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NUCLEAR EFFECTS IN ELECTRON SPIN
RESONANCE OF CRYSTALLINE SOLIDS

I.URSU and S.V.NISTOR

Bucharest - ROMANIA

Nuclear Effects in Electron Spin
Resonance of Crystalline Solids*

by

I. Ursu and S.V. Nistor

Institute for Atomic Physics, Bucharest

Abstract

A survey on the theory of paramagnetic ions in crystals is given. It serves as a background for presenting some recent applications in which nuclear properties are studied by means of the ESR method. The following applications are discussed: the finer effects in the hyperfine structure of ESR spectra, the temperature dependence of the hyperfine coupling of S-state ions, the observation of nuclear isotopic shift in ESR.

I. INTRODUCTION

Since its discovery by Zavoisky in 1945, electron spin resonance (ESR) sometimes called electron paramagnetic resonance or briefly paramagnetic resonance, has been developed rapidly and applied to a wide range of research problems. Essentially it forms a branch of high resolution spectroscopy using frequencies in the microwave region ($\sim 10^9$ to 10^{11} Hz). However, ESR differs from simple microwave spectroscopy in being concerned with paramagnetic materials:

Due to its high sensitivity it is mainly used for detecting small quantities of paramagnetic impurities or paramagnetic defects in different hosts ranging from liquids to crystalline

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solids from organic compounds to ionic crystals, semiconductors of metals.

It is well known that for an electron having a spin $S = 1/2$ the angular momentum is $1/2 h$ and the magnetic moment associated with the spin of electron is given by

$$\vec{\mu}_s = -g_e \beta_e \vec{S} \quad (1)$$

where $\beta = \frac{eh}{2mc}$ is the Bohr magneton and g the magnetogyric ratio of the electron equal to 2.0023. In a magnetic field \vec{H} the component of the spin angular momentum in the field direction is restricted to $\pm 1/2 h$. Thus, a graph of magnetic energy $E = -\vec{\mu}_s \cdot \vec{H}$ against magnetic field strength consists of two straight lines, which are the corresponding energy levels.

The resonance condition for a transition between these two Zeeman components is therefore

$$h\nu = g_e \beta_e H \quad (2)$$

With a magnetic field of several thousand gauss, the ESR may be induced by suitably polarized microwave radiation, the Boltzman distribution of spins between the two states ensuring a net absorption of microwave energy. An ESR spectrometer is essentially a device for supplying microwave power to a cavity and detecting the changes in its quality factor Q , the microwave cavity being placed in a strong homogeneous magnetic field. The resonance is sought by slowly varying the magnetic field through the value indicated by eq.2 and the signal may be displayed either on an oscilloscope or by means of a recording potentiometer.

Unlike the above simplest case of free electrons, in the case of paramagnetic impurities, the ESR spectra does not consist of a single absorption line at $g_e = 2.0023$ as other interactions due to the electronic orbital and nuclear angular momentum as well

as the effect of crystalline neighbourhood should be considered.

The presence of these interactions yields more complicated ESR spectra and their interpretation becomes a difficult task as many times long and complicated calculations had to be performed. Despite this fact as soon as powerful theoretical and experimental methods became available the number of results concerning the paramagnetic centers in different hosts continuously increased.

Aside its intrinsic interest, ESR spectroscopy has more applications some of them which relate to the theory of solids. Our purpose is to present some applications in which the so called hyperfine interactions due to the interaction of unpaired electrons with the nuclei play the major role. This begins with a discussion about the interactions which should be taken into account in describing the energy levels of an unpaired electron spin system in a crystalline solid. More details about the crystal field interaction will be given. Also we plan to discuss the dynamical effect of the crystal lattice introducing the orbit-lattice Hamiltonian. In this connection the spin-lattice relaxation process will be mentioned.

Next we shall discuss the hyperfine interactions in ESR spectroscopy. A review of hyperfine effects in ESR of crystalline solids will be given. Further, the effect of temperature dependence of hyperfine splitting will be presented.

Finally we shall focus our attention on some experiments concerning the observation of nuclear isotopic shift in ESR spectra. The experimental and theoretical work of Marshall et al on Fe^{3+} in MgO and Ca^{3+} in calcite is the basis of this discussion.

II. FREE ION AND CRYSTAL-FIELD INTERACTIONS IN ESR

Simple systems in isolation like the above mentioned example of free electrons in a magnetic field experiencing either no external interactions or perhaps a few specified interactions represent usefull ideals from which may be developed complex systems which more closely approach those conditions that are normally encountered in the laboratory.

Such an example is the system of paramagnetic ions contained in a crystalline lattice. In this case the analysis of the energy levels should be started [1-7] by considering the "free ion interactions".

The major one is the Coulombian interaction between the electrons and the nucleus,

$$V_F = \sum_{k=1}^N \left(\frac{\vec{p}_k^2}{2m} - \frac{ze^2}{r_k} \right) + \sum_{k>j}^N \frac{e^2}{r_{kj}} \quad (3)$$

where the sumation goes over the N electrons belonging to a paramagnetic ion. Usually the corresponding energy splittings are of the order 10 cm^{-1} .

Without going into details [8] it should be noted that solving the corresponding Schrodinger equation and considering a Russell-Saunders coupling, the corresponding energy levels called terms are described by the quantum numbers $(SLM_L M_S)$ or $(SLJM)$ in which $J = S + L$. Generally the interest is limited to the lowest term as ESR transitions usually can be observed between its sublevels.

The next important interaction is the spin-orbit interaction which can be written as

$$V_{LS} = \sum_{j \neq k} (a_{jk} \vec{l}_j \cdot \vec{s}_k + b_{jk} \vec{l}_j \cdot \vec{l}_k + c_{jk} \vec{s}_j \cdot \vec{s}_k) \quad (4)$$

where a_{jk} , b_{jk} and c_{jk} are constants. Inside a manifold with the same L and S the equation (4) can be rewritten as

$$V_{LS} = \lambda \vec{L} \cdot \vec{S} \quad (5)$$

where λ is the spin-orbit coupling parameter. With an energy contribution of order 10^2 cm^{-1} this interaction can be considered a perturbation. The calculations show that every term splits into a set of spectral multiplets described by the quantum numbers (JM_J) .

Before proceeding to a further analysis of the free ion interactions it is worthwhile to discuss the interaction between the paramagnetic ion and its environment as this interaction yields splittings ranging from 10^4 cm^{-1} for electrons located in the outer shells to $10^2 - 10^1 \text{ cm}^{-1}$ for those situated in the inner shells.

In an ionic solid the constituent ions may be considered to first order as motionless point charges located at sites of minimum electric potential. For a crystal these sites will be distributed throughout the space of the solid in some regular and periodic fashion so that each point, whether it will be an ion site or an arbitrary point, will possess overall as well as local symmetries which may be determined from the crystal structure details. At each charge-free point of this structure, the electric field potential function V will necessarily satisfy Laplace's equation $\Delta V = 0$. This is a consequence of the assumptions of point charge immobility and of the total ionicity. Arguments based upon these idealizations will therefore be of limited utility since totally ionic as well as completely rigid structures are not realizable. However, such idealizations are

quite useful not only as models for supplying first-order approximations but also as devices for elaborating upon various interaction processes. With this crystal field model, for any field point (r, θ, φ) , the potential function can be expressed as

$$V(r, \theta, \varphi) = \sum_i \frac{e_i}{|\vec{r} - \vec{r}_i|} \quad (6)$$

This expression, which is real, may be simplified a great deal by taking advantage of the fact that each product function $r^n y_n^m(\theta, \varphi)$ is a solution to Laplace's equation so that equation (6) may be rewritten as

$$V(r, \theta, \varphi) = \sum_i \sum_{n,m} \left(\frac{e_i}{r_i} \right) \left(\frac{r}{r_i} \right)^n y_n^m(\theta_i, \varphi_i) y_n^m(\theta, \varphi) \quad (7)$$

where r_i, θ_i, φ_i and e_i are the coordinates and the electric charge of the i th crystal site, the index i being summed over all sites.

Equation (7) can also be written as

$$V(r, \theta, \varphi) = \sum_{n,m} A_n^m r^n y_n^m(\theta, \varphi) \quad (8)$$

where each A_n^m is a constant determined by the charge distributions in the crystal lattice. It can be shown by symmetry arguments that for each type of lattice the number of nonvanishing terms in eq. (8) is even smaller. Moreover, the terms with $n \geq 6$ should not be taken into account in the crystal-field potential expression. This is a consequence of the rule

$$\langle \lambda, \mu | y_n^m | \lambda, \mu' \rangle = 0 \quad (9)$$

unless $n \leq 2\lambda$ and $m = \mu - \mu'$ which must be considered into all energy level calculations.

As soon as an ion is brought into a crystal and located at a normal lattice site, its energy spectrum will be in varying

degrees altered as a consequence of the electric field generated by the other ions of the crystal. Depending upon its strength and symmetry, this field whose potential is of the form given by eq. (8) will in principle produce some splittings of the $(2S + 1)(2L + 1)$ - fold degenerate term. This removal of degeneracy, also referred to as quenching of angular momentum, was firstly treated in a fundamental manner by Bethe, who took account of crystalline point symmetry through the application of the theory of groups [9]. Aside from symmetry considerations, crystalline electric fields may be classified as being weak intermediate or strong, the classification referring to a comparison of the effects of the crystal-field relative to the Russell-Saunders and spin-orbit coupling interactions. Examples of weak crystal-field effects are given by the rare-earth series ions incorporated in various hosts. In similar hosts ions of the incomplete 3d, 4d or 5d series provide examples of intermediate and strong crystal-field effects.

As the crystal-field theory has been increasingly applied it became clear that the picture which used electrostatic field was too simple and more attention had to be given to molecular-orbital-type models. However, symmetry considerations usually decide the number of free parameters required, and will have to be included in any new theory. Thus the form of many of the crystal-field theory results will be retained, although with different matrix elements.

Another step toward a better description of the interactions inside a crystal consists of taking into account the lattice vibrations. Their effect was firstly considered in order to explain the relaxation processes, and mainly the spin-lattice relaxation process. Speaking about this process it should be noted that in any

ESR experiment in which microwave energy is supplied to a spin system, this energy flows out to a thermal reservoir by a mechanism which keeps a difference of populations between the resonant levels of the spin system, thus allowing the observation of ESR absorption. The block diagram showing the stages involved in the flow of energy from the microwave field into the thermal reservoir is shown in figure 1. If we define characteristic times T_1 and T_2

Fig. 1

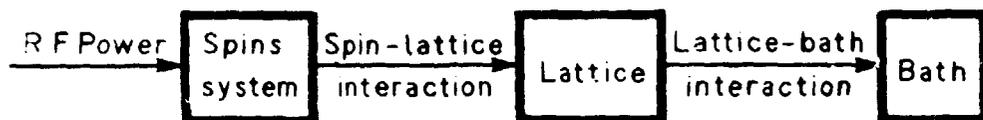
then the time taken for energy to travel from spins to bath is

$$\tau \sim T_1 + T_2 \quad (1)$$

The first proposal of a spin-lattice interaction mechanism goes far beyond in 1939 when Krönig [10] published what was essentially a phenomenological treatment of spin-lattice relaxation based upon the premise that "when the lattice vibrates, the orbital motion undergoes periodic changes due to variations in the electric field of the crystal and these changes react upon the spins causing them to alter their orientation with respect to the constant external magnetic field".

In a modern language we may say that the lattice vibrations within the real crystal modulate the crystalline electric field acting upon the magnetic ion in question and thereby induce spin transitions. There is no direct interaction between the crystal-field of the lattice and the spin but there is between the lattice and the orbital motion of the electron and the spin is made aware of this through the spin-orbit interaction.

Therefore our next problem will be to find the orbit-lattice hamiltonian describing the above mentioned interaction. Let now examine the disturbance produced by a longitudinal wave



< Fig. 1

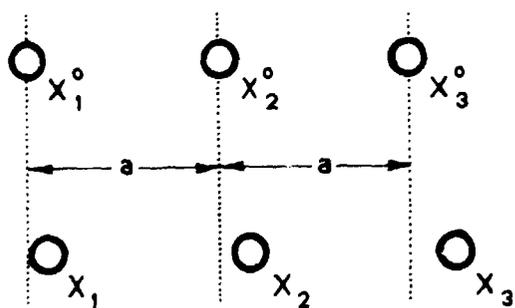


Fig. 2

in the vicinity of the paramagnetic ion. If the coordinates of three adjacent ions (the paramagnetic ion and two nearest neighbours) are x_1^0 , x_2^0 and x_3^0 (see fig. 2)

Fig. 2

then in the presence of the lattice wave these will become x_1 , x_2 and x_3 , where

$$x_1 = x_1^0 + \delta(x_1^0) \quad (11)$$

$$x_2 = x_2^0 + \delta(x_2^0)$$

$\delta(x)$ is some function of x describing the wave and $\delta(x_i)$ is its value for $x = x_i$. From equation (11) we have

$$x_2 - x_1 \approx a + a\delta'(x_1^0) \quad (12)$$

$$x_3 - x_2 \approx a + a\delta'(x_2^0) \quad (13)$$

and

$$[(x_3 - x_2) - (x_2 - x_1)] \approx a^2\delta''(x_1^0) \quad (14)$$

Thus in general, the mean separation of magnetic ion and ligand is changed and furthermore $(x_3 - x_2)$ is no longer equal to $(x_2 - x_1)$, i.e., there is no longer a centre of symmetry in the system. This implies not only a change in even order crystal-field parameters but the introduction of odd terms. However, it is known these odd terms have no matrix elements within a manifold of d or f states so they can be neglected. The important point to note is that when both longitudinal and transverse waves are included, the crystal field expansion will contain terms such as V_2^1 , V_4^1 , V_4^3 in addition to more familiar terms V_2^0 , V_2^2 , V_4^0 , etc. The order of magnitude of these vibrating potentials will be

that of corresponding static terms reduced in the ratio of the local lattice strain ϵ where

$$\epsilon = \frac{(x_2 - x_1) - (x_2^0 - x_1^0)}{x_2^0 - x_1^0} = \frac{\Delta a}{a} \quad (15)$$

To see this formally, we write the change in crystal-field potential due to lattice waves as

$$\Delta V = \sum_{n,m} \Delta V_n^m = \sum_{n,m} a_n^m \gamma_n^m \quad (16)$$

in the same way as for the static field, where the coefficients

a_n^m are simply the changes in the static coefficients A_n^m . As $A_n^m \propto a^{-(n+1)}$ we have

$$a_n^m = \Delta A_n^m \approx \left(\frac{\partial A_n^m}{\partial a} \right) \Delta a = -(n+1) A_n^m \epsilon \quad (17)$$

For order of magnitude estimates

$$\Delta V = \sum_{n,m} \Delta V_n^m \sim \sum_{n,m} V_n^m \epsilon \quad (18)$$

which represents with the approximation of a constant factor the orbit-lattice interaction Hamiltonian.

It represents a time-dependent perturbation acting on the system of spins plus phonons, and is able to induce transitions of the kind $|M, \bar{N}(v)\rangle \rightarrow |M-1, \bar{N}(v)+1\rangle$, where a paramagnetic ion jumps from state $|M\rangle$ to a lower state $|M-1\rangle$ losing a quantum of energy $h\nu$ which is converted into lattice energy, i.e., a single phonon of frequency ν is created.

For a two level system the characteristic relaxation time is given by

$$\frac{1}{T_1} = W_{21} \left\{ 1 + \exp\left(-\frac{h\nu}{kT}\right) \right\} \quad (19)$$

so we need to calculate only the downward relaxation rate W_{21} . To

to this we use the standard result of time-dependent perturbation theory:

$$w_{21} = \frac{1}{h^2} |\langle \delta | H_{0L} | i \rangle|^2 \rho(\nu) \quad (20)$$

where $|i\rangle$ and $|\delta\rangle$ represent the initial and final states of the system of spins plus phonons and $\rho(\nu)$ is the density of phonon states. As V_n^m operate only on electronic wave-functions and ϵ only on phonon states, their matrix elements may be separated and we have

$$w_{21} = \frac{1}{h^2} |\langle \psi_1 | \sum_{n,m} V_n^m | \psi_2 \rangle|^2 |\langle \bar{N} + 1 | \epsilon | \bar{N} \rangle|^2 \rho(\nu) \quad (21)$$

But the strain matrix elements are those of the simple harmonic oscillator

$$|\langle \bar{N} + 1 | \epsilon | \bar{N} \rangle|^2 = \frac{(\bar{N} + 1) h \omega}{2 M \nu^2} \quad (22)$$

so finally we have

$$\frac{1}{T_1} = \left(\frac{24 \pi^3}{h \rho \nu^3} \right) \nu^3 \coth \left(\frac{h \nu}{2 k T} \right) |\psi_1 | \sum V_n^m | \psi_2 \rangle|^2 \quad (23)$$

where ρ is the density of the crystal. The difference between longitudinal and transverse sound velocities was neglected. As, it is often the experimental case, $\frac{h \nu}{k T} \ll 1$ so we may write,

$$\frac{1}{T_1} \approx \left(\frac{48 \pi^3 h}{h^2 \rho \nu^3} \right) \nu^2 T |\langle \psi_1 | \sum V_n^m | \psi_2 \rangle|^2 \quad (24)$$

showing that T_1 is proportional to T^{-1} a result which has been proved experimentally in many cases.

III. HYPERFINE INTERACTIONS

After this brief discussion of crystal-field effects we shall focus our attention on hyperfine interactions due to coupling of the electrons with the electric and magnetic moments of the nucleus.

Electrostatic hyperfine interaction

We begin with the electrostatic hyperfine interaction which although less important in practice ($10^{-3} - 10^{-4} \text{ cm}^{-1}$) is conceptually simpler. Atomic energy levels are usually calculated under the simplifying assumption of a point nucleus with a charge Ze . If the finite nuclear dimensions are taken into account, the changes in the atomic energy levels are exceedingly small, and for nuclear spins different from zero are best observed through the removal of the degeneracy of atomic levels. The Hamiltonian responsible for the splittings can be obtained starting from the expression of the mutual electrostatic energy between two charge distributions $\rho_n(r_n)$ and $\rho_e(r_e)$

$$W_E = \iint \frac{\rho_n(r_n)\rho_e(r_e)dr_e dr_n}{|\vec{r}_n - \vec{r}_e|} \quad (25)$$

which can be expanded using the classical formula:

$$\frac{1}{|\vec{r}_n - \vec{r}_e|} = \sum_{k=0}^{\infty} \sum_{q=-k}^k \frac{r_n^k}{r_e^{k+1}} C_k^q(\theta_n, \varphi_n) C_k^{q*}(\theta_e, \varphi_e) \quad (26)$$

where $C_k^q(\theta, \varphi) = \sqrt{\frac{4\pi}{2k+1}} y_k^q(\theta, \varphi)$ are the normalized spherical harmonics. Neglecting the small penetration of the electrons inside the nucleus we take $r_e > r_n$ and write

$$W = \sum_{k,q} A_k^q B_k^{q*} \quad (27)$$

where

$$A_k^q = \int \rho_n(r_n) r_n^k C_k^q(\theta_n, \phi_n) dr_n \quad (28)$$

$$B_k^q = \int \rho_e(r_e) r_e^{-(k+1)} C_k^q(\theta_e, \phi_e) dr_e$$

If the state of nucleus is described by a wave function $\psi_n(R_1, \dots, R_A)$ of the coordinates of its A nucleons, the nuclear charge density can be written as the expectation value of the operator density of charge at the point r_n ,

$$\rho_n(r_n) = \langle \psi_n | \sum_{i=1}^A e_i \delta(r_n - R_i) | \psi_n \rangle \quad (29)$$

where e_i is $+e$ for proton and zero for neutron. From (27) and (28) A_k^q can be written as an expectation value $A_k^q = \langle \hat{A}_k^q \rangle$ where

$$\hat{A}_k^q = \sum_i e_i r_i^k C_k^q(\theta_i, \phi_i) \quad (30)$$

R_i, θ_i, ϕ_i being the polar coordinates of the A nucleons. Similarly B_k^q is the expectation value of the electron operator \hat{B}_k^q , where

$$\hat{B}_k^q = -e \sum_{i=1}^N r_i^{-(k+1)} C_k^q(\theta_i, \phi_i) \quad (31)$$

The energy of electrostatic interaction between the electrons and the nucleus is then the expectation value of a Hamiltonian

$$\hat{H}_E = \sum_{k,q} \hat{A}_k^q \hat{B}_k^q \quad (32)$$

From (30) and (31) it is clear the operators \hat{A}_k^q and \hat{B}_k^q are tensor operators of order k . The tensor operator \hat{A}_k^q with $2k + 1$ components \hat{A}_k^q is called the multipole moment of order k of the nucleus.

For diagonal matrix elements which interests us odd

values of k are forbidden if we assume, as seems well established experimentally, that stationary nuclear states have well defined parities. In particular, nuclei should have no permanent electric dipole moments ($k = 1$) as was experimentally established.

The term $k = 0$ of the electrostatic interaction corresponds to the simple case of coupling with a point charge Ze . Since nuclear radius R is much smaller than electronic radius a , the various terms of W_E decrease rapidly, roughly as $(\frac{R}{a})^k$. For this reason there is little experimental evidence of electrostatic interactions for $k > 2$ and usually only quadrupole interactions are considered.

The components of the nuclear quadrupole moment operator can be written in the form:

$$\begin{aligned}\tilde{A}_2^0 &= \frac{1}{2} \sum_i e_i (3z_i^2 - r_i^2) \\ \tilde{A}_2^{\pm 1} &= \pm \sqrt{\frac{3}{2}} \sum_i e_i z_i (x_i \pm iy_i) \\ \tilde{A}_2^{\pm 2} &= \sqrt{\frac{3}{8}} \sum_i e_i (x_i \pm iy_i)^2\end{aligned}\tag{33}$$

According to the Wigner-Eckart theorem the \tilde{A}_2^q has for a nuclear spin 1, within the manifold of the $(2I + 1)$ substates $I_z = m$ the same matrix elements as the Hermitian tensor operator formed from the components of the vector 1,

$$\begin{aligned}\hat{Q}_2^0 &= \langle I \| \alpha \| I \rangle \frac{1}{2} [3I_z^2 - I(I+1)] \\ \hat{Q}_2^{\pm 1} &= \pm \langle I \| \alpha \| I \rangle \frac{1}{2} \sqrt{\frac{3}{2}} (I_z I_{\pm} + I_{\pm} I_z) \\ \hat{Q}_2^{\pm 2} &= \langle I \| \alpha \| I \rangle \sqrt{\frac{3}{8}} I_{\pm}^2\end{aligned}\tag{34}$$

In the same manner for the electronic operator \tilde{B}_2^q it is

possible to write equivalent operators in the limit of a LS term,

$$\begin{aligned}\hat{H}_2^0 &= -e\langle r_q^{-3} \rangle \langle III \alpha || I \rangle \frac{1}{2} [3L_z^2 - L(L+1)] \\ \hat{H}_2^{\pm 1} &= \pm e\langle r_q^{-3} \rangle \langle III \alpha || I \rangle \frac{1}{2} \sqrt{\frac{3}{2}} (L_z L_{\pm} + L_{\pm} L_z) \\ \hat{H}_2^{\pm 2} &= -e\langle r_q^{-3} \rangle \langle III \alpha || I \rangle \sqrt{\frac{3}{8}} L_{\pm}^2\end{aligned}\quad (35)$$

where $\langle r_q^{-3} \rangle$ is the mean value of the third power of electron distance from nucleus, averaged over the electronic-wave functions.

Finally, we find the electric quadrupole interaction Hamiltonian for an ion with LS coupling to be given by

$$\begin{aligned}\hat{H}_E &= -\frac{\theta^2 Q \langle r_q^{-3} \rangle}{r(2I-1)} \langle III \alpha || I \rangle \left[\frac{1}{2} [3L_z^2 - L(L+1)] [3I_z^2 - I(I+1)] + \right. \\ &\quad \left. + \frac{3}{8} [(L_z L_{\pm} + L_{\pm} L_z) (I_z I_{\pm} + I_{\pm} I_z) + (L_z L_{\pm} + L_{\pm} L_z) (I_{\pm} I_z + I_z I_{\pm})] + \right. \\ &\quad \left. + \frac{3}{8} (L_{\pm}^2 I_{\pm}^2 + L_{\pm}^2 I_{\pm}^2) \right]\end{aligned}\quad (36)$$

where

$$\langle III \alpha || I \rangle = \frac{eQ}{r(2I-1)} \quad (37)$$

and the factors $\langle III \alpha || I \rangle$ are listed in tables [6].

In electron spin resonance we encounter sometimes the difficulty, which exists also for free atoms, of deciding what value to use for the quantity $\langle r_q^{-3} \rangle$. The most used hypothesis is that it has the same value as the parameter $\langle r^{-3} \rangle$ that appears in the magnetic hyperfine structure and that it can be determined from the latter if the value of the nuclear magnetic moment is known independently. However, the distortion of the charge cloud of the inner closed shells of electrons produces an appreciable change in the electric field gradient at the nucleus due to magnetic electrons in contrast to the analogous effect (diamagnetic shielding) in the magnetic case, which is quite small and

generally negligible compared to other effects that produce uncertainties in the value of $\langle r^{-3} \rangle$, particularly in solids. We may formally represent the effect of this distortion by writing $\langle r_q^{-3} \rangle = (1 - R_q) \langle r^{-3} \rangle$ where the contributions to R_q from the various closed shells may be either positive (shielding) or negative (antishielding).

Magnetic hyperfine interaction

This interaction is usually stronger ($10^{-2} - 10^{-3} \text{ cm}^{-1}$) than the electrostatic hyperfine interaction. The theory can be developed along the same lines as for the electrostatic interactions, that is, to assign electric-current densities to the electrons and to the nucleus and to calculate their interactions according to the laws of classical electromagnetism. One would thus define magnetic multipole operators for the nucleus which like the electric ones, would be tensor operators of integral order k . If one recalls the opposite parity properties of the electric field and of the magnetic field it is understandable that even, rather than odd values of k are forbidden for permanent magnetic multipoles. The first nonvanishing nuclear magnetic multipole is thus a magnetic dipole, the next a magnetic octopole. As magnetic octopoles have never been observed by means of magnetic resonance in bulk matter we shall limit ourselves at discussing the interaction with magnetic dipoles.

In the non-relativistic Pauli description of the electron the Hamiltonian in the presence of a potential A is

$$H_M = \frac{1}{2m} \left(\vec{p} + \frac{e}{c} \vec{A} \right)^2 + g_e \beta (\vec{S} \nabla \times \vec{A}) \quad (20)$$

where \vec{S} is the spin of electron and

$$\vec{A} = \frac{\vec{\mu} \times \vec{r}}{r^3} = \nabla \times \frac{\vec{\mu}}{r} \quad (39)$$

is the potential vector \vec{A} of a magnetic dipole $\vec{\mu}$.

The spin dependent part of (38) can then be written as

$$H_S = g_e \beta_e (\vec{S} \cdot \vec{\nabla})(\vec{\mu} \cdot \vec{\nabla}) - \frac{1}{3} (\vec{S} \cdot \vec{\mu}) \nabla^2 \left(\frac{1}{r}\right) - \frac{2\beta}{3} g_e (\vec{S} \cdot \vec{\mu}) \nabla^2 \left(\frac{1}{r}\right) \quad (40)$$

where only terms linear in A were taken into account.

The magnetic interaction of the nuclear moment with the electron spin $H_M = \langle \psi_e | H_S | \psi_e \rangle$ is obtained by multiplying (41) by the electronic density $\rho = \psi_e^* \psi_e$ and integrating over the electron coordinates. For $\lambda \neq 0$, H_S as given by (40) is a regular function where the first term is equal to

$$H'_S = g_e \beta_e \left(\frac{3(\vec{S} \cdot \vec{r})(\vec{\mu} \cdot \vec{r})}{r^5} - \frac{\vec{S} \cdot \vec{\mu}}{r^3} \right) \quad (41)$$

which is the usual dipole-dipole interaction and the second term vanishes because of Laplace's equation.

When λ tends toward zero the first term H'_S of (40) behaves like a spherical harmonic of order 2 under a rotation of the coordinate system. Hence if ψ_e is expanded in a sum of spherical harmonics $\psi_e = \sum_L a_L \phi_L$, the only nonvanishing contribution to $\langle \psi_e | H'_S | \psi_e \rangle$ will come from terms $\langle \phi_L | H'_S | \phi_{L'} \rangle$ such that $L+L' \geq 2$. Because a wave function ϕ_L is of order λ^L near the origin in the matrix element $\langle \phi_L | H'_S | \phi_{L'} \rangle = \int \phi_L^* H'_S \phi_{L'} \lambda^2 d\lambda d\tau$ the integrand varies as $\lambda^{(L+L'+2-3)}$ and the corresponding integral always remains finite since $L+L' \geq 2$. According to the theory of the Coulomb potential the second term of (41) is equal to $\frac{8\pi}{3} g_e \beta_e \vec{S} \cdot \vec{\mu} \delta(\vec{r})$ and by integration gives $\frac{8\pi}{3} g_e \beta_e \vec{S} \cdot \vec{\mu} |\psi_e(0)|^2$ which is finite for s electrons and zero for others.

Now we can write the Hamiltonian for the magnetic

interaction of the electron with the nucleus as

$$H = g_e \beta_e g_n \beta_n \vec{I} \left[\frac{\vec{L}}{\lambda^3} - \frac{\vec{S}}{\lambda^3} - 3 \frac{\vec{L}(\vec{S} \cdot \vec{\lambda})}{\lambda^5} + \frac{8\pi}{3} \vec{S} \delta(\vec{\lambda}) \right] \quad (42)$$

In terms of equivalent operators within a ground term (L,S) of electrons for which $\lambda \neq 0$ the magnetic hyperfine coupling can then be written as

$$H = g_e \beta_e g_n \beta_n \langle \lambda^{-3} \rangle [(\vec{L} \cdot \vec{I}) + \epsilon L(L+1)(\vec{I} \cdot \vec{S}) - \frac{3}{2}(\vec{L} \cdot \vec{I})(\vec{L} \cdot \vec{S}) - \frac{3}{2}\epsilon(\vec{L} \cdot \vec{S})(\vec{L} \cdot \vec{I})] \quad (43)$$

where

$$\epsilon = \frac{1}{2S} \langle L | \epsilon | L \rangle \quad (44)$$

The configuration interaction method

In the calculations of the crystal-field effects we have assumed that the configuration is a good quantum number and on the basis of this assumption we would have expected equation (43) to give reasonable agreement with experiment. In fact, in the important case of iron group ions the agreement is very poor. The explanation resides in the fact that d -electrons, especially those of low principal quantum number n have hyperfine couplings very much stronger than those of other electrons with $\lambda \neq 0$. It follows that if a term (L,S) whose ground configuration has no unpaired d -electrons, contains a small admixture of functions belonging to configurations with unpaired d -electrons, there may be an appreciable change in the hyperfine coupling although all other properties of the ground term remain practically unchanged. It is therefore reasonable to look for small admixtures that contain unpaired d -electrons into the ground configuration.

The conventional configuration assigned to the ions of the iron group ions in their ground state is

$$C_0 = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^n \quad (45)$$

In the ground term constructed from this configuration according to Hundt's rule the total spin S is either $n/2$ or $5 - n/2$ depending on whether $n \leq 5$ or $n \geq 5$. This configuration does not allow for a term such as $A_0 \vec{I} \vec{S} = -g_e \beta_e g_n \beta_n \langle \lambda^{-3} \rangle K \vec{I} \vec{S}$ in the hyperfine Hamiltonian however such a term is found to be necessary in order to fit the experimental data. It is convenient to introduce a quantity x characteristic of the density of unpaired spins at the nucleus:

$$x = \frac{4\pi}{5} \left\langle \sum_k \delta(\vec{r}_k) S_{kz} \right\rangle_{S_z = S} \quad (46)$$

Its expectation value is to be taken over state $S_z = S$ of the ground term. x is related to K by

$$K \langle \lambda^{-3} \rangle = -\frac{2}{3} x \quad (47)$$

For each ion of the iron group x is found to depend little on the surroundings of the ion, which makes it plausible that it is a feature of the free ion. x is also found experimentally to vary little (no more than 25%) inside the iron group ions [13,14].

Let us denote by C_1 the excited configuration

$$C_1 = 1s^2 2s^2 2p^6 3s R_\delta 3p^6 3d^n = 3s R_\delta (C_0 - 3s^2) \quad (48)$$

where R_δ means an s -orbital which is orthogonal to all the s -orbitals of C_0 . In that case the new wave function of the spin system is

$$\psi = \alpha \psi_0 + \beta \psi_1 \quad (49)$$

where β is a small arbitrary quantity.

It was hoped by Abragam and Pryce [15] that the bulk of

the anomalous hyperfine structure in the iron group was due to the configuration C_1 , and a numerical calculation of x was attempted leading [16] to a value of $x = -0.3 \times 10^{-3}$ a.u. instead of the experimental value $x = -3$ a.u.

As a result of such failures calculations of anomalous hyperfine structures were done latter using the so-called core polarization method to be described further.

The method of core polarization

The idea of magnetic polarization of an atomic or ionic core of closed electronic shells by an unfilled external shell with a total spin S originates in the earlier work of Sternheimer [17].

The idea is physically very simple; let us consider a paramagnetic ion, say Fe^{3+} in the state $S_z = S = +\frac{5}{2}$ where the spins of its five $3d$ electrons are all "up". The electrostatic repulsion between an s -electron of an inner shell with spin up, say $1s^+$ and these $3d$ electrons will not be the same as for the electron $1s^-$ as a consequence of the exclusion principle which prevents two electrons with parallel spins from occupying the same position in space.

The main task of any theory would be consequently to calculate the spin densities differences at origin of spins up and down,

$$x = \frac{4\pi}{5} \sum_{\lambda} \{ |\phi_{i\lambda}^+(0)|^2 - |\phi_{i\lambda}^-(0)|^2 \} \quad (51)$$

In contrast to the configuration interaction approach the wave function ψ for the ground state is now written as a single Slater determinant constructed solely from orbitals belonging to

the unperturbed configuration C_0 . The difference from the conventional function ψ_0 is in the use of trial wave functions where $P_{n\ell}^+(\gamma)$ is not required to be equal to $P_{n\ell}^-(\gamma)$. This method is called the unrestricted Hartree-Fock (UHF) method. We shall not describe the procedure used for writing down and solving the equations obeyed by the spin-polarized orbitals in (UHF) method. Details and bibliography can be found in the review articles of Freeman and Watson [13,14]. What is interesting is the fact that the calculated values of x are in surprisingly good agreement with experiment, considering uncertainties involved in calculation. The calculation shows that the electronic densities behave as if electrons with parallel spins did attract each other. This is why, for the inner shells $1s$, $2s$ where electrons with spins up are attracted away from the nucleus by $3d$ electrons, the spin density is negative, i.e., opposite to the orientation of the ionic spin. On the other hand the spin density is positive for $3s$ and $4s$ electrons.

Finer effects in the hyperfine structure of ESR spectra

Due to the discovery of electron-nuclear double resonance (ENDOR) method by Feher [18] the accuracy of hyperfine structure parameters measurements greatly increased. Consequently, smaller effects could be observed and measured by ESR technique. Such an effect is the hyperfine structure anomaly related to the finite size of atomic nuclei.

When an electron gets into the nucleus the magnetic properties of the latter cannot be considered anymore as those of a point-like magnetic moment. Instead the electron deals with the detailed distribution of the magnetization inside the nucleus which has a

part due to the magnetic spin-moments of the individual nucleus and a part related to their orbital motion. For two different isotopes these distributions may have different shapes and the ratio of their contributions to the magnetic hyperfine structure has no reason to be equal to the ratio of the nuclear magnetic moments.

Another effect related to the former is the fact that although two isotopes have the same charge Ze , this charge may be distributed differently inside the two nuclei, which is another reason why the ratio of the hyperfine structures may differ from that of the nuclear moments.

Let $A'_\delta \vec{I}' \vec{S}$ and $A''_\delta \vec{I}'' \vec{S}$ be the scalar parts of the hyperfine interactions for two isotopes with spins I' and I'' and magnetic moments $\vec{\mu}'$ and $\vec{\mu}''$. The hyperfine anomaly can be defined as the parameter ϵ resulting from the relation:

$$\frac{A'_\delta}{A''_\delta} = \frac{g'_n}{g''_n} (1 + \epsilon) \quad (52)$$

The ratios A'_δ/A''_δ and g'_n/g''_n can be obtained from ENDOR measurements. Consequently ϵ can be compared with the theoretical values derived from nuclear models thus providing a test of their validity. For light nuclei ϵ is 10^{-6} but for heavy ones $\epsilon > 1\%$ which could be observed experimentally. However in the analysis of ENDOR data one should be very careful as other effects like second order magnetic hyperfine structure or pseudo-nuclear Zeeman effects could simulate a hyperfine anomaly.

The temperature dependence of hyperfine coupling of S-state ions

Some years ago Walsh, Jenner and Bloembergen studying the temperature dependence of the hyperfine coupling of Mn^{2+} in MgO have observed a decrease of the hyperfine coupling parameter A with increasing temperature whereas hydrostatic pressure experiments predicted an increase of A with temperature caused by thermal expansion of the lattice. The interpretation of this behaviour as given by Simenex and Orbach [20] is based on a mechanism which involves the admixture of excited configurations of the form $3d^4ns$ into the ground $3d^5$ configuration by a dynamic phonon-induced noncubic field. Since this dynamic field is electrostatic in character the admixed s -states will have spin parallel to the spin of the $3d^5$ ground state. This will result in a net decrease of hyperfine field since the hyperfine coupling in the ground $3d^5$ configuration is primarily produced by core polarization. Because use is made of phonon to induce the s -like admixtures, the net change in hyperfine field will be proportional to the mean square strain $\langle \epsilon^2 \rangle$, quantity which increases as the fourth power of the temperature at low temperatures.

In order to estimate this effect quantitatively a perturbation approach is used for the computation of strain induced s -admixture.

Conventional perturbation theory yields

$$\psi'_{3d_\alpha} = \psi_{3d_\alpha} - \sum \frac{\langle \psi_{ns} | V_{OL} | \psi_{3d_\alpha} \rangle}{E(3d_\alpha) - E(ns)} \psi_{ns} \quad (53)$$

where α labels the particular $3d$ orbital being considered and

$$V_{OL} = \sum_{m=0, \pm 2} V(\Gamma_{3g}, 2) C(\Gamma_{3g}, 2, m) \epsilon(\Gamma_{3g}, m) + \sum_{m=\pm 1, 0} V(\Gamma_{5g}, 2) C(\Gamma_{5g}, 2, m) \epsilon(\Gamma_{5g}, -m) (-1)^m \quad (54)$$

Here $\epsilon(\Gamma_{ig}, m)$ are linear combinations of the strain tensor components transforming as the m subvector of the Γ_{ig} irreducible representation of cubic group, $C(\Gamma_{ig}, 2, m)$ are the normalized spherical harmonics. The coupling parameters calculated in a point charge approximation are:

$$V(\Gamma_{3g}, 2) = \frac{6ee_0f_1^2}{R^3}, \quad V(\Gamma_{5g}, 2) = \frac{4ee_0f_1^2}{R^3} \quad (55)$$

Performing the computations, the new ground state determinant will be

$$|{}^6S, M_S = \frac{5}{2}\rangle = |\psi'_{3d,2}, \psi'_{3d,1}, \dots, \psi'_{3d,-2}\rangle \quad (56)$$

and the perturbed hyperfine field is found from the matrix element of

$$H_{hyp} = \frac{8\pi}{3} g e^\beta e_L^2 S_z i \delta(\vec{r}_i) \quad (57)$$

Finally one obtains the hyperfine coupling constant

$$A(T) = A(0) \left[1 - CT^4 \int_0^{\theta/T} \frac{x^3 dx}{e^x - 1} \right] \quad (58)$$

In the above equation θ is the averaged Debye temperature of the crystal, and C is a parameter depending on the properties of the crystal lattice. The calculations were performed in the long wave-length approximation.

Although the value of C calculated by Simanek and Orback was an order of magnitude too small, the form of the above relation fitted very well the results of Walsh, Jr, et al. Latter,

Menne, Ames and Lee [21] extended the theory of Simanek and Orbach to rare-earth ions in cubic symmetry and obtained the expression,

$$A(T) = A(0) \left[1 - CT^6 \int_0^{\theta/T} \frac{x^5 dx}{e^x - 1} \right] \quad (59)$$

They fitted this expression to their measured temperature variation of A for Eu^{2+} in CaF_2 and found excellent agreement with the form of the variation, although their calculated C value was again an order of magnitude too small.

Several reasons were supposed to contribute to the discrepancy between experimental and calculated values of C . The inadequacy of the point-charge model in calculations of the orbit-lattice coupling constant is well known [20,22]. Indeed Simanek and Huang [23] have greatly improved the fit to C_{exp} by including covalency effects. An other source of errors could be the use of the long wavelength approximation. Meanwhile, measurements on Mn^{2+} in CaO and SrO [24] and in BaO [25] revealed that in the latter two hosts the region of linear variation extended to a temperature too low to be consistent with Simanek and Orbach theory. It was pointed out in both cases that the lattice conditions favor a low force constant accompanying the impurity and therefore a modification of the Debye spectrum owing to the existence of a low frequency resonant mode.

An improved version of the theory for rare-earth S-state ions in cubic crystals was developed later by Menne [26] and by Lee and Huang [27]. It incorporates a computation procedure valid over the entire phonon-wavelength range and contributions from both the acoustic branch based on a Debye spectrum and the optical branches based on an Einstein spectrum are determined. A good qualitative agreement with experimental data on Eu^{2+} in CaF_2 , SrF_2 and

BaF_2 was obtained. Also, recently the temperature dependence of hyperfine splitting of Gd^{3+} in ThO_2 could be explained [28] only, in the frame of this improved theory. However, like in the previous case, the quantitative agreement between experimental and calculated values of the coefficients was very poor. It seems that covalency and overlap should be considered seriously in any future theory. Despite these difficulties, it should be noted that valuable information concerning the lattice vibrations like the Debye temperature [29] or the presence of local modes of oscillations [24,25] have been already obtained using this effect.

The observation of nuclear isotopic shift in ESR

Although the isotope effect in ESR is expected to be very small, the group of Marshall et al., has been able to report such an effect studying the ESR spectra of substitutional Fe^{3+} in calcite [30] and substitutional Ca^{3+} in MgO in sites with axial symmetry [31]. This effect was observed as a slight magnetic field displacement between the effective fine structure components of Fe^{56} and Fe^{57} isotopes in the first case, respectively of Ca^{52} and Ca^{53} in the second case.

The observation of this effect became possible due to following facts: (i) the paramagnetic ions had at least two isotopes, each in sufficient abundance to be readily detectable and their spectral components were completely resolved, (ii) the system had a nonzero crystal field splitting energy, (iii) the crystal-field splitting energy was sufficiently large compared to the widths of the resonance absorptions that its magnitude may be determined to within one part in 10^4 , (iv) the resonance lines were sufficiently

narrow and the EPR spectrometer had enough stability and magnetic field homogeneity in order to ensure an accuracy equivalent to determining absorption-line field positions to within ± 10 mOe.

To develop a satisfactory interpretation of the isotope effect in the ESR absorption spectrum of a crystal-ion system, it would be advantageous if there existed a well-established theory to account for the $2D$ parameter determining the splitting of the ground term in an axial crystal-field. The inadequacy of the crystal-field theory in dealing with this problem led to considerable work in this area which involved application of configuration mixing and covalency reduction of local symmetry, etc. Consequently, rather than attempting to incorporate all interactions in theory and then deriving the isotope effect, a simpler approach was adopted by Marshall et al. [31].

In this approach the splitting in question is assumed to arise from some interactions which, in the second order, connect the ground term with the other noncubic terms of this ion. The form of such a splitting is taken to be

$$2D = \sum_{p \neq 0} \frac{V^2(p)}{E(p) - E(0)} \quad (60)$$

where $V(p)$ is a matrix element which connects $|p\rangle$, an excited noncubic term of the ion, with $|0\rangle$, the ground term. This formalism enjoys the advantage of being adaptable to take account of the fact that the paramagnetic ion along with its host is a dynamical system. It means that in fact each electronic level is a manifold potential well with each sheet of the manifold associated with a specific oscillational mode of the crystal-ion system, each virtual transition of the second order perturbation expression in Eq. (60) taking place between electron-vibration

states rather than between pure electronic states. Thus, a given magnetic resonance absorption line will appear as the superposition of all such individual absorptions and its mean-field position will be determined by a Boltzmann averaging of the crystal-field splitting energy. With the above assumptions the mean crystalline field splitting energy for a given mode of oscillation can be written as

$$2\bar{D} = \left(\sum_n \exp\left(-\frac{n\hbar\omega}{kT}\right) \right)^{-1} \sum_{p \neq 0} \sum_{\lambda, n} |\langle \lambda | n \rangle|^2 \exp\left(-\frac{n\hbar\omega}{kT}\right) \frac{V^2(p)}{\Delta E(p) + \delta E} \quad (61)$$

where $\Delta E(p) = E(p) - E(0)$, $\delta E = (\lambda + \frac{1}{2})\hbar\omega' - (n + \frac{1}{2})\hbar\omega$, ω and ω' are the frequencies characteristic of the given mode of oscillation in the ground and excited electronic states, respectively and the $|n\rangle$ and $|\lambda\rangle$ refer to oscillator wavefunction of the ground and excited electronic states respectively. With some specific assumptions [31] regarding the nature of the potential wells associated with the ground and excited electronic wells, equation (61) greatly simplifies and yields the following approximate result:

$$\frac{\delta\bar{D}}{D_0} = - \frac{\bar{D} - D_0}{2D_0} \frac{\delta M}{M} \quad (62)$$

This equation provides three predictions: (i) that the isotopic shift in \bar{D} should be proportional to the change in nuclear mass (ii) that the temperature dependence of $\delta\bar{D}$ should be similar but of opposite sign to the temperature dependence of \bar{D} ; and (iii) that a reasonable estimate of $\delta\bar{D}/D_0$ should be obtainable from data on temperature dependence of \bar{D} . The first prediction explains the data on Fe^{3+} in calcite [30]. In this case it was found that the shift in the crystal-field parameters of Fe^{3+}

with respect to Fe^{56} is of opposite sign and half that of the shift for Fe^{54} . The second prediction is also fulfilled as the temperature dependence of $\delta\bar{D}$ for Cr^{52} isotope relative to Cr^{53} goes in opposite direction with the temperature dependence of \bar{D} . Finally, from the experimental data for \bar{D} a relative isotope shift in \bar{D} for chromium was calculated to be of the order of 1 part in 10^4 , which is the shift experimentally observed [31].

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