THE SHAPE AND TEMPERATURE DEPENDENCE OF THE ELECTRON-SPIN RESONANCE LINES OF LOCALIZED ELECTRON CENTERS IN CRYSTALS

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The hyperfine structure of localized electron centers in crystals is evaluated and their electron spin resonance is considered, taking the vibrations of the ions (atoms) into account. We have obtained the shape of the electron paramagnetic resonance (EPR) lines and its temperature dependence. It turns out that they have the Lorentz shape. The EPR of F-centers in NaCl type crystals is considered as an example. The theoretical results agree with experiments. The determination of the EPR half width makes it possible to evaluate the spin-lattice relaxation time. Numerical estimates performed for F-centers lead to agreement between the theoretical results and experiments.

INTRODUCTION

IN those papers which are known up to the present and which are devoted to the theory of the electron paramagnetic resonance (EPR) of localized electron centers, it is assumed that the ions were immovably fixed at lattice sites.[1-5] In a number of cases it was possible in this approximation to explain the shape of the overall EPR spectrum of localized centers.[1,2] The shapes of the separate lines, however, were not explained satisfactorily in a quantitative way. Attempts to estimate the line broadening taking dipole-dipole interactions between spatially separated localized centers into account led therefore to a discrepancy of one or two orders of magnitude between the theoretical results and the experiments. In this approximation, of course, one cannot consider the temperature dependence of either the shapes of the separate lines or the shape of the overall EPR spectrum.

There are, nevertheless, recent experimental evidences of an appreciable temperature dependence of the EPR spectrum shape.[6,7] Moreover, direct experimental measurements performed with F-centers[7] show that the spin-lattice interaction is the decisive factor for the shape.

We shall develop in the present paper a theory of EPR of localized centers which will include the hyperfine interaction of a localized electron with the magnetic moments of the nuclei of the vibrating crystal. The latter turns out to be not a small perturbation, in contradistinction to the situation in investigations in the theory of spin-lattice relaxation, and will be taken into account in the zeroth approximation of the theory. The calculations will be performed in the approximation of extremely long wavelengths of the lattice vibrations which turns out to be justified in the case under consideration.

The theory leads to a Lorentz shape of the separate lines and to its correct temperature dependence. The Lorentz shape agrees also with the results of phenomenological investigations. Portis[8] has given a satisfactory explanation of the saturation effect of the EPR of F-centers assuming that the shape of the separate lines is close to the Lorentz shape. A similar assumption enabled Wolga and Strandberg[9] to obtain the correct shape of the smoothed out EPR line of F-centers.

1. THE HAMILTONIAN AND THE ENERGY SPECTRUM OF THE SYSTEM

The Hamiltonian of the system (a localized electron interacting with the lattice vibrations, with the nuclear magnetic moments, and with the external static magnetic field) can be written in the form

$$\hat{H} = \hat{T} + \hat{V}(\mathbf{r}, \mathbf{u}) + \hat{H}_{\text{vib}} + \hat{H}_s + \sum_n \hat{Q}_n, \qquad (1)$$

where $\hat{T}$ is the electronic kinetic energy operator, $\hat{V}(\mathbf{r}, \mathbf{u})$ the operator of the interaction energy between the electron and the lattice, which does not take into account the hyperfine interaction (this term contains, in particular, also the operator of the energy of the electron in the periodic crystalline field); $\hat{H}_{\text{vib}}$ the lattice vibration energy oper-

ator, $\hat{H}_3$ the operator of the energy of the interaction between the electronic magnetic moment μ and the external static magnetic field $\mathcal{3C}$, $\sum_n \hat{Q}_n$ the operator of hyperfine interaction of the localized electron with the magnetic moments of the nuclei in the neighborhood, $\mathbf{u}$ the displacement vector of an arbitrary lattice point, and $\mathbf{n}$ the vector determining the position of a lattice site. The Hamiltonian (1) does not contain spin-orbit interaction terms as we shall in the following consider systems for which $\bar{L} = 0$.

For small displacements $\mathbf{u}$ we can expand the operators $\hat{V}$ and $\hat{Q}_n$ in a power series in $\mathbf{u}$ and restrict ourselves to the linear terms in the expansion. Equation (1) can then be rewritten as follows

$$\hat{H} = \hat{T} + \hat{V}_0(\mathbf{r}) + \mathbf{u}\,(\text{grad}\,\hat{V})_0 + \hat{H}_{\text{vib}}$$
$$+ \hat{H}_3 + \sum_n \hat{Q}_n^0 + \sum_n \mathbf{u}\,(\text{grad}\,\hat{Q}_n)_0 \qquad (2)$$

Writing $\mathbf{u}$ as an expansion in a complete set of functions

$$\mathbf{u} = \sum_{\kappa,\alpha} \mathbf{u}_{\kappa\alpha}\chi_\kappa(\mathbf{r}), \qquad (3a)$$

$$\chi_\kappa(\mathbf{r}) = \sqrt{2/L^3}\,\sin(\kappa\mathbf{r} + \pi/4) \qquad (3b)$$

and using in (2) dimensionless normal coordinates, we get

$$\hat{H} = \hat{T} + \hat{V}_0(\mathbf{r}) + \sum_{\kappa,\alpha}\mathbf{B}_{\kappa\alpha}\mathbf{q}_{\kappa\alpha} + \tfrac{1}{2}\sum_{\kappa\alpha}\hbar\omega_{\kappa\alpha}(q_{\kappa\alpha}^2 - \partial^2/\partial q_{\kappa\alpha}^2)$$
$$+ \hat{H}_3 + \sum_n \hat{Q}_n^0 + \sum_{n,\kappa,\alpha}\mathbf{A}_{\kappa\alpha}^n\,\mathbf{q}_{\kappa\alpha}\,. \qquad (4)$$

where α is the number of the branch of the lattice vibrations and $\omega_{\kappa\alpha}$ the frequency of the κ-th vibration of the α-th branch.

The energy spectrum of the system can be obtained without writing down explicitly the operator coefficients $\mathbf{B}_{\kappa\alpha}$ and $\mathbf{A}_{\kappa\alpha}^n$. The energy of the spectrum is determined by minimizing the functional

$$J = \int \Psi^*\,\hat{H}\Psi d\tau \dots dq_{\kappa\alpha}\dots dS_z\dots di_{nz}\dots \qquad (5)$$

The symbolic integration over the spin coordinates of the electron S_z and of all the nuclei of the surroundings of the defect $\dots, i_{nz}, \dots$ means summation over the spin variables.

We shall choose the wave function of the system in the form

$$\Psi = \psi(\mathbf{r})\,\Phi(\dots q_{\kappa\alpha}\dots)\chi(S_z, \dots, i_{nz}, \dots). \qquad (6)$$

Substituting (6) into (5), restricting ourselves to the contact terms in the hyperfine interaction operator and in the approximation of strong magnetic fields, we get

$$J = \bar{T} + \bar{V}_0 + \sum_{\kappa\alpha}\bar{\mathbf{B}}_{\kappa\alpha}\int\Phi^*\mathbf{q}_{\kappa\alpha}\,\Phi\dots dq_{\kappa\alpha}\cdots$$
$$+ \tfrac{1}{2}\int\Phi^*\sum_{\kappa\alpha}\hbar\omega_{\kappa\alpha}\Big(q_{\kappa\alpha}^2 - \frac{\partial^2}{\partial q_{\kappa\alpha}^2}\Big)\Phi\cdots dq_{\kappa\alpha}\cdots$$
$$+ (\mu/S)\,S_z\mathcal{H}_z + \sum_n(8\pi\mu\mu_n/3SI_n)\,|\psi(\mathbf{r} = \mathbf{R}_n)|^2\,S_zI_{nz}$$
$$+ \sum_{n\kappa\alpha}\bar{\mathbf{A}}_{\kappa\alpha}^n\int\Phi^*\mathbf{q}_{\kappa\alpha}\Phi\dots dq_{\kappa\alpha}\dots, \qquad (7)$$

where I_{nz} is the quantum number of the operator of the z-component of the spin of the n-th nucleus. The bars on top indicate averaging over $\psi(\mathbf{r})$. Without loss of generality it was assumed in (7) that the axis of the system coincided with the direction of the external static field.

Varying (7) with respect to Φ^* leads to the following equation for Φ

$$\Big\{\tfrac{1}{2}\sum_{\kappa\alpha}\hbar\omega_{\kappa\alpha}(q_{\kappa\alpha}^2 - \partial^2/\partial q_{\kappa\alpha}^2) + \sum_{\kappa\alpha}\Big(\bar{\mathbf{B}}_{\kappa\alpha} + \sum_n\bar{\mathbf{A}}_{\kappa\alpha}^n\Big)\mathbf{q}_{\kappa\alpha}\Big\}$$
$$\times \Phi(\dots q_{\kappa\alpha}\dots) = \lambda\Phi(\dots q_{\kappa\alpha}\dots) \qquad (8)$$

One can write Eq. (8) in the form

$$\Big\{\tfrac{1}{2}\sum_{\kappa\alpha}\hbar\omega_{\kappa\alpha}[(q_{\kappa\alpha} - q'_{\kappa\alpha})^2 - \partial^2/\partial q_{\kappa\alpha}^2]$$
$$- \sum_{\kappa\alpha}\tfrac{1}{2}\hbar\omega_{\kappa\alpha}q'^2_{\kappa\alpha}\Big\}\Phi = \lambda\Phi, \qquad (9)$$

$$q'_{\kappa\alpha} = q'_{\kappa\alpha} + q^0_{\kappa\alpha}, \qquad (10)$$

$$q'_{\kappa\alpha} = -(\bar{\mathbf{B}}_{\kappa\alpha}\mathbf{k}_{\kappa\alpha})/\hbar\omega_{\kappa\alpha}, \qquad (11)$$

$$q^0_{\kappa\alpha} = -\Big[\sum_n(\bar{\mathbf{D}}_{\kappa\alpha}^n\mathbf{k}_{\kappa\alpha})\,I_{nz}S_z\Big]\Big/\hbar\omega_{\kappa\alpha}, \quad \bar{\mathbf{D}}_{\kappa\alpha}^n I_{nz}S_z = \bar{\mathbf{A}}_{\kappa\alpha}^n, \qquad (12)$$

where $\mathbf{k}_{\kappa\alpha}$ is a unit vector with components

$$k_{\kappa\alpha x} = \sin\theta_{\kappa\alpha}\cos\varphi_{\kappa\alpha}, \quad k_{\kappa\alpha y} = \sin\theta_{\kappa\alpha}\sin\varphi_{\kappa\alpha}, \quad k_{\kappa\alpha z} = \cos\theta_{\kappa\alpha},$$

with $\theta_{\kappa\alpha}$ and $\varphi_{\kappa\alpha}$ being polar angles determining the direction of the vector $\mathbf{q}_{\kappa\alpha}$.

It follows from (9) that

$$\lambda = \sum_{\kappa\alpha}\hbar\omega_{\kappa\alpha}\Big(n_{\kappa\alpha} + \tfrac{1}{2}\Big) - \sum_{\kappa\alpha}\tfrac{1}{2}\hbar\omega_{\kappa\alpha}q''^2_{\kappa\alpha}, \cdot \qquad (13)$$

$$\Phi = \prod_{\kappa\alpha}\Phi_{n_{\kappa\alpha}}(q_{\kappa\alpha} - q'_{\kappa\alpha}), \qquad (14)$$

where $\Phi_{n_{\kappa\alpha}}$ are the eigenfunctions of an oscillator with its equilibrium position at the point $q''_{\kappa\alpha}$.

Using (13) and (14) we get for J

$$J = \bar{T} + \bar{V}_0 + \sum_{\kappa\alpha}\hbar\omega_{\kappa\alpha}\Big(n_{\kappa\alpha} + \tfrac{1}{2}\Big) + (\mu/S)\,S_z\mathcal{H}_z$$
$$+ \sum_n(8\pi\mu\mu_n/3SI_n)\,\psi^2(\mathbf{r} = \mathbf{R}_n)\,S_zI_{nz} - \tfrac{1}{2}\sum_{\kappa\alpha}q''^2_{\kappa\alpha}\hbar\omega_{\kappa\alpha}. \qquad (15)$$

The electron-coordinate part of the wave function (6) is determined by minimizing (15) with respect to $\psi(\mathbf{r})$. The evaluation of the $\psi(\mathbf{r})$ corresponding to the minimum of J and the substitution of that function into (15) determines the energy terms of the system. We note in passing that the presence in (15) of spin dependent terms can in

no way appreciably influence the wave function parameters, as these terms are several orders of magnitude smaller than all the others. We can thus to a high degree of accuracy use for our calculations the ψ-function evaluated without taking the "magnetic" terms into account. $\psi(\mathbf{r})$ has been evaluated in this approximation for a number of localized electron centers (see, for instance, references 10 and 11).

The frequency of the quantum transition involving a change in the electron spin and the emission (absorption) of phonons is determined by the expression

$$\hbar\Omega = q\mu\,\mathcal{H}_z + \sum_n (8\pi\mu\mu_n / 3SI_n)\,\psi^2(\mathbf{r} = \mathbf{R}_n)\,I_{nz}$$

$$+ \sum_{\varkappa\alpha} \hbar\omega_{\varkappa\alpha}\,(\eta_{\varkappa\alpha} - \mathbf{n}'_{\varkappa\alpha}) - \sum_{\varkappa\alpha} \hbar\omega_{\varkappa\alpha}\,q'_{\varkappa\alpha}\,q^0_{\varkappa\alpha}/S_z. \qquad (16)$$

By comparison with the paramagnetic resonance frequency in a crystal with "clamped" ions, (16) contains a term (the third one) corresponding to the emission (absorption) of phonons accompanying the electron-spin transition. The fourth term determines the constant shift of the EPR frequency in a vibrating lattice. This last term must lead to an additional change in the g-factor of an electron in a crystal.

2. SHAPE AND TEMPERATURE DEPENDENCE OF EPR LINES

To evaluate the absorption coefficient for lines corresponding to the frequencies (16) we can use the general expression for the intensity of the absorption of electromagnetic radiation by localized centers given by Krivoglaz and Pekar[12]

$$\tau_e = K\,(2\pi i)^{-1} \oint dz \cdot z^{-(\omega_e+1)} \exp \sum_{\varkappa\alpha} (q_{\varkappa\alpha 1} - q_{\varkappa\alpha 2})^2$$

$$\times \left[\tfrac{1}{2}(n_{\varkappa\alpha} + 1)\,z^{\omega_{\varkappa\alpha}} + \tfrac{1}{2}\,n_{\varkappa\alpha}\,z^{-\omega_{\varkappa\alpha}} - n_{\varkappa\alpha} - \tfrac{1}{2}\right]. \qquad (17)$$

In the case under consideration $q_{\varkappa\alpha_1}$ and $q_{\varkappa\alpha_2}$ are the equilibrium positions of the normal coordinates in the ground state (as far as the electron spin is concerned) and the excited states. The coefficient K depends in the given case on the amplitude of the incident radio-frequency field and on the temperature determining the difference in population of the magnetic levels. If $2\mu\mathcal{H}/kT \ll 1$, K is inversely proportional to the temperature. The integration is over a closed contour encircling the point $z = 0$,

$$\hbar\omega_e = \sum_{\varkappa\alpha} \hbar\omega_{\varkappa\alpha}\,(n_{\varkappa\alpha} - n'_{\varkappa\alpha}), \qquad (18)$$

$$n_{\varkappa\alpha} = [\exp(\hbar\omega_{\varkappa\alpha}/kT) - 1]^{-1}. \qquad (19)$$

It follows from (10) that

$$q_{\varkappa\alpha 1} - q_{\varkappa\alpha 2} = q^0_{\varkappa\alpha,\,1/2} - q^0_{\varkappa\alpha,\,-1/2}, \qquad (20)$$

where $q^0_{\varkappa\alpha,\,1/2}$ and $q^0_{\varkappa\alpha,\,-1/2}$ are the values of $q^0_{\varkappa\alpha}$ for $S_z = 1/2$ and $S_z = -1/2$.

It is convenient to go over to new variables $z = \rho e^{i\varphi}$ in (17) and to put $\rho = 1$. Separating moreover the real and imaginary parts of τ_e one sees easily that the imaginary part of τ_e is identically equal to zero. Using also the fact that the integrand in the expression for the real part of τ_e is even we can rewrite (17) in the form

$$\tau_e = (K/\pi)\int_0^{\pi} d\varphi \cos\left[\sum_{\varkappa\alpha} \tfrac{1}{2}\,a_{\varkappa\alpha} \sin\omega_{\varkappa\alpha}\,\varphi - \omega_e\varphi\right]$$

$$\times \exp\left\{\sum_{\varkappa\alpha} a_{\varkappa\alpha}\left(n_{\varkappa\alpha} + \tfrac{1}{2}\right)[\cos\omega_{\varkappa\alpha}\,\varphi - 1]\right\}, \qquad (21)$$

$$a_{\varkappa\alpha} = (q^0_{\varkappa\alpha,\,1/2} - q^0_{\varkappa\alpha,\,-1/2})^2. \qquad (22)$$

It is appropriate to emphasize once again that the summation over α in (21) includes all branches of the dispersion. One can, however, show that in the case under consideration the optical frequencies do not play an important role in (21). To show that, we estimate the indices of the exponentials corresponding to the optical vibrations. We shall restrict ourselves for the sake of simplicity to lattices containing two ions in the elementary cell. One can in that case determine the displacements of the positive and negative ions $\mathbf{u}_+$ and $\mathbf{u}_-$ in the lattice from the following equations

$$M_+\mathbf{u}_+ + M_-\mathbf{u}_- = 0, \qquad (23a)$$

$$(e/n^2\Omega_0)\,(\mathbf{u}_+ - \mathbf{u}_-) = \mathbf{P}, \qquad (23b)$$

where M_+ and M_- are the masses of the positive and negative ions, Ω_0 the volume of the elementary cell, n the refractive index in the crystal, and $\mathbf{P}$ the vector of the specific inertial polarization of the crystal in the case of extremely long wavelengths. It follows from (23) that

$$\mathbf{u}_+ = \mathbf{P}\Omega_0 n^2 / e\,(1 + M_+/M_-); \qquad \mathbf{u}_- = -M_+\mathbf{u}_+/M_-. \qquad (24)$$

An expansion of $\mathbf{P}$ in a series in terms of a complete set of functions $\chi_\varkappa(\mathbf{r})$ and the transition to dimensionless coordinates using the relations

$$\mathbf{q}_\varkappa = \sqrt{4\pi/\hbar\omega_0 c}\,\mathbf{P}_\varkappa \qquad (25)$$

leads to the following expression for $\mathbf{u}_+$

$$\mathbf{u}_+ = \frac{\Omega_0 n^2 M_-}{e\,(M_- + M_+)} \sum_\varkappa \sqrt{\frac{\hbar\omega_0 c}{4\pi}}\,\mathbf{q}_\varkappa\chi_\varkappa(\mathbf{r}), \qquad (26)$$

where ω_0 is the frequency of the limiting optical vibrations, $c = 1/n^2 - 1/\epsilon$, and ϵ is the dielectric constant of the crystal

We shall assume that the radius of the state of the localized electron is not much larger than the lattice constant (this occurs in a wide range of crystals). In that case only the hyperfine interaction with the nearest ions in the lattice will play an important role. Let these be, for instance, the positive ions of the first coordination sphere surrounding the defect (the estimate is not essentially altered if we take several coordination spheres into account). For our estimate we can put

$$(\text{grad } \hat{Q}_n)_0 = (8\pi\mu\mu_n / 3SI_n)(\nabla\psi^2)_{r=R_n^+} S_z I_{nz}.$$

Using (26) we get for q_κ^0 opt

$$q_{\varkappa,\,\text{opt}}^0 = -\frac{8\pi\mu\mu_n\Omega_0 n^2 M_-}{3\hbar\omega_0 SI_n (M_- + M_+)e}\sqrt{\frac{\hbar\omega_0 c}{4\pi}}\sum_n \chi_\varkappa (R_n^+)(\nabla\psi^2)_{r=R_n^+}\,\mathbf{k}. \tag{27}$$

The summation is over the positive ions of the first coordination sphere.

A direct numerical estimate of the index of the exponent in (21) using (22) and (27) and strongly overestimating shows that this index is practically equal to zero $(10^{-15} - 10^{-16})$. A similar estimate of the sum in the argument of the cosine in (21) leads to the result that here also the role of the optical vibrations is insignificant. As we shall show directly in the following, the index of the exponent in (21) is for the case of the acoustic vibrations, generally speaking, not small (of the order of unity). The interaction with the long wavelength acoustical vibrations turns out to be very substantial, which follows both from the expression for the coupling constant for the spin-lattice interaction

$$C_{\varkappa\alpha} = \sqrt{\hbar / \omega_{\varkappa\alpha}\rho}\sum (\text{grad } \hat{Q}_n)_0\, \mathbf{k}_{\varkappa\alpha}, \tag{28}$$

and from the general physical picture of the phenomenon.*

We note that for the optical vibrations the coupling constant is equal to

$$C_{\text{opt}} = \frac{\Omega_0 n^2 M_-}{e(M_- + M_+)}\sqrt{\frac{\hbar\omega_0 c}{4\pi}}\sum_n (\text{grad } \hat{Q}_n)\,\mathbf{k}. \tag{29}$$

For small κ, $C_{\kappa\alpha}$ will thus be appreciably larger than C_{opt}. Taking the above remarks into account we can with great accuracy in (21) in both sums over κ and α retain only the three branches of the acoustical vibrations.

For the actual case of the extremely long wavelengths we can introduce the normal coordinates of the acoustical vibrations using the relations

*One sees easily that for the spin resonance phenomenon the long wavelength phonons with frequencies $\omega \sim 2\mu H/\hbar$ play the most important part. This follows, though, directly from the expression given in the following for u_z, where the second integral with the limits $\omega_1 \sim 2\mu H$ and ω_0 does not play a part.

$$\mathbf{u}_{\varkappa\alpha} = \mathbf{q}_{\varkappa\alpha}\sqrt{\hbar / \rho\omega_{\varkappa\alpha}}. \tag{30}$$

Taking (30) and (12) into consideration we can write $q_{\kappa\alpha}^0$ in the form

$$q_{\varkappa\alpha}^0 = \omega_{\varkappa\alpha}^{-1/2}\sum_n (\mathbf{E}^n \mathbf{k}_{\varkappa\alpha})\,\chi_\varkappa (R_n)\,S_z I_{nz}. \tag{31}$$

$$\mathbf{E}^n = -\frac{\overline{(\text{grad } Q_n)_0}}{I_{nz}S_z\sqrt{\hbar\rho}}. \tag{32}$$

We note that (32) is independent of $I_{nz}S_z$. It follows from (22) and (31) that

$$a_{\varkappa\alpha} = \omega_{\varkappa\alpha}^{-3}\sum_{nn'} (\mathbf{E}^n \mathbf{k}_{\varkappa\alpha})(\mathbf{E}^{n'}\mathbf{k}_{\varkappa\alpha})\,\chi_\varkappa (R_n)\,\chi_\varkappa (R_{n'})\,I_{nz}I_{n'z}. \tag{33}$$

By generously overestimating, we find from a numerical estimate similar to (27) but for the acoustical vibrations that the sums

$$\frac{1}{2}\sum_{\varkappa\alpha} a_{\varkappa\alpha}\,[\cos\omega_{\varkappa\alpha}\,\varphi - 1], \qquad \frac{1}{2}\sum_{\varkappa\alpha} a_{\varkappa\alpha}\sin\omega_{\varkappa\alpha}\,\varphi$$

are appreciably less than unity (of the order of 10^{-6}). Therefore

$$\tau_e \approx \frac{K}{\pi}\int_0^\pi \cos\omega_e\varphi \cdot \exp\left\{\sum_{\varkappa,\alpha} a_{\varkappa\alpha}n_{\varkappa\alpha}\,[\cos\omega_{\varkappa\alpha}\,\varphi - 1]\right\}d\varphi. \tag{34}$$

Replacing the summation over κ by an integration over κ-space we are by a direct integration over θ_α and φ_α and a summation over α led to the following result

$$\tau_e \approx (K / \pi)\int_0^\pi d\varphi \cos(\omega_e\varphi) \exp\left\{M\int_0^{\varkappa_0} [\cos\omega_\varkappa\,\varphi - 1]\,n_\varkappa\varkappa^{-1}d\varkappa\right\}, \tag{35}$$

$$M = (6\pi^2)^{-1}(2 / c_\perp^3 + 1 / c_\parallel^3)\sum_{nn'} (\mathbf{E}^n \mathbf{E}^{n'})\,I_{nz}I_{n'z}, \tag{36}$$

where $c_\parallel$ and $c_\perp$ are the velocities of the longitudinal and transverse waves. We note that $M > 0$. To obtain (35) we took into account that in the sums over κ in which the extremely long wavelengths play the dominant part, $\kappa R_n \ll \pi/4$ and thus $\sin(\kappa R_n + \pi/4) \approx 1/\sqrt{2}$.

For the integration it is convenient to write (35) in the form

$$\tau_e \approx (K / \pi)\int_0^{2\omega_1} d\varphi \cos(\omega_e\varphi) \exp\left\{M\int_0^{\varkappa_0} [\cos\omega_\varkappa\,\varphi - 1]\,n_\varkappa\varkappa^{-1}d\varkappa\right\}$$

$$+ (K / \pi)\int_{2\omega_1}^\pi d\varphi \cos(\omega_e\varphi) \exp\left\{M\int_0^{\varkappa_0} [\cos\omega_\varkappa\,\varphi - 1]\,n_\varkappa\varkappa^{-1}d\varkappa\right\}, \tag{37}$$

where ω_1 is the frequency within the interval $(0, \omega_0)$ which satisfies the condition

$$\omega_1 \ll kT / \hbar. \tag{38}$$

We shall show that the first integral in (37) is appreciably less than the second one. To do this we note that

$$\int_0^{\omega_e} \frac{\cos\omega\varphi - 1}{\exp(\hbar\omega/kT) - 1} \frac{d\omega}{\omega}$$

cannot be positive. Its largest value is equal to zero.

$$u_1 = \frac{K}{\pi} \int_0^{2/\omega_1} d\varphi \cos(\omega_e\varphi)$$

$$\times \exp\left\{ M \int_0^{x_e} (\cos\omega_x\varphi - 1) n_x x^{-1} dx \right\} \leqslant \int_0^{2/\omega_1} d\varphi = 2/\omega_1.$$

We write the second integral in the form

$$u_2 = \frac{K}{\pi} \int_{2/\omega_1}^{\pi} d\varphi \cos(\omega_e\varphi)$$

$$\times \exp\left\{ M \left[\int_0^{\omega_1} \frac{\cos\omega\varphi - 1}{\exp(\hbar\omega/kT) - 1} \frac{d\omega}{\omega} + \int_{\omega_1}^{\omega_0} \frac{\cos\omega\varphi - 1}{\exp(\hbar\omega/kT) - 1} \frac{d\omega}{\omega} \right] \right\}$$

One can show that in the index of the exponent the first integral (J_1) plays the dominant role. To show this we expand $n(\omega)$ in powers of $\hbar\omega/kT$. We can restrict ourselves by virtue of (38) in J_1 to the first term of the expansion. The second integral J_2 is only increased when we replace $n(\omega)$ by $kT/\hbar\omega$. Thus

$$J_1 = \left[\frac{1 - \cos\omega_1\varphi}{\omega_1} - \varphi \int_0^{\omega_1\varphi} \frac{\sin x}{x} dx \right] \frac{kT}{\hbar}, \quad (39a)$$

$$J_2 \leqslant \frac{kT}{\hbar} \left[\frac{1 - \cos\omega_0\varphi}{\omega_0} - \frac{1 - \cos\omega_1\varphi}{\omega_1} \right.$$

$$\left. - \varphi \int_0^{\omega_0\varphi} \frac{\sin x}{x} dx + \varphi \int_0^{\omega_1\varphi} \frac{\sin x}{x} dx \right]. \quad (39b)$$

$\omega_1\varphi > 1$ in the range of values of φ $(2/\omega_1, \pi)$. Using the asymptotic expression for the sine integral we can write (39) in the form

$$J_1 = (kT/\hbar)(1/\omega_1 - \pi\varphi/2) \approx -kT\pi\varphi/2\hbar, \quad (40a)$$

$$J_2 \leqslant (kT/\hbar)(1/\omega_0 - 1/\omega_1). \quad (40b)$$

It follows from (40) that J_1 is larger than the right hand side of (40b). Therefore

$$u_2 = \frac{K}{\pi} \int_{2/\omega_1}^{\pi} d\varphi \cos(\omega_e\varphi)\exp\left(-\frac{\pi}{2} \frac{kT}{\hbar} M\varphi \right). \quad (41)$$

Integrating, we get

$$u_2 \approx \frac{K}{\pi} \frac{\exp(-2m/\omega_1)}{m^2 + \omega_e^2} \left(m\cos\frac{2\omega_e}{\omega_1} - \omega_e\sin\frac{2\omega_e}{\omega_1} \right), \quad (42)$$

$$m = MkT\pi/2\hbar. \quad (43)$$

Since for the range of frequencies of interest (for which τ_e is still appreciable) $2\omega_e/\omega_1 \ll 1$, we find

$$u_2 \approx \frac{K}{\pi} \frac{m}{m^2 + \omega_e^2}. \quad (44)$$

Comparing (44) and $u_1 \leq 2/\omega_1$ it follows that in this interval $u_2 \gg u_1$.

Therefore

$$\tau_e \approx \frac{K}{\pi} \frac{m}{m^2 + \omega_e^2}, \quad (45)$$

if ω_1 is chosen within the range

$$m \leqslant \omega_1 \leqslant kT/\hbar. \quad (46)$$

Numerical estimates show that $m \approx 10^6 - 10^7$ sec^{-1}. Therefore (46) is not a strong inequality restricting the range of temperatures. For $\omega_1 \approx 10^9$, for instance, $T \geq 0.01°$ K.

Equation (45) is a general expression for the absorption coefficient at frequency ω_e. It can be seen from this expression that the curve has the Lorentz shape. The half width of the line δ is determined by the expression

$$\delta = 2m. \quad (47)$$

The total intensity of the absorption in the line turns out to be equal to

$$\int_{-\infty}^{+\infty} \tau_e d\omega_e = K. \quad (48)$$

It follows from (47) and (43) that the EPR line half width increases linearly with temperature. The absorption coefficient at the maximum

$$\tau_{e\,max} = K/\pi m, \quad (49)$$

is thus

$$\tau_{e\,max}\delta = 2K/\pi. \quad (50)$$

3. THE SHAPE OF THE EPR LINES OF F-CENTERS

For the sake of simplicity we restrict ourselves to such colored crystals for which the hyperfine interaction of the electron with the nuclei of the first coordination sphere, for instance with alkali halide nuclei of the NaCl type is substantial (the generalization to the case of interactions with several coordination spheres does not present any difficulties in principle). It is well known that there are in that case 19 lines corresponding to the different values of the z-component of the total spin I_z. The intensity of each of the 19 lines is determined by the interaction of the electron spin with the lattice vibrations without taking the statistical weight of the state with a well defined value of I_z into account.

The consideration given above shows that the line corresponding to one of the possible distributions of the values of I_{nz} (for given I_z) is broad-

ened. The intensity of each of the 19 lines τ_e is thus made up of the intensities of broadened lines with a well defined distribution of I_{nz}

$$\tau_e = \frac{K}{\pi} \sum_i \frac{m_i}{m_i^2 + \omega_e^2} , \qquad (51)$$

where the summation extends over all states with different I_{nz} but fixed I_z.

One shows easily, using (51), that the total line intensity turns out to be equal to $K\sigma$, where σ is the statistical weight of the state. One sees easily that (51) has also the Lorentz shape for ω_e which are small or large compared to the m_i. The range of intermediate values is small so that (51) to a good approximation has the Lorentz shape for the whole interval over which the frequency varies. What has been said above substantiates the assumption of the phenomenological theory of the saturation effect of the EPR of F-centers which agrees well with experiments, if one assumes that the shape of each of the 19 lines is the Lorentz shape[8] in their "tails."

To obtain the overall shape of the EPR line of F-centers in accordance with experiments it was also just assumed[9] that each of the 19 lines had a Lorentz shape. It was then again emphasized that to obtain the correct shape of the EPR band it is sufficient that the Lorentz shape occur in the "tails" of the curve.

The frequency dependence of the absorption coefficient of the whole EPR band can be written in the form

$$\tau = \frac{K}{\pi} \sum_{iI_z} \frac{m_i}{m_i^2 + (\omega_e - \omega_{I_z})^2} , \qquad (52)$$

if we use (51), where ω_{I_z} is the frequency of the maximum of each of the 19 lines.

Equations (51) and (52) enable us to obtain the temperature dependence of the band width in the frequency range near the maximum. If $\omega_e \ll m_i$, it follows from (51) that

$$\tau_e \approx \left\{ \frac{K}{\pi} \sum_i m_i^{-1} - \omega_e^2 \sum_i m_i^{-3} \right\} . \qquad (53)$$

We shall as an example determine the line width in the neighborhood of the maximum for $\tau_{e\alpha}$ $= (1 - \alpha)\tau_{max}$ where $\alpha < 1$. It follows from (53) that the line width is equal to

$$\delta_\alpha = 2 \left[\alpha \sum_i m_i^{-1} \Big/ \sum_i m_i^{-3} \right]^{1/2} . \qquad (54)$$

Taking (43) into account we find that

$$\delta_\alpha \sim T . \qquad (55)$$

A similar consideration enables us to obtain the temperature dependence of the width of the whole EPR band in the neighborhood of the maximum. The dependence turns out to be more complicated. The band width increases slowly with the temperature in accordance with the experimental results.[6,7]

One sees easily that the m_i depend on the values of the gradient of the wave function of the localized electron at different lattice sites. A comparison of the results of the theory developed in the foregoing with experiment may thus serve as a method to determine the gradient of the wave function. This can be especially simply done for those crystals in which the localized electron interacts only with one magnetic moment of the nuclei of the surrounding atoms (such a situation occurs, for instance, for F-centers in MgO crystals).

In conclusion we note that knowing the width of the absorption lines enables us to estimate the spin-lattice relaxation time t. In the weak coupling limit (which is valid in the case under consideration) t is inversely proportional to the line width. Preliminary estimates performed for F-centers, show that $t \approx 10^{-5} - 10^{-6}$ sec. This magnitude agrees well with the corresponding experimental results (see, for instance, reference 8).

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