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Phonon-mediated exchange interaction of impurity centers in crystals

M. F. Deĭgen, N. I. Kashirina, and L. A. Suslin

Semiconductor Institute, Ukrainian Academy of Sciences

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The interaction of impurity centers via the phonon field in ionic and atomic crystals is calculated with account taken of the permutation symmetry. The latter leads to the appearance of exchange terms in the effective-interaction operator. Estimates show that the proposed interaction is comparable in order of magnitude with the Coulomb exchange.

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1. Consider exchange interaction of two impurity centers via the crystal-lattice oscillations. The coupling of the centers with the lattice is effected by the usual electron-phonon interaction.1) The dependence of the energy of the indirect interaction on the spin operator is the result of allowance for the permutation symmetry. It is assumed for simplicity that the impurity centers have spin-$\frac{1}{2}$.

The initial Hamiltonian is of the form

$$\hat{\mathrm{H}}=\hat{\mathrm{H}}_0+\hat{\mathrm{H}}_1, \tag{1}$$

where $\hat{\mathrm{H}}_0$ includes the Hamiltonian of the individual centers and of the phonon system, while $\hat{\mathrm{H}}_1$ is the operator of the interaction of the first and second centers with the lattice vibration—the perturbation operator. The orthonormalized zeroth-approximation wave functions are chosen in the form

$$[2(1\pm I_1^2)]^{-1/2}(|i\rangle\pm|j\rangle), \quad |i\rangle=a(1)b(2)|0\rangle, \quad |j\rangle=a(2)b(1)|0\rangle,$$

where a(1) and b(2) are the wave functions of the impurity centers, $|0>$ is the wave function of the ground state of the phonon system, and I_1 is the overlap integral.

The second-order perturbation-theory correction to the system energy can be represented in the form

$$\Delta\varepsilon^{\pm}=(1\pm I_1^2)^{-2}(D_{ii}\pm D_{ij}), \tag{2}$$

where

$$D_{ij}=\sum_l{}' (E_0-E_l)^{-1}\langle i|\hat{\mathrm{H}}_1|l\rangle\langle l|\hat{\mathrm{H}}_1|j\rangle. \tag{3}$$

The upper sign in (2) pertains to the singlet state, and the lower to the triplet state.

Denoting the difference $\Delta\varepsilon+ - \Delta\varepsilon -$ by $2J_{\text{phon}}$, we can write, accurate to terms $\propto I_1^2$ (see, e.g., Ref. 2) that part of (2) which depends on the total spin of the system, in the form

$$\hat{\mathrm{H}}_{\text{фон}}=-2J_{\text{фон}}\hat{\mathrm{S}}_1\hat{\mathrm{S}}_2, \quad J_{\text{фон}}=D_{ij}-2I_1^2D_{ii}. \tag{4}$$

Here $\hat{\mathrm{S}}_1$ and $\hat{\mathrm{S}}_2$ are respectively the operators of the electron spins of the first and second centers. The indirect-exchange operator (4) is outwardly similar to the Heisenberg Coulomb-exchange operator. Of course, these interactions are quite different in character. Since the electron-phonon interactions with the acoustic and optical lattice vibrations are different,

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we shall consider the two types separately.

The electron-phonon operators are given by (see, e.g., Ref. 3)

$$\hat{\mathrm{H}}_1=N^{-1/2}\sum_{\mathbf{q}}F(\mathbf{q})\,(b_{\mathbf{q}}-b_{-\mathbf{q}}{}^{+})\,(e^{i\mathbf{q}\mathbf{r}_1}+e^{i\mathbf{q}\mathbf{r}_2}); \tag{5}$$

N is the number of unit cells of the crystal, and

$$F(\mathbf{q})=\begin{cases}-ia(\hbar q/2Mc_s)^{1/2}, & (6a)\\ -ie(2\pi\hbar\Omega/\bar{\varepsilon}Vq^2)^{1/2}. & (6b)\end{cases}$$

Here (6a) stands for acoustic phonons, (6b) for optical phonons, a is the deformation-potential constant, M and V are respectively the mass and volume of the unit cell, c_s is the velocity of the longitudinal sound waves, Ω is the limiting frequency of the optical phonons, $\bar{\varepsilon}^{-1}=\varepsilon_\infty^{-1}-\varepsilon_0^{-1}$, and $\bar{\varepsilon}$ is the effective permittivity of the crystal.

We ignore, for simplicity, the changes introduced into the phonon spectrum by the impurities themselves. In this case the lattice vibrations contribute only to the electron-electron interaction.

2. For the situation in which the energy interval between the ground and first excited electronic levels of the impurity exceed significantly the characteristic energies of the phonons, we need take into account as intermediate states in (3) only the phonon excitations of the system. Substitution of (5) in (3), calculation of the matrix elements, and summation over the wave vectors, leads to the following expressions:

$$J_{\mathrm{ac}}=2a^2I_1(I_1I_2+I_1I_3-2I_4)/\rho_0c_s^2; \tag{7a}$$

here ρ_0 is the crystal density

$$J_{\mathrm{opt}}=2e^2I_1(I_1I_5+I_1I_6-2I_7)/\bar{\varepsilon}, \tag{7b}$$

where in (7a) and (7b)

$$I_2=\int|a(1)|^4d\tau_1,\quad I_3=\int|a(1)b(1)|^2d\tau_1,$$

$$I_4=\int a(1)b^*(1)|a(1)|^2d\tau_1,\quad I_5=\int|a(1)a(2)|^2\frac{d\tau_1\,d\tau_2}{r_{12}},$$

$$I_6=\int|a(1)b(2)|^2\frac{d\tau_1\,d\tau_2}{r_{12}},\quad I_7=\int a(1)b^*(1)|a(2)|^2\frac{d\tau_1\,d\tau_2}{r_{12}}.$$

3. For a number of impurities in ionic crystals, expression (7b) is incorrect because the limiting frequency of the longitudinal optical phonons can exceed the ionization energy I (as, for example, for zinc impurities in InSb). In the case $\hbar\Omega\gg I$ we get

$$J'_{\mathrm{opt}}=-e^2(I_8-I_1^2I_6)/\bar{\varepsilon}, \tag{7c}$$

where

$$I_8=\int a(1)b(2)a^*(2)b^*(1)\,\frac{d\tau_1\,d\tau_2}{r_{12}}.$$

4. The effectiveness of the proposed interaction was estimated by comparing (7a)–(7c) with the Coulomb exchange. The latter can be represented in the macroscopic approximation in the form

$$J_{\mathrm{opt}}=e^2(I_8-I_1^2I_6)/\varepsilon_\infty+2e^2I_1(I_1I_9-I_{10})/\varepsilon_0, \tag{8}$$

where

$$I_9=\int|a(1)|^2\frac{d\tau_1}{r_{b1}},\quad I_{10}=\int a(1)b^*(1)\,\frac{d\tau_1}{r_{a1}}.$$

The integrals in (7b), (7c), and (8) have been thoroughly investigated in molecule theory.[4] All the terms of expressions (7b), (7c), and (8) turn out, generally speaking, to be of the same order of magnitude.

The first term in (8) describes the electron-electron part of the Coulomb exchange. The total interaction

$$\hat{\mathrm{H}}_\Sigma=-2J_\Sigma\hat{\mathrm{S}}_1\hat{\mathrm{S}}_2$$

is the sum of the Coulomb exchange and the exchange due to phonons. As seen from a comparison of (7c) and (8), the electron-electron part of J_{Coul} is exactly cancelled by that part of J'_{opt} which contains ε_∞. Thus, for the case described in Sec. 3, we get

$$\hat{\mathrm{H}}_\Sigma=\hat{\mathrm{H}}_{\mathrm{ac}}-\frac{1}{\varepsilon_0}[2e^2(I_8-I_1^2I_6)+4e^2I_1(I_1I_9-I_{10})]\hat{\mathrm{S}}_1\hat{\mathrm{S}}_2. \tag{9}$$

The first and second terms of this expressions are due to phonons. We note that the second and third terms are equal to the exchange energy of the "diatomic molecule" divided by ε_0. For impurities in atomic crystals, as can be easily verified, the expression for $\hat{\mathrm{H}}_\Sigma$ agrees outwardly with (9), but only $\hat{\mathrm{H}}_{\mathrm{ac}}$ in this expression is due to phonons.

Expressions (7a), (7b), (8), and (9) are quite sensitive to the choice of the wave functions of the impurity electrons. For estimates we used the wave functions of the effective-mass method. We then obtain from (7a) and (7b), accurate to terms proportional to $\exp(-2R/a^*)$, where a^* is the effective radius of the state and R is the distance between the impurities

$$J_{\mathrm{ac}}\approx-\frac{a^2}{4\pi\rho_0c_s^2a^{*3}}e^{-2\rho}\left(1+\rho+\frac{1}{3}\rho^2\right)\left(-\frac{3}{\rho}+5-\rho-\frac{1}{3}\rho^2\right), \tag{10a}$$

$$J_{\mathrm{opt}}\approx-\frac{e^2}{4\bar{\varepsilon}a^*}e^{-2\rho}\left(1+\rho+\frac{1}{3}\rho^2\right)\left(-\frac{3}{\rho}-11+\frac{25}{3}\rho-\frac{5}{3}\rho^2\right),\quad \rho=R/a^*. \tag{10b}$$

With decreasing radius of the state, the contribution of the acoustic oscillations to the total exchange increases more rapidly than the contributions J_{Coul} and J_{opt}. Thus, for example, in silicon (where there is no interaction via optical oscillations at all), the ratio $|J_{\mathrm{ac}}/J_{\mathrm{Coul}}|$ changes from 0.2 at $a^*=18.2$ Å (lithium impurity) to 5.5 at $a^*=8.8$ Å (bismuth impurity). The presented state radii were calculated from the measured ionization energies, the deformation-potential constant was assumed to be 10 eV, $\rho_0\sim2.3$ g/cm^3, $c_s\sim4\times10^5$ cm/sec, $\varepsilon_0\sim12$, and $R\sim90$ Å. Thus, even in an atomic crystal the contribution of the lattice vibrations to J_ϵ can be appreciable.

In estimates of J_Σ in ionic crystals, certain caution must be exercised because the contributions of the J_{Coul} and of the interaction via the optical vibrations are of the same order in absolute magnitude. An important role is played also by the sign of J_ϵ: the contribution J_{ac} becomes ferromagnetic at $\rho\geqslant2.1$; J_{opt} determined from (10b) is ferromagnetic at all ρ; the sign of J_{Coul} in crystals with $\varepsilon_0/\varepsilon_\infty\sim1.7$ (e.g., ZnS, CdTe) changes with increasing R. The sign of J_Σ has therefore a complicated dependence on R and on the crystal parameters.

The fact that $J_{\rm Coul}$ goes through zero in a number of systems, however, is evidence that $\hat{H}_E$ is apparently due to phonons in a definite range of impurity concentrations. Numerical calculations have shown that the ratio $|J_{\rm opt}/J_{\rm Coul}|$ at $\rho=8$ can vary in a wide range: it is of the order of 0.5 for InSb, AlSb, and PbS, it is equal to 4–6 for many alkali-halide compounds, ZnO, and Cu_2O, and exceeds 10 for CdS, RbI, and CsI. Of course, the contribution of the phonons to J_e increases when account is taken of other mechanisms that couple the electrons with the lattice vibrations (the piezoelectric effect, the optical deformation potential).

Besides the spectroscopic manifestations (the values of the resonance frequencies, the widths of the EPR and APR absorption lines, etc.), interaction via phonons can manifest itself in principles in effects that depend on the magnetic ordering of the impurity. Of interest from this point of view is gallium arsenide, where ferromagnetic ordering of the iron impurity was observed at a concentration 10^{19} cm^{-3} (Ref. 5). At a^* of the order of the lattice constant (~5.6 Å), $a\sim 15$ eV, $c_s\sim 4\times 10^5$ cm/sec, $\rho_0=5$ g/cm^3, $\varepsilon_0=11.3$, and $\varepsilon_\infty=10.6$ it turns out that $J_E\approx J_{\rm ac}\approx 118\times 10^{-3}$ eV. This value of the exchange energy accounts fully for the observed ordering temperatures (77–300 K). None the less, this estimate is more readily qualitative, since the deformation-potential method is not valid for impurities with small state radii, and to describe the electron-phonon coupling it is necessary to employ improved procedures.

[1)] One must not confuse the proposed interaction with that considered by Aminov and Kochelaev.[1] The latter is of relativistic character and is therefore smaller by several orders of magnitude.

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On the renormalization of the velocity of sound in phase transitions involving a change in valency

A. M. Tsvelik and A. F. Barabanov

Institute of High-Pressure Physics, USSR Academy of Sciences

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The effect of the hybridization of conduction electrons with a localized f-electron energy level, ϵ_f, lying near the Fermi surface on the longitudinal sound velocity, C, is considered. It is shown that the hybridization enhances the screening of the ion-ion interaction as ϵ_f approaches the Fermi surface. This explains the experimentally-observed mimimum in the pressure dependence of the velocity of sound. The strong intrasite correlation of the f electrons leads to an asymmetry in the minimum of $C(\epsilon_f)$ as the ϵ_f level passes through the Fermi surface. The results are compared with the results of the measurement of the velocity of sound in Ce as it undergoes the γ–α transition.

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1. There occurs in a number of rare-earth metals and their compounds (e.g., in Ce and SmS) as the pressure and temperature are varied an electron phase transition connected with the existence of a narrow localized-f-electron band near the Fermi level.[1] A theoretical model for such a transformation has been worked out in a number of papers[4–6] on the basis of the transition of f electrons into the conduction band as the pressure is increased.[2,3] In this case the presence of strong repulsion between the f electrons at the same time lattice site turns out to be important for the existence of the phase transition.

Later, it was shown[7,8] that allowance for the hybridization of the *spd*-f electrons enables us to account for the intermediate-valence state. It is known that an increase in the compressibility occurs in the vicinity of a phase transition involving a change in valency.[1] In particular, it has been observed that the longitudinal velocity of sound $C(P)$ in Ce has a minimum in the region of the γ-α transition, which occurs in Ce at a pressure ~7 kbar.[9] The γ-α transition in Ce is isomorphous, the number of f electrons per site changing in the transition from $n_f=0.94$ to $n_f=0.33$.[10,11]

In the present paper, using Ce as an example, we show that allowance for the hybridization of the f electrons with the conduction electrons enables us to account for the presence of the $C(P)$ minimum associated with transitions involving a change in valency. This effect has been considered by Kocharyan and Khomskiĭ,[12] but their approach is purely phenomenological

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