Effects of space-frequency correlation and EPR on supergratings

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The Green's function method is used to calculate the magnetic susceptibility $\chi(\omega)$ of dilute paramagnets with allowance for the spin correlation via the phonon field. The equation obtained for χ'' depends both on the frequency distribution function and on the coordinates of the spins. It is shown that allowance for the correlations leads to the appearance of a "dip" on the EPR line, the magnitude of the dip being determined by the distribution function of the centers over the volume of the crystal. In the case of EPR on a "supergrating" (i.e., if the paramagnetic-center density contains a spatially-periodic component), the effect is not small if the wavelength of the resonant phonon coincides with the period of the supergrating. The depth of the dip is proportional to the spin-phonon coupling constant, and the width of the dip is equal to the reciprocal lifetime of the phonon.

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1. INTRODUCTION

In the study of the shape of the electron paramagnetic resonance (EPR) line or of the rate of the spin-lattice relaxation (SLR) in sufficiently dilute paramagnets, the direct dipole-dipole interaction between the spins does not manifest itself in the experiment. In these cases it is customary to use the single-particle approximation, the mathematical formulation of which features the neglect of the correlation, due to the spin-phonon interaction, between the different spins. The magnetic susceptibility is in this case an additive quantity (in terms of the number of spins) and is equal to $N\chi_j$, where N is the number of particles and χ_j is the magnetic susceptibility of one particle.

Aminov and Kochelaev[1] have considered the EPR line shift due to spin-phonon interaction $\mathcal{H}_{\rm int}$, and the complete Hamiltonian (1) in the calculations. However, the spin Green's functions were calculated in the lowest order in $\mathcal{H}_{\rm int}$ without allowance for the correlations between the different centers, and could therefore be obtained in fact from the single-particle Hamiltonian. The influence of the paramagnetic spins on the acoustic phonons were considered by Al'tshuler and Kochelaev[2] and by Fedders[3] for the case of non-concentrated paramagnets, and also by Elliott and Parkinson[4] and by Hoenerlage[5] for paramagnetic spins with periodic structure. In[2,3] however, the correlations between the spatially remote spins were neglected, and the results of[4,5] cannot be applied to spins randomly distributed over the volume of the crystal.

Yet the use of the single-particle Hamiltonian in place of the Hamiltonian of the total system (i.e., the neglect of the correlations between the different spins) in the calculation of the EPR line shape, of the phonon spectrum, or of the rate of the SLR calls for a justification. Interest attaches to the effect of the correlation between the spins in dilute paramagnets, in the EPR spectra, and in the SLR, and also their dependence on the character of the spin distribution.

The criterion for the applicability of the single-particle approach will be formulated as the requirement that the correlation corrections be small.

2. EPR LINE SHAPE WITH ALLOWANCE FOR THE CORRELATION CORRECTIONS

Let the system under consideration be described by the Hamiltonian (for simplicity we confine ourselves to the case $S=1/2$)

$$\mathcal{H}=\sum_{j=1}^{N}(\mathcal{H}_Z^j+\mathcal{H}_{int}^j)+\mathcal{H}_L. \qquad (1)$$

Here

$$\mathcal{H}_Z^j=\omega_0^jS_Z^j,\quad \mathcal{H}_{int}^j=\sum_\alpha\sum_k B_k^\alpha S_\alpha^j e^{i\mathbf{kR}_j}(a_k+a_{-k}^+), \qquad (2)$$

where $\alpha=X,Y,Z$; $\mathbf{R}_j$, ω_0^j, and S_α^j are the coordinate, the resonant frequency, and the α-th projection of the spin of the j-th paramagnetic center, B_k^α is the spin-phonon coupling constant, $k=(\mathbf{k},s)$, $\mathbf{k}$ is the wave vector, s is the polarization of the acoustic phonon, and a_k^+ and a_k are the creation and annihilation operators of the k-th phonon. Here ω_0^j depends in random fashion on the number j of the center, so that in the case of inhomogeneous broadening the fluctuations of ω_0^j determine the width σ and the shape of the EPR absorption line.

The external static magnetic field **H** is directed along the Z axis, and the alternating magnetic field along the Y axis: $H_{1x}=H_1\sin\omega t$. We consider the lattice in the harmonic approximation:

$$\mathcal{H}_L=\sum_k\omega_k(n_k+{}^1/_2),\quad n_k=a_k^+a_k. \qquad (3)$$

If H_1 is small enough, then the complex magnetic susceptibility of the system can be written in the linear-response approximation[6]:

$$\chi_{XX}(\omega)=-2\pi(g\beta)^2G_{XX},\quad G_{XX}=\langle\langle S_X|S_X\rangle\rangle_\omega,\quad S_\alpha=\sum_{j=1}^{N}S_\alpha^j, \qquad (4)$$

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so that $\chi(\omega)=\chi'(\omega)+i\chi''(\omega)$ is expressed in terms of the Fourier transform of the time-dependent temperature Green's function G_{XX} at the frequency ω of the external alternating field. The imaginary part of expression (4) determines the line shape of the EPR absorption signal.

It is seen from the definition (4) that it is convenient to introduce the spin Green's functions that connect the spin operators of two particles: $G_{\mu X}^{jj'}=\langle\langle S_\mu^j|S_X^{j'}\rangle\rangle$, where $\mu=+,-,Z$; $S_\pm=S_X\pm iS_Y$. For $G_{\mu X}^{jj'}$ we can write down equations of motion (see, e.g., [4,5]). The latter contain the mixed spin-phonon Green's functions $\langle\langle S_\mu^j(a_k\pm a_{-k}^+)|S_X^{j'}\rangle\rangle$. We have confined ourselves to allowance for nine equations for the foregoing Green's functions. This approximation, as we shall show, already includes the correlation effects and enables us to take into account the direct process in the SLR.[1)] The results are thus valid at sufficiently low temperatures, when single-phonon processes predominate.

Using the approximations assumed in[1-5], and confining ourselves to frequencies close to resonance, i.e.,

$$|\omega-\omega_0^j|\ll\omega,\quad \omega>0, \tag{5}$$

we arrive at a system of N linear algebraic equations for the Fourier transforms of the sought Green's functions $G_\mu^{jj'}\equiv G_{\mu X}^{jj'}(\omega)$. Since the derivation of analogous equations is described in detail in the literature (see, e.g.,[4], and especially Eqs. (2.25), which are analogous to Eqs. (6) of our paper when (5) is taken into account), we present here only the final result:

$$G_-^{jj'}=-\delta_{jj'}\frac{\langle S_Z^j\rangle}{\pi\Omega_-^j}+4\frac{\langle S_Z^j\rangle}{\Omega_-^j}\sum_{j''\neq j}\sum_k B_k^+\frac{\omega_k}{\omega^2-\omega_k^2}\times\exp\{i\mathbf{k}\mathbf{R}_{jj''}\}[B_{-k}^+G_+^{j''j'}+B_{-k}^-G_-^{j''j'}], \tag{6}$$

where $\mathbf{R}_{jj'}=\mathbf{R}_j-\mathbf{R}_{j'}$,

$$B_k^\pm={}^1/_2(B_k^X\mp iB_k^Y),\quad B_{-k}^+=-B_k^{-*},\quad -k=(-\mathbf{k},s).$$

The function $G_+^{jj'}$ is expressed in terms of $G_-^{jj'}$:

$$G_{-X}^{jj'*}(\omega)=-G_{+X}^{jj'}(-\omega),$$

from which we see that, since $\Omega_\pm^j=\omega\pm\omega_0^j+a_\pm^j$, it follows that

$$\frac{G_+^{jj'}}{G_-^{jj'}}\sim\frac{\omega-\omega_0^j}{\omega+\omega_0^j}.$$

Here

$$a_\pm^j=\sum_k B_k^ZB_{-k}^Z\frac{(\omega\pm\omega_0^j)(2\langle n_k\rangle+1)\mp\omega_k\Theta_k^j}{(\omega\pm\omega_0^j)^2-\omega_k^2}+2\sum_k B_k^+B_{-k}^-(2\langle n_k\rangle+1)\frac{\omega}{\omega^2-\omega_k^2}. \tag{7}$$

The function $G_+^{jj'}$ in the right-hand side of (6) can be neglected alongside with $J_-^{jj'}$, in view of (5).

The first term[2)] in expression (7) for a_-^j describes a two-quantum process, in which the passage of a spin between Zeeman levels is accompanied by simultaneous emission (or absorption) of a phonon ω_k and a phonon ω. An estimate shows that near resonance, if (5) is satisfied, the contribution of this relaxation mechanism is negligibly small in comparison with the ordinary single-phonon mechanism. For B_k we have used the approximation

$$B_k^X=B_k^Y=B_k^Z=(\varepsilon\omega_k/N_0)^{1/2}, \tag{8}$$

where ε is the spin-phonon coupling constant and N_0 is the number of unit cells in the crystal.

Thus, the EPR line broadening due to the spin-phonon coupling, and the shift of the resonance frequencies are determined by the second term of (7). The contribution of Re a_-^j to the EPR frequency shift was considered in[1].

The phonon broadening of the EPR line is expressed in terms of the SLR time $T_1\sim(\mathrm{Im}\,a_-^j)^{-1}$. Since we are considering temperatures so low that single-phonon processes predominate, so that $T_1^{-1}<10^{3-4}$ Hz, the experimentally observed inhomogeneous EPR line width is $\sigma\gtrsim10^7\ \mathrm{Hz}\gg T_1^{-1}$ for most objects. Thus, the case of most practical significance is

$$\sigma\gg T_1^{-1}. \tag{9}$$

The inequality (9) is the main condition for the conversions of the perturbation-theory series in our problem, as will be shown below.

The reason for the broadening of σ may be hyperfine and superhyperfine interactions. The scatter of the local fields and of the deformations due to the crystal-lattice defects. We denote the shape of the inhomogeneously broadened EPR line by $g(\omega_0^j-\bar\omega)$ ($\bar\omega$ is the central frequency of the line), and introduce accordingly in N-dimensional space defined by the aggregate $\omega_0^1,\omega_0^2,\ldots,\omega_0^N$ (ω-space). However, as seen from Eq. (6), G_- depends also on the coordinates of the centers (R-space). We introduce the distribution function in the $\omega\times R$ space:

$$W(\omega_0^1,\omega_0^2,\ldots,\omega_0^N,\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_N),$$

so that $Wd\omega dR$ is the probability that the spins will land simultaneously in the ω-space volume element $d\omega=\Pi_{j=1}^N d\omega_0^j$ and in the configuration-space element $dR=\Pi_{j=1}^N d^3\mathbf{R}_j$ ($\iint Wd\omega dR=1$).

The problem is thus simplified and consists now of finding the distribution of the solutions N of Eqs. (6) given the distribution function $W(\omega,R)$. This problem can be solved if the spin-phonon coupling constants are small enough to admit of a corresponding iteration series. Assuming that the smallness of the higher-order terms in the iteration series is a sufficient condition for its convergence, we write down the solution (6) after the first iteration step and sum the result in accordance with (4) over j and j'. For the Green's function of the total spin we obtain

$$2G_{XX}=G_-=-\frac{N}{\pi}\left\langle\overline{\frac{\langle S_Z^j\rangle}{\Omega_-^j}}\right\rangle_R+\frac{4}{\pi}\sum_{\substack{j,j'\\ j\neq j'}}\sum_k B_k^+B_{-k}^-\times\frac{\omega_k}{\omega^2-\omega_k^2}\left\langle\exp\{i\mathbf{k}\mathbf{R}_{jj'}\}\overline{\frac{\langle S_Z^j\rangle\langle S_Z^{j'}\rangle}{\Omega_-^j\Omega_-^{j'}}}\right\rangle_R. \tag{10}$$

The superior bar in (10) denotes averaging over ω, while $\langle\cdots\rangle_R$ denotes averaging over the configurations. The second term in (10) reflects a new effect—spin correlation via the phonon field. The iteration series (10) converges if T_1^{-1} is small enough. In fact, averaging over ω in (10), together with condition (9), makes it possible to use for $G_-^{jj'}(\omega)$ the pole approximation[6] (i.e., $\mathrm{Im}\,(1/\Omega_-^j)\to\pi\delta(\omega-\omega_0^j)$). After integrating with respect to ω, the first term in the iteration series (9) is equal to $G_-^0(\omega)=\mathrm{const}\cdot g(\omega-\bar{\omega})\sim 1/\sigma$ and the second term is equal to $G_-^{(1)}(\omega)\sim T_1^{-1}/\sigma^2$. The succeeding terms decrease in proportion to $(T_1^{-1}/\sigma)^k$.

3. RANDOM DISTRIBUTION. ZEEMAN FREQUENCIES INDEPENDENT OF THE CENTER COORDINATES

Let

$$W=\prod_{j=1}^{N}g(\omega_0^j-\bar{\omega})\rho(\mathbf{R}_j),\quad \rho(\mathbf{R}_j)=V_0^{-1}$$

(V_0 is the volume of the crystal). This case is trivial in the sense that, at the accuracy at which Eqs. (6) were obtained, the result does not differ from that dictated by the single-particle approach, i.e., the EPR signal is an exact replica of the distribution function of the resonant spin frequencies. This conclusion follows from an analysis of the equation for the spatial Fourier components

$$G(\omega,\mathbf{q})=\sum_{jj'}G^{jj'}(\omega)\exp(i\mathbf{q}\mathbf{R}_{jj'})$$

and is too cumbersome to present here. The absence of correlation effects is a consequence of the satisfaction of two conditions: 1) multiplicativity of the distribution function, and 2) randomness of the impurity distribution over the crystal volume.

The fact that no multiparticle effects manifest themselves in the EPR line shape in the case of a random uncorrelated distribution of the impurities in the volume does not mean, however, that the single-particle approach is altogether valid under these conditions. Indeed, let us dwell on the problem of relaxation of N paramagnetic spins which do not interact directly with one another. In the $N=1$ approximation, standard perturbation theory yields for the rate of the direct process $(S=\frac{1}{2})$[7]

$$T_1^{-1}=\pi\sum_k|B_k^+B_{-k}^-|[2\langle n_k\rangle+1][\delta(\omega-\omega_k)-\delta(\omega+\omega_k)],\tag{11}$$

where $\langle n_k\rangle=n(\omega_k)$ is the Planck factor. On the other hand, the relaxation of the spin packet that make up the inhomogeneously broadened line is determined by the imaginary part of the poles of the Green's function,[6] and according to (6) and (7) we can also obtain T_1^{-1} from (11), but now $\langle n_k\rangle$ is the statistical mean value of the operator n_k (3) over the total Hamiltonian (1).

Let us estimate $\langle n_k\rangle$. To this end we use the results of the preceding paper,[8] where we obtained the phonon correlation function for a random distribution of the spins over the volume of the crystal

$$\langle\langle(a_k-a_{-k}^+);(a_{-k}-a_k^+)\rangle\rangle_\omega=\frac{1}{\pi}\frac{n(\omega)\Gamma_k(\omega)}{[(\omega^2-\omega_k^2)/2\omega_k+\Pi_k(\omega)]^2+\Gamma_k^2(\omega)}.\tag{12}$$

Here $\Pi_k(\omega)$ and $\Gamma_k(\omega)$ are the real and imaginary parts of the polarization operator, and we obtain for $S=\frac{1}{2}$ and $\omega>0$, using the approximation (8),

$$\Gamma_k(\omega)=-\pi C\langle S_z\rangle\varepsilon\omega_k g(\omega-\bar{\omega}),\tag{13}$$

$$\Pi_k(\omega)=C\langle S_z\rangle\varepsilon\omega_k\int_0^\infty\frac{g(\omega'-\bar{\omega})}{\omega-\omega'}d\omega',\tag{14}$$

where $g(\omega-\bar{\omega})$ is the line-shape function and $C=N/N_0$ is the spin concentration. Thus, $\langle n_k\rangle$ and $\langle S_z\rangle$ can be jointly obtained from the solution of the system of integral equations

$$\langle 2n_k+1\rangle=\frac{1}{2\pi}\int_{-\infty}^{\infty}\langle\langle a_k-a_{-k}^+;a_{-k}-a_k^+\rangle\rangle_\omega d\omega,\tag{15}$$

$$\langle 2S_z\rangle=\frac{1}{2\pi}\int_{-\infty}^{\infty}\langle\langle S_+;S_-\rangle\rangle_\omega d\omega.\tag{16}$$

The system (15), (16) can be approximately solved by a procedure similar to that described in Zubarev's review,[9] by substituting in the right-hand sides the corresponding mean values for the extremely small spin-phonon coupling constant. Replacing in this manner $\langle S_z\rangle$ by $-(\frac{1}{2})\tanh(\beta\omega/2)$ in (13) and (14), we substitute (12) in (15). If $g(\omega-\bar{\omega})$ is a Lorentzian of width σ and $\gamma\equiv\frac{1}{2}\varepsilon C\tanh(\beta\omega/2)\gg\sigma^2/\omega_k$, then calculation of the integral yields

$$\langle 2n_k+1\rangle\approx\frac{2n(\omega_k')+1}{2}\left[1+\frac{\omega_k-\bar{\omega}}{((\omega_k-\bar{\omega})^2+4\gamma\omega_k)^{1/2}}\right],\tag{17}$$

where ω_k' is an insignificantly renormalized frequency of the phonon k. In the case of the opposite inequality, $\gamma\omega_k\ll\sigma^2$, the result hardly differs from the Planck factor $2n(\omega_k)+1$ dictated by the single-particle approach.

Thus, the multiparticle effects (the concentration effects) can appear in the SLR even for a random distribution of the impurity centers, since the condition $\gamma\omega_k\gg\sigma^2$ can be easily reached at reasonable values of ε, C, and T. The relaxation time becomes dependent on the detuning of the microwave and is twice as long at the center of the EPR as on the wing.

4. MANIFESTATION OF FREQUENCY-SPATIAL CORRELATION IN THE EPR LINE SHAPE

Assume that all N spins are of the same sort, and that the inhomogeneous broadening of the EPR line is determined by the interaction of the latter with defects in the crystal-lattice structure. It is assumed that the spins do not distort the field of the defects and are randomly distributed over the volume, i.e.,

$$W(\omega,R)=W_\omega(\omega,R)W_R(R)=W_\omega(\omega,R)V_0^{-N},$$

where $W_\omega(\omega,R)$ is the N-dimensional distribution function of the frequencies at a given configuration of R and $W_R(R)dR$ is the probability of realizing the latter. Then, at fixed positions of the defects, the resonant frequency of the j-th center depends only on the proper coordinate

$\mathbf{R}_j$. We regard $\omega_0^j = \omega_0(\mathbf{R}_j)$ as a random scalar field; $W_\omega(\omega_0^1, \ldots, \omega_0^N)$ is the N-dimensional distribution function that defines this field. In the approximation used to obtain (10), it suffices to take into account the one-dimensional and two-dimensional distribution functions

$$W_\omega^{(1)}(\omega_0^j, \mathbf{R}_j) = g(\omega_0^j - \bar\omega, \mathbf{R}_j),$$

$$W_\omega^{(2)}(\omega_0^j, \mathbf{R}_j; \omega_0^{j'}, \mathbf{R}_{j'}) = \underbrace{\int \ldots \int}_{N-2} \prod_{j'' \neq j, j'}^{N} d\omega_0^{j''} W_\omega(\omega, R).$$

The functions $W_\omega^{(i)}$, $i \leqslant N$ are subject to the consistency condition, i.e., $W^{(i)}$ depends only on the coordinates of i centers.[10]

We confine ourselves to the case of a homogeneous isotropic field $\omega_0(\mathbf{R})$ (physically this means macroscopic homogeneity and isotropy of the sample), so that

$$g(\omega_0^j - \bar\omega, \mathbf{R}_j) = g(\omega_0^j - \bar\omega),$$

$$W_\omega^{(2)}(\omega_0^j, \mathbf{R}_j; \omega_0^{j'}, \mathbf{R}_{j'}) = W_\omega^{(2)}(\omega_0^j, \omega_0^{j'}, R_{jj'}),$$

the average frequency $\overline{\omega_0^j} = \bar\omega$ does not depend on the coordinate, the second moment $\overline{\omega_0^j \omega_0^{j'}} \equiv B_{jj'}$ depends only on the distance $R_{jj'} = |\mathbf{R}_j - \mathbf{R}_{j'}|$ between two centers, and we assume that the interaction of the spins with the defect leads to a normal distribution of the frequencies. Then[10]

$$W_\omega^{(2)}(\omega_0^j, \omega_0^{j'}, R_{jj'}) = \frac{1}{2\pi\sigma^2 (1-K_{jj'}^2)^{1/2}} \times \exp\left\{-\frac{(\omega_0^j - \bar\omega)^2 + (\omega_0^{j'} - \bar\omega)^2 + 2K_{jj'}(\omega_0^j - \bar\omega)(\omega_0^{j'} - \bar\omega)}{2\sigma^2 (1-K_{jj'}^2)}\right\}. \quad (18)$$

Since we are interested in the qualitative aspects of the problem, we approximate the correlation coefficient $K_{jj'}$ by a very simple piecewise-smooth function[3]:

$$K_{jj'} = \frac{B_{jj'} - \bar\omega^2}{\overline{\omega^2} - \bar\omega^2} \approx \begin{cases} 1 - (R_{jj'}/R_c)^l, & R_{jj'} < R_c \\ 0, & R_{jj'} > R_c \end{cases}. \quad (19)$$

The correlation radius R_c introduced in (19) is of the order of the average distance between the line-broadening defects.[4] Using (18) and (19), let us estimate the correction $G^{(1)}$ due to the second term in (10). Substituting (8) in (10) we obtain after summing over k in the isotropic Debye model

$$\mathrm{Im}\, G_-^{(1)} = -\frac{18\varepsilon}{\omega_D^3} v\omega^3 \sum_{\substack{jj' \\ j \neq j'}} \left\langle \frac{1}{R_{jj'}} \sin\left(\frac{\omega}{v} R_{jj'}\right) \frac{\overline{\langle S_z^j \rangle \langle S_z^{j'} \rangle}}{\Omega_-^j \Omega_-^{j'}} \right\rangle_R, \quad (20)$$

where v is the average speed of sound in the crystal and ω_D is the Debye frequency.

In the high-temperature approximation ($\beta\omega \ll 1$) the averaging of the factor $\langle S_z^j \rangle \langle S_z^{j'} \rangle / \Omega_-^j \Omega_-^{j'}$ is carried out for an arbitrary $K_{jj'}$, after which the results can be averaged over the configurations that realize the random distribution. The integral over the volume of the crystal is taken in general form subject to the additional requirements

$$\frac{\omega}{v} R_c \ll 1, \quad \left|\frac{\omega - \bar\omega}{\bar\omega}\right| \ll 1.$$

The first means that the correlation radius is smaller than the wavelength of the resonant phonon. At microwave frequencies $\sim 10^{10}$ Hz and at $v \sim 6\times 10^5$ cm/sec this condition becomes a restriction on the concentration of the broadening defects, $N_{\mathrm{def}}/V_0 \gg 10^{15}$ cm^{-3}, which is perfectly reasonable. The second requirement means in fact under EPR experimental conditions $\sigma \ll \bar\omega$ and is always satisfied.

The result of the calculations can be represented in the form ($l = 2$)

$$\mathrm{Im}\, G_{xx} = G_{xx}^{(0)} \left\{1 + 9\sqrt{2}\pi^2 \frac{N}{V_0} R_c^3 \beta\omega \left(\frac{\omega}{\omega_D}\right)^3 \frac{\varepsilon}{\sigma} \times \left[1 - 4\sqrt{\pi}\sigma^2 \frac{1 - \exp\{-(\omega - \bar\omega)^2/2\sigma^2\}}{(\omega - \bar\omega)^2}\right]\right\}. \quad (21)$$

$G_{xx}^{(0)}$ is determined by the first term of (10) and is proportional to $g(\omega - \bar\omega)$ (in this case—Gaussian). The correlation function reaches a maximum at the line center, where it is negative. In addition, $G^{(1)}$ is proportional to ε/σ, and also to the mean number of the spins in the volume of the sphere with the correlation radius $4\pi N R_c^3 / 3V_0$.

Thus, if a spatial-frequency correlation is realized and the spin-phonon coupling constant is large enough, one should expect a "dip" to appear in the center of the inhomogeneously broadened EPR line. The magnitude of the effect is proportional to the reciprocal temperature $\beta = \hbar/k_B T$ and can be determined in principle from the temperature dependence of the shape of the inhomogeneously broadened EPR line. The relative value of the maximally expected effect, according to (21), is

$$\frac{G_{xx}^{(1)}(\bar\omega)}{G_{xx}^{(0)}(\bar\omega)} \approx -320 \frac{N}{V_0} R_c^3 \beta\bar\omega \left(\frac{\bar\omega}{\omega_D}\right)^3 \frac{\varepsilon}{\sigma}. \quad (22)$$

Let $N/V_0 = 10^{19}$ cm^{-3}, $(\omega/\omega_D)^3 \varepsilon/\sigma \approx T_1^{-1}/\sigma = 10^{-3}$, $T = 4.2$ K, $\omega = 2\pi \cdot 10^{10}$ Hz, then $G^{(1)}/G^{(0)} \approx -3 \cdot 10^{17} R_c^3$. Consequently, the effect is observable if $R_c \approx 0.7 \cdot 10^{-6}$ cm, i.e., if the paramagnetic centers, the distance between which is $\lesssim 100$ Å, have frequencies correlated in accordance with (18), then the EPR signal intensity at the center of the line will decrease by 30% at $T = 4.2$ °K and will be restored with increasing temperature.

5. ONE-DIMENSIONALLY PERIODIC DISTRIBUTION OF CENTERS

In this section we neglect the correlation between the resonance frequencies of two spins, so that, just as in the case of the random distribution (Sec. 3),

$$W = \prod_{j=1}^{N} g(\omega_0^j - \bar\omega)\rho(\mathbf{R}_j).$$

Now, however, we consider a parametric-center distribution function in R space in the form

$$\rho(X, Y, Z) = \frac{1}{V_0}\left(1 + m\cos\frac{2\pi Z}{a}\right), \quad 0 \leqslant m \leqslant 1. \quad (23)$$

A distribution close to (23) can be realized in holographic gratings when the impurities introduced into the crystal are capable of going over from a nonparamagnetic state to a paramagnetic state (or vice versa) under the influence of laser radiation.[11] In this case a is the holographic-grating constant, and the modulation factor m is determined by the effectiveness of the realignment of the centers. Another obvious example of realization of (23) is a one-dimensional supergrating with period a. In either case, $\rho(Z)$ need not necessarily be a harmonic function. It is more correct to regard (23) as the zeroth and first terms of the expansion of $\rho(Z)$ in a Fourier series.

We proceed to an analysis of $G_{XX}^{(1)}$. The multiplicativity of W permits an immediate averaging over the frequencies. As a result

$$\frac{\overline{\langle S_z^j\rangle\langle S_z^{j'}\rangle}}{\Omega_-^j\Omega_-^{j'}}=\left[\frac{\overline{\langle S_z^j\rangle}}{\Omega_-^j}\right]^2\sim g^2(\omega-\bar\omega)$$

does not depend on the number of the centers and is taken outside of the sign of summation over j and j'. The remaining factor $\exp(i\mathbf{k}\cdot\mathbf{R}_{jj'})$ can be easily averaged with a weight (23). After summation over j and j', we get

$$\left\langle\sum_{jj'}^{N}\exp(i\mathbf{k}\mathbf{R}_{jj'})\right\rangle_R=2\pi N\delta(k_X)\delta(k_Y)[4\delta(k_Z)+m\delta(k_a+k_Z)+m\delta(k_a-k_Z)], \tag{24}$$

where $k_a=2\pi/a$. Expression (24) was obtained in the limit N, $N_0\to\infty$, $N/N_0=C=\text{const}$. The first term in the square brackets of (24) corresponds to a random distribution of the impurity centers and make no contribution to $G_{XX}^{(1)}$. The two other terms in (24) show that the correlation between the spins present in the one-dimensional supergrating is due to two phonons (six, if account is taken of the three polarization branches) that propagate in both directions along the Z axis of the crystal and whose wavelength is the constant of the supergrating.

Direct substitution of (24) in (10) leads to a divergence as $\omega\to\omega_{k_a}$ because we have so far not taken into account phonon scattering not connected with the considered centers in the crystal. Addition of terms that take into account the interaction in the phonon system to the Hamiltonian (3) of the ideal harmonic grating leads to a smearing of the pole in the expression for $J_{XX}^{(1)}$, so that $\omega_k/(\omega^2-\omega_k^2)$ in (10) is replaced by the factor

$$[(\omega^2-\omega_k^2)/\omega_k+i2\Gamma_k(\omega_k)]^{-1}. \tag{25}$$

The damping $\Gamma_k(\omega_k)$ depends on the magnitude and on the mechanism of the phonon interaction with the lattice-structure defect. Thus, if the crystal is close to ideal and the mass defect and the local deformations due to the prescence of paramagnetic impurities can be neglected, then the phonon mean free path is determined at low temperatures by the sample dimensions, i.e., $\Gamma_k(\omega_k)\approx 2\pi v_s V_0^{-1/3}$. In other cases $\Gamma_k(\omega_k)$ can substantially exceed this value. Phonon scattering by point defects and dislocations was considered in[12].

Substituting (25) and (24) in (10) we obtain ultimately

$$\operatorname{Im}(G_{XX})=G_{XX}^{(0)}[1+{}^1/_2\pi\langle S_Z\rangle g(\omega-\bar\omega)mC\varepsilon(L_\parallel+2L_\perp)], \tag{26}$$

where

$$G_{XX}^{(0)}=N\langle S_z^j\rangle g(\omega-\bar\omega);$$

$$L_s=\frac{\omega_s\Gamma_{k_a}(\omega_s)}{[(\omega^2-\omega_s^2)/2\omega_s]^2+\Gamma_{k_a}^2(\omega_s)},\quad \omega_s=\frac{2\pi v_s}{a},\quad s=\parallel,\perp;$$

$$\mathbf{k}_a=\{0,0,k_a\}.$$

Here $v_\parallel$ and $v_\perp$ are the velocities of the longitudinal and transverse acoustic oscillations. The effect due to the second term in the square brackets of (26) becomes substantial when the two conditions $\omega\approx\bar\omega$ and $\omega\approx\omega_s$ are satisfied. Whereas the first condition denotes simply resonance at the Zeeman frequency, the second is the condition $\omega_{\text{micro}}\equiv\omega$ that the microwave mode be at resonance with the acoustic mode, whose wavelength coincides with the constant of the supergrating. Just as in the case of correlation between resonant frequencies of the spins, this effect can be observed in the form of a dip on the EPR line. The relative depth of the dip in the case of exact resonances $\omega=\bar\omega=\omega_s$ is

$$\frac{G_{XX}^{(1)}}{G_{XX}^{(0)}}\approx-\pi mC\frac{\nu_s\varepsilon}{4\sigma}\frac{\omega_s}{\Gamma_{k_a}(\omega)}\operatorname{th}\frac{\beta\omega}{2} \tag{27}$$

and in the case, say, $C=10^{-5}$, $\omega_s/\Gamma_{k_a}(\omega)\sim10^3$, $m\sim10^{-3}$ it can reach several dozen percent at typical ε and σ when $\varepsilon/\sigma\sim10^4$ and $T=4\,^\circ\text{K}$ (ν_s is the multiplicity of degeneracy of the acoustic branch s).

If $g(\omega-\bar\omega)$ is a Lorentzian with width σ, then expression (26) can be written in different form:

$$\chi''(\omega)=\chi_0\left[1+T_2^2(\omega-\bar\omega)^2+\sum_s\frac{x_s}{1+\tau_s^2(\omega-\omega_s)^2}\right]^{-1}. \tag{28}$$

The quantity $x_s=\frac{1}{2}T_2\varepsilon\tau_s\omega_s mC|\langle S_Z\rangle|$ now plays the same role at the saturation factor, i.e., the EPR signal is saturated resonantly at the frequency ω_s of the supergrating even at low microwave powers. If the phonon lifetime is $\tau_s=\Gamma_{k_a}^{-1}(\omega_s)\gg T_2=2/\sigma$, then the dip is narrow and its width is $\Delta\sim2\tau_s^{-1}\ll\sigma$. The depth of the dip is determined by the spin-phonon coupling, and the position is determined by the period of the supergrating.

From the point of view of the experimental verification of the theory, the authors regard as the most promising an investigation of EPR with holographic gratings,[9] since the condition $\omega=\omega_s$ is reached at typical values $\omega_{\text{micro}}=2\pi\cdot10^{10}$ Hz, $v_s=6\times10^5$ cm/sec, and $a=6000$ Å. We note that by observing the dip of the EPR line for supergratings in sufficiently pure samples with small phonon damping, it is possible to determine the sound velocities of the longitudinal and transverse acoustic mode $v_s=a\omega_{\text{micro}}/2\pi$ with practically the same accuracy with which ω_{micro} and a can be measured.

6. CONCLUSION

Spin correlation via the phonon field causes, generally speaking, the single-particle approach to be invalid in the calculation of $\chi(\omega)$ or T_1 (Sec. 2). In the case of an inhomogeneously broadened EPR line, the correlation corrections contain the factor $(\varepsilon/\sigma)C\tanh(\beta\omega/2)$, which makes $\chi(\omega)$ non-additive (in the number of spins) and causes T_1 to depend on the concentration (Sec. 1), and also gives rise to new temperature dependence of these quantities. An estimate of these effects has shown the following: If the centers are randomly distributed and if a correlation exists between the spatial and frequency distributions, the maximum attainable depth of the dip in the EPR signal is of the order of 10% at $R_c \approx 70$ Å and $N/V_0 = 10^{19}$ cm^{-3}, at an inhomogeneous EPR line width $\sigma = 1$ Oe, and at a spin-lattice relaxation rate $T_1^{-1} \approx 10^3$ Hz. The periodic distribution of the centers over the crystal leads to a depth of the dip on the order of several dozen per cent at the usually realized EPR parameters (see Sec. 5) and at a relative concentration $mC \sim 10^{-8}$ of the periodically distributed centers. The spin-lattice relaxation time depends, when the multiparticle characteristics are taken into account, on the microwave detuning and its values from the center and on the wing of the EPR signal can differ by a factor of two.

Particular interest attaches to the investigation of EPR with holographic gratings made up of paramagnetic impurities. If the wavelength of the resonant phonon coincides with the period of such a grating, a strong correlation appears between spins separated by distances on the order of or smaller than the phonon mean free path. This correlation is realized via phonons with wave vectors directed along the axis of the supergrating. One can expect holographic supergratings to act under conditions of resonant pumping as acoustic analogs of lasers, and to serve as a source of coherent hypersonic waves.

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1) To take Raman relaxation processes into account it would be necessary to solve equations for higher Green's functions of the type $\langle\langle S_\mu^j a_k + a_q \mid Sx^{j'} \rangle\rangle$.

2) An expression for Θ_k^j is given in[8].

3) The law governing the decrease of the correlation function with distance is determined by the actual model of the interaction of the spins and defects; Eq. (19) should be regarded as a rough but convenient method of representing, in the form of a polynomial, functions of the type exp $(-R_{jj'}^l/R_c^l)$, in terms of which $K(R_{jj'})$ is expressed.

4) The considered correlation (frequency-spatial correlation) is determined exclusively by the random field of the lattice defect and does not depend on the paramagnetic spins; however, as seen from (10), it causes the spin Green's functions $G^{jj'}$ to be finite at $j \neq j'$.

5) It follows from the communication of Bishop, Strom, and Taylor,[15] reporting EPR of photoexcited localized cases in amorphous arsenic, that in amorphous semiconductors one can obtain supergratings with large spin concentration.

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