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THE AUSTRALIAN NATIONAL UNIVERSITY

RESEARCH SCHOOL OF PHYSICAL SCIENCES

DEPARTMENT OF SOLID STATE PHYSICS

ANNUAL REPORT 1974

STAFF

Professor and Head of Department	W.A. Runciman, DSc (Edin.), FInstP, FAIP, FGA
Senior Fellow	D.J. Newman, BSc, ARCS, PhD (Lond.) (from July)
Research Fellows	E.R. Vance, BSc (Melb.), PhD (Monash)
	B. Window, BSc (Q'ld.), PhD (Monash) (until February)
	N.B. Manson, BSc, PhD (Aberd.)
	B.L. Dickson, MSc (Well.), DIC, PhD (Lond.)
	G. Smith, BSc (Glas.), PhD (N'cle, UK) (from July)
	D.C. Price, BSc, PhD (Monash) (from July)
	I.N. Douglas, BSc, PhD (Cant.) (from October)
Visiting Fellow	R.T. Cox, BSc (Q'ld.), D es Sci (Grenoble) (until September)
Postdoctoral Fellow	A. Edgar, BSc, PhD (Cant.) (from September)
Research Assistant	M. Marshall, BSc, PhD (until June)

TECHNICAL STAFF

Senior Technical Officer	W.H.M. Miles
Technical Officers	G. Sampietro
	J.P. Carlton

INTRODUCTION

The major research interest of the Department is the spectroscopic study of paramagnetic centres in non-metallic materials. The substances being studied include oxides and fluorides doped with transition metal ions, minerals and gemstones. Optical instrumentation covers a wide range of the electromagnetic spectrum from the ultraviolet at 54,000 cm^{-1} to the far infrared at 32 cm^{-1}. Mössbauer spectrometers and a newly installed electron paramagnetic resonance spectrometer are also in use. Magnetic circular dichroism (MCD), magnetic linear dichroism (MLD) and magnetically induced circular emission (MICE) are being used and are providing an abundance of interesting data.

In the majority of cases experiments are carried out with a crystal sample at helium temperatures and with an external perturbation applied to the sample; the more common perturbations are uniaxial stress, large electric fields (Stark effect) and magnetic fields (Zeeman effect). The Department is particularly strong in its ability to study Zeeman effects and has several high magnetic field facilities available. Superconducting solenoids provide steady fields of up to 80 kG, and the pulsed magnet in the Magnet Laboratory of the Department of Engineering Physics produces fields up to 220 kG for several seconds.

The success of experiments in solid state physics is dependent on the availability of high quality materials. Crystal growth and preparation methods are being developed and in the past year apparatus for hydrothermal growth has been installed and used for growing undoped and doped quartz crystals.

Considerable advances in the understanding of the optical and Mössbauer spectra of minerals have been made this year. New phenomena due to electron-vibration interactions have been observed for Ni^{2+} in oxides.

GENERAL

The first National Congress of the Australian Institute of Physics was held in Adelaide in May. Professor Runciman presented an invited paper on "The Optical Spectroscopy of Minerals and Gemstones", and was invited to Chair the session on "Solid State and Optics".

Professor Runciman continued to act as Chairman of the Helium Advisory Committee of the Research School of Physical Sciences and Dr. N.B. Manson also joined the Committee.

Dr. G.E. Stedman (University of Canterbury) visited the Department for a week during November for discussions on collaborative studies.

Professor Runciman left for London on December 8th for a period of study leave based in the Spectroscopy Group in the Physics Department of the Imperial College of Science and Technology. Dr. D.J. Newman has been appointed Acting Head of Department for this period.

During 1974 a new building has been planned which will accommodate the Department of Solid State Physics, the Computer Centre, a lecture theatre and a commonroom. Construction has started and the building is due for completion by the end of 1975.

The Department acknowledges the continued cooperation of the Research School of Earth Sciences in providing electron microprobe analyses and the Department of Nuclear Physics in irradiating samples. It also notes with pleasure the continuing interaction with members of the Research School of Chemistry.

STAFF CHANGES

Dr. B. Window resigned his Research Fellowship in February to take up a position at Sydney University.

Dr. D.J. Newman arrived in July from Queen Mary College, London.

Dr. G. Smith arrived in July from the University of Tokyo.

Dr. D.C. Price arrived in July from the University of Liverpool.

Dr. I.N. Douglas arrived in October from the University of East Anglia.

Dr. A. Edgar arrived in September from the University of Canterbury.

Dr. R.T. Cox, a Visiting Fellow for one year on leave of absence from C.E.A. - C.E.N., Grenoble, returned there in September.

Dr. M. Marshall left in June on termination of his appointment.

RESEARCH PROGRAMME

1. THEORETICAL AND COMPUTATIONAL WORK

The theoretical side of the Department has been greatly strengthened and a close interaction between theory and experiment has been established at all stages from planning to the interpretation and publication of research.

1.1. Data analysis

A considerable fraction of our effort goes into the interpretation of spectroscopic data. Calculations are carried out on departmental Hewlett-Packard 9820 and 9821 calculators and the Univac 1108 in the Computer Centre. A terminal providing a direct link to the Computer Centre has recently been installed in the Department.

1.2. Local distortions

A general theory of local distortions near substituted ions in crystals has been developed, and is being applied to determine the effects of various substituted systems in fluorite crystals.

1.3. S-state ions

A general review of the techniques and the interpretation of ESR data on "S-state" ions (with configuration $\ell^{(2\ell+1)}$) has been completed by Dr. D.J. Newman in conjunction with Prof. Dr. W. Urban of Bonn. In this connection, a relation between matrix elements in ℓ^2 and $\ell^{(2\ell+1)}$ configurations has been established using hole-particle formalism.

2. MINERALS

The study of minerals by the technique of optical spectroscopy has been continued and extended.

2.1. Diamond

MCD and absorption spectra at temperatures of 10-70K in the range 12000-30000 cm^{-1} were measured for an electron-irradiated Type Ia diamond. Most absorption bands gave a mixture of A- and B-type MCD, characteristic of transitions from a non-degenerate ground state to degenerate excited states.

2.2. Charge transfer

Preliminary temperature dependence investigations of the 20800 cm^{-1} band occurring in the spectra of andalusite have shown a well defined temperature behaviour which may be attributed to a charge transfer process involving Ti^{4+} cations. This behaviour is linked with problems associated with ligand-metal overlap which arise from the fact that Ti^{4+} contains no electrons in its 3d shell. These initial investigations have led to more critical studies being made on other minerals with appreciable titanium content, such as brown tourmaline, melanite garnet, blue kyanite and rutile.

2.3. Natural garnets

Mössbauer spectra suggested that most of the Fe^{3+} in spessartine is not at the octahedral site where it is situated in pyrope, grossular and andradite. Thus, in assigning optical absorption bands one should note there will be two independent Fe^{3+} spectra.

MCD and absorption data were used to obtain the intensities and positions of bands in 14000-31000 cm^{-1} and the bands were then assigned to particular species by comparing intensities in garnets of different compositions.

2.4. Rhodonite

Earlier assignments of absorption bands in 4000-30000 cm^{-1} to Mn or Fe were based on unpolarized spectra, as only the spectrum of high-iron rhodonite crystals had been measured. This year, some low-iron rhodonite crystals of sufficient size for absorption spectrum measurements were acquired and their polarized spectra measured at room and helium temperatures. Reliable band assignments could then be made by comparing the spectra of high- and low-iron rhodonites and some earlier assignments were shown to be incorrect. Some of the Mn^{2+} crystal field independent bands in the low-iron rhodonite spectrum showed the temperature-dependence characteristic of pair-transitions.

2.5. U^{4+} in zircon

Analysis was completed of the polarized spectra of U^{4+} in $ZrSiO_4$. Using ten parameters an energy-level fit was obtained for

30 observed levels with a standard deviation of 112 cm^{-1}. Theoretical g-values have been compared with results obtained from Zeeman experiments and MCD.

2.6. U^{5+} in zircon

Further studies have been conducted on the optical spectrum of U^{5+} in synthetic zircon, the U^{5+} being charge compensated by Y^{3+} and $A\ell^{3+}$. The strongest lines, at ~6700 and 9000 cm^{-1}, of the U^{5+} spectrum were found to have different $g_{\perp}$ values in the ground states, showing the lines to derive from different centres, in spite of the fact that the lines appeared to be intensity-correlated over a concentration range of ~0.003 - 0.3 wt% U^{5+}. U^{5+} in zircon is apparently favoured by trivalent, rather than divalent charge compensators, although some dependence of the valence state of U in synthetic zircon was found on the atmosphere used in high-temperature annealing.

2.7. Fission fragment damage in zircon

Tracks due to slow-neutron-induced fission of uranium impurities in synthetic zircon were observed directly by electron microscopy for dosages in the 10^{10} - 10^{13} fission events.cm^{-3} range. Fission-fragment irradiation of zircon was observed to produce lattice disorder, as found from x-ray studies, and ultimately amorphism, after a dose of about 10^{16} fission events. cm^{-3}. The radiation damage process was found to be qualitatively similar to the α-recoil damage process in natural zircon. A fission fragment, however, was deduced to cause ~10^{4} times more lattice disordering than an α-recoil event. Fission fragment, fast neutron and γ-irradiation had little effect on the optical properties of zircon, although γ-irradiation induced ultraviolet absorption bands near 40000 cm^{-1} in undoped zircon.

2.8. Amethyst quartz

Previous work had indicated that the purple colouration of the quartz gemstone, amethyst, is produced by small quantities of iron impurity. We have now obtained evidence from spectra in the near infrared, visible and ultraviolet spectral regions for a definite model of the structure of these impurity centres. They consist of (the rarely found) Fe^{4+} ions occupying tetrahedrally coordinated silicon lattice sites.

2.9. Hydrothermal crystal growth

Apparatus was acquired for hydrothermal crystal growth (growth from aqueous solutions at temperatures up to 600°C and pressures up to 3000 atmospheres). Large single crystals of pure quartz were grown. Attempts to grow transition metal doped quartz were less successful, due to the low solubilities of transition metal ions in the hydrothermal solutions and the low impurity tolerance of the quartz lattice. However, iron doped crystals were successfully grown for use in studies of the optical and magnetic properties of iron in quartz.

3. TRANSITION METAL IONS IN SIMPLE OXIDES

Studies of iron group transition metal ions doped into MgO, CaO and SrO have been continued during the present year using the techniques of optical absorption, magnetic circular dichroism (MCD) and magnetic linear dichroism (MLD).

3.1. $MgO:Ni^{2+}$, $CaO:Ni^{2+}$, $SrO:Ni^{2+}$

In the case of $CaO:Ni^{2+}$ a new phenomenon for 3d ions has been observed. The Ni^{2+} ion replaces the larger Ca^{2+} ion at a site with O_h symmetry and gives rise to a low frequency local mode of T_{1u} symmetry. This mode couples and interacts strongly with the electronic energy levels of the Ni^{2+} ion and for each degenerate energy level gives rise to several vibronic absorption features. Normally, the energy of the electron-vibration coupled system is given by the electronic energy plus the vibrational energy. However, in $CaO:Ni^{2+}$ the interaction between the two is large and has given rise to the splitting and consequently the energy is not given by the simple addition of the two components. The motion of the electron and the vibration are not independent but rather are very much interrelated.

This effect has never been reported before for a 3d ion in a solid, nor indeed for any single substituted ion in a solid. Considerable effort is being placed in trying to identify the effect in other systems. Already, MCD and MLD measurements have established that similar effects take place in $MgO:Ni^{2+}$.

In a separate study the MCD of the $^3A_{2g} \rightarrow {}^3T_{2g}$ absorption band of $MgO:Ni^{2+}$ has been reported. It is established that the band is

predominantly magnetic dipole in origin with the two sharp lines arising from zero-phonon transition to the Γ_3 and Γ_4 spin-orbit components of the $^3T_{2g}$ crystal field level. It is presumed that the rest of the structure in the band arises from the coupling of A_{1g} even modes onto the allowed magnetic dipole transitions.

3.2. $MgO:Cr^{3+}$ ($KNaGaF_6:Cr^{3+}$)

$MgO:Cr^{3+}$ has been studied in MCD. The two strong spin-allowed absorption bands, $^4A_2 \rightarrow {}^4T_{2g}$ and $^4A \rightarrow {}^4T_{1g}$, are established to be forced electric dipole in origin with the majority of the intensity arising from the coupling with T_{1u} vibrations. In addition, the energy of two quartet levels is established from the presence of magnetic dipole zero-phonon lines. A separate study by magnetically induced circular emission (MICE) of the $MgO:Cr^{3+}$ R line emission has established that the sideband arises from the coupling to T_{1u} and T_{2u} vibrations, contrary to conclusions drawn by other workers.

In connection with the $MgO:Cr^{3+}$ study and related material, $KNaGaF_6:Cr^{3+}$ has been investigated. The Cr^{3+} ion is at a site of O_h symmetry surrounded by six cation nearest neighbours. It is no surprise then that similar conclusions are drawn - in particular, that the spin-allowed bands gain their intensity from T_{1u} coupling. However, in addition, weak MCD features are observed. Some have been assigned to spin-forbidden transition but the origins of others are still difficult to account for.

3.3. $MgO:Co^{2+}$, $CaO:Co^{2+}$, $SrO:Co^{2+}$

The low-temperature absorption and MCD measurements of $MgO:Co^{2+}$, $CaO:Co^{2+}$ and $SrO:Co^{2+}$ are currently under study. $MgO:Co^{2+}$ is the most interesting in that it shows several interesting weak features in the MCD, but which cannot be accounted for by conventional single-ion Co^{2+} absorption.

3.4. $MgO:Fe^{2+}$

A sharp magnetic dipole zero-phonon close to the $^5T_{2g} \rightarrow {}^5E_g$ absorption band in the infrared of the $MgO:Fe^{2+}$ spectrum remains a puzzle. At one stage three lines were identified in this region; however, on annealing the strain from the crystal these converge to give just one line. This line gives a small magnetic field splitting

(2 cm^{-1} at 5T) with a σ absorption moving to lower energy and a π line to higher energy.

3.5. Luminescent CaO

Sharp lines in luminescent CaO have been studied further by Zeeman and stress perturbation spectroscopy. Heat-treatment effects on the lines have also been made. Zeeman results on the unreported emission line at 14646 cm^{-1} were similar to those found for the well-documented $^3P \rightarrow {}^1S$ emission line at 17420 cm^{-1} due to the F centre. The stress results showed that the 14646 cm^{-1} line is due to a more insular centre than the F centre but the details of these results are not understood as yet. H may be responsible for the 14646 cm^{-1} line and heat-treatment and proton-irradiation studies are in progress to examine this proposition. The effect of heat-treatment on lines at 5777 and 17512 cm^{-1}, due to an even-electron system in orthorhombic I symmetry, are at variance with those reported by other authors.

4. HEXAVALENT URANIUM

Zeeman experiments on a zero-phonon line seen in the emission of uranium doped CaF_2 have shown that the emission arises from a centre with trigonal and inversion symmetry and it was concluded that the centre could only be a UO_2^{2+} or a UO_6^{6-} grouping.

The magnetic field measurements have clearly shown that the emitting level is a doublet. This is the first time that the emission level of a hexavalent uranium ion has been shown to be degenerate. The same conclusion has now been established for $LiF:U^{6+}$, using MICE measurements. Similar studies on the emission from uranyl compounds have not shown any magnetic effects.

5. ELECTRON PARAMAGNETIC RESONANCE

The Department's new 35GHz EPR spectrometer arrived in September and was satisfactorily installed and tested. Although low temperature measurements are planned, the present configuration is adequate for measurements at room temperatures. An experimental programme on S-state ions has therefore been initiated. The first project in this programme is an attempt to identify and measure the EPR spectrum

of Gd^{3+} cluster sites in calcium fluoride crystals. Preliminary results indicate that such clusters do not form below dopant concentrations of 1 per cent.

6. MÖSSBAUER SPECTROSCOPY

In the past year a number of projects on the general theme of applying Mössbauer spectroscopy to mineralogical studies have been carried out.

6.1. Rhodonite

Four rhodonite, $(Fe,Ca,Mn,Mg)SiO_3$, samples containing differing amounts of iron were studied and the distribution of ferrous iron amongst the five possible cation sites was determined.

6.2. Staurolite

The mineral staurolite has pseudo-orthorhombic symmetry, the origin of which appears to be due to aluminium sites. Most of the iron is tetrahedrally coordinated, whereas iron substituted into the partly filled Aℓ sites is octahedrally coordinated. Room temperature Mössbauer spectra cannot distinguish the two types of iron, but staurolite was found to order magnetically near 5K. Spectra have been obtained at <5K and are being analysed to obtain relative site populations.

6.3. Spinels

The spinels $(Mg_x\ Fe_{1-x})Aℓ_2O_4$, $0 \leqslant x \leqslant 1$, can be up to 20% inverse (i.e. up to 20% the ferrous iron will be in octahedral Aℓ sites). As with staurolite, Mössbauer spectra should enable the two iron sites to be distinguished. A number of synthetic and natural spinels have been examined. The natural samples show only tetrahedrally coordinated ferrous ions, though the spectra are complicated by small deviations from cubic symmetry which arise from the distribution of iron and magnesium nearest neighbours. The spectra at room temperature of the synthetic spinel $FeAℓ_2O_4$ show two broad asymmetric peaks, but at lower temperatures these become narrower and a small doublet appears inside the more intense lines. The temperature dependence of this doublet line is currently being examined to see if it originates from octahedrally coordinated iron.

6.4. Olivines

A study of natural and synthetic olivines, $(Fe,Ca,Mg,Mn)_2SiC_4$, in the temperature range 2-900K, is being made. The higher temperatures enable the contribution to the spectra of the iron in each of the two possible cation sites to be resolved. A small preference of Fe^{2+} for the slightly larger and more distorted M_2 site was confirmed. By the use of single crystals at high temperatures the direction of the principal axes of the electric field gradient around both sites has been determined individually.

At low temperatures, the iron-rich olivines show magnetic ordering. A detailed study is underway on fayalite, Fe_2SiO_4, to examine the nature of an anomaly in the magnetic susceptibility that occurs some 30^{o} below the Néel temperature of 65K.

6.5. Paramagnetic hyperfine spectra

Spectra have been taken of dilute ferric iron in two diamagnetic lattices, mullite ($3A\ell_2O_3.2SiO_2$) and spinel ($MgA\ell_2O_4$). At low temperatures the relaxation rate of Fe^{3+} is slow and magnetic hyperfine interactions can be observed. The spectra for mullite have been analysed in detail to obtain the crystal field parameters, quadrupole splittings and internal magnetic fields at the Fe^{3+} nuclei in the approximate octahedral and tetrahedral sites. The spectra from spinel are currently being analysed. Two unusual features observed with iron in mullite were the slow relaxation of the Fe^{3+} ions at room temperature, and that at low temperatures the application of a small magnetic field had little effect on the observed spectra. Both these effects result from the low symmetry of the sites occupied by the Fe^{3+} ions and the resulting strong mixing of the three Kramers doublets of the $^6S_{5/2}$ ground state.

6.6. Magnetically ordered minerals

A number of iron or iron-manganese rich minerals are being examined at 4.2K to determine if magnetic ordering occurs, as more detailed information on the iron sites can be obtained from a magnetically split spectrum. Minerals examined thus far which order magnetically include garnets, astrophyllites, johannsenite-hedenbergites and ilmenites.

6.7. Natural radiation damage in minerals

Mössbauer and x-ray studies were made of some heat-treated metamict allanites. The results were similar to those reported by other workers, except that CeO_2 was observed to "precipitate" in one sample at temperatures as low as 500°C, a much lower temperature than that reported by other workers for allanite. The betafite-like phase was observed to "precipitate" in a metamict samarskite at temperatures as low as 400°C. The behaviour of these metamict minerals was found to resemble that of metamict zircon in some respects.

6.8. Fe^{2+} in rhombohedral carbonates

^{57}Fe Mössbauer measurements are being made to determine both the structure and temperature dependence of the low-energy electronic states of Fe^{2+} in several naturally-occurring and synthetic compounds of the calcite group. The features of the measurements of current interest are the temperature dependence of the Mössbauer quadrupole splitting, which may be affected by a Jahn-Teller coupling, and the spin-lattice relaxation rate. Calculations of both of these quantities are in progress.

PUBLICATIONS

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(1) Not a member of this University.

(2) Former member.

(3) Member of the Research School of Chemistry.