80/77

2.1.8.9

18/1972

THE AUSTRALIAN NATIONAL UNIVERSITY

RESEARCH SCHOOL OF PHYSICAL SCIENCES

DEPARTMENT OF SOLID STATE PHYSICS

ANNUAL REPORT 1971

Staff

Professor and Head of Department	W.A. Runciman, D.Sc. (from February)
Research Fellows	B.C. Munday, B.Sc., Ph.D.
	D. Sengupta, M.Sc., M.S., Ph.D. (from July)
	D.J. Mackey, B.Sc., Ph.D. (from October)
Research Assistants	J.T. Gourley, B.Sc., Dip.Ed., Ph.D. (from March)
	I.R. Herbert, B.Sc. (from July)
	M. Marshall, B.Sc. (from May)

Technical Staff

Senior Technical Officer	W.H.M. Miles (from May)
Technical Officer	G. Sampietro (from October)

INTRODUCTION

The department aims to carry out research in a few selected areas of solid state physics, a branch of physics which appears to provide about half the employment for physicists in industrial nations. Initially much of the effort will be devoted to topics which will utilize the magnet

facilities available, including the 165 and 300 kilogauss pulsed magnets in the Magnet Laboratory operated by the Department of Engineering Physics. A programme on magnetic oxides started in the Department of Engineering Physics will close down early in 1972, and then the main emphasis will be on the spectroscopic properties of a wide variety of non-metallic solids, including ionic crystals, organic materials and semiconductors.

Professor Runciman arrived in February to take charge of the new Department of Solid State Physics and the staff numbers built up rapidly during the year to a total of three Research Fellows, three Research Assistants and two technical staff. The first graduate student has arrived and a second is due to start early in 1972. Similarly, on the equipment side, there has been a steady build-up and major items include a Cary 17 spectrophotometer for spectroscopic studies in the ultraviolet and visible regions and a Perkin-Elmer 180 spectrophotometer for the infrared region. Experimental arrangements have been devised to allow the study of crystals at liquid helium temperature. The one inch bore superconducting solenoid has been commissioned and will be used for the study of magnetic circular dichroism of crystals as well as for Zeeman experiments. The two inch vertical bore superconducting solenoid has been refitted with a second replacement coil, and has been satisfactorily tested to 79 kilogauss.

GENERAL

Professor Runciman acted as Chairman for a Symposium on Imperfections in Alkali Halides held at the National Standards Laboratory in March.

Professor Runciman attended the 8th Australian Spectroscopy Conference held at Monash University in August. He was Chairman of the session on Solid State Spectroscopy and gave a paper on the high resolution infrared spectroscopy of diamond based on research carried out at A.E.R.E., Harwell, prior to taking up his appointment.

RESEARCH PROGRAMME

(1) Magnetic oxides

The programme of research on magnetic oxides started in the Department of Engineering Physics has been continued and has made use of the 300 kilogauss pulsed magnet operated by the Department of Engineering Physics. The main part of this research programme has been an investigation of V_2O_3 and $(V_{1-x}Cr_x)_2O_3$. In particular, a search is being made for a possible spin-flop transition when a large magnetic field is applied to the antiferromagnetic phase. Considerable difficulty was experienced in preparing the samples, and most of the work was performed on specimens which contained considerable amounts of V_3O_5. It was hoped that the V_3O_5 (which is a non-magnetic insulator) would not interfere significantly. All specimens showed the expected large resistivity jump at the Néel point and a deep cusp was observed in the temperature dependence of the Young's modulus, the

latter indicating a magnetic component of elastic compliance. Magnetic fields up to 240 kilogauss were applied at temperatures down to 4.2°K. The Young's modulus was altered by these large fields but the resistivity was unchanged, suggesting a modification of the magnetic order rather than of the band structure. New specimens of single phase V_2O_3 have been prepared and measurements of the Young's modulus in zero field show a better defined anomaly in the antiferromagnetic phase. It is hoped that these specimens will provide more explicit information on the effects of large applied fields.

A series of measurements determining the Néel temperatures in the MgO-NiO and MgO-MnO systems were performed in conjunction with Dr. T. Sabine of the AAEC. Unfortunately there was considerable confusion about the exact compositions of the samples prepared at the AAEC and the work has been terminated short of a satisfactory conclusion. An earlier investigation of the magnetoelastic properties of some dilute alloys of Cr was completed and published.

(2) Ultraviolet and visible spectroscopy, including near infrared

The absorption spectrum of MgO (Fe^{2+}) had been studied previously and the $^5T_2 \rightarrow {}^5E$ transition identified. Re-examination of the spectrum at liquid helium temperature revealed two additional sharp lines very close to the $^5T_2 \rightarrow {}^5E$ band. Upon raising the sample temperature to 77°K two additional lines were observed. All these lines disappeared as the temperature was further raised. The lines were attributed to the spin-forbidden $^5T_2 \rightarrow {}^3T_1$ transition. Two lines observed at liquid helium temperature are due to transitions from lowest spin-orbit split component of $^5T_2$ level to the $^3T_1$ level. At higher temperature the next higher spin-orbit level of $^5T_2$ state is populated and transitions from this state to $^3T_1$ produce the other lines. A detailed energy level calculation was carried out in the strong-field coupling scheme. The lines are not sharp enough to attempt any Zeeman effect work, but the possibility of splitting the lines by applying uniaxial stress to the sample is now being explored.

A programme to study the optical properties of rare-earth ions has been started. One of the systems being investigated is Ba_2GdNbO_6 with 1-2% of rare-earth impurity. In this phosphor the rare-earth sites are expected to have cubic symmetry. Phosphors doped with europium and samarium have already been prepared and these samples show a red fluorescence. A series of rare-earth orthoferrite compounds ($REFeO_3$) are also being prepared. Difficulties have been encountered in getting enough light through these samples, and attempts are now under way to prepare single crystals of these materials.

The fluorescence spectrum at liquid helium temperature of CaO doped with bismuth consists of two alternating series of lines in the near ultraviolet. The high energy series is significantly enhanced relative to the other in magnetic fields up to 77 kilogauss, but no resolvable Zeeman effect has been observed. This phenomenon has led to a revision of the energy level scheme previously proposed. This is believed to be the first example

of magnetic enhancement of fluorescence, which is probably analogous to the magnetically induced absorption lines found in $CaF_2(Sm^{2+})$ and $SrF_2(Sm^{2+})$. As expected the enhancement appears to grow quadratically with field strength, but saturation is significant above 50 kilogauss.

(3) Magnetic circular dichroism

Magnetic circular dichroism equipment has just been installed and will be used in conjunction with the horizontal bore superconducting magnet to study spectra at various temperatures down to 4.2°K. MCD studies will initially be carried out on MgO and CaO doped with metal ions. This research will complement the results of conventional spectroscopy in ascertaining the symmetry and oxidation state of the dopant ions formed by heat treatment, chemical reduction and irradiation. The additional information provided by MCD includes evaluation of g values and degeneracies of various energy levels and the possibility of locating weak transitions not normally observed in absorption spectra.

(4) Mössbauer spectroscopy

In order to supplement the results of the optical research programme being carried out in the department, a Mössbauer spectroscopy system has been established. This technique is particularly useful for studying the magnetic properties of the relevant crystalline materials under the influence of high external magnetic fields. The construction of an efficient and linear Mössbauer drive and spectrometer has been carried out within the department. Initial spectra obtained with the system have shown that the linearity is excellent and the apparatus capable of driving the quite large masses needed for low temperature magnetic field studies. To enable low temperatures to be achieved a cryostat, designed to allow quick sample changing, is now under construction. Counting systems for this project are being designed in conjunction with Lucas Heights Research Establishment.

(5) Infrared spectroscopy

Using the Perkin-Elmer 180 infrared spectrophotometer, measurements have been carried out at room temperature and liquid helium temperatures on MgO, CaO and SrO to determine the fundamental lattice vibration and multiphonon absorption spectra of these substances in the wavelength range 2000 cm^{-1} to 180 cm^{-1}. Samples of thickness ranging from several millimetres down to an effective thickness of 5 micron, were prepared enabling full spectra to be obtained. An analysis is being carried out in terms of the various infrared active fundamental and sum modes of vibration of the crystal lattice. A similar preliminary study has been made for the materials of the group, germanium, silicon and diamond. An investigation is also being carried out on the absorption line spectrum of OH^- impurity centres associated with vacancies, positive holes and trivalent ion impurities in MgO and CaO. Several new absorption lines have been discovered in this group in the range 4000 to 2000 cm^{-1}. These are being investigated using various techniques which include the application of electric fields, stress, low temperatures and heating of the crystals in various atmospheres. Previously

unreported absorption lines have also been found in the infrared region, associated with the luminescence centres in CaO. It is thought that these may be due to H^+ impurities associated with the colour centres of CaO. These are also being investigated using the above techniques. In parallel with work carried out in the visible and near infrared, the infrared spectrum of various thicknesses of the mineral serpentine, $Mg_6Si_4O_{10}(OH)_8$, have been recorded to determine the fundamental OH^- and lattice absorptions, as an aid to the investigation of its crystal structure.

(6) Crystal growth and preparation

A major part of any solid state study is concerned with the growing and cutting of suitable samples. One furnace has been constructed for crystal growth and treatment up to 1000°C and a commercial muffle furnace has been installed for heat treatment to 1250°C. A Capco crystal cutter has been installed for cutting thin crystal sections down to about 150 microns in thickness. Coarse and fine grinding, followed by polishing, complete the crystal preparation procedures.

PUBLICATIONS

Munday, B.C. and Street, R.[++], Spin density wave processes in chromium metal, Journal of Physics F: Metal Physics, 1, 498-510, (1971).

Munday, B.C., Magnetoelastic behaviour of dilute chromium alloys, physica status solidi (a) 8, (1971).

[++]Physics Department, Monash University.