Magnetic Resonance of the Solid State

A Conference Report by ***D. J. E. Ingram***

A MEETING of the Radiofrequency Spectroscopy Group was held in Newcastle on September 22nd and 23rd to discuss recent work on "Magnetic Resonance of the Solid State". The number attending this meeting and the keen interest in the work reported were striking evidence of the increasing power of these new techniques as a probe into the details of solid-state structure and interactions. The general theme of the discussion was the study of impurities and defects in ionic crystals, which appropriately linked with the research being carried out by Dr. Schneider's group at Newcastle itself. The study of impurity and defect centers is a subject in which magnetic resonance is making very considerable contributions at the moment, in a somewhat similar way to its applications in detailed organic analysis and the investigation of free-radical systems on the more chemical side.

The meeting was particularly fortunate in having Professors M. H. L. Pryce and B. Bleaney as its first two speakers. The early development of electron resonance and its application to ionic crystals was largely due to the excellent cooperation between the theoretical and experimental groups headed by these two scientists, and one of the most encouraging features of the present meeting was the evidence of the continued and active cooperation between these two sides of the subject. The particular items of direct concern to the discussion were outlined in an introductory survey by Professor Pryce and can be briefly summarized as: (1) impurity atoms, (2) trapped electrons and holes, (3) vacancies, (4) interstitial atoms, dislocations and strains, and (5) excited states. The unpaired electrons associated with these centers allow electron resonance to be used to probe into their detailed structure and to measure their concentrations with high sensitivity. The disturbing effects of these centers on the normal constituents of the crystal can also be measured by the shifts and line-shape changes which they produce in the nuclear-resonance spectra, and hence both electron and nuclear resonance can be used in their study.

One of the most interesting points that the conference served to underline was the great advantage of employing both techniques for simultaneous attack on any given solid-state problem. It is probably fair to say that, until recently, research workers were interested in making measurements either with electron resonance or with nuclear resonance, and that very few employed both techniques. This outlook is now rapidly altering as the advantages of combining the information obtained from each is becoming so apparent. This becomes even more striking when *simultaneous* electron and nuclear-resonance experiments are carried out on the same sample, as in "Overhauser" or "double resonance" techniques. It would appear that the advent of these double-resonance methods might almost be taken as a second milestone in the history of resonance work, and from now on one might expect electron and nuclear resonance to be used together instead of as separate research tools.

A large amount of detailed information can still be obtained from each technique on its own, of course, as is illustrated by the measurements on "superhyperfine structure" produced by atoms surrounding the impurity centers. Professor Bleaney described some of Tinkham's work on manganese impurity atoms in zinc fluoride as a good example of this. The basic lattice structure is shown in Fig. 1 where one of the manganese impurity atoms is shown substituted for the normal zinc atom. It is seen that this is surrounded by six fluorine atoms, four of these lying in a plane at the corners of a rectangle and at equal distances from the manganese atom, while the other two lie above and below at a distance slightly greater than the first four. In the normal electron-resonance spectrum of manganese, when there is no interaction with the surrounding atoms, each electronic transition is split into six single, well-resolved hyperfine components, due to the nuclear spin of

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Mn^{55}, $I = 5/2$. If there is any covalent binding and charge transfer between the impurity atom and its neighbors, however, there will be an additional interaction between the unpaired electron and the nuclear moments of the surrounding atoms. The exact coupling with each will depend on the direction that the external magnetic field makes with the bond between the given fluorine atom and the manganese, and since each fluorine nucleus has two possible orientations in the applied field ($I = 1/2$), there will be 2^6 slightly different interactions for any arbitrary direction. If the field is applied along one of the three orthogonal axes, x, y, or z, however, there will be equal coupling to the four fluorine nuclei in the plane, and this will produce a splitting of the single manganese hyperfine line into five components of intensity ratio 1: 4: 6: 4: 1. The other two fluorines are also equally coupled, but with a slightly smaller interaction, and they will therefore produce a further splitting of each component into three with an intensity ratio of 1: 2: 1. The complete predicted pattern for such a "superhyperfine interaction" is therefore as shown in Fig. 2(b), and the actual spectrum observed is shown above it in Fig. 2(a). Although the detailed analysis of such complex patterns can be somewhat difficult it is evident that very detailed information can be obtained on the actual bonding of the impurity atom to its neighbors. Moreover some important points, such as whether the impurity atom enters the lattice substitutionally or interstitially, can often be determined immediately from the symmetry of the resulting spectral splittings. The use of hyperfine-structure analysis of impurity centers and trapped electrons was also illustrated in detail by some of the following papers.

The information that can be obtained from asymmetries in the electron resonance spectrum was also illustrated very vividly by the work that Professor J. Wertz

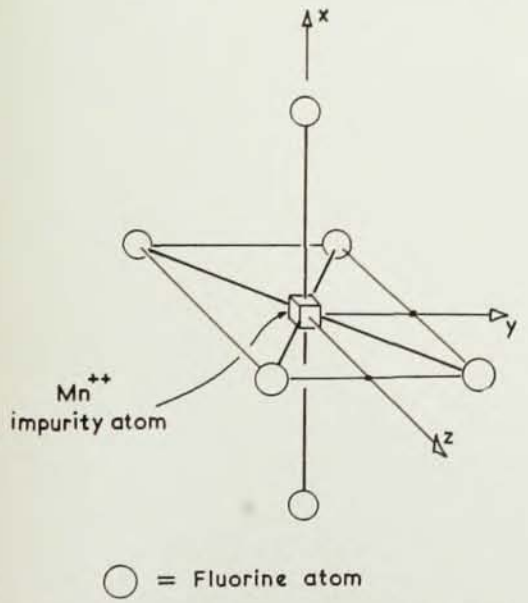

Fig. 1. Structure of zinc fluoride lattice around a manganese impurity atom.

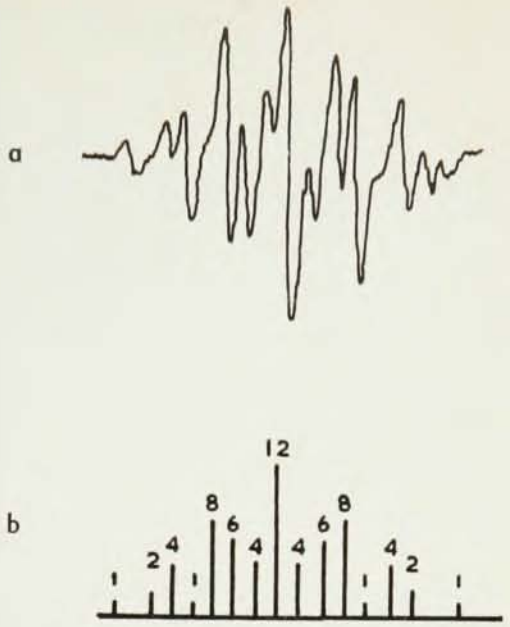

Fig. 2a. Observed "superhyperfine structure" due to fluorines on one manganese hyperfine component. (Derivative tracing after Tinkham.)

Fig. 2b. Predicted intensities for the superhyperfine pattern with field along an orthogonal axis. Numbers indicate line intensities.

described on vacancies in the magnesium oxide lattice structure. Particular interest is now being focused on the nature of V centers in such crystals, such a center being produced when a positive ion is missing from the lattice. In order to preserve neutrality of charge an electron must therefore also be missing from one of the neighboring ions, and this missing electron may be viewed as a positive "hole" in the electron shells of the surrounding atoms. Such a state of affairs is illustrated schematically in Fig. 3, where the positive ions are represented by the squares and the negative ions by the circles. The vacancy is indicated by the dotted square in the center and the associated missing electron by the positive charge, surrounded by a triangle, and located on the negative ion at A. In a symmetrical crystal structure this "hole" will have as much tendency to reside on any of the other neighboring ions B, C or D as on A, and hence can be regarded as moving in a delocalized symmetrical orbit about the vacancy site. The electron-resonance signal observed from such a center will therefore be completely isotropic, with no g-value variation.

If, on the other hand, a positively charged impurity atom such as Cr^{3+} is located in the lattice close to this vacancy, such as at the position labeled E, then the "hole" will be localized on the negative ion at A due to the electrostatic repulsion. There is now an axis of symmetry through the site of the vacancy and the location of the hole, and hence an anisotropic resonance spectrum is obtained, with a different g value when the field is applied along the axis than when perpendicular to it.

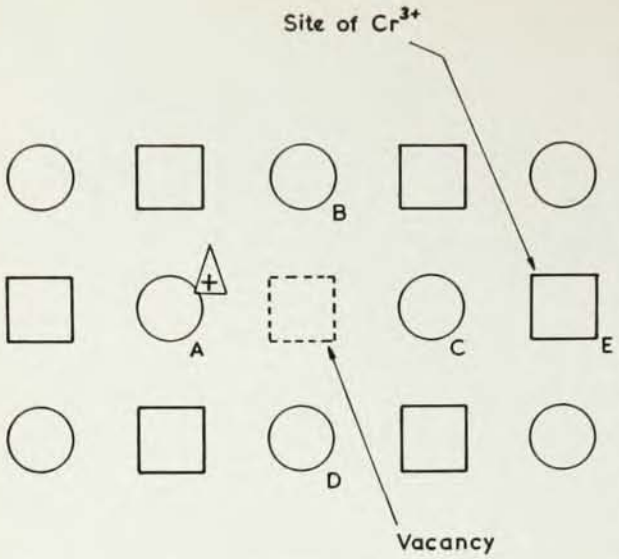

Fig. 3. Location of V center in magnesium oxide lattice. Open squares represent positive ions. Open circles represent negative ions.

It is therefore evident that information on the surroundings of the center as well as on its own structure can be obtained from such measurements. Examples were also given of cases in which the variation in the mobility of the holes with temperature could be determined from changes in the resonance spectra.

The final session of the meeting was devoted to cyclotron resonance in metals and semiconductors. This was introduced by Professor A. F. Kip who outlined the peculiar difficulties in studying metals, and the recent ideas which had enabled these to be overcome. In a simple cyclotron resonance experiment the oscillating microwave electric field is applied in the same plane as the orbit of the rotating electron and at right angles to the applied magnetic field. In this way the rotational motion of the electron can abstract energy from the oscillating field, and this is detected by a fall in the transmitted power. Only electrons in the correct phase take part in this interaction, however, and as a result of this "phase focusing" a large number of electrons tend to become concentrated at the same point in each cycle. If the number of conduction electrons involved is very high, as in a metal, this produces a large oscillating polarization and internal electric field, which tend to shift the position of the resonance peak and smear out the absorption line. It initially appeared that this effect might prove an insuperable difficulty and it would not be possible to observe cyclotron resonance in metal conductors.

Recently, however, it has been shown that the difficulties associated with phase focusing should be overcome if experiments are carried out under anomalous skin-depth conditions with the oscillating electric field and the dc magnetic field applied accurately parallel to the surface of the metal. This is outlined schematically in Fig. 4, where the rectangular block represents a piece of metal with a skin depth of δ, as indicated. The magnetic field, H, is applied parallel to the top surface so that the electrons will be rotating in orbits in a plane normal to the paper. One such orbit is shown at such a depth that only its top portion reaches into the skin depth and is affected by the oscillating electric field. This field is now applied in the same direction as the magnetic field and its effect on such an electron will therefore be a lateral movement from left to right. The electron's orbit is thus converted into a spiral instead of into an enlarged circle with phase-focused electrons. Under resonance conditions the given electron will suffer the same force each time it comes up within the skin depth, and a discrete absorption will thus be obtained with no interfering effects of induced polarization. It may be noted that a whole series of subharmonic resonance frequencies is also predicted for such an experiment, since electrons rising to the skin depth after two, or three, periods will also be in the right phase to interact. Recent experiments on very pure samples of tin and copper have strikingly confirmed this theory, with the subharmonic resonance peaks stretching back into low field values.

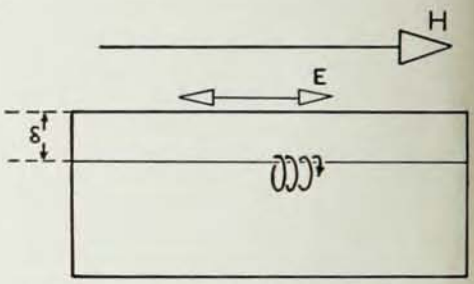

Fig. 4. Observation of cyclotron resonance in metals. H is the dc magnetic field, E the microwave electric field, and δ the skin depth.

This work on the cyclotron resonance of metals is somewhat symbolic of magnetic resonance at the moment. On each occasion when it has appeared that most of the useful and possible measurements have been done, some new principle or technique has come to light which has opened up a whole new field of experiment. Now, with the advent of double resonance, and the ever widening applications of resonance to impurity and defect studies, irradiation damage, and free-radical problems, a wide field of research still lies wide open to these methods.

In this connection the regular meetings envisaged by the Radiofrequency Spectroscopy Group should serve a very useful purpose in bringing many of the workers in this field together, for comparison of results and cross-fertilization of ideas. The Newcastle meeting seemed particularly successful in this way and Dr. E. E. Schneider is to be congratulated on the very efficient organization of the whole proceedings.