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Electron Paramagnetic Resonance (A Review)

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For the purposes of this review, the term *electron paramagnetic resonance* is taken to refer to the resonant absorption of electromagnetic radiation by electronic systems which possess *permanent* magnetic moments (due, in general, to the orbital as well as to the spin angular momentums of electrons) and which are therefore paramagnetic. The term *paramagnetic resonance,* which is frequently encountered, refers strictly to the magnetic resonance of permanent magnetic dipoles of any type, including nuclear magnetic resonance. On the other hand, the term *electron resonance* includes cyclotron resonance (diamagnetic resonance).

In a short article of this nature, it is clearly impossible to discuss, in detail, all aspects of such a wide field. Rather, the intention is to discuss the basic principles of the electron paramagnetic resonance technique together with some results in certain fields which illustrate its range, applications, and potentialities.

1. Introduction

The phenomenon of electron paramagnetic resonance (epr) is now very well understood, owing to the extensive research carried out, particularly during the last twenty years. In addition to the intrinsic interest of the phenomenon, it is well established as an analytical tool in physics, chemistry, biology, and related fields of study.

The classes of systems which can be investigated by the epr technique are broadly categorised below.

(*a*) *Transition group ions* These groups consist of atoms or ions in which one or more of the inner electron shells is incompletely filled (e.g. the 3d shell in the iron-group ions).

(*b*) *Organic free radicals* By definition, these systems have unpaired electrons and hence a permanent magnetic moment. Most free radicals tend, by their very nature, to be very reactive and hence short-lived. Special techniques have been developed for investigating paramagnetic systems having such short lifetimes (~milliseconds).

The application of epr techniques to the study of free radicals has been of great use in chemical and biological fields of research.

(*c*) *Defects in solids* Electrons and/or holes may be trapped at a wide variety of defects in solids (e.g. impurity atoms, vacancies) which may be produced by chemical means, radiation damage, or mechanical damage.

(*d*) *Metals* The conduction electrons in metals and semiconductors have a paramagnetic susceptibility, and epr has been observed in a wide variety of materials.

(*e*) *Gases* A number of gases are paramagnetic either in their natural state (e.g. oxygen) or else when sustaining a gas discharge.

2. Basic Principles

For a free ion having total angular momentum **J**, situated in a magnetic field **B**, the energy levels are

$$W_{M_J} = g\beta B M_J \qquad (1)$$

where β is the Bohr magneton, and M_J, the projection of **J** in the direction of **B**, ranges from $-J$ to $+J$ in integral steps. The g-factor (spectroscopic splitting factor) is given by Landé's formula:

$$g = 1 + \left(\frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}\right) \qquad (2)$$

where **L** and **J** are orbital and spin angular momentums respectively.

Since the selection rule for magnetic dipole transitions is $\Delta M = \pm 1$, the quantum of energy required to induce an electron spin resonance transition is given by

$$\mathrm{h}\nu = g\beta B \tag{3}$$

Considerations of sensitivity of detection lead to the conclusion that the minimum detectable number of electron "spins" is proportional to $(\nu)^{-7/2}$. In practice, the maximum operating frequency is limited by a number of practical features, of which an important one is the availability of large enough magnetic fields which are also homogeneous enough over the volume of a practicably sized sample. The most popular frequency band is centred about 9.5 kMc/sec (X-band microwaves), and for $g \sim 2$ the required magnetic field $\simeq 3.3$ kG. Oscillators with good frequency stability and power outputs ranging from 100 mW to a few watts are readily available. epr spectrometers operating at K-band frequencies (24 kMc/sec, 8 kG), and Q-band frequencies (34 kMc/sec, 12 kG) are also in frequent use. Recent developments in the fields of millimetre waves and superconducting magnets have facilitated the development of spectrometers operating at 75 kMc/sec (24 kG) and 150 kMc/sec (48 kG). A limiting factor at these latter frequencies is the small amount of power presently available ($\sim$milliwatts).

Thus, in practice, the epr technique is a branch of microwave spectroscopy. Because of the existence of highly monochromatic sources of radiation, dispersive elements are not needed in the spectrometer, a source of radiation, an absorption cell (cavity), and a detector being the essential components of the spectrometer. Considerable ingenuity has been exercised in improving methods of detection [1] and, in practice, the minimum detectable number of "spins", for a line width of 10 G, is $\sim 10^{12}$ for a microwave power level at the sample of 10 mW. For a sample having a volume ~ 1 cm^3, this represents a minimum detectable concentration of "spins" as low as 1 part in 10^{10}.

3. General Features of epr Spectra

The features of an epr spectrum which yield useful information can be collected under five headings.

(*a*) *g-factor* This factor determines the value of the magnetic field at which the resonance will be observed, for a given operating frequency. The vast majority of experimentally observed g-factors lie between about 1.5 and 2.5 and the important quantity is the "g-shift" $(g - g_0)$, where $g_0 = 2.00229$ is the free-electron g-factor. $|(g - g_0)|$ is proportional to the amount of spin-orbit coupling for the electron.

(*b*) *Fine structure* This is related to the existence of a zero-field splitting of the spin degeneracy of the energy levels of the paramagnetic system.

(*c*) *Hyperfine structure* This is due to the interaction between the magnetic dipole moment and/or nuclear quadrupole moment of the nuclei of the paramagnetic system with the unpaired electrons.

(*d*) *Relaxation behaviour* There are many types of process by which paramagnetic systems may relax to their lowest energy state after being excited in a resonant absorption process. The nature of the coupling between the paramagnetic system and the phonons present in the host medium is extremely important in this context.

(*e*) *Intensity* The integrated intensity of an epr spectrum is directly proportional to the number of paramagnetic systems taking part in the resonance process.

The width of epr lines can be due to a variety of factors. For instance, there are many situations in which fine structure is unresolved, or there may be a "spread" of g-values due to, for example, internal strains in a crystal. Unresolved hyperfine structure gives rise to "inhomogeneous" broadening ("Gaussian" line shape), whereas "lifetime" broadening, due to very short relaxation times ($\sim 10^{-7}$ sec or less), gives "homogeneous" broadening ("Lorentzian" line shape). If the concentration of paramagnetic centres is high enough, magnetic dipole-dipole interactions may cause significant broadening although, in the same situation, exchange interaction may cause a counteracting line-narrowing effect. Line widths ranging from ~ 0.1 to 1000 G are observed in practice.

4. The Interpretation of epr Spectra

In fluids, motional effects "average-out" many of the interactions which can produce structure in an epr spectrum. So, for illustrative purposes, the spectrum of a paramagnetic system in a crystalline solid will be considered.

The paramagnetic system is influenced by many interactions, such as spin-orbit interaction, the interaction of the externally applied magnetic field with the electronic and nuclear magnetic moments, and electrostatic and covalent interactions with the crystalline environment. epr is usually concerned with transitions between the low-lying energy levels of a paramagnetic ion, and the concept of a "Spin Hamiltonian" has been extremely valuable in describing the magnetic behaviour of these levels [2]. The spin-orbit interaction terms and the interaction with the externally applied magnetic field (ignoring electron-nuclear interactions for the present) are treated as perturbations of the Hamiltonian of the paramagnetic ion in the crystal. No representation is chosen for spin angular-momentum operators, and the perturbation is carried out to second order. Thus an expression is obtained which is an explicit function of the spin angular-momentum operator and whose eigen-values are the energies of the ion. The form of the Spin Hamiltonian, $\mathscr{H}_S$, is determined by symmetry considerations, and epr is an extremely powerful means for determining the local symmetry of paramagnetic ions. In the case of axial symmetry, for example, $\mathscr{H}_S$ has the simple form:

$$\mathscr{H}_S = \beta \mathbf{B}.\mathbf{g}.\mathbf{S} + \mathbf{S}.\mathbf{D}.\mathbf{S} \qquad (4)$$

Here, the coefficients **g** and **D** are symmetric second-rank tensors which are intimately related to the splittings of the low-lying energy levels and to the spin-orbit coupling. D determines the zero-field splitting of the energy levels. For **B** parallel to the axis of symmetry, it follows that the positions of the fine-structure lines are determined by:

$$B = B_0 - 2D\,(M_S - \tfrac{1}{2}) \qquad (5)$$

Hence D, which is now expressed in gauss, can be easily measured.

It must be emphasised that the S appearing in (4) is an effective spin, such that $(2S + 1)$ is equal to the number of energy levels whose magnetic properties are described by the Spin Hamiltonian.

Electron-nuclear interactions are described by adding a term to $\mathscr{H}_S$ having the general forms **S.A.I**, where **I** is the spin of the nucleus, which splits the electronic transitions into $(2I + 1)$ hyperfine components. The magnitude of A is proportional to $< 1/r^3 >$, where r is the electron-nuclear separation, except in the case of s-electrons where A is proportional to $|\psi(0)|^2$, the square of the magnitude of the electron wave function at the nucleus. Hence, hyperfine structure can be extremely valuable in identifying paramagnetic centres and, in addition, yields useful information regarding the distribution of the electron wave function around the nucleus of the paramagnetic ion and also, in some circumstances, the distribution around neighbouring nuclei which possess magnetic moments. The electron-nuclear double resonance (endor) technique [3] is especially useful in this context, as it is capable of resolving much smaller hyperfine splittings than the conventional epr technique.

The great value of the Spin Hamiltonian concept is that the symmetry and structure of the epr spectrum can be specified in terms of a very small number of parameters. It is then possible, in principle at least, to calculate the electron wave functions and energy levels of the paramagnetic ion.

In the foregoing discussion, it was assumed that the unpaired electrons were localised near the site occupied by the paramagnetic ion and **g** and **D** are determined by the spin-orbit interaction and the splittings of the low-lying energy levels of the ion. If the unpaired electrons are extremely delocalised, as for certain paramagnetic centres in semiconductors, then the spin resonance properties of the centre are determined by the energy band structure of the host crystal [4].

In summary, it can be said that the two outstanding features of the epr technique are its great sensitivity and the information it yields regarding the symmetry of paramagnetic systems.

5. epr in Semiconductors

5.1. Shallow Donor Impurities

epr has proved to be a very important tool both in identifying impurities in a wide variety of inorganic semiconductors (Group-IV semiconductors, Group-III/V and Group-II/VI compounds) and also in elucidating the detailed structure of the impurity centres.

The shallow donor impurities [5] (phosphorus, arsenic, antimony, bismuth, lithium) in silicon and germanium are paramagnetic, because of the unpaired "donor" electron, and have proved a fruitful field for investigation by the epr technique [6]. On the one hand, the host materials can be prepared as extremely pure single crystals having a relatively simple crystal structure (diamond-type structure); this has enabled a large amount of information to be obtained relating to epr of covalently bonded, tetrahedrally coordinated ions. On the other hand, the results of epr have formed a very important contribution to the understanding of the detailed structure of the donor centres. For instance, group theoretical arguments predicted that the lowest energy levels of the donor impurity centres in silicon should consist of a singlet state separated from a doublet state and a triplet state, but without predicting which of these states was lowest in energy. Only the lowest state of the donor centre is involved in the epr experiments and, since the epr spectrum exhibited isotropic hyperfine structure, it was concluded that the singlet state is the ground state, since this is the only one with $|\psi(0)| \neq 0$.

The g-factors of the shallow donor centres are related to the energy gap between the conduction and valence bands, to the spin-orbit splittings of the energy bands, and to the electron effective mass. In both silicon, where $(g - g_0) = -0.003$, and germanium, where $(g - g_0) = -0.29$, the agreement between theory and experiment is very good [7, 8].

If a single crystal of silicon is subjected to a uniaxial compression (strains up to $\sim 10^{-3}$), then the equivalence of the six conduction-band minima is removed. As a result, there is admixing of the shallow donor-impurity doublet/triplet state with the ground state, and hence there is a reduction of the isotropic hyperfine interaction. From such experiments, it was calculated that the separation between the doublet/triplet level and the ground state was 0.015 eV for phosphorus-doped silicon, and that the deformation potential was 8 eV approximately [9].

The epr spectra of shallow donor impurities in germanium are essentially similar to those in silicon, although experiments have been less fruitful for two principal reasons. Firstly, the spin-orbit splitting of the valence band is about one order of magnitude larger than in silicon, resulting in much shorter spin-lattice relaxation times. Secondly, random local strains in the crystal produce a spread of g-values for the impurities and hence cause line-broadening.

Phosphorus-doped silicon has proved to be an excellent medium for studying a wide range of relaxation phenomena because of the long electron spin-lattice relaxation times (as long as 10^3 sec). Additional advantages are the purity of the single crystals and the comparatively simple energy level system (for phosphorus the nuclear spin quantum number $I = \frac{1}{2}$, hence the hyperfine structure consists of two lines only, and also there are no quadrupole effects). In contrast, in many other materials of interest from the point of view of relaxation processes (e.g. potential maser materials), the comparison between theory and experiment is complicated by the presence of a wide variety of lattice defects and by non-stoichiometry.

Because of the long relaxation times, it is possible to produce a polarisation of the nuclear spin ensemble by a variety of techniques [6]. The nuclear polarisation P is defined through

$$P = \langle I_z \rangle / I \tag{6}$$

where $\langle I_z \rangle$ is the ensemble average of the component of I in the direction of the externally applied magnetic field $\mathbf{B}$. Values of P which are greater by a factor $\sim 10^2$ over the thermal equilibrium value have been obtained. Nuclear physicists are very interested in obtaining targets containing polarised nuclei for scattering experiments and the investigation of nuclear decay modes, parity non-conservation, and the angular distribution of α-, β-, and γ-rays. It is possible to obtain nuclear polarisations without the use of microwave radiation by means of the interaction between "hot" conduction electrons (electrons not in thermal equilibrium with the lattice) and magnetic nuclei. So far, indium antimonide has been investigated most closely in this respect [10].

The endor technique has a much greater power (by a factor $\sim 10^3$) for resolving hyperfine interactions than the conventional epr technique, providing that the epr transitions can be partially saturated; it was first developed in connexion with shallow donor impurities in silicon [3]. For these impurities, the donor electron wave function extends over many hundreds of unit cells, and hyperfine interactions with the randomly distributed Si^{29} nuclei (5% abundant, $I = \frac{1}{2}$, whereas $I = 0$ for 95% abundant Si^{28}) are the dominant source of the inhomogeneous broadening of the epr lines. With the aid of the endor technique, the Si^{29} hyperfine structure can be resolved as far as the twenty-third nearest neighbour of shallow donor impurity. Since the hyperfine interaction energy is related to the amplitude of the donor electron wave function at the Si^{29} sites, important information is obtained regarding the spatial extent of the donor electron wave function. From the calculated form of this wave function, Feher was able to estimate that the conduction-band minima in silicon lie 85% of the way from the centre of the Brillouin zone to the zone boundary.

5.2. Deep Impurity Levels

A large number of elements, particularly the transition-series ions, give "deep" levels (ionisation energy ~0.5 eV) in many semiconductors [6, 4]. Considerable attention has been devoted to the electrical properties of these materials when transition-series impurities are present, but there is difficulty, in general, in associating observed electrical properties with a specific impurity, for three principal reasons. Firstly, the solubilities of these elements are low (10^{14} to 10^{17} atoms/cm^3). Secondly, the electrical properties are time-dependent, presumably owing to precipitation of the impurities. Thirdly, the electrical properties of different impurity elements are similar.

Since these impurities have relatively high ionisation energies, the unpaired electrons are localised. In contrast to the shallow donor centres, the parameters of the epr spectrum are determined by the local environment of the paramagnetic ion rather than by the energy band structure of the crystal. The position of the Fermi level in the forbidden energy gap can be varied by doping with suitable concentrations of shallow donor or acceptor impurities, and various ionisation states of the deep-lying levels may thus be obtained. It is not possible to determine from electrical measurements the type of site occupied by the deep impurities or their electronic structures. epr experiments, carried out notably by G. W. Ludwig and H. H. Woodbury [4], have revealed, from the symmetry of the observed spectra, that the transition-series ions can occupy substitutional or interstitial sites and may also occur as impurity pairs. In addition, it has been possible to deduce the electronic structures of the transition-ion impurities from the fine structure of the epr spectra.

5.3. Other Applications of the epr Technique in Semiconductors

epr and endor studies have been made on silicon carbide containing the Group-V impurity, nitrogen, and the Group-III impurity, boron [11]. Silicon carbide may exist in cubic or hexagonal forms in which the atoms are tetrahedrally coordinated, but epr has been observed only in the hexagonal form, 6H. From an analysis of the hyperfine spectra of the two impurities, combined with X-ray and electrical data, it was concluded that they occupied carbon sites in the lattice. The epr technique has also proved useful for studying the kinetics of defect formation in some of those materials whose resistivities may be so large that electro-optical experiments are difficult to perform. In these materials, the Fermi level lies near the centre of the energy gap; the procedure is to dope with a paramagnetic impurity whose ground state also lies near the centre of the energy gap. The impurity will gain or lose electrons as the Fermi level passes through it, and hence the intensity of the epr signal can be used as a monitor for the motion of the Fermi level [12].

The epr technique has also been used to monitor optically stimulated electron transfer processes. For instance, electron/hole recombination times have been measured, the interchange of electrons between shallow donor impurities and the conduction band has been investigated, and the transfer of electrons between donor and acceptor centres has been monitored [6].

epr signals which are attributed to adsorbed oxygen atoms on damaged surfaces have been observed in specimens of silicon and germanium whose surfaces had been sand-blasted or which were in powder form. The intensity, line width, and g-value of the spectra depend on the extent of the mechanical damage, the oxygen content of the ambient atmosphere, and the heat-treatment. According to Muller *et al* [13], there is a logarithmic dependence of the number of adsorbed oxygen atoms per unit area on the oxygen partial pressure in the ambient atmosphere.

6. Effects of Radiation Damage

Paramagnetic defects are formed in many diamagnetic substances which have been subjected to irradiation by electromagnetic radiation in the visible, ultraviolet, or X-ray regions of the spectrum, or by nuclear radiations. There is an enormous literature dealing with radiation damage in solids but, although the field is not a new one, there are still many controversial problems. The identification of defects is perhaps the central problem, and in many cases the epr technique has been able to yield valuable information regarding the symmetry of defects and interactions with the surroundings. Ignoring organic compounds, the solids in which the epr spectra of radiation damage defects have been studied can be roughly grouped as follows: covalent solids (Group-IV semiconductors), ionic solids (especially the alkali halides and magnesium oxide), and plastics.

epr spectra attributed to radiation-damage centres have been observed in both n- and p-type silicon and germanium irradiated by high-energy electrons (150 to 650 keV) and fast neutrons. Most attention has so far been devoted to electron-irradiated materials [14], since the defects have a relatively simple form; typically, an interstitial atom remains within a few lattice spacings of its associated vacancy. Important information has been obtained concerning the role of impurities in trapping radiation-induced primary defects and also concerning the mobilities of the primary defects. The defects on which most attention has been focused are the Si/Bl and Si/G8 centres. In both cases, epr measurements have given evidence that the primary defect is a vacancy and that it is trapped near an oxygen atom or a phosphorus atom respectively.

Measurements of the intensity of the epr spectra arising from divacancies have shown that the production rate is dependent on the orientation of the electron beam relative to the crystal axes, the optimum orientation being along the <111> directions.

By measuring the decay rate for the Si/G8 spectrum, Corbett and Watkins were able to calculate the energy barrier against dissociation.

Colour centres in alkali halides have been extensively studied by the epr and endor techniques. For example, in the case of an F-centre, an electron is trapped at a negative ion vacancy, and the centre is paramagnetic. In general, the epr lines are inhomogeneously broadened owing to unresolved hyperfine interactions with the surrounding ions. The endor technique has been invaluable in resolving these hyperfine interactions and thus in determining the spatial variation of the wave function of the trapped electron [15]. Other classes of colour centres such as V- and U-centres are also paramagnetic, and epr has been observed for interstitial hydrogen atoms.

The epr technique has been applied extensively to the study of radiation-induced (photons, electrons, neutrons) defects in oxide glasses, in which the most common defects are oxygen vacancies of a variety of types. A complicating factor in the interpretation of the epr spectra is the random orientation of the SiO_4 tetrahedra of the glassy structure. However, the paramagnetic centres are expected to have axial symmetry, and in this situation it is possible to obtain values for their *g*-factors and hyperfine-interaction constants from the "powder-pattern" epr spectra.

In X-irradiated plastics, such as Perspex, Fluon, polystyrene and polyethylene, the observed epr spectra are assumed to be due to broken C-C bonds in the polymer chain. The complex structures of the spectra are interpreted as being due to hf interaction with protons of fluorine nuclei [16]. An epr signal has also been observed in ultraviolet-irradiated Perspex and, from the growth/irradiation time characteristic, it has been associated with residual monomer [17].

7. epr in Stressed Materials

A number of epr experiments have been carried out on crystals such as nickel fluosilicate, magnesium oxide, and ruby, subjected to hydrostatic pressures up to 60 kb [18-20]. For instance, the wurtzite-to-blende structure transition in polymorphic zinc sulphide has been observed through a change in the fine-structure constant of the added impurity Mn^{2+}.

It is expected that the crystal field potential at a lattice site, which depends on the relative position of the electric charges in the lattice, will be a function of stress and temperature. The observed changes in the parameters describing the epr spectra have been related to measured values of compressibilities.

In many situations, the application of a uniaxial stress gives important additional information regarding the electron states for which epr is observed. The most important effect of the resulting strain is to lower the symmetry of the environment of the paramagnetic ion and thus to reduce any orbital degeneracy of its ground state. Generally, this gives longer relaxation times and smaller line widths owing to a reduction in the effect of random strains present in the crystal [6].

The strength of polymers is thought to be related to the rate at which chemical bonds rupture in macromolecules. Free radicals are formed in this process and appear to accumulate at rupture sites [20]. Polymers such as vulcanised rubber, Perspex, and caprone fibres have been studied by the epr technique whilst subjected to uniaxial tensile stresses, and the growth of the free-radical signal was monitored. In this way, the kinetics of the accumulation of free radicals has been compared with the creep curves [21]. These observations indicate that the epr technique can be a useful tool in the study of the degradation and deformation of stressed or mechanically damaged polymers.

8. Metals

In metals, experimental work using the epr technique has been aimed at the accurate measurement of g-values and of line widths which, in the case of metals having a cubic crystal structure, are directly related to the spin-lattice relaxation time T_S. Hence the spin-orbit coupling interaction is expected to be important in determining the line width, and the observed line widths in various metals should be related to $|(g - g_0)|$ for the conduction electrons in that metal [22]. Also, the temperature dependence of the line width (proportional to $1/T_S$) should be the same as that of the electrical resistivity (proportional to $1/T_r$, where T_r is the "resistive" relaxation time) and this has been observed in a number of alkali metals, and in aluminium.

To-date, epr has been observed from conduction electrons in a number of the alkali metals (Li, Na, K, Ce, Rb), and also for Be, Cu, Al, and the semimetals Te, Bi, Sb, and B.

Conduction electron spin resonance has also been observed in Li/Mg alloys containing up to 12 at. % Mg [23]. Magnesium has a larger spin-orbit coupling constant than lithium and so the dependence of line width (and hence T_S) upon the spin-orbit coupling interaction can be studied systematically.

9. Conclusion

It is difficult to give a firm assessment of the usefulness of the epr technique in the field of materials science since the limits of the field are not precisely defined. epr experiments in the case of mechanically stressed plastics and some inorganic solids give results which are of direct relevance to the field of materials science. In addition, however, the extreme sensitivity of the technique and the information which it can yield regarding the symmetry of paramagnetic defects give it a valuable supporting role.

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