THEORY OF EPR LINE SHAPE OF IMPURITY CENTERS IN NONMETALLIC CRYSTALS

M. D. GLINCHUK and M. F. DEĬGEN

Semiconductor Institute, Academy of Sciences, Ukrainian SSR

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A theory of the EPR line shape of impurity centers in nonmetallic crystals is developed within the framework of the quantum kinetic equation. The angular dependences of the line half-widths on the orientation of the crystal in an external static magnetic field are obtained. The case of Cr^{3+} in $ZnWO_4$ is considered as an example. The correlation between the angular dependences of the EPR line half-widths and the magnitude of the line splitting in an external electric field which has been observed experimentally [1] is explained. The principal spin-phonon interaction mechanism responsible for line broadening can be established by comparing the theory and experiment.

1. INTRODUCTION

In a number of experimental papers (see, for example,[1,2]) an angular dependence of the EPR line half-width of impurity centers in crystals has been established. The effect of an external electric field on the EPR spectrum in crystals without a center of inversion has been investigated in[1,3,4]. The non-equivalence of the ionic positions in the unit cell produces a splitting of the EPR line in an external electric field. The magnitude of the splitting depends on the orientation of the crystal in the external magnetic field and has an angular dependence. Bugaĭ et al.[1] have established a correlation between the angular dependences of the EPR line half-widths in the absence of an electric field and the magnitude of the splitting of the line in an electric field. Mims and Gillen[5] attempted to explain this correlation effect, proposing that the angular dependence of the half-width is associated with the effect of the electric fields of the impurity centers incorporated in the crystal. Estimates have shown that to explain this effect high concentrations of defects of the order of 10^{18} cm^{-3} are necessary.

A theory of EPR line shape is developed below, using the quantum kinetic equation (see, for example,[6,7]). The theory explains the angular dependences of the EPR line half-widths and the correlation between these and the magnitude of the line splitting in an external electric field. The theory contains no presumption of the presence of charged defects in the crystal.

2. BASIC EQUATIONS

We write the Hamiltonian of the system consisting of the paramagnetic center and the crystal in the form

$$\hat{W} = \hat{\mathscr{H}} + \hat{V} + \hat{F} + \hat{G}, \qquad (1)$$

where $\hat{\mathscr{H}}$ is the operator for the energy of the paramagnetic center in the crystal (the dynamic subsystem), $\hat{V}$ is the operator for the energy of interaction of the paramagnetic center with an external ac magnetic field, $\hat{F}$ is the Hamiltonian of the surroundings of the paramagnetic center (dissipative sub-system), and $\hat{G}$ is the operator for the energy of interaction of the dynamic and dissipative subsystems.

The equation of motion for the density matrix of the entire system is

$$\partial\rho / \partial t = i[\rho, \hat{W}]. \qquad (2)$$

The equation of motion for the density matrix of the dynamic subsystem using the usual assumptions[7] has the form

$$\sigma_{mn} + i\omega_{mn}\sigma_{mn} + i[\hat{V},\sigma]_{mn} = \begin{cases} \sum_k (w_{km}\sigma_{kk} - w_{mk}\sigma_{mm}), & m = n \\ -\dfrac{1}{\tau_{mn}}\sigma_{mn}, & m \neq n. \end{cases} \qquad (3)$$

Here m and n number the energy levels of the dynamic subsystem, w_{km} is the probability of transition per unit time from state k to state m,

$$w_{km} = 2\Gamma_{mkkm}, \quad \omega_{mn} = \varepsilon_m - \varepsilon_n,$$
$$\frac{1}{\tau_{mn}} = \frac{1}{2}\sum_k (w_{mk} + w_{nk}) - 2\Gamma_{mmnn} + \Gamma_{mmmm} + \Gamma_{nnnn}. \qquad (4)$$

The interaction operator is

$$G = \sum_{l\lambda} F_l^{-\lambda} Y_l^\lambda, \qquad (5)$$

where Y_l^λ is the λ component of an irreducible tensor operator of weight l in spin space, F_l is the corresponding quantity in the space of the variables of the dissipative subsystem:

$$\Gamma_{mkln} = \sum_{q\lambda\mu} \Phi_q^{-\lambda-\mu}(\omega_{ln})\,(Y_q^\lambda)_{mk}(Y_q^\mu)_{ln}, \qquad (6a)$$

$$\Phi_q^{\lambda\mu}(\omega_{ln}) = \int_{-\infty}^{\infty} e^{-i\omega_{ln}t}\langle F_q^\lambda(t)F_q^\mu(0)\rangle dt. \qquad (6b)$$

Here $\omega_{mk} = \omega_{nl}$.

We choose for the operator for the energy of the dynamic subsystem

$$\hat{\mathscr{H}} = D\left[\hat{J}_z^2 - \frac{1}{3}J(J+1)\right] + E[\hat{J}_x^2 - \hat{J}_y^2] + \beta\sum_{i=1}^{3} g_i H_i \hat{J}_i. \qquad (7)$$

Here $\hat{J}$ and J are respectively the angular momentum operator of the spin and its eigenvalue, D and E are the crystal field constants. Similar spin Hamiltonians describe the behavior of iron-group ions in tungstates, corundum ($E = 0$), and in many other crystal systems.

Below we shall compare theory with experiment in the case of Cr^{3+} in $ZnWO_4$. In this case $J = 3/2$, $D \gg g\beta H$. In first-order perturbation theory the energy levels and wave functions in the zeroth approximation have the following form:

$$\varepsilon_{1,2} = -D \mp {}^1/_2 g\beta H\sqrt{1 + 3\sin^2\theta}, \quad \varepsilon_{3,4} = D \mp {}^3/_2 g\beta H\cos\theta; \qquad (8a)$$

$$\psi_1 = 2^{-1/2}[\sqrt{1+a}\,\chi_{-1/2} - \sqrt{1-a}\,\chi_{1/2}],$$
$$\psi_2 = 2^{-1/2}[\sqrt{1-a}\,\chi_{-1/2} + \sqrt{1+a}\,\chi_{1/2}],$$
$$\psi_3 = \chi_{-3/2}, \quad \psi_4 = \chi_{3/2}, \quad a = \frac{\cos\theta}{\sqrt{1+3\sin^2\theta}}, \tag{8b}$$

where χ_m are the eigenfunctions of the operator $\hat{J}_z$ and θ is the angle between the direction of a dc magnetic field located in the xz plane and the z axis.

3. EPR LINE SHAPE. COMPARISON WITH EXPERIMENT.

The operator for the energy of interaction between the spin and an ac magnetic field has the form

$$\hat{V} = \hat{V}^0 \cos\Omega t, \quad \hat{V}^0 = 2\gamma H_1 \hat{J}_x, \tag{9}$$

where Ω is the frequency of the electromagnetic field, γ is the gyromagnetic ratio, and H_1 is the amplitude of the ac electromagnetic field. We choose the frequency Ω to correspond to the transition between levels 2 and 1 (lower Kramers doublet).

Using the stationary solutions of the kinetic equations, we obtain for the dynamic susceptibility

$$\chi(\Omega) = \frac{\gamma^2\cos^2\theta}{1+3\sin^2\theta}\frac{[(\Omega-\omega_{21})+i\tau_{21}^{-1}](\sigma_{22}^0-\sigma_{11}^0)}{(\Omega-\omega_{21})^2+1/\tau_{21}^2}, \tag{10}$$

where $\sigma^0_{mm} = \exp(-\epsilon_m/kT)/\Sigma_m \exp(-\epsilon_m/kT)$ is the equilibrium density matrix. Note that in (10) we have neglected small terms of order $(V^0_{mn})^2$.

The imaginary part of the magnetic susceptibility, which determines the absorption line shape, is

$$\chi''(\Omega) = \frac{\gamma^2\cos^2\theta}{1+3\sin^2\theta}\frac{\tau_{21}^{-1}(\sigma_{22}^0-\sigma_{11}^0)}{(\Omega-\omega_{21})^2+1/\tau_{21}^2}. \tag{11}$$

It is seen from (11) that the absorption line is Lorentzian in shape with half-width equal to τ_{21}^{-1}.

After calculating the matrix elements in (6a) using the wave functions (8b) in the high-temperature approximation ($\omega_{mn}/kT \ll 1$), we obtain

$$1/\tau_{21} = A_0 + A_1a^2 + A_2a\sqrt{1-a^2} + A_3\sqrt{1-a^2} + A_4a. \tag{12}$$

Here the coefficients A_i are real and are linear combinations of the functions $\Phi_l^{\lambda\mu}(\omega)$ (ω are the frequencies of the dynamic subsystem, including $\omega = 0$).

For comparison with experiment (klystron frequency Ω fixed, external magnetic field magnitude H variable), Eq. (11) is transformed from $\chi''(\Omega)$ to $\chi''(H)$. Expanding $\Phi_q^{\lambda\mu}(\omega_{ij})$ in a series and retaining only the first approximation ($g\beta H/D \ll 1$), assuming that $\Phi_q^{\lambda\mu}(\omega_{ij})$ varies little with a change of magnetic field by an amount of the order of the line width, and taking the parity of the functions $\Phi_q^{\lambda\mu}(\omega)$ into account in the high temperature approximation, we obtain for the half-width

$$\frac{1}{\tau_{21}} = \frac{1}{\sqrt{1+3\sin^2\theta}}[C_0 + C_1a^2 + C_2a\sqrt{1-a^2}]. \tag{13}$$

Here the coefficients C_i are linear combinations of the functions $\Phi_l^{\lambda\mu}(\omega)$, ω takes on values 0, Ω, 2Ω (the explicit form of the coefficients is omitted here because of its complexity).

An analogous treatment for the transition 4 → 3 (upper Kramers doublet) leads to the following expression for the half-width:

$$\frac{1}{\tau_{43}} = [B_1\cos\theta + B_2\sin\theta]/\cos^2\theta. \tag{14}$$

Here the real coefficients B_i are given in the form of a linear combination of the Fourier transforms of the correlators $\Phi_1^{\lambda\mu}(\omega)$ at frequencies 0, 2Ω. We remark that the calculation of the matrix elements in obtaining (14) was carried out using zero- and first-order wave functions.

The theory was compared with the experimental results of[1] (Cr^{3+} in $ZnWO_4$) for the transitions 2–1 and 4–3. The curves of the angular dependences obtained in[1] are raised a little above the abscissa axis. This is evidently connected with the spin-spin interaction of the paramagnetic centers. The comparison of theory with experiment was made for values of the half-width in the absence of the spin-spin background. These were defined as the difference between the observed and minimum values of the half-width.

Figures 1 and 2 give the results of the comparison for the transitions 2–1 and 4–3, respectively. It is seen that with a proper choice of parameters the theoretical curves reproduce the experimental ones in their main features.

The results simultaneously explain also the correlation of the angular dependence of the half-width with the magnitude of the splitting of the line in an external electric field. Equations (8) and (9) in[1] for $\varphi = 0$ (magnetic field in the xz plane) coincide respectively with Eqs. (13) and (14).

The comparison with experiment also allows one to make a judgement concerning the principal mechanism of line broadening. Agreement with experiment can be secured by taking into account in the energy of the interaction of the spin with its surroundings terms with $l = 1$, which correspond to interactions linear in the spins. This follows directly from the fact that the form of Eqs. (13) and (14) does not change if in the coefficients C_i and B_i terms with $1 = 2$, which correspond to interactions quadratic in the spins, are left out. Qualitatively, this can be explained by considering the upper and lower Kramers doublets as systems corresponding to an effective spin of $1/2$.

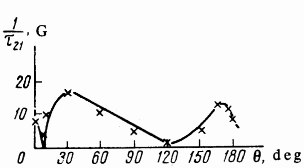

FIG. 1. Angular dependence of the EPR line half-width (lower Kramers doublet): continuous curve—theory, points—experimental values from [1].

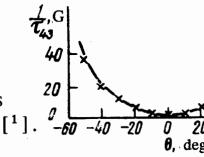

FIG. 2. Angular dependence of the EPR line half-width (upper Kramers doublet): continuous curve—theory, points—experimental values from [1].

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192