EPR LINE SHAPE DUE TO HYPERFINE CONTACT INTERACTION WITH RANDOMLY DISTRIBUTED NUCLEI

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The correlation spectrum function is found by the Margenau-Anderson statistical method for the case of exponential decrease of the interaction energy which broadens the spectral line. This case is realized for an EPR line whose shape is due to the hyperfine contact interaction with nuclei. The line shape is considered, and its moments are calculated as a function of the radius of the state of the center and the concentration of magnetic nuclei. The conditions for which the line shape is Gaussian are indicated. A comparison is made with the experimental data of Feher.[6] The agreement is good.

1. INTRODUCTION

THE statistical method, which in the limiting case is the method of the microcanonical ensemble, was introduced into the theory of the shape of lines in optical spectra by Margenau[1] and then applied by Anderson[2,3] to the problem of spin-spin interactions in EPR.

Recently, this theory has received further fruitful development and application to EPR, in the consideration of dipole-dipole and exchange interactions.[4, 4a]

In this paper line shape is considered for the case when the principal broadening mechanism is the hyperfine contact interaction with nuclei. The results, which are compared with experiment, are obtained on the basis of a hydrogen-like model for the local electronic center.

The contact hyperfine interaction is the principal broadening mechanism for a number of local centers in semiconductors. One can distinguish two cases. In one of these the percentage of magnetic isotopes of the lattice nuclei approaches 100% and the EPR line shape (more precisely, the shape of the envelope of spin-packets) is determined by the distribution of nuclear spin orientations. An example of this is the Gaussian line of the F-center in the NaCl-type lattice.[5] In the other case, the one of interest to us, there are isotopes with nonmagnetic nuclei, and the line shape will depend not only on the combination of spin orientations, but also on the spatial distribution of magnetic nuclei relative to the center. The donor states of group V elements in silicon are a typical example.[6,7]

The only parameter which depends on the nature of the center in a given crystal and affects the line shape and moments is the Bohr radius of the center. Thus, by knowing in essence only the ionization energy of the local center, one can give a rather satisfactory description of the shape of an EPR line broadened by the contact mechanism.

The simplifications introduced when considering crystals and associated with the transition from a summation over crystal lattice sites to an integration over a continuum does not lead to large quantitative errors, particularly when the concentration of magnetic nuclei is small (cf. [4,8]). These simplifications do not exist of course, if the centers giving the EPR signals are in an amorphous matrix.

2. CORRELATION FUNCTION OF THE SPECTRUM

1. Let there be N magnetic nuclei (spin $I = 1/2$) randomly dispersed in a volume V (in the limit $N \to \infty$, $V \to \infty$, $n = N/V = \text{const}$). The electron from the paramagnetic center (spin S) interacts by contact with the N nuclei. The interaction operator is

$$\hat{\mathcal{H}} = \sum_{i=1}^{N} \frac{8\pi}{3} g\beta \frac{\mu_n}{I} |\psi(\mathbf{r}_i)|^2 \hat{S}\hat{I}. \qquad (1)$$

Here $\psi(\mathbf{r}_i)$ is the value of the wave function of the local center at the site of the i-th nucleus. For simplicity, the magnetic moments of the nuclei are taken to be identical.

In a strong magnetic field the shift of the EPR frequency due to the interaction (1) is

$$\omega = \sum_i \omega(\mathbf{r}_i) m_i, \tag{2a}$$

where

$$\omega(\mathbf{r}_i) = \frac{4\pi}{3\hbar} g\beta \frac{\mu_n}{I} |\psi(\mathbf{r}_i)|^2, \quad m_i = \pm 1, \tag{2b}$$

and the resonance frequency in the absence of interaction (1) is set equal to zero.

In the simple hydrogen-like model for the center we have

$$|\psi(\mathbf{r}_i)|^2 = \eta(\alpha^3/8\pi) e^{-\alpha r_i}. \tag{2c}$$

In Eq. (2c), $\alpha = 2/a$, a is the Bohr radius of the center, η is a dimensionless quantity equal to $|u_0(\mathbf{r}_i)|^2/\langle u_0^2(\mathbf{r})\rangle_{av}$, where u_0 is the Bloch function at the edge of the energy band, and the average in the denominator is carried out over an elementary cell.[7] Consequently, $\omega(\mathbf{r})$ from Eq. (2a) has the form

$$\omega(\mathbf{r}) = ve^{-\alpha r}, \quad v = \frac{1}{6\hbar} g\beta \frac{\mu_n}{I} \alpha^3 \eta. \tag{3}$$

If $\omega(\mathbf{r})$ is written, as is sometimes convenient, in magnetic field units, the factor $g\beta$ will be absent.

2. We shall find the shape of the EPR line under the above conditions. Let q represent the set of variables $(\mathbf{r}_1 \ldots \mathbf{r}_N; m_1 \ldots m_N)$. The probability of a microstate is

$$dW(q) = \rho(q)\, dq.$$

Let $\mathscr{E}(\omega; d\omega)$ be the volume of the phase space of q such that, if q falls in $\mathscr{E}(\omega; d\omega)$, then

$$\omega \leqslant \sum_i \omega(\mathbf{r}_i) m_i \leqslant \omega + d\omega.$$

Then the intensity of the spectral line

$$I(\omega)\, d\omega \sim \int_{\mathscr{E}(\omega;\, d\omega)} \rho(q)\, dq.$$

The coefficient of proportionality is chosen from the normalization condition

$$\int_{-\infty}^{+\infty} I(\omega)\, d\omega = 1.$$

If the a priori probabilities of all microstates are the same, then

$$I(\omega)\, d\omega \sim \int_{\mathscr{E}(\omega;\, d\omega)} dq,$$

i.e., simply, the intensity of the line $I(\omega)d\omega$ is proportional to the "number" of configurations leading to a given frequency shift.[1] We shall consider the a priori probabilities of the configurations q in our case to be the same and the probability of a spin configuration to be independent of the probability of a coordinate configuration.

If out of the N nuclear spins a fixed number N_1 were to have $m_i = 1$, then the intensity would equal

$$I_{N_1}(\omega)\, d\omega = V^{-N} \int_{\mathscr{E}_{N_1}(\omega;\, d\omega)} d\mathbf{r}_1 \ldots d\mathbf{r}_N, \tag{4}$$

where the volume $\mathscr{E}_{N_1}(\omega; d\omega)$ of coordinate space is determined from the condition

$$\omega \leqslant \sum_{i=1}^{N_1} \omega(\mathbf{r}_i) - \sum_{i=N_1+1}^{N} \omega(\mathbf{r}_i) \leqslant \omega + d\omega. \tag{5}$$

The factor V^{-N} is introduced for normalization. The observed line shape is

$$I(\omega)\, d\omega = \sum_{N_1} f(N, N_1) I_{N_1}(\omega)\, d\omega, \tag{6}$$

where $f(N, N_1)$ is the probability that a given spin configuration exists; it is known that

$$f(N, N_1) = \frac{1}{2^N} \frac{N!}{(N - N_1)!\, N_1!}$$

$$\approx \left(\frac{2}{\pi N}\right)^{1/2} \exp\{-2(N_1 - N/2)^2/N\}. \tag{7}$$

The latter expression in (7) is true for the actual values of N_1 in (6).

Transforming in (4) to an integration over all space with the Dirac δ-function

$$\delta\left[\omega - \sum_i \omega(\mathbf{r}_i) m_i\right]$$

and replacing thereafter the δ-function by its Fourier transform, we obtain[1, 3]

$$I_{N_1}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i\omega t} Z^{N_1} Z^{*\, N - N_1}\, dt, \tag{8}$$

where

$$Z = \frac{1}{V} \int e^{-i\omega(\mathbf{r})t}\, d\mathbf{r}. \tag{8a}$$

The function $\omega(\mathbf{r})$ is given in our case by Eq. (2b) or (3), and the integration in (8a) is carried out over the volume allocated to the nucleus.

For sufficiently large N, N_1, and V, the quantity Z from (8a) is transformed by Margenau's method,[1, 3] so that

$$Z^{N_1} = (1 - n_1 V'/N_1)^{N_1} = e^{-n_1 V'}, \tag{9}$$

$$V' = \int (1 - e^{-i\omega(\mathbf{r})t})\, dt = 4\pi \int_{r_0}^{\infty} (1 - e^{-i\omega(\mathbf{r})t}) r^2\, dr. \tag{10}$$

In Eq. (9), $n_1 = N_1/V$; the last equality in (10) is valid if $\omega(\mathbf{r})$ is a spherically symmetric function, as in case (3); r_0 in (10) is the minimum distance between the nucleus and the center, which in the

case of a crystal is given by the geometry of its lattice.

Substituting (9) into (8), we have

$$I_{N_1}(\omega)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}e^{i\omega t}\exp\{-i(2n_1-n)\operatorname{Im}V'-n\operatorname{Re}V'\}\,dt. \tag{11}$$

If $n_1 \neq n/2$, then, in addition to broadening, the interaction leads to a shift of the line center, caused by the imaginary part of V′.

However, if we substitute $I_{N_1}(\omega)$ from (8) into Eq. (6) and make use of Eq. (7), then for an experimentally observable line we obtain, after a transformation of the type (9), the expression

$$I(\omega)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}e^{i\omega t}\,e^{-nV_1(t)}\,dt, \tag{12}$$

in which $V_1 = \operatorname{Re} V'$. It is natural that $I(\omega) = I_{N/2}(\omega)$, since $N/2$ is the most probable value of N_1 and the line is symmetrical, since V_1 is an even function of t.

Thus, the correlation function of the spectrum is $F(t) = \exp(-nV_1(t))$, where in the case (3)

$$V_1(t)=4\pi\int_{r_0}^{\infty}[1-\cos\omega(r)t]\,r^2\,dr. \tag{12a}$$

The problem now is to calculate the function $\varphi(t) = -nV_1$.

3. We introduce a dimensionless parameter characterizing the center in the hydrogen-like model $u = \alpha r_0$. Setting $x = \exp(-\alpha r)$, we obtain, considering (3) and (12a)

$$\varphi=-n\cdot 4\pi\alpha^{-3}\int_0^{e^{-u}}\frac{\ln^2 x}{x}(1-\cos vtx)\,dx. \tag{13}$$

The function φ can be represented as a series

$$\varphi=-\pi n\alpha^{-3}\sum_{m=1}^{\infty}\frac{(-1)^{m+1}(vt)^{2m}}{(2m)!\,m^3}C_{2m}, \tag{14a}$$

where

$$C_{2m}=[1+2mu+{}^1/_2(2mu)^2]e^{-2mu}. \tag{14b}$$

For centers with large state radii we have $u < 1$ and $C_{2m} \lesssim 1$; $C_{2m} = 1$, if $r_0 = 0$.

As is seen from (14a), when t is small, φ varies as t^2, so that the wings of the line $I(\omega)$ are always Gaussian. If the parameter α and the concentration are such that in Eq. (12) the first term of the series (14) already gives the correct result, then the entire curve is Gaussian to a rather high degree of accuracy. For further analysis and calculation it is convenient to go over to the dimensionless variables $\bar{\omega} = \omega/(M_2)^{1/2}$ and $\tau = t(M_2)^{1/2}$, where M_2 is the second moment of $I(\omega)$. The calculations of M_2 (see Sec. 3) lead to the following expressions for $I(\bar{\omega})$ and $\varphi(\tau)$:

$$I(\bar{\omega})=\frac{1}{2\pi}\int_{-\infty}^{+\infty}e^{i\bar{\omega}\tau}e^{\varphi(\tau)}\,d\tau,$$

$$\varphi(\tau)=-\left(\frac{\tau^2}{2}-\frac{\tau^4}{4!2^3}z^2\frac{C_4}{C_2^2}+\frac{\tau^6}{6!3^3}z^4\frac{C_6}{C_2^3}-\cdots+\frac{(-1)^{m+1}\tau^{2m}}{(2m)!\,m^3}z^{2m-2}\frac{C_{2m}}{C_2^m}+\cdots\right). \tag{15}$$

In (15) the parameter

$$z^2=\frac{32}{3}\frac{1}{N_a}=\frac{u^3}{\pi n_0 r_0^3}\frac{1}{f},$$

where N_a is the number of magnetic nuclei contained in a sphere of radius $a = 2/\alpha$, and f is the relative concentration of magnetic nuclei, so that $n = n_0 f$, where n_0 is the concentration of atoms. The ratio C_{2m}/C_2^m is given by Eq. (14b). It is easy to see that this ratio does not exceed unity and approximates unity if u is small. Thus, when u is small the number of terms in the series (15) necessary for calculating $I(\bar{\omega})$ is determined solely by N_a. For centers with small state radii it is necessary to take C_{2m}/C_2^m into account also, so that two parameters—u and f—determine $\varphi(\tau)$. Note that if $r_0 = 0$, all $C_{2m} = 1$, and $\varphi(\tau)$ is again determined only by N_a.

For the case of small u, when it is unimportant to take C_{2m}/C_2^m into account, we see from (15) that when $\tau \ll 3(N_a)^{1/2}$ we may set $\varphi(\tau) \approx -\tau^2/2$. With C_{2m}/C_2^m we obtain the analogous inequality

$$\tau \ll 3\sqrt{N_a}(1+2u+2u^2)(1+4u+8u^2)^{-1/2}=\tau_{\text{crit}}.$$

These inequalities allow us to estimate the values of the concentration f ($N_a \sim f$) for which the line $I(\omega)$ is Gaussian. For this, τ_{crit} must be sufficiently large. If we take τ_{crit} of the order of several units, the number N_a for which the line becomes Gaussian is greater than one. We shall consider this question from a somewhat different point of view in the next section.

Without pausing to investigate in detail the asymptotic behavior of $\varphi(\tau)$ as $\tau \to \infty$ (and, consequently, of $I(\omega)$ for small ω), we remark that $\varphi(\tau)$ increases as $\tau \to \infty$ approximately as a polynomial in $\ln \tau$. The asymptote is different when there is dipole-dipole interaction; then $\varphi(\tau) \sim |\tau|$, $\tau \to \pm\infty$.[2-4] Remote nuclei give a contribution to $I(\omega)$ as $\omega \to \infty$. Since the interaction (3) falls off exponentially, the hyperfine dipole-dipole interaction may be more important for distant nuclei (we are speaking here of nuclei lying outside the Bohr orbit of the center). It is clear that taking the hyperfine dipole-dipole interaction into account in analyzing $I(\omega)$ near the maximum ($\omega = 0$) can be important for centers with large values of u (small state radii).

3. MOMENTS OF THE LINE

Any n-th moment of the spectral line

$$M_n = \int_{-\infty}^{+\infty} \omega^n I(\omega)\, d\omega$$

can be determined from the correlation function F(t)[3]:

$$M_n = i^n F^{(n)}(0).$$

For calculating M_n one needs to know only $\varphi(t) = -nRe\, V'$ (see Eq. (10)). For an even function φ only the even moments remain. For them we have

$$M_2 = -\varphi''(0), \quad M_4 = 3\varphi''(0)^2 + \varphi^{IV}(0),$$

$$M_6 = -15\varphi''(0)^3 - 15\varphi''(0)\varphi^{IV}(0) - \varphi^{VI}(0), \ldots \qquad (16)$$

In our case, it follows from the series (14a), (15) that

$$M_2 = \pi n a^{-3} C_2 = \frac{\pi n_0}{36 r_0^3}\left(\frac{\mu_n}{I}\right)^2 \eta^2 u^3 (1 + 2u + 2u^2) e^{-2u} f,$$

$$M_4 = 3M_2^2\left[1 + \frac{4}{9N_a}\frac{C_4}{C_2^2}\right],$$

$$M_6 = 15M_2^3\left[1 + \frac{4}{3N_a}\frac{C_4}{C_2^2} + \frac{2^{10}}{3^5 N_a^2}\frac{C_6}{C_2^3}\right], \ldots \qquad (17)$$

It is seen from (17) that M_2 is inversely proportional to the cube of the Bohr radius of the center and the cube of the lattice constant, and is proportional to the relative concentration of magnetic nuclei. If $a \to \infty$ ($u \to 0$), then M_2 goes to zero as a^{-3}, which is to be expected.[9] But if $a \to 0$ ($u \to \infty$), the magnitude of M_2 falls exponentially. Maximum M_2 is reached at $u = 2.3$, i.e., when $a \approx 0.87 r_0$ (if $r_0 \neq 0$). When $r_0 = 0$ the magnitude of M_2 is obtained by setting $C_2 = 1$.

The higher moments are expressed in terms of the second moment and polynomials in powers of $1/f$ (or $1/N_a$). If the sum of the terms with f in the square brackets turns out to be less than one, then the moments $M_{2n} = (2n-1)!!M_2^n$, and the line will be Gaussian. Since the wings of the line are always Gaussian, and the higher moments are determined by the wings, the condition for "Gaussicity" of the fourth and sixth moments is of interest. For $u \ll 1$ (practically for $u < 0.5$), $C_{2m}/C_2^m \approx 1$ and the line $I(\omega)$ will be Gaussian according to the fourth moment if $N_a \gg 4/9$. In order for the sixth moment also to be associated with a second relation characteristic of a Gaussian, we must have $N_a \gg 3$. Consequently, the sixth moment superposes a somewhat greater limitation on the condition for the transition of the line shape to Gaussian. For arbitrary u it is possible to obtain the dependence of f_{crit} on u from (17), f_{crit} being such a concentration that when $f \gg f_{crit}$ the line $I(\omega)$ is Gaussian, and when $f \leq f_{crit}$ the line shape deviates from Gaussian. We shall not write out explicitly the dependence $f_{crit}(u)$ obtained from the sixth moment, but shall merely point out that for the Si lattice, when u has the values 0.3, 0.5, 1.0, 1.5, and 2, the corresponding values of f_{crit} (in percent) are 0.34, 1.3, 6.5, 14.5, and 24.

4. COMPARISON WITH EXPERIMENT

Feher[6] investigated the EPR line of donor electrons of Sb, P, As, and Bi[10] in Si. The line width was determined by the hyperfine interaction with the nuclei of the magnetic isotope Si^{29} ($\mu_n = 0.555$ nuclear magnetons, $I = 1/2$). For a sample with natural content of Si^{29} ($f = 0.047$) the line shape is Gaussian; its width at half-height ΔH and $\Gamma = M_4/3M_2^2$ were measured. Measurements on samples alloyed with phosphorus, in which the Si^{29} content was reduced to $f = 0.0012$, showed that the EPR line deviates significantly from the Gaussian shape and $\Gamma = 1.8 \pm 0.1$.[6]

In calculations from this experimental data it is necessary to know the magnitude of $\alpha = 2/a$. The radius of the Bohr orbit can be calculated from the ionization energy, since $a = Ea_0/\epsilon E_i$, where ϵ is the dielectric permeability of the substance ($\epsilon = 11.7$ for Si), E is the ionization energy of hydrogen, a_0 is the Bohr radius, and E_i is the ionization energy of the donor center into the conduction band. The values of E_i given in Feher's paper[6] and in [10,11] differ somewhat. We shall take the values for E_i given in [11]. The table illustrates the results of calculations from Eq. (17);

$$\Delta H = 2\sqrt{2\ln 2}\sqrt{M_2}$$

(for the Gaussian shape). The fact that the shape

Donor	Ionization energy, eV	$u = \alpha r_0$	Relative widths ΔH		ΔH	
			Theory	Experiment	Theory	Experiment
Sb	0.043 (0.040)*)	0.331	1.	1	1.8	2.3
P	0.045 (0.044)	0.346	1.07	1.09	2.0	2.5
As	0.054 (0.050)	0.416	1.4	1.26	2.6	2.9
Bi	0.071	0.546	2.03	1.96	3.8	4.5**)

*)The data in parentheses are from[6].

**)The data for Bi are from the review article[10].

should be Gaussian for $f = 0.047$[7] is clear from the criteria indicated here. Thus, for As, we have $N_a \approx 14$, and for P, $N_a \approx 25$. The coefficient C_4/C_2^2 in (17) varies from 0.8 for Bi to 0.91 for Sb, so that the value of Γ calculated from (17) is 1.06 for Bi and even closer to unity for the others.

With the exception of As, the relative widths ΔH agree well with the experiments. These relative widths, as follows from (17), are determined mainly by $E_i^{3/2}$ ($u \sim 1/a \sim E_i$). The absolute values are in somewhat worse agreement with experiment. To obtain these, we used the following values in (17): $\eta = 186$ (this quantity is given in [12] with a deviation of ±18), $n_0 = p/d^3$; for Si, $p = 8$, $d = 5.43$ Å, $r_0 = (3)^{1/2} d/4$. Note that if we take $E_i = 0.050$ eV for As (see table) but keep the values from [11] for the other E_i, then the ratio $\Delta H_{As}/\Delta H_{Sb}$ agrees better with experiment.

For As the quantity $\Gamma_{exp} = 1.3 \pm 0.1$, compared to $\Gamma_{exp} = 1 \pm 0.1$ for Sb and P (Eq. (17) gives this same value for the latter two elements). Although N_a for As is indeed less than for Sb and P, this is nevertheless insufficient to explain Γ_{exp}. Moreover, calculation from (17) for P when $f = 0.0012$ leads to $\Gamma = 1.63$, which is in poor agreement with experiment. In this latter case $N_a \approx 0.6 < 3$, so that the criterion for Gaussian line shape is not satisfied. The theory gives the possibility of calculating the line shape in this case.

It should be kept in mind that silicon is not a very good object for comparison with a theory in which the model for the center is hydrogen-like. The wave function of the donor, in the first place, is anisotropic, and, in the second place, it by no means falls off monotonically from the center because of interference from functions of different wavelengths.[7] The calculations of M_2 given in the papers of Kohn[7] and Feher[6] utilize lattice sums and accurate values of the function at the lattice sites and therefore give more accurate quantitative results. The decrease in accuracy of the calculation of the EPR line widths in Si in this paper as compared to the calculation of lattice sums is compensated by the greater generality and clearness of the results and chiefly by the isolation of the dependence of the line shape and its moments on the physical parameters of the problem.

The theory may be generalized in a number of ways—calculation of the moments when $|\psi|^2$ is more complex than as given by a 1s hydrogen function; simultaneous computation of the hyperfine dipole-dipole interaction, etc. The moment calculation reduces essentially to a volume integral of powers of $\omega(\mathbf{r}_i)$, where $\omega(\mathbf{r}_i)$ is given by Eq. (2b).

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57