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THE USE OF ULTRASONIC WAVES AND PHONONS IN STUDYING PARAMAGNETIC CRYSTALS*

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A review is made of the use of acoustic paramagnetic resonance and phonon spectroscopy using superconducting tunnel junctions to study paramagnetic ions in dielectric crystals with special emphasis on those which undergo a Jahn–Teller effect. Some examples of the use of these methods is given, particularly of work done at the University of Nottingham.

ИСПОЛЬЗОВАНИЕ УЛЬТРАЗВУКОВЫХ ВОЛН И ФОНОНОВ ДЛЯ ИЗУЧЕНИЯ ПАРАМАГНИТНЫХ КРИСТАЛЛОВ

В работе дается обзор применения акустического парамагнитного резонанса и фононной спектроскопии с использованием сверхпроводящих туннельных непреходов для изучения парамагнитных ионов в диэлектрических кристаллах, причём особое внимание уделяется тем кристаллам, в которых наблюдается эффект Яна–Теллера. Приведены некоторые примеры использования этих методов, в частности, работа, выполненая в Ноттингемском университете.

I. INTRODUCTION

The study of paramagnetic impurities doped into a dielectric crystal has been an active field for many years. Many investigations using electron spin resonance, optical spectroscopy, specific heat and thermal conductivity measurements have been made on such system. In recent years there has been special interest in paramagnetic ions which are very strongly coupled to the crystal lattice. These ions are likely to undergo the Jahn—Teller effect. This arises when the environment of a paramagnetic ion can distort to a lower symmetry and lower the electronic energy of the ion. The elastic energy of the crystal lattice increases but a new position of lower total energy can be achieved. This Jahn—Teller distortion may be static or dynamic. A recent review of the theory of Jahn—Teller effects, including a full

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bibliography, is given by Bates [1]. Bates also gives references to experimental work on Jahn—Teller systems by electron spin resonance and various forms of optical spectroscopy as well as by phonon spectroscopic methods.

Because of the strong ion-lattice coupling found in Jahn—Teller ions, phonon spectroscopy is an especially useful tool in studying these systems. This review is concerned with two of these methods, acoustic paramagnetic resonance and phonon spectroscopy using superconducting tunnel junctions. Another useful ultrasonic method uses acoustic relaxation losses, the method can be found described in the papers by King et al. [2, 3] and the references given there.

Before the methods themeselves and some of the results obtained are described, an important general point must be made. The paramagnetic ions with we are concerned are very strongly coupled to the crystal lattice and are hence very sensitive to small distortions of the crystal lattice environment in which they are placed. Small random internal strains in the lattice broaden the resonance and govern the line shape; in some instances the most obvious features of a resonance line can be due to the internal strain distribution in the crystal. An important example is given by Buisson and Nahmani [4]. The sources of the random internal strains may be dislocations, charge compensation centres or the ions themselves which are doped into the dielectric crystal.

II. ACOUSTIC PARAMAGNETIC RESONANCE

The technique of acoustic paramagnetic resonance (a.p.r.) is now well established. It has been described by Tucker and Rampton [5].

Experiments are made using a conventional pulse-echo technique with a piezoelectric transducer in a microwave re-entrant cavity. Quartz rod transducers and evaporated thin film cadmium sulphide transducers have been used. The magnitude of an ultrasonic echo is plotted as a function of magnetic field using a box-car detector to improve the signal to noise ratio. Most experiments have been made in the frequency range 9 GHz to 10 GHz. The paramagnetic absorptions increase with increasing frequency so there is an advantage in using high frequencies. The use of high frequences causes two problems. First, when using a conventional pulse-echo ultrasonic system with piezoelectric transducers the specimen surfaces must be well polished to give good echoes. The wavelength of ultrasonic waves at 9 GHz in most dielectric materials is similar to an optical wavelength and thus polishing to optical standards is required. Second, the scattering of ultrasonic waves by thermal phonons increases with frequency and in order to make a.p.r. experiments at 9 GHz temperatures below 20 K must be used. A.p.r. experiments have been made at other frequencies, see for example Lange [6] who used 1 GHz and 3 GHz or Pointon and Taylor [7] who used 16 GHz.

III. PHONON SPECTROSCOPY USING SUPERCONDUCTING TUNNEL JUNCTIONS

Spectroscopy in the frequency range approximately 90 GHz to 1.5 THz can be made by using the phonons generated by superconducting tunnel junctions. A full review of the technique has been given by Eisenmenger [8].

A superconducting tunnel junction consists of a pair of thin superconducting metal films separated by a thin insulating layer which is usually formed of the metal oxide. If a low potential is applied to the junction, a small current will flow due to tunnelling by thermally excited quasi-particles. If the potential difference is increased to a value larger than the superconducting energy gap, a large current passes due to the breaking of Cooper pairs with tunnelling. The quasi-particles after tunnelling can lose energy in two ways, by relaxing to states just above the energy gap and emitting a phonon and then by recombining to form a Cooper pair and emitting a second phonon. The resulting phonon emission spectrum has two special features, a peak at 2Δ, the energy gap of the material, due to recombination phonons and a sharp cut-off at a maximum frequency of $eV - 2\Delta$, where V is the applied voltage, due to relaxation phonons. A small modulation voltage superimposed on the steady bias modulates the intensity of the 2Δ recombination phonons and also the relaxation phonons at $eV - 2\Delta$. Hence by detecting only at the modulation frequency a spectroscopic tool is available. The detection is by means of a superconducting tunnel junction biassed to a voltage less than the energy gap, where the current is due to thermally excited quasi-particles. Incident phonons, of an energy greater than the energy gap of the detector, break the Cooper pairs and increase the quasi-particle population and hence the tunnel current. The frequency range available in using this method is determined by the detector energy gap which forms the lower limit and the generator energy gap which forms the upper limit because of phonon re-absorption. The upper limit may be greater if a thin aluminium generator is used because re-absorption is much less in aluminium than in tin or a lead-bismuth alloy, the other generator materials which have been used.

The modulation method may be either a continuous sine wave when a lock-in amplifier is used for detection or pulse modulation when a box-car is employed.

IV. RESULTS

A brief survey of results is given here, especially of work done by members of the Physics Department of the University of Nottingham.

The chromous ion has been of interest for a number of years in both magnesium oxide and aluminium oxide. A.p.r. result on chromous ions in MgO have been obtained by Marshall and Rampton [9] and by Rampton and Shellard [10].

Shellard and Rampton used a modified apparatus in which a uniaxial compression could be applied to the sample while a.p.r. was observed. The theoretical interpretation of these is due to Fletcher and Stevens [11] and Ham [12]. Recently we have obtained further information of this system using superconducting tunnel junctions [13]. The rather similar problem of chromous ions in CaO has been studied by a.p.r. unpublished work by Rampton and Shellard shows that the spin-orbit splitting and the tunnelling splitting of the chromous ion are both much smaller in CaO than in MgO.

The chromous ion and the isoelectric magnetic ion have been studied in aluminium oxide. A.p.r. results have been presented by Anderson et al. [14, 15, 16]. The effect of an applied electric field on the a.p.r. line shapes was shown by Anderson et al. [16] and established that the lines were broadened by random internal electric fields due to charged defects. The theory of these ions has been developed by Bates [17] for Cr^{2+} in Al_2O_3 and by Bates et al. [18] for Mn^{3+} in Al_2O_3. Work has been done on these systems using superconducting tunnel junctions with results approximately in agreement with the theoretical predictions [18, 19].

V. CONCLUSIONS

In order to understand the behaviour of paramagnetic ions in dielectric crystals in cases where the Jahn—Teller effect is of importance, experimental information is required on the lowlying energy levels. A.p.r. and superconducting tunnel junction phonon spectroscopy are useful tools and have already provided much useful informations.

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