

have been measured over the temperature range from 3 to 300°K. Phonons are the dominant carriers of the thermal energy. It is suggested that the thermal conduction in the molecular solids such as orthorhombic sulfur and cubic (white) phosphorus is caused by lattice phonons only; the phonons associated with the internal vibrations of the  $S_8$  or  $P_4$  units do not contribute to the conduction because their propagation velocities are zero. Since only a fraction of the phonons can carry heat and since their mean free path in the solid at the melting point is only about one molecular diameter, the molecular solids have thermal conductivities much lower than those of monatomic solids of similar average atomic mass. In monatomic solids such as orthorhombic (black) phosphorus there are no molecular groups. Thus all of the phonons contribute to the heat transport, their mean free paths at the melting point are of the order of twenty interatomic distances, and the thermal conductivities of such solids are high.

The  $\beta$ -rhombohedral form of boron has a crystal

structure somewhere between the molecular and monatomic types. Its measured thermal conductivity has a value intermediate between the limits predicted by the molecular and monatomic models. Because of the similarity in the crystal structures of the several polymorphs of boron, it is believed that the other polymorphs as well as many of the interstitial compounds of boron will also have low thermal conductivities quite close to that of the  $\beta$ -rhombohedral form.

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### Nuclear Resonance of Solids Doped with Paramagnetic Impurities\*

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This paper is an extension of the work of Rorschach on the interactions of dipolar nuclei with paramagnetic impurities in dielectric crystals. The influence of the average "static" moment on the nuclear resonance linewidth is considered. It is suggested that by measuring  $T_1$  and the nuclear resonance linewidth as a function of temperature, magnetic field intensity, and sample orientation it is possible to determine the autocorrelation time of paramagnetic ions as a function of these parameters.

#### INTRODUCTION

SINCE Bloembergen<sup>1</sup> showed that nuclear spins could be relaxed in an insulating crystal by small amounts of paramagnetic impurities, several publications have appeared indicating information could be obtained concerning paramagnetic ions using nuclear magnetic resonance. Most of the attention has been given to the effect of impurities on the spin-lattice relaxation time  $T_1$  of the nuclei. However, Verber, Mahon, and Tantilla<sup>2</sup> have demonstrated that paramagnetic ions also broaden the nuclear resonance at low temperatures. By utilizing the results obtained from both  $T_1$  and linewidth measurements it is possible to eliminate most of the uncertainties of the theory, and thereby get more reliable information concerning the paramagnetic ions and their behavior in the crystal. In the theory section an ex-

pression is derived for the effect of paramagnetic ions on the nuclear-resonance linewidth based on Van Vleck's<sup>3</sup> method and Rorschach's<sup>4</sup> treatment of the motion of the paramagnetic moment. This calculation gives rise to an expression for the second moment containing the autocorrelation time of the paramagnetic ion, the ion concentration, and the average of the square and the square of the average of the  $z$  component of the magnetic moment for the paramagnetic ion. Also a discussion is given for  $T_1$  based on Rorschach's paper.

#### THEORY

##### Linewidth

The nuclear-resonance linewidth of a system of nuclear spins can be calculated using Van Vleck's moment theory, and is in excellent agreement with experiment. If electron paramagnetic impurities are

\* Work supported by National Science Foundation.

<sup>1</sup> N. Bloembergen, *Physica* **15**, 386 (1949).

<sup>2</sup> C. M. Verber, H. P. Mahon, and W. H. Tantilla, *Phys. Rev.* **125**, 1149 (1962).

<sup>3</sup> J. H. Van Vleck, *Phys. Rev.* **74**, 1168 (1948).

<sup>4</sup> H. E. Rorschach, Jr., *Physica* **30**, 38 (1964).

present in the sample with high enough concentrations they may contribute significantly to the linewidth because of their very large magnetic moment relative to the nuclear moment. It should be possible to take this into account by using Van Vleck's theory and a consideration of the effective moment of the impurity as seen by the nuclei.

According to the theory of Van Vleck the dipolar term in the truncated Hamiltonian between like spins is

$$(H_d^0)_{I-I} = 1/4\gamma_I^2\hbar^2 \sum_{j,k} (1-3\cos^2\theta_{jk}) \times r_{jk}^{-3}(3I_{zj}I_{zk} - \mathbf{I}_j \cdot \mathbf{I}_k);$$

the mean-square linewidth due to like spins is

$$\langle \Delta\omega^2 \rangle_{I-I} = \frac{3}{4}\gamma_I^4\hbar^2 I(I+1) \sum_k (1-3\cos^2\theta_{jk})^2 r_{jk}^{-6}; \quad (1)$$

the coupling between unlike spins is

$$(H_d^0)_{I-J} = \gamma_I\gamma_J\hbar^2 \sum_{ij} (1-3\cos^2\theta_{ij}) r_{ij}^{-3} I_{zi} J_{zj};$$

and the contribution to the second moment is

$$\langle \Delta\omega^2 \rangle_{I-J} = \frac{1}{3}\gamma_I^2\gamma_J^2\hbar^2 J(J+1) N_I^{-1} \sum_{i,j} (1-3\cos^2\theta_{ij})^2 r_{ij}^{-6}. \quad (2)$$

In Eq. (2), it is assumed that the magnetic moment of the nonresonant spin (represented by  $J$ ) is independent of the magnetic field, temperature, crystal orientation, and lifetime of spin  $I$ . This, of course, is not true in all cases. In particular, if the spins  $J$  are paramagnetic ions the probability of occupation of a lower magnetic substate can be significantly greater than  $(2J+1)^{-1}$ . That is, the Boltzmann factor can not be safely approximated as being unity, as is done in the derivation of Eq. (2). Another important consideration that must not be overlooked is the average lifetime of spin  $J$  relative to spin  $I$ .

It should be possible to account for these effects by determining the  $z$  component of the magnetic moment of spin  $J$ ,  $(\mu_z^*)$ , effective in broadening the resonance of the spins  $I$ . Rorschach has proposed a theory to determine  $(\mu_z^*)$  using harmonic analysis and random time-dependent perturbation theory. The theory involves determining the magnitude of that part of the spectrum of the magnetic field due to spin  $J$  that is "sufficiently" near the Larmor frequency of nuclear spins  $I$  to be effective in interacting with the nuclei adjacent to  $J$ . If the spectral density is denoted by  $J(\omega)$ , then the average static moment which is effective in broadening the nuclear-resonance line is determined by that part of the spectrum with frequencies between  $\pm T_2^{-1}$ . Rorschach assumed that the autocorrelation function for spin  $J$ , hereafter referred to as the impurity, was

$$\kappa(\tau) = \langle \mu_z \rangle^2 + (\langle \mu_z^2 \rangle - \langle \mu_z \rangle^2) e^{-\tau/\tau_c}. \quad (3)$$

$\tau_c$  is the autocorrelation time for the impurity.  $\langle \mu_z^2 \rangle$  and  $\langle \mu_z \rangle^2$  can be computed using statistical mechanics, provided the energy levels are known and the impurity spins are more strongly coupled to the lattice than to each other. The Fourier transform of  $\kappa(\tau)$  is the spectral density given by

$$J(\omega) = \int_{-\infty}^{\infty} \kappa(\tau) e^{i\omega\tau} d\tau = \langle \mu_z \rangle^2 2\pi\delta(\omega) + (\langle \mu_z^2 \rangle - \langle \mu_z \rangle^2) \frac{2\tau_c}{1+\omega^2\tau_c^2}, \quad (4)$$

where  $\delta(\omega)$  is the Dirac delta function. The square of the average  $z$  component of the moment, effective in perturbing the nuclear spins, is thus given by

$$\begin{aligned} (\mu_z^*)^2 &= \frac{1}{2\pi} \int_{-1/T_2}^{1/T_2} J(\omega) d\omega \\ &= \langle \mu_z \rangle^2 + \frac{2}{\pi} (\langle \mu_z^2 \rangle - \langle \mu_z \rangle^2) \tan^{-1}\tau_c/T_2. \end{aligned} \quad (5)$$

Now to correct Eq. (2) we must replace  $\frac{1}{3}\gamma_I^2\gamma_J^2\hbar^2 J(J+1)$  by  $\langle \mu_z^* \rangle^2$ . One then gets

$$\langle \Delta\omega^2 \rangle_{I-J} = \gamma_I^2 (\mu_z^*)^2 N_I^{-1} \sum_{i,j} \beta_{ij}, \quad (6)$$

where  $\beta_{ij} = (1-3\cos^2\theta_{ij})^2 r_{ij}^{-6}$ . Now assuming the impurities are located at equivalent sites in the crystal and the number of impurities is denoted by  $N_J$ , Eq. (6) becomes

$$\langle \Delta\omega^2 \rangle_{I-J} = \gamma_I^2 (\mu_z^*)^2 (N_J/N_I) \sum_j \beta_{ij}. \quad (7)$$

The mean-square linewidth  $\langle \Delta\omega^2 \rangle$  total is the sum of the two contributions  $\langle \Delta\omega^2 \rangle_{I-I}$  and  $\langle \Delta\omega^2 \rangle_{I-J}$ . It is convenient to consider

$$\xi = \frac{\langle \Delta\omega^2 \rangle_{I-J}}{\langle \Delta\omega^2 \rangle_{I-I}} = \frac{4 N_J (\mu_z^*)^2 \sum \beta_{ij}}{9 N_I \mu_I^2 \sum \beta_{jk}}, \quad (8)$$

where  $\mu_I^2 = \frac{1}{3}\gamma_I^2\hbar^2 I(I+1)$ . In Eq. (8), the sum in the denominator is over all nuclear spins in the lattice, whereas the sum in the numerator may not include all spins. Nuclear spins very close to an impurity have their Larmor frequency shifted far into the wings of the absorption line and contribute significantly to the second moment. However, in observing the resonance line shape, the wings of the resonance are usually not observed. This means one can omit terms in the sum close to the impurity. A criterion for the critical radius inside of which the terms should be omitted is that the dipole field of the impurity at the critical radius be equal to the local field of the nuclei alone. A measure of the nuclear local field is the root-mean-square second moment.

$$\langle \Delta H^2 \rangle^{1/2} = (\mu_z^*) / (b')^3, \quad (9)$$

where  $b'$  is the critical radius. Typically  $b'$  is about ten lattice spacings, which means the lattice sum can be replaced by an integral

$$\sum_j' \beta_{ij} \simeq 2\pi \int_{b'}^{\infty} \int_0^{\pi} \rho_I (1 - 3 \cos^2 \theta)^2 r^{-4} \sin \theta d\theta dr$$

$$= \rho_I \frac{16\pi}{15} (b')^{-3}. \quad (10)$$

Here  $\rho_I$  is the number of nuclear spins per unit volume. If a simple cubic lattice of nuclear spins is considered, one has for the sum in the denominator of Eq. (8)

$$\sum_k \beta_{jk} = 16.4 f(\lambda) a^{-6},$$

where  $f(\lambda) = (\lambda_1^4 + \lambda_2^4 + \lambda_3^4 - 0.187)$ . The  $\lambda_i$  represent the direction cosines of the external magnetic field referred to the principal axes of the crystal and  $a$  is the distance between adjacent nuclei. For a simple cubic lattice  $\rho_I = a^{-3}$  and the ratio of the lattice sums become

$$\frac{\sum_j' \beta_{ij}}{\sum_k \beta_{jk}} = 0.204 (a/b')^3 f^{-1}(\lambda). \quad (11)$$

For a simple cubic lattice

$$\langle \Delta H^2 \rangle^{1/2} = 6.06 \mu_I a^{-3} f^{1/2}(\lambda). \quad (12)$$

Combining Eqs. (8)–(12), one obtains

$$\xi = 0.55 (N_J/N_I) (\langle \mu_z^* \rangle / \mu_I) f^{-1/2}(\lambda). \quad (13)$$

Finally using Eqs. (5) and (13),  $\xi$  becomes

$$\xi = 0.55 (N_J/N_I) \mu_I^{-1} f^{-1/2}(\lambda) \times [\langle \mu_z^2 \rangle + 2/\pi (\langle \mu_z^2 \rangle - \langle \mu_z \rangle^2) \tan^{-1}(\tau_c/T_2)]^{1/2}. \quad (14)$$

All of the magnetic field and temperature dependence for  $\xi$  is contained in  $\langle \mu_z^2 \rangle$ ,  $\langle \mu_z \rangle^2$ , and possibly in  $\tau_c$ . However, if one knows the energy-level configuration for the impurity, the field and temperature dependence of  $\langle \mu_z^2 \rangle$  and  $\langle \mu_z \rangle^2$  can be calculated. By measuring the magnetic field and temperature dependence of  $\xi$ , one can then conclude the dependence of  $\tau_c$  on these parameters.

It should be pointed out that it is not necessary for the impurity spins to change magnetic substates to give rise to a fluctuating  $z$  component of magnetic moment. For example, the energy levels of the impurity may fluctuate due to lattice vibrations through the crystal-line field splitting. Therefore the autocorrelation time of the impurity  $\tau_c$  may not be simply related to either the spin-lattice or the spin-spin relaxation time of the impurity. The significance of  $\tau_c$  would depend on the type of impurity and its interaction with the lattice.

### Relaxation Time

Bloembergen<sup>1</sup> has shown that nuclear spin-lattice relaxation in dielectric solids by means of paramagnetic impurities is the result of two processes operating serially: spin-energy diffusion and direct relaxation.

Diffusion of Zeeman energy towards an impurity by means of mutual spin-flips occurs as a result of the gradient in magnetic energy density created by the direct relaxation of nuclei near the impurity through a dipole-dipole interaction. This direct relaxation is effective only at short ranges due to the inverse sixth-power radial dependence of the transition probability. Thus, it is possible to consider only a spherical volume of radius  $R$  surrounding one impurity and containing  $N'$  nuclei as representative of the total crystal. There are  $\rho_J$  of these spheres per unit volume of the crystal,  $\rho_J$  being the impurity concentration. The Hamiltonian for one of these representative volumes may then be written in spherical polar coordinates in the familiar form of the sum of six components, arranged according to their selection rules.

$$H''_{I-J} = \sum_{i=1}^{N'} \gamma_I \gamma_J \hbar^2 r_i^{-3} [A' + B' + C' + D' + E' + F'], \quad (15)$$

where

$N' = N_I/N_J$  = number of nuclear spins associated with each impurity spin

$$A' = I_{zi} J_z (1 - 3 \cos^2 \theta_i); \quad \Delta m_i = \Delta m_p = 0$$

$$B' = -\frac{1}{4} [I_i^- J^+ + I_i^+ J^-] (1 - 3 \cos^2 \theta_i);$$

$$\Delta m_i = -\Delta m_p = \pm 1$$

$$C' = D'^* = -\frac{3}{2} [I_i^+ J_z + J^+ I_{zi}] \sin \theta_i \cos \theta_i \times e^{-i\phi_i};$$

$$\Delta m_i = 0; \quad \Delta m_p = \pm 1; \quad \Delta m_i = \pm 1; \quad \Delta m_p = 0$$

$$E' = F'^* = -\frac{3}{4} I_i^+ J^+ \sin^2 \theta_i \times e^{-i2\phi_i}; \quad \Delta m_i = \Delta m_p = +1.$$

$I$  is the spin operator for  $i$ th nuclear spin

$J$  is the spin operator of the impurity spin.

Because of the large energy difference between nuclear transitions and impurity transitions, the only term of interest is the third term ( $C'$ ) which involves a nuclear transition with the impurity remaining in its same magnetic substate.

Using first-order perturbation theory of the  $j$ th term of  $H_{I-J}''$  to calculate the probability that the  $j$ th nucleus will undergo a downward transition while the impurity does not change its state, one obtains

$$W_j = 9/4 \gamma_I^2 |\langle \frac{1}{2}, \alpha | I_j^+ | -\frac{1}{2}, \alpha \rangle|^2 \times \sin^2 \theta_j \cos^2 \theta_j r_j^{-6} J(\omega_j), \quad (16)$$

where  $\alpha$  represents the quantum numbers that specify the state of the impurity and  $J(\omega_j) = |\langle \frac{1}{2}, \alpha | \mu_z(t) | -\frac{1}{2}, \alpha \rangle|^2$  is the intensity of the Fourier spectrum of  $\mu_z(t)$  evaluated at the resonant frequency of nucleus  $j$ . Since  $|\langle \frac{1}{2}, \alpha | I_j^+ | -\frac{1}{2}, \alpha \rangle|^2 = 1$ , the transition probability is

$$W_j = 9/4 \gamma_I^2 r_j^{-6} \sin^2 \theta_j \cos^2 \theta_j J(\omega_j). \quad (17)$$

All variations in  $r_j$ ,  $\theta_j$ , and  $\phi_j$ , due to lattice vibrations have been neglected, on the assumption that the impurity is much more effective in relaxing the nuclei than are the lattice vibrations.

In order to evaluate  $J(\omega)$  it is necessary to assume

some mathematical description of  $\mu_z$ . Following Rorschach, it is assumed that  $\mu_z$  is a randomly fluctuating stationary function of time, which can be described by the autocorrelation function given in Eq. (3).

The spectral density given in Eq. (4) gives the amplitude of that part of the random motion of  $\mu_z$  occurring at frequency  $\omega$ . Substituting Eq. (4) into Eq. (17) and averaging over the solid angle yields, for the average direct interaction transition probability of these nuclei at a radius  $r$  from the impurity,

$$\langle W(r) \rangle = (C/2)r^{-6} \\ = \frac{3}{5}\gamma_I^2(\langle \mu_z^2 \rangle - \langle \mu_z \rangle^2)(\tau_c/(1+\omega_0^2\tau_c^2))r^{-6}. \quad (18)$$

The substitution of the average Larmor frequency  $\omega_0$  for  $\omega$  is valid for all nuclei except for those within a distance  $b'$  of the impurity, whose resonant frequency is shifted out of the resonance line shape. This radius  $b'$ , the critical radius, may or may not correspond to the spin-diffusion barrier radius  $b$ , as pointed out by Blumberg,<sup>5</sup> but the two are of comparable magnitude and usually small compared with the distance between impurities. Now by integrating Eq. (18) from  $b'$  to  $R$ , where  $R$  is the radius of the sphere associated with each impurity, one has for the spin-lattice relaxation time

$$T_1 = 3(b')^3/4\pi C\rho_I, \quad (19)$$

where  $\rho_I$  is the impurity concentration  $(4/3\pi R^3)^{-1}$ .

<sup>5</sup> W. E. Blumberg, Phys. Rev. **119**, 97 (1960).

This agrees with Blumberg's expression for the rapid-diffusion  $T_1$ .

Rorschach<sup>4</sup> has recently derived a general expression for  $T_1$  which has two asymptotic forms, according to the magnitude of a dimensionless parameter. This parameter  $\delta$  is equal to  $\frac{1}{2}(\beta/b)^2$ , where  $\beta$  is the pseudopotential radius as defined by DeGennes<sup>6</sup> and  $b$  is the barrier radius for spin diffusion. For  $\delta \ll 1$ , the asymptotic form is the same as that above, while for  $\delta \gg 1$ , the form is that of the original diffusion limited expression of DeGennes.

It should be pointed out that, if one knows the energy-level configuration of the impurity and the impurity concentration, then the only unknown in the expression for  $T_1$  is the autocorrelation time  $\tau_c$  of the impurity. By measuring  $T_1$  as a function of magnetic field, temperature, and sample orientation one should be able to determine  $\tau_c$  as a function of these experimental parameters as in the case for  $\xi$ .

## CONCLUSION

Preliminary measurements of the second moment and  $T_1$  have been made on  $\text{CaF}_2:\text{Eu}^{2+}$  for two concentrations as a function of temperature and magnetic field intensity. The results tend to confirm the essential features of the theory. Currently a number of other rare-earth and iron-group ions doped in  $\text{CaF}_2$  are being studied and the results will be published shortly.

<sup>6</sup> P. G. DeGennes, J. Phys. Chem. Solids **7**, 345 (1958).

## Phonon-Assisted Electroabsorption\*

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Recently several experiments have been reported on electroabsorption spectra in indirect-bandgap materials. These observations refer essentially to the change in absorption produced by an applied electric field  $\mathcal{E}$  in the material under study. The particular photon-energy region explored has been that where phonon-assisted interband absorption obtains. Usually, considerable structure appears in the experimental curves. The absorption change  $\Delta\alpha$  varies quite radically with photon energy both in amplitude and in sign. All theories extant on the phenomenon of electroabsorption are concerned with direct-bandgap transitions. In the light of recent experimental results, however, in the neighborhood of indirect transitions, it is appropriate to calculate the electroabsorption spectrum for phonon-assisted processes in order to have a more applicable theoretical model with which to compare experimental results. The present paper reports just such a calculation. A formula for  $\Delta\alpha$  is presented in the case of phonon-assisted interband absorption.

## INTRODUCTION

RECENTLY, several experiments have been reported on electroabsorption spectra in indirect-

bandgap materials.<sup>1-3</sup> These observations refer essentially to the change  $\Delta\alpha$  in absorption produced by an applied electric field  $\mathcal{E}$  in the material under study. The particular photon energy region explored has been

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