Indirect interaction of paramagnetic centers via the plasmon field

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The indirect interaction of paramagnetic centers via the plasmon field and the shift in the magnetic levels of the center caused by this field are considered. This interaction leads to the appearance of terms of fourth order in the spin operators in the Hamiltonian. The proposed interaction is compared with direct exchange and the Ruderman–Kittel effect.

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INTRODUCTION

In this paper the indirect interaction between paramagnetic centers that arises as a result of their coupling with plasmon oscillations in crystals is investigated. A possible mechanism of such a coupling was proposed earlier by the authors[1,2] and invoked to elucidate paramagnetic relaxation in semiconductors[1)]. Its meaning reduced to the following: the electric field of the plasma oscillations perturbs the orbital motion of the electron of the paramagnetic center and, owing to the spin-orbit coupling, acts on the spin. Such an effect is especially important for paramagnetic ions whose position in the crystal lattice is not a center of inversion. The observation in NMR of effects similar to those described makes it possible in principle to incorporate in the discussion systems of magnetic nuclei too.

1. THE INDIRECT INTERACTION

We shall consider two paramagnetic centers in a crystal. The energy operator of such a system has the form

$$\hat{\mathbf{H}}=\hat{\mathbf{H}}_1+\hat{\mathbf{H}}_2+\hat{\mathbf{H}}_{pl}+\hat{\mathbf{H}}_{1pl}+\hat{\mathbf{H}}_{2pl}, \tag{1}$$

where $\hat{\mathrm{H}}_1$, $\hat{\mathrm{H}}_2$ are the Hamiltonians of the paramagnetic centers, and $\hat{\mathrm{H}}_{pl}$ is the Hamiltonian of the plasma oscillations. The operator $\hat{\mathrm{H}}_{ipl}$ (i = 1, 2) describes the interaction of the i-th center with the plasmons[1,2]:

$$\hat{\mathbf{H}}_{ipl}=\frac{4\pi ne}{\varepsilon}\left(\frac{\hbar}{2Nm^*}\right)^{1/2}\sum_p \hat{\mathbf{D}}_p^{(i)}\sum_{\mathbf{k}}\frac{k_p}{k\omega_k^{1/2}}[a_{\mathbf{k}}e^{i\mathbf{k}\mathbf{R}_i}-a_{\mathbf{k}}^+e^{-i\mathbf{k}\mathbf{R}_i}],$$
$$\hat{\mathbf{D}}_p^{(i)}=\sum_{jk}\alpha_{pjk}\{\hat{S}_j^{(i)}S_k^{(i)}\} \tag{2}$$

(p, j, k) = (x, y, z). Here $\mathbf{R}_i$ is the coordinate of the i-th center, n is the electron concentration, Nm^* is the effective mass of the charge carriers, ϵ is the dielectric permittivity of the crystal, a_k (a_k^+) is the operator annihilating (creating) a plasmon with momentum $\hbar k$ and frequency ω_k, α_{pjk} are the components of the tensor of the electric-field effect, and $\hat{S}^{(i)}$ is the electron-spin operator. The operators $\hat{D}_p^{(i)}$ have the meaning of components of the spin electric-dipole moment of the i-th center. If we are considering the interaction of a paramagnetic center with plasmons in a system of valence-band electrons, we must omit ϵ and the effective-mass asterisk in formulas (2).

The operator describing the indirect interaction is obtained from (1) by means of the well-known unitary transformation, with subsequent separation of the terms containing the variables of the two centers:

$$\tilde{\mathbf{H}}_{12}=-\frac{i}{2\hbar}\int_{-\infty}^{0}d\tau\{[\hat{\mathbf{H}}_{1pl}(0),\ \hat{\mathbf{H}}_{2pl}(\tau)]+[\hat{\mathbf{H}}_{2pl}(0),\ \hat{\mathbf{H}}_{1pl}(\tau)]\}. \tag{3}$$

The operators appearing in (3) are written in the interaction picture. Substituting (2) into (3), averaging over the plasmon variables and neglecting the retardation we obtain

$$\tilde{\mathbf{H}}_{12}=\frac{2}{\pi\sqrt{27}\,\varepsilon a^3}\{\hat{\mathbf{D}}^{(1)}\hat{\mathbf{D}}^{(2)}\Gamma_1(\alpha)+R_{12}^{-2}(\hat{\mathbf{D}}^{(1)}\mathbf{R}_{12})(\hat{\mathbf{D}}^{(2)}\mathbf{R}_{12})(\Gamma_2(\alpha)-3\Gamma_1(\alpha))\}, \tag{4}$$

where

$$\Gamma_1(\alpha)\approx\frac{1}{\alpha^3}\left[\pi-\frac{1}{2}\sin(\alpha\sqrt{3})+\frac{\sqrt{3}}{8\alpha}\cos(\alpha\sqrt{3})+\frac{1}{4\alpha^2}\sin(\alpha\sqrt{3})\right], \tag{5}$$

$$\Gamma_2(\alpha)\approx-\frac{1}{\alpha^2}\left[\frac{\sqrt{3}}{2}\cos(\alpha\sqrt{3})+\frac{1}{4\alpha}\sin(\alpha\sqrt{3})+\frac{3}{8\alpha^3}\sin(\alpha\sqrt{3})\right],$$

$\mathbf{R}_{12}$ is the distance between paramagnetic centers, a is the screening length and $\alpha = R_{12}/a\sqrt{3}$. The treatment given presupposes that $\alpha > 1$.

One's attention is drawn to the oscillations of $\tilde{\mathbf{H}}_{12}$ on variation of the distance between the centers or on variation of the concentration of the electrons taking part in the plasma oscillations (in the latter case, the screening length varies).

2. SHIFT OF THE LEVELS

Separating out the terms pertaining to only one center in the transformed starting Hamiltonian and performing the necessary calculations, we obtain for the shift ΔE_α of the magnetic level α:

$$\Delta E_\alpha=\frac{1}{3^{5/2}\pi\varepsilon a^3}\sum_p\sum_\gamma J_{\gamma\alpha}\langle\alpha|\hat{\mathbf{D}}_p|\gamma\rangle\langle\gamma|\hat{\mathbf{D}}_p|\alpha\rangle, \tag{6}$$

$$J_{\gamma\alpha}=\sqrt{3}-t_{\gamma\alpha}\ln(2+\sqrt{3}) \tag{6a}$$

$$+\begin{cases}-(t_{\gamma\alpha}^2-1)^{1/2}\ln\left|\dfrac{-2t_{\gamma\alpha}-1+\sqrt{3}(t_{\gamma\alpha}^2-1)^{1/2}}{2+t_{\gamma\alpha}}\right|, & t_{\gamma\alpha}^2>1\\ -(1-t_{\gamma\alpha}^2)^{1/2}\left[\dfrac{\pi}{2}-\arcsin\dfrac{1+2t_{\gamma\alpha}}{2+t_{\gamma\alpha}}\right], & t_{\gamma\alpha}^2<1\end{cases},$$

where $t_{\gamma\alpha} = \omega_{\gamma\alpha}/\Omega$; $\omega_{\gamma\alpha}$ is the energy gap (in frequency units) between the levels γ and α, and Ω is the Langmuir frequency.

For the actual case $\Omega \gg \omega_{\gamma\alpha}$, (6) takes the form

$$\Delta E_\alpha=(9\pi)^{-1}(1-\pi/3\sqrt{3})\langle\alpha|\hat{\mathbf{D}}^2|\alpha\rangle/\varepsilon a^3. \tag{7}$$

Numerical estimates show that the shift in the electron magnetic levels because of the interaction with the plasmons reaches ones to tens of megaHertz.

3. DISCUSSION OF THE RESULTS

It is of interest to compare the indirect-interaction mechanism that we have proposed with direct exchange and the Ruderman-Kittel interaction. We note, first of all, that the interaction (4) is more long-range (a term $\sim 1/aR_{12}^2$ is present) than the two interactions mentioned. Of importance is the fact that the coupling constant in (4) (i.e., the tensor components α_{pjk}) can be determined from independent experiments on the effect of external electric fields on the EPR spectra of the impurities. We shall carry out a quantitative comparison for paramagnetic impurities in nonmetallic crystals. At the usual impurity concentrations ($10^{16} - 10^{19}$ cm^{-3}) direct exchange is unimportant. In fact, for centers of large radius (e.g., group-V elements in silicon) the concentrations are such that the average distance between impurities amounts to not less than 100 Å. The estimates performed in[4] show that the influence of direct exchange can be ignored. This is even more valid for deep centers (states of radii $\sim$1 Å) at similar concentrations.

A comparison with the Ruderman-Kittel mechanism can be properly carried out for nuclear systems. In the case of electron centers, the reliable information on the magnitude of the exchange parameters that is needed to estimate the effectiveness of the Ruderman-Kittel interaction is absent. Moreover, for nuclear systems the coupling constants in (4) are determined from the electric-field effects in the NMR. The hyperfine-interaction constants are also known.

For reasonable values of the parameters (electric-field coupling $D \approx 10^{-24}$ esu, hyperfine constants $\approx 10^{-19}$ erg, impurity concentration $N = 10^{18}$ cm^{-3} and charge-carrier concentration $n = 10^{18}$ cm^{-3}), the ratio of the energy of the indirect exchange via the plasmons to the Ruderman-Kittel interaction is found to be equal to 10^6. This comparison is even more favorable for the interaction of impurities via the valence-band electrons. Because of the sharp decrease of the quantity a the field $\tilde{H}_{12}$ increases, while the Ruderman-Kittel effect, both for electron and for nuclear centers, becomes ineffective[5].

Evidently, the interaction considered here will also turn out to be important in disordered alloys containing paramagnetic metals as one of the components.

It follows from (2) that $\tilde{H}_{12}$ can be represented in the form

$$\tilde{H}_{12} = \sum_{jklm} J_{jklm} \{\hat{S}_j^{(1)} \hat{S}_k^{(1)}\} \{\hat{S}_l^{(2)} \hat{S}_m^{(2)}\},$$

$$J_{jklm} = \frac{2}{\pi\sqrt{27}\,\varepsilon a^3} \sum_{pp'} \alpha_{pjk}\alpha_{p'lm}[\delta_{pp'}\Gamma_1(\alpha) + n_p n_{p'}(\Gamma_2(\alpha) - 3\Gamma_1(\alpha))], \quad (8)$$

where $n = \mathbf{R}_{12}/R_{12}$. It can be seen that this interaction is fourth-order in the spin operators. Thus, here we have proposed a physical mechanism leading to fourth-order invariants in the spin operators.

We shall now estimate the quantities J_{jklm}, both for electron and for nuclear paramagnetic systems. It is assumed that the interaction is effected via the valence-band plasmons. Then, for electron centers (we consider the example Mn^+:Si, $\alpha \sim 1.5 \times 10^{-19}$ esu, $N(Mn^+) = 10^{18}$ cm^{-3}), we obtain $J \sim 0.1$ K (interaction with the nearest neighbors is taken into account). In the case of nuclear systems (As^{75}:GaAs) it is found that $J = 2 \times 10^{-7}$ K.

[1)] In the articles of Khabibullin and Kiyashchenko [3], the indirect interaction of optically active impurities via the plasmon field was considered. The results obtained are thus not connected with spin magnetism.

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