

Effect of exciton coherence in spectra of paired impurity clusters in molecular crystals

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An analytic expression is obtained, within the context of the density-matrix and linear-response theories, for the EPR line width in the spectrum of a triplet exciton of a paired AB center (A and B are differently oriented molecules in a crystal cell), for coherent motion and with allowance for single-phonon and two-phonon processes. The temperature dependence of the EPR line width is investigated for an impurity AB cluster in deuterio-naphthalene crystal, and the temperature corresponding to the maximum of a homogeneously broadened EPR line is analyzed as a function of the exciton-phonon coupling constants.

The temperature dependences of the shapes, widths, and intensities of EPR lines in the spectra of paired impurity clusters in a deuterio-naphthalene crystal were experimentally investigated¹ using the methods of optical detection of magnetic resonance and spin echo. A theoretical analysis of these results, with allowance for single-phonon processes, was carried out in Ref. 2. It was impossible there, however, to reconcile in this approximation the calculated and experimental temperatures (T_{\max}) corresponding to the maximum EPR line width of the triplet exciton of a paired AB center (A and B are differently oriented molecules in the crystal). The difference between these values reached $\sim 60\%$.

We show in the present paper that this effect can be explained by taking two-phonon processes into account. Using the density-matrix and linear-response theories we obtain an analytic expression for a homogeneously broadened EPR line of the considered paired impurity cluster. We analyze the value of the maximum temperature as a function of the exciton-phonon interaction constants. Account is taken of the influence of the anisotropy of the spectroscopic-splitting g -factor.

1. SYSTEM HAMILTONIAN

The initial Hamiltonian describing an impurity AB center is of the form³

$$H = H_{ex} + H_l + H_{int}, \quad (1)$$

where H_{ex} is the exciton Hamiltonian and determines the spectrum of the system in the absence of exciton-phonon coupling:

$$H_{ex} = \sum_{\alpha} (E_{\alpha} + H_{z\alpha} + H_{r\alpha}) B_{\alpha} + B_{\alpha} + J(B_A + B_B + B_B + B_A), \quad (2)$$

B_{α}^{+} and B_{α} are operators corresponding to creation and annihilation of excitation on the α th molecule of the cluster ($\alpha = A, B$); E_{α} is the electron-level energy of the α th molecule; J is a matrix element of the resonant (exchange) interaction between neighboring (A and B) molecules of the impurity;

$$H_{z\alpha} = \beta \mathbf{H} \hat{g}_{\alpha} \mathbf{S} \quad (3)$$

is the Zeeman interaction between the excited α th molecule

and the stationary magnetic field \mathbf{H} (\mathbf{S} is the electron-spin operator, g_{α} —tensor of spectroscopic splitting of α th molecule);

$$H_{r\alpha} = \mathbf{S} \hat{D}_{\alpha} \mathbf{S} \quad (4)$$

is the fine-structure (FS) energy operator (\hat{D}_{α} —FS tensor of the α th molecule).

Assume that the AB center in question contains a single exciton, i.e.,

$$B_A + B_A + B_B + B_B = 1, \quad (5)$$

and that both molecules of the cluster have identical electron levels (resonance case): $E_A = E_B = E$. The Hamiltonian (2) can then be written in the form

$$H_{ex} = \sum_{\mu} E_{\mu} A_{\mu} + A_{\mu} + \frac{1}{2} (H_{zA} + H_{zB} + H_{rA} + H_{rB}) + V, \quad (6)$$

where E_{μ} is the energy of the μ th Davydov component:

$$E_{\mu} = E - (-1)^{\mu} J. \quad (7)$$

A_{μ}^{+} and A_{μ} are the creation and annihilation operators of the symmetric and antisymmetric states of the impurity AB pair:

$$A_{\mu}^{+} = 2^{-1/2} [B_A + (-1)^{\mu} B_B], \quad (8)$$

$$A_{\mu} = 2^{-1/2} [B_A + (-1)^{\mu} B_B].$$

The operator

$$V = 1/2 (H_{zA} - H_{zB} + H_{rA} - H_{rB}) A \quad (9)$$

describes the correlation of the spatial and spin motions; in Eq. (9) we have

$$A = A_1 + A_2 + A_2 + A_1. \quad (10)$$

The interaction V is determined by the anisotropy of the g factor of the spectroscopic splitting and by the anisotropy of the FS which are, respectively, smaller by 3–4 and 1–2 orders than the resonant interaction. The influence of V on the exciton motion will therefore be small and can be taken into account by perturbation theory. The energy levels of the Hamiltonian (6) are shown in the figure.

The transition matrix elements A_{ik} which we need in the subsequent calculations are given by

$$+ \delta_{\mu\mu'} \frac{2\omega_{\mu\tilde{\mu}} \Delta_{ss'}}{\omega_{\mu\tilde{\mu}}^2 - \omega_{ss'}^2} + \delta_{\mu\tilde{\mu}'} \sum_{s_1} \frac{2\Delta_{ss_1} \Delta_{s_1s'}}{(\omega_{\mu\tilde{\mu}} + \omega_{ss_1})(\omega_{\mu\tilde{\mu}} + \omega_{s's_1})} \times \left[\delta_{ss'} \frac{\omega_{\mu\tilde{\mu}}^2}{\omega_{\mu\tilde{\mu}}^2 - \omega_{ss'}^2} + (1 - \delta_{ss'}) \frac{\omega_{\mu\tilde{\mu}}}{\omega_{ss'}} \right], \quad (11)$$

where

$$\Delta_{ss'} = \frac{1}{2} \langle s | H_{ZA} - H_{ZB} + H_{FA} - H_{FB} | s' \rangle \quad (12)$$

and $\mu, \mu' = 1, 2; \tilde{\mu}, \tilde{\mu}' = 2, 1; s, s' = 1, 2, 3$. The correspondence between the indices μs and i is shown in the figure.

The operator H_I in the Hamiltonian (1) describes the energy of the phonons in the crystal ($\hbar = 1$):

$$H_I = \sum_j \omega_j b_j^+ b_j, \quad (13)$$

b_j^+ and b_j are phonon creation and annihilation operators in the state j .

The operator H_{int} determines the exciton-phonon interaction:

$$H_{int} = \sum_j g_j (b_j^+ + b_j) A + \sum_{j,j'} g_{jj'} (b_j^+ + b_j) (b_{j'}^+ + b_{j'}) A, \quad (14)$$

g_j and $g_{jj'}$ are the respective interaction constants for one- and two-phonon processes.

Our analysis has shown that the main contribution to the exciton-phonon interaction is made by modulation of the positions of the electron levels E_α of the individual molecules. Modulation of the resonance interaction J does not lead to any substantial effects.

2. SYSTEM EQUATIONS OF MOTION

Let us write down an equation for the density matrix describing a dynamic system with a Hamiltonian (6)

$$i \frac{d\rho}{dt} = \hat{L}\rho, \quad (15)$$

where the Liouville operator is of the form

$$\hat{L} = [H_{ex}, \dots] + i\pi \sum_{klmn} (A_{nm} A_{kl} |k\rangle\langle l| \dots |n\rangle\langle m| + A_{mn} A_{lk} |m\rangle\langle n| \dots |l\rangle\langle k|) \sum_j \{ g_j^2 [n_j \delta(E_{nm} + \omega_j) + (n_j + 1) \delta(E_{nm} - \omega_j)]$$

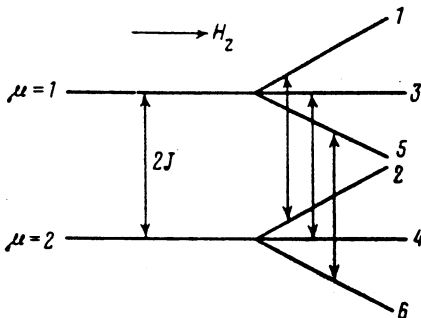


FIG. 1. Energy-level diagram of triplet exciton pair center in coherent motion.

$$+ \sum_{j'} g_{jj'}^2 [n_j (n_j + 1) \delta(E_{nm} + \omega_j - \omega_{j'}) + n_{j'} (n_{j'} + 1) \delta(E_{nm} - \omega_j + \omega_{j'})] \} - i\pi \sum_{ilm} (A_{lm} A_{mk} \dots |l\rangle\langle k| + A_{ml} A_{km} |k\rangle\langle m| \dots) \times \sum_j \{ g_j^2 [n_j \delta(E_{lm} + \omega_j) + (n_j + 1) \delta(E_{lm} - \omega_j)] + \sum_{j'} g_{jj'}^2 [n_j (n_j + 1) \delta(E_{lm} + \omega_j - \omega_{j'}) + n_{j'} (n_{j'} + 1) \delta(E_{lm} - \omega_j + \omega_{j'})] \}. \quad (16)$$

Here $n_j = [\exp(\omega_j/kT) - 1]^{-1}$, and account is taken also of the most effective two-phonon processes that cause the transitions:⁴ $E_{nm} = \omega_j - \omega_{j'}$.

The EPR line shape is determined by the imaginary part of the complex susceptibility. According to the linear-response theory, it is given at $H_x(t) \perp H_z$ by

$$\chi(\omega) = \int_0^\infty i \langle [S_x(t), S_x] \rangle_0 e^{i\omega t} dt, \quad (17)$$

where

$$\langle [S_x(t), S_x] \rangle_0 = \sum_{i,j} (P_i - P_j) \langle i | S_x | j \rangle \chi_{ij}(t) \quad (18)$$

and

$$P_i = \exp\left(-\frac{\omega_i}{kT}\right) / \sum_i \exp\left(-\frac{\omega_i}{kT}\right), \quad (19)$$

$$\chi_{ij}(t) = \text{Sp}_0 S_x \exp(-i\hat{L}t) |i\rangle\langle j|. \quad (20)$$

Differentiating (20) and taking into account the explicit form of the operator \hat{L} [Eq. (16)], we obtain the equation of motion for $\chi_{ik}(t)$:

$$\frac{d\chi_{ik}}{dt} + iE_{ik} \chi_{ik} = \pi \sum_{l,m} \{ (A_{il} A_{km} \chi_{lm} - A_{km} A_{ml} \chi_{il}) \times \sum_j [g_j^2 (n_j \delta(E_{km} + \omega_j) + (n_j + 1) \delta(E_{km} - \omega_j))] + \sum_{j'} g_{jj'}^2 (n_j (n_j + 1) \delta(E_{km} + \omega_j - \omega_{j'}) + n_{j'} (n_{j'} + 1) \delta(E_{km} - \omega_j + \omega_{j'})) \} + (A_{ml} A_{kl} \chi_{ml} - A_{lm} A_{ml} \chi_{lk}) \times \sum_j [g_j^2 (n_j \delta(E_{lm} + \omega_j) + (n_j + 1) \delta(E_{lm} - \omega_j))] + \sum_{j'} g_{jj'}^2 (n_j (n_j + 1) \delta(E_{lm} + \omega_j - \omega_{j'}) + n_{j'} (n_{j'} + 1) \delta(E_{lm} - \omega_j + \omega_{j'})) \}. \quad (21)$$

We change in (21) from summation over the phonon states to integration over the frequencies, taking into account the

linear dispersion law for the acoustic oscillations excited at low temperatures ($T \sim 1$ K). We shall assume here that the constants g_1 and g_2 which describe the exciton-phonon interaction for one- and two-phonon processes are constant in the considered frequency region.

We seek the solution of (21) in the form

$$\chi_{ik}(t) = e^{-i\omega t} \chi_{ik}. \quad (22)$$

Taking into account the maximum values of the matrix elements A_{ik} in (11), namely $A_{ik} \sim 1$, which correspond to transitions between the lower and upper Davydov components (these transitions are shown by arrows in the figure), we obtain

$$\omega_{46} = \bar{E} - i\bar{z} + i[(\bar{z}^2 - \Delta E^2) + 2i\Delta E \Delta z]^{\frac{1}{2}}, \quad (23)$$

where

$$\bar{E} = \frac{E_{35} + E_{46}}{2}, \quad \Delta E = \frac{E_{35} - E_{46}}{2}, \quad (24)$$

$$\bar{z} = g_1^2 \xi_1 (2n_0 + 1) + g_2^2 \xi_2, \quad \Delta z = g_1^2 \xi_1 + g_2^2 \Delta \xi,$$

with

$$\begin{aligned} \xi_1 &= \frac{V_0}{2\pi c^3} \omega_0^2, \\ \xi_2 &= \left(\frac{V_0}{2\pi c^3} \right)^2 \int_0^\infty \omega^2 (\omega_0 + \omega)^2 [n(\omega) + 2n(\omega)n(\omega_0 + \omega) \\ &\quad + n(\omega_0 + \omega)] d\omega, \\ \Delta \xi &= \left(\frac{V_0}{2\pi c^3} \right)^2 \int_0^\infty \omega^2 (\omega_0 + \omega)^2 [n(\omega) - n(\omega_0 + \omega)] d\omega. \end{aligned} \quad (25)$$

Here V_0 is the volume of the unit cell of the crystal, c is the phase velocity of the acoustic phonons, and $\omega_0 = 2J$. We have considered only transitions of frequency ω_{46} , since transitions of frequency ω_{35} have not been observed in experiment.² We have also used the approximation $n(\omega_{34}) \approx n(\omega_{56}) \approx n(\omega_0) = n_0$.

The width of the EPR line is determined by the imaginary part of the transitions ω_{46} :

$$\Gamma(T) = -\text{Im } \omega_{46} = g_1^2 \xi_1 [X - (\alpha_1^2 + \beta_1^2)^{1/2} \cos(\varphi/2)], \quad (26)$$

where we use the notation

$$X = 2n_0 + 1 + \left(\frac{g_2}{g_1} \right)^2 \frac{\xi_2}{\xi_1}, \quad \varphi = \arctg \frac{\beta_1}{\alpha_1}, \quad (27)$$

$$\alpha_1 = X^2 - \left(\frac{\Delta E}{g_1^2 \xi_1} \right)^2, \quad \beta_1 = \frac{2\Delta E}{g_1^2 \xi_1} \left[1 + \left(\frac{g_2}{g_1} \right)^2 \frac{\Delta \xi}{\xi_1} \right].$$

We obtain the maximum value of the temperature from the condition

$$\frac{d}{dT} \Gamma(T) |_{T=T_{\max}} = 0. \quad (28)$$

For $\Delta E/g_1^2 \xi_1 \ll 1$ we obtain from (28) an approximate expression for the maximum temperature:

$$2n_0(T_{\max}) + 1 + \left(\frac{g_2}{g_1} \right)^2 \frac{\xi_2(T_{\max})}{\xi_1} = 3^{1/2}. \quad (29)$$

It is seen from (28) that T_{\max} is a function of the ratio g_2/g_1 of the exciton-phonon coupling constants. For the typical values $c = 10^5$ cm/s and $V_0 = 10^{-22}$ cm³, the ratio ξ_2/ξ_1 is large. Therefore even a small nonlinear interaction influences substantially the value of T_{\max} . Direct calculation using Eq. (29) shows that the experimentally observed $T_{\max} = 1.7$ K corresponds to $g_2/g_1 = 1.3 \cdot 10^{-1}$. An investigation of the temperature dependence of the EPR line width of *AB* centers yields thus information not only on the linear but also on the nonlinear components of the exciton-phonon interaction.

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