rangle \)

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^1T_1 & -\sqrt{3}/2 & 1/2 & \sqrt{2} \\
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\]

\( \langle t_{\text{e}}S' \parallel V(1T_2) \parallel eS' \rangle \)

\[
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\hline
^1A_1 & -\sqrt{2}/3 \\
^3T_1 & \sqrt{2}/3 & -1 & -\sqrt{2}/3 & -1/\sqrt{2} \\
^1E & 1/\sqrt{3} & 1/\sqrt{2} \\
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\( \langle t_{\text{e}}S' \parallel V(1T_2) \parallel eS' \rangle \)

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^1T_1 & -1/2 & \sqrt{3}/2 & 1/2 & \sqrt{2} \\
^1T_1 & -\sqrt{3}/2 & 1/2 & \sqrt{2} \\
\end{array}
\]
Point-group Tables (from "Properties of the Thirty-Two Point Groups", Koster et al., M.I.T. press, Massachusetts (1963))

Character Table and Basis Functions for the Groups D₃ and C₃ᵥ.

<table>
<thead>
<tr>
<th>Γ</th>
<th>D₃</th>
<th>E</th>
<th>E</th>
<th>2C₃</th>
<th>2C₃</th>
<th>3C₂</th>
<th>3C₂</th>
<th>Time</th>
<th>Bases for D₃</th>
<th>Bases for C₃ᵥ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Γ₁</td>
<td>E</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>a</td>
<td>R</td>
<td>R or z</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Γ₂</td>
<td>E</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>a</td>
<td>S₁ or z</td>
<td>S₁</td>
<td></td>
</tr>
<tr>
<td>Γ₃</td>
<td>2</td>
<td>2</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>a</td>
<td>(S₂ - iS₃),</td>
<td>(S₂ - iS₃),</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- (S₂ + iS₃),</td>
<td>-(S₂ + iS₃)</td>
<td></td>
</tr>
</tbody>
</table>

Gamma 4

| Γ₄ | 2 | -2 | 1 | -1 | 0 | 0 | c | ϕ(1/2,-1/2), | ϕ(1/2,-1/2), |
|    |   |   |   |   |   |   |   | ϕ(1/2,1/2), | ϕ(1/2,1/2) |

Gamma 5

| Γ₅ | 1 | -1 | 1 | i | -i | b | ϕ(3/2,-3/2) | ϕ(3/2,-3/2) |
|    |   |   |   |   |   |   | -iϕ(3/2,3/2) | -iϕ(3/2,3/2) |

Gamma 6

| Γ₆ | 1 | -1 | 1 | -i | i | b | -ϕ(3/2,3/2) | -ϕ(3/2,3/2) |
|    |   |   |   |   |   |   | +iϕ(3/2,-3/2) | +iϕ(3/2,-3/2) |

Multiplication Table for the Groups D₃ and C₃ᵥ.

$$
\begin{array}{cccccccc}
\Gamma₁ & \Gamma₂ & \Gamma₃ & \Gamma₄ & \Gamma₅ & \Gamma₆ & \Gamma₁ & \Gamma₂ \\
\Gamma₁ & \Gamma₂ & \Gamma₃ & \Gamma₄ & \Gamma₅ & \Gamma₆ & \Gamma₂ & \Gamma₁ \\
\Gamma₁ & \Gamma₃ & \Gamma₄ & \Gamma₅ & \Gamma₆ & \Gamma₁ & \Gamma₂ & \Gamma₁ \\
\Gamma₁ & \Gamma₂ & \Gamma₃ & \Gamma₄ & \Gamma₅ & \Gamma₆ & \Gamma₁ & \Gamma₂ \\
\Gamma₁ & \Gamma₂ & \Gamma₃ & \Gamma₄ & \Gamma₅ & \Gamma₆ & \Gamma₁ & \Gamma₂ \\
\Gamma₁ & \Gamma₂ & \Gamma₃ & \Gamma₄ & \Gamma₅ & \Gamma₆ & \Gamma₁ & \Gamma₂ \\
\end{array}
$$
Coupling Coefficients for the Groups $D_3$ and $C_3v$

$$u_6 = Ku_3; \quad u_5 = -Ku_6$$

$$u_5\psi_6 = -\psi_6 \quad u_5\psi_5 = \psi_5$$

<table>
<thead>
<tr>
<th>$\psi_5^{1/2}$</th>
<th>$u_5\psi_5^{1/2}$</th>
<th>$u_5\psi_5^{1/2}$</th>
<th>$u_5\psi_5^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi_3$</td>
<td>$i$</td>
<td>$0$</td>
<td>$\psi_3^{1/2}$</td>
</tr>
<tr>
<td>$\psi_2$</td>
<td>$-i$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$u_5\psi_3$</th>
<th>$u_5\psi_3^1$</th>
<th>$u_5\psi_{3/2}$</th>
<th>$u_5\psi_{3/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi_1$</td>
<td>$0$</td>
<td>$1/\sqrt{2}$</td>
<td>$1/\sqrt{2}$</td>
</tr>
<tr>
<td>$\psi_2$</td>
<td>$0$</td>
<td>$i/\sqrt{2}$</td>
<td>$-i/\sqrt{2}$</td>
</tr>
<tr>
<td>$\psi_3$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>$\psi_4$</td>
<td>$1$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$u_5\psi_4$</th>
<th>$u_5\psi_{4/2}$</th>
<th>$u_5\psi_{4/2}$</th>
<th>$u_5\psi_{4/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi_1$</td>
<td>$0$</td>
<td>$i/\sqrt{2}$</td>
<td>$-i/\sqrt{2}$</td>
</tr>
<tr>
<td>$\psi_2$</td>
<td>$0$</td>
<td>$-i/\sqrt{2}$</td>
<td>$i/\sqrt{2}$</td>
</tr>
<tr>
<td>$\psi_3$</td>
<td>$1$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>$\psi_4$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$u_5\psi_5$</th>
<th>$u_5\psi_{5/2}$</th>
<th>$u_5\psi_{5/2}$</th>
<th>$u_5\psi_{5/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi_1$</td>
<td>$0$</td>
<td>$0$</td>
<td>$i/\sqrt{2}$</td>
</tr>
<tr>
<td>$\psi_2$</td>
<td>$0$</td>
<td>$-i/\sqrt{2}$</td>
<td>$-i/\sqrt{2}$</td>
</tr>
<tr>
<td>$\psi_3$</td>
<td>$1$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>$\psi_4$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>$u_5\psi_6$</th>
<th>$u_5\psi_{6/2}$</th>
<th>$u_5\psi_{6/2}$</th>
<th>$u_5\psi_{6/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi_1$</td>
<td>$0$</td>
<td>$-i/\sqrt{2}$</td>
<td>$i/\sqrt{2}$</td>
</tr>
<tr>
<td>$\psi_2$</td>
<td>$0$</td>
<td>$i/\sqrt{2}$</td>
<td>$-i/\sqrt{2}$</td>
</tr>
<tr>
<td>$\psi_3$</td>
<td>$1$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>$\psi_4$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
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</table>

<table>
<thead>
<tr>
<th>$u_6\psi_5$</th>
<th>$u_6\psi_{5/2}$</th>
<th>$u_6\psi_{5/2}$</th>
<th>$u_6\psi_{5/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi_1$</td>
<td>$1/\sqrt{2}$</td>
<td>$1/\sqrt{2}$</td>
<td>$0$</td>
</tr>
<tr>
<td>$\psi_2$</td>
<td>$i/\sqrt{2}$</td>
<td>$-i/\sqrt{2}$</td>
<td>$0$</td>
</tr>
<tr>
<td>$\psi_3$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>$\psi_4$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
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</table>

<table>
<thead>
<tr>
<th>$u_6\psi_6$</th>
<th>$u_6\psi_{6/2}$</th>
<th>$u_6\psi_{6/2}$</th>
<th>$u_6\psi_{6/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi_1$</td>
<td>$1/\sqrt{2}$</td>
<td>$1/\sqrt{2}$</td>
<td>$1/\sqrt{2}$</td>
</tr>
<tr>
<td>$\psi_2$</td>
<td>$i/\sqrt{2}$</td>
<td>$-i/\sqrt{2}$</td>
<td>$i/\sqrt{2}$</td>
</tr>
</tbody>
</table>
Character Table and Basis Functions
for the Groups $D_2$ and $C_{2v}$

\[
\begin{array}{cccccccc}
 & E & \bar{E} & C_2' & \bar{C}_2' & C_2'' & \bar{C}_2'' \\
D_2 & & & & & & & \\
\hline
\Gamma_1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
\Gamma_2 & 1 & 1 & -1 & 1 & -1 & 1 & 1 \\
\Gamma_3 & 1 & 1 & 1 & -1 & -1 & 1 & 1 \\
\Gamma_4 & 1 & 1 & -1 & -1 & 1 & 1 & 1 \\
\Gamma_5 & 2 & -2 & 0 & 0 & 0 & 0 & 0 \\
\end{array}
\]

Bases
\[
\begin{array}{cccc}
\text{Bases} & \text{for } D_2 & \text{Bases} & \text{for } C_{2v} \\
\hline
\Gamma_1 & \text{R or } xyz & z & \\
\Gamma_2 & \text{S}_x \text{ or } y & \text{S}_x \text{ or } x & \\
\Gamma_3 & \text{S}_y \text{ or } z & \text{S}_y \text{ or } xy & \\
\Gamma_4 & \text{S}_y \text{ or } x & \text{S}_y \text{ or } y & \\
\Gamma_5 & \phi(1/2, -1/2), \phi(1/2, -1/2) & \phi(1/2, 1/2) & \phi(1/2, 1/2) \\
\end{array}
\]

Multiplication Table for the Groups
\[
D_2 \text{ and } C_{2v}
\]

\[
\begin{array}{cccccccc}
\Gamma_1 & \Gamma_2 & \Gamma_3 & \Gamma_4 & \Gamma_5 & \Gamma_1 \\
\hline
\Gamma_1 & \Gamma_2 & \Gamma_3 & \Gamma_4 & \Gamma_5 & \Gamma_1 \\
\Gamma_2 & \Gamma_4 & \Gamma_1 & \Gamma_5 & \Gamma_1 & \Gamma_2 \\
\Gamma_3 & \Gamma_1 & \Gamma_2 & \Gamma_3 & \Gamma_3 & \Gamma_4 \\
\Gamma_4 & \Gamma_5 & \Gamma_1 & \Gamma_3 & \Gamma_1 & \Gamma_5 \\
\Gamma_5 & \Gamma_1 + \Gamma_2 & \Gamma_1 + \Gamma_4 & \Gamma_1 & \Gamma_5 & \\
\end{array}
\]

Character Table and Basis Functions for the Groups $C_2$ and $C_s$

\[
\begin{array}{cccccccc}
 & E & \bar{E} & C_2 & \bar{C}_2 & C_2' & \bar{C}_2' \\
C_s & E & \bar{E} & \sigma & \bar{\sigma} & \text{Time} & \text{Bases} & \text{Bases} \\
\hline
\Gamma_1 & 1 & 1 & 1 & 1 & a & \text{S}_x \text{ or } z & \text{S}_x \text{ or } x \text{ or } y \\
\Gamma_2 & 1 & 1 & -1 & -1 & a & \text{S}_y \text{ or } S_x \text{ or } x \text{ or } y & \text{S}_y \text{ or } S_x \text{ or } z \\
\Gamma_3 & 1 & -1 & i & -i & b & \phi(1/2, 1/2) & \phi(1/2, 1/2) \\
\Gamma_4 & 1 & -1 & -i & i & b & \phi(1/2, -1/2) & \phi(1/2, -1/2) \\
\end{array}
\]

Multiplication Table for the Groups
\[
C_2 \text{ and } C_s
\]

\[
\begin{array}{cccc}
\Gamma_1 & \Gamma_2 & \Gamma_3 & \Gamma_4 \\
\hline
\Gamma_1 & \Gamma_2 & \Gamma_3 & \Gamma_4 \\
\Gamma_1 & \Gamma_2 & \Gamma_3 & \Gamma_4 \\
\Gamma_2 & \Gamma_1 & \Gamma_3 & \Gamma_4 \\
\Gamma_2 & \Gamma_1 & \Gamma_3 & \Gamma_4 \\
\end{array}
\]
## Compatibility Table

<table>
<thead>
<tr>
<th>$O_h$</th>
<th>$I_1^a$</th>
<th>$I_2^a$</th>
<th>$I_3^a$</th>
<th>$I_4^a$</th>
<th>$I_5^a$</th>
<th>$I_6^a$</th>
<th>$I_7^a$</th>
<th>$I_8^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O$</td>
<td>$I_1^a$</td>
<td>$I_2^a$</td>
<td>$I_3^a$</td>
<td>$I_4^a$</td>
<td>$I_5^a$</td>
<td>$I_6^a$</td>
<td>$I_7^a$</td>
<td>$I_8^a$</td>
</tr>
<tr>
<td>$T_d$</td>
<td>$I_1^a$</td>
<td>$I_2^a$</td>
<td>$I_3^a$</td>
<td>$I_4^a$</td>
<td>$I_5^a$</td>
<td>$I_6^a$</td>
<td>$I_7^a$</td>
<td>$I_8^a$</td>
</tr>
<tr>
<td>$T_h$</td>
<td>$I_1^a$</td>
<td>$I_2^a$</td>
<td>$I_3^a$</td>
<td>$I_4^a$</td>
<td>$I_5^a$</td>
<td>$I_6^a$</td>
<td>$I_7^a$</td>
<td>$I_8^a$</td>
</tr>
<tr>
<td>$D_{4h}$</td>
<td>$I_1^a$</td>
<td>$I_2^a$</td>
<td>$I_3^a$</td>
<td>$I_4^a$</td>
<td>$I_5^a$</td>
<td>$I_6^a$</td>
<td>$I_7^a$</td>
<td>$I_8^a$</td>
</tr>
<tr>
<td>$C_{4v}: H(z)$</td>
<td>$I_1^a$</td>
<td>$I_2^a$</td>
<td>$I_3^a$</td>
<td>$I_4^a$</td>
<td>$I_5^a$</td>
<td>$I_6^a$</td>
<td>$I_7^a$</td>
<td>$I_8^a$</td>
</tr>
<tr>
<td>$C_{2v}: H(v)$</td>
<td>$I_1^a$</td>
<td>$I_2^a$</td>
<td>$I_3^a$</td>
<td>$I_4^a$</td>
<td>$I_5^a$</td>
<td>$I_6^a$</td>
<td>$I_7^a$</td>
<td>$I_8^a$</td>
</tr>
<tr>
<td>$C_{2v}: H(w)$</td>
<td>$I_1^a$</td>
<td>$I_2^a$</td>
<td>$I_3^a$</td>
<td>$I_4^a$</td>
<td>$I_5^a$</td>
<td>$I_6^a$</td>
<td>$I_7^a$</td>
<td>$I_8^a$</td>
</tr>
<tr>
<td>$C_{2v}: E(z)$</td>
<td>$I_1^a$</td>
<td>$I_2^a$</td>
<td>$I_3^a$</td>
<td>$I_4^a$</td>
<td>$I_5^a$</td>
<td>$I_6^a$</td>
<td>$I_7^a$</td>
<td>$I_8^a$</td>
</tr>
<tr>
<td>$C_{2v}: E(v)$</td>
<td>$I_1^a$</td>
<td>$I_2^a$</td>
<td>$I_3^a$</td>
<td>$I_4^a$</td>
<td>$I_5^a$</td>
<td>$I_6^a$</td>
<td>$I_7^a$</td>
<td>$I_8^a$</td>
</tr>
<tr>
<td>$C_{2v}: E(w)$</td>
<td>$I_1^a$</td>
<td>$I_2^a$</td>
<td>$I_3^a$</td>
<td>$I_4^a$</td>
<td>$I_5^a$</td>
<td>$I_6^a$</td>
<td>$I_7^a$</td>
<td>$I_8^a$</td>
</tr>
</tbody>
</table>

### Additional Notes

- $I_1^a$, $I_2^a$, $I_3^a$, $I_4^a$, $I_5^a$, $I_6^a$, $I_7^a$, $I_8^a$ represent the irreducible representations of the point group $O_h$.
APPENDIX II

ENERGY LEVEL DIAGRAMS (d^8 TRIGONAL)

and

A CUBIC FIELD ENERGY LEVEL DIAGRAM (d^7) AFTER

SR0NI(D8)  DQ=-320  B=800  
C=3600  ξ=-600  V'=-.5V
SR0NI(D8) DQ = -350, B = 700, C = 3000, η = -600, V' = -2/3V

TRICOSAL FIEL D P A R A M E T E R, V (CM-1)

ENERGY (CM-1)
SR0NI(D8) \( DQ = -350 \), \( B = 800 \)
\( C = 3500 \), \( \omega = -600 \), \( V' = -V \)
SR0NI(D8) DQ=-600, B=900
C=3900 $\eta=-600$ $V'=0.25V$

TRIGONAL FIELD PARAMETER, $V$(CM-1)
—Energy level diagram for a d⁷ electronic configuration encompassed by a field of octahedral symmetry for \( \gamma \) equals \(-450\) cm\(^{-1}\), \( B \) equals \(35\) cm\(^{-1}\), and \( C \) equals \(4B\).