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Polaron effects in exchange clusters ($V^{2+} - F^- - V^{2+}$ in $KMgF_3$)

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Abstract. We have calculated the phonon contribution to the energy of a superexchange. It is shown that the phonon contribution to the exchange interaction is comparable on the order of magnitude with the Coulomb superexchange. The numerical calculations are performed for a molecular cluster consisting of an exchange-coupled pair $V^{2+} - F^- - V^{2+}$ and 10 nearest ions F^- in $KMgF_3$. The distinctions of a temperature dependence of the exchange interaction caused by phonons are discussed. In systems with the close located electronic levels, the account of interaction with a phonon field reduces in occurrence of resonant terms in the exchange interaction of paramagnetic ions. The similar terms result in occurrence of the exponential temperature dependence in an exchange interaction. As an example, the exchange pair of Cu^{2+} ions in $K_2CuCl_4 \cdot 2H_2O$ has been considered. The experimentally observed anomalously strong temperature dependence of the exchange interaction of copper ions in this system can be described by the contribution of the resonant terms caused by a phonon contribution to the exchange interaction. The total exchange can be described by the dependence $I_\Sigma \approx I_0 - I_1(e^x - 1)^{-1}$, where I_Σ is the complete exchange interaction in a system including the phonon contribution (the second term), $x = \delta/k_0T$ with the parameters $I_0 \cong 0.29$ K, $I_1 \cong 0.22$ K, $\delta \cong 192$ K. The parameter δ corresponds to the splitting of a doubly degenerated lowest term of the copper ion in the crystalline field.

Keywords: an orbital-lattice interaction, exchange-coupled pairs, indirect spin-spin interactions.

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1. Introduction

The account of permutation symmetry effects in wavefunction for many-electron system is a basis of the microscopic theory of magnetism. For a long time in the theory of exchange interactions (EI), the influence of a phonon system on the size of an exchange splitting (as well as the influence of elementary excitations of another nature on EI) was not taken into account. Aggregate colour centers (an exchange-coupled pairs of F^- -centers or F_2^- -centers) in alkali-halide crystals were intensively studied in the Kiev school in the 50s of the last century by M.F. Deigen [1]. The historical analysis of the first works devoted to the theory of the aggregate colour centers and bipolarons (BPs) [1-3] shows that the nonrelativistic magnetic exchange takes place in addition to the electron-phonon interaction (EFI) taken into account in functionals of the ground state. The stability of two-center BPs is provided by the exchange

contribution caused by electron-phonon interaction to the energy of a two-electron system (in this system, the Coulomb exchange is ferromagnetic).

For the first time, the phonon contribution to the energy of the simplest aggregate centers such as F_2^- -centers and BPs was investigated in the framework of continuum approximation [1-4]. This direction of the aggregate center theory is currently developed, too [5-8]. The availability of the coupled two-electron states such as F_2^- -centers and two-center BPs was possible to be explained only due to the account of permutation symmetry in these electron systems. The functional of the ground state in these systems, besides terms, concerning the kinetic energy and Coulomb energy, contained the contributions caused by interaction of electrons with the field of optical E_{opt} and acoustical E_{ac} waves. These additional terms depend on a distance R between centers of the polarizing well for two polarons and between vacancies for two F^- -centers. In spite of the

fact that, for deriving these terms, the traditional Fröhlich canonical transformation [9] was not performed just in those had been contained the sources of the theory of indirect interactions of the paramagnetic centers. Moreover, if as the zeroth approximation we choose the energy and the wavefunctions of isolated F -centers or polarons (i.e., include the zeroth approximation terms into the Hamiltonian describing the interaction of an isolated F -center with phonons), the explicit form for the energies of indirect interactions of these centers E_{opt} and E_{ac} can be obtained by methods of the perturbation theory. However for the derivation of the effective Hamiltonian of indirect interactions (EHII), the permutation symmetry of the system must be taken into account. For the first time, it was made when modeling the interaction on the phonons of shallow paramagnetic centers [10]. In an implicit form, the exchange energy caused by phonons contained already in functionals of the ground states of F_2 -centers and BPs (strong coupling), however the purpose of the works [1-3] was to find a minimum of the basic state, and the separation of a spin-dependent part from the total energy was not carried out.

Thus for a long time, the availability of spin-dependent exchange terms in the energy of the F_2 -center ground state remained as though unrecognized. However, from the viewpoint of researching magnetic interactions, just the spin-dependent part in the energy of two-electron systems holds the greatest interest.

Spin-dependent terms in the energy of an indirect interaction of two shallow impurities through a phonon field were obtained using the method of the perturbation theory in [10, 11]. In these works, the main attention was focused on the spin-dependent part of the energy of the indirect interaction, and the terms that had not an exchange character were omitted. And only after solution of a similar task by the methods of strong coupling [12], noticed was the complete analogy of the systems considered in [10-12] with those containing F_2 -centers and well investigated by M.F. Deigen [1].

Presently, interest in the study of exchange-coupled pairs of impurities has regenerated in the context of an opportunity to use such two-electron systems as a basis for the development of quantum computers that could operate using both the spin [13] and nuclear resonances [14, 15]. In both schemes, EI between impurities provides the interaction between qubits. The results of the work [16] show that the polarons and BPs are good candidates to logical switching in the molecular circuits of conducting polymers. Therefore, theoretical studies of the energy spectrum of simplest two-electron systems such as BPs (free and coupled) and exchange-coupled pairs in crystals are not only of pure theoretical interest, but of practical importance as well.

Step of going from shallow paramagnetic centers (PC) to the PC of small radius, the direct exchange interaction concedes a place to a superexchange through intermediate anion (diamagnetic, as a rule). Therefore,

naturally this bring up the question of influence of the orbital-lattice interaction on the energy of exchange splitting of more complex systems including the intermediate diamagnetic atoms. Our work is devoted to construction of the effective Hamiltonian describing the indirect interaction (EHII) between two deep PC of small radius, spatially divided by a diamagnetic anion.

2. Effective Hamiltonian of indirect interaction

Let's consider the elementary system consisting of two PC with the spins $\mathbf{S}_1 = \mathbf{S}_2 = 1/2$ in a crystal. The Hamiltonian of this system has the following form

$$\hat{\mathbf{H}} = \hat{\mathbf{H}}_0 + \hat{\mathbf{H}}_f + \hat{\mathbf{H}}_{\text{int}}, \quad (1)$$

where $\hat{\mathbf{H}}_{\text{int}}$ describes the interaction between electrons of PC and the field of elementary excitations, $\hat{\mathbf{H}}_0$ includes all Coulomb interactions in a system, $\hat{\mathbf{H}}_f$ is the Hamiltonian of the elementary excitation field. Let's carry out the canonical transformation $e^{-i\mathbf{S}\hat{\mathbf{H}}e^{i\mathbf{S}}}$ with the operator $\mathbf{S} = -\int_{-\infty}^0 \hbar^{-1} \hat{\mathbf{H}}_{\text{int}}(\tau) d\tau$.

The operator of PC interaction through a boson field (further, for definiteness, phonons) can be written in the most general form as

$$\hat{\mathbf{H}}_{\text{int}} = \sum_{\mathbf{q}} F(\mathbf{q})(\mathbf{b}_{\mathbf{q}} - \mathbf{b}_{-\mathbf{q}}^+) \sum_{i=1}^N V(\mathbf{q}, r_i) \quad (2)$$

where $\mathbf{b}_{\mathbf{q}}^+$ ($\mathbf{b}_{\mathbf{q}}$) are the Bose operators of creation (annihilation) of phonons with the wavevector \mathbf{q} , N is the number of electrons in the system, the functions $F(\mathbf{q})$ and $V(\mathbf{q}, r_i)$ depend on a specific kind of PC interacting with bosons, r_i is the coordinate of i -th electron. For the large radius centers $V(\mathbf{q}, r_i) = \exp(i\mathbf{q}r_i)$.

After statistical averaging over the electronic coordinates and boson field variables, we derived the following expression for the energy of singlet (S) and triplet (A) states

$$E_{S,A} = \sum_{\mathbf{q}} F^2(\mathbf{q}) \left\{ (\hbar\omega_{\mathbf{q}})^{-1} |\Phi_{S,A}(\mathbf{q})|^2 - \sum_{\theta} \left(\frac{\langle n_{\mathbf{q}} \rangle}{\hbar(\omega_{\mathbf{q}} - \omega_{\theta})} - \frac{\langle n_{\mathbf{q}} \rangle + 1}{\hbar(\omega_{\mathbf{q}} + \omega_{\theta})} \right) \right\} \times \left| \langle \Psi_{S,A} | \sum_{\theta} \exp(i\mathbf{q}r_i) | \Psi_{\theta} \rangle \right| \quad (3)$$

where $\Phi_{S,A}(\mathbf{q}) = \langle \Psi_{S,A} | \sum_i V(\mathbf{q}, r_i) | \Psi_{S,A} \rangle$. For large radius PC, the functions $\Phi_{S,A}(\mathbf{q})$ represent the

electronic form-factors of impurity systems in the singlet and triplet states, correspondingly: $\omega_{\mathbf{q}}$ is the phonon frequency with the wavevector \mathbf{q} , $\langle n_{\mathbf{q}} \rangle$ is the mean number of excitations with the wavevector \mathbf{q} , θ is the number of excited states in this electron system, ω_{θ} is the frequency of θ -th excited state of the electron system.

Let's pay attention that, for two-level system with the wavefunctions Ψ_S and Ψ_A , owing to the selection rules, the temperature dependence caused by $\langle n_{\mathbf{q}}(T) \rangle$ cannot appear.

3. Zero-point phonon contribution in the energy of a superexchange

Designating the energy difference $E_S - E_A$ as $2J_{\Sigma}$, we rewrite the spin-dependent part of the impurity system energy as

$$\hat{\mathbf{H}}_{\Sigma} = -2J_{\Sigma} \mathbf{S}_1 \mathbf{S}_2. \quad (4)$$

For the system containing more than two electrons, it is possible to generalize the expression (4) to the form

$$J_{\Sigma} = (n_1 n_2)^{-1} \sum_{i=1}^{n_1} \sum_{j=1}^{n_2} J_{ij}, \quad (5)$$

where the summation is carried out over all the nonpaired electrons, n_1 and n_2 are the numbers of these electrons in the first and second systems, accordingly.

Let's consider a many-electron system. The approximated wavefunction is chosen as the Slater determinant made of one-electron spin-orbitals. For the simplicity, it is considered that Ψ_S and Ψ_A are orthonormalized. Let's also assume that the elementary system for which the concept of a superexchange is entered consists of four electrons (one electron per each PC and two pairing electrons per an intermediate diamagnetic anion).

As a specific object the exchange-coupled pair of ions of $V^{2+} - F^{-} - V^{2+}$ ($\mathbf{S}_1 = \mathbf{S}_2 = 3/2$) in KMgF_3 is considered. The chosen object is well investigated both experimentally [17] and theoretically [18]. The contribution of an orbital-lattice interaction to the energy of a superexchange was investigated in [19]. In this work, the calculations of the superexchange through phonons were carried out by formal substitution of the operator for the van Vleck orbital-lattice interaction into the expressions for the energy of the superexchange derived in [18]. Thus, naturally, the terms describing the contribution of the ion configuration have been lost. Formally, such terms could appear only in the first order of a perturbation theory, and the averaging over the phonon variables yielded to zero result.

The expression for EHII in the terms (3) has a general form and holds for a many-electron

wavefunction, which is used in the theory of the superexchange. The maximal contribution to the energy of a superexchange caused by zero phonons will give terms in (3) described by the expression

$$2J = \sum_q (-\hbar\omega_q)^{-1} \left(\left| \langle \Psi_S | \hat{\mathbf{H}}_{\text{int}} | \Psi_S \rangle \right|^2 - \left| \langle \Psi_A | \hat{\mathbf{H}}_{\text{int}} | \Psi_A \rangle \right|^2 \right). \quad (6)$$

This expression corresponds to the ion configuration of the four-electron system $d(4)(+R) - p(1,2)(0) - d(3)(-R)$. The nucleus coordinates of ions participating in the superexchange ($R, 0, -R$) is specified in brackets. The designations accepted in [18] are used hereinafter.

Let's pay attention to that we spend the canonical transformation before the averaging over the electron coordinates. If the similar transformation eliminating linear on the operator of electron-phonon interaction was carried out after averaging over the electronic coordinates, we would find the members of the higher order in the spin variables. For the concrete case of the exchange-coupled pair $V^{2+} - F^{-} - V^{2+}$ in KMgF_3 , we derive the operator of an orbital-lattice interaction in the van Vleck form and use the orthonormalized orbitals of four-electron system according to the rules, stated in [18]. Then for the energy of exchange splitting determined by the expression (4), with the account of (3) and (5), neglecting the orbital-lattice interaction of diamagnetic anion F^{-} , we derive the equation

$$J_0^{\text{ph}} = -\frac{4}{9} \sum_{j=1,2,3} V_{j33} \left[2V_{j34} T - 2V_{j33} T^2 - 2V_{j34} S^2 - 4V_{j33} S^2 T - 4V_{j33} S^4 \right] \left\langle \frac{Q_j^2 (1 + \exp(2iqR))}{\hbar\omega_q} \right\rangle. \quad (7)$$

where the summation is carried out over all the normal coordinates of a molecular cluster consisting of the exchange pair $V^{2+} - F^{-} - V^{2+}$ and ten nearest neighbours of V^{2+} ions. The overlapping integrals are determined by the expressions $S = \langle a_1 | a_4 \rangle = -\langle a_1 | a_3 \rangle$, and $T = \langle a_3 | a_4 \rangle$, where the orbitals a_1 and a_2 correspond to the p_x orbital of diamagnetic anion F^{-} , the orbitals a_3 and a_4 corresponds to d_{xz} one of paramagnetic ion of V^{2+} , $V_j(r_3, r_4)$ are the first derivatives over normal coordinates of crystal potential in the location electrons with coordinates r_3, r_4 .

When deriving the expression (7), we used the property of permutation symmetry of the orbital-lattice interaction operator. The similar symmetry is possible only for simultaneous accounting the electrons interaction with the nearest neighbours of both centers. Thus, it is necessary to include into consideration all 11 fluorine ions. At the approximated calculations of matrix elements of the operators $V_j(r_3, r_4)$, the traditional

expansion on electron coordinates of PC should be carried out relatively to the nearby intermediate ion F^- , participating in a superexchange. The similar expansion will not disturb the permutation symmetry of the initial Hamiltonian.

Let's pay attention to the fact that the maximal contribution in EI through phonons will be given by terms that appropriate to the normal coordinates interacting with the isolated PC. Therefore, the formal application of the expression (7) to the four-electron system with d_{xz} -orbitals of magnetic ions can result in occurrence of the exchange splitting deprived of the physical sense for our system. Such terms will describe the orbital-lattice interaction of V^{4+} ions.

The ground state of the considered V^{2+} ion is an orbital singlet, and therefore the only normal oscillation appropriated to completely symmetric displacement of six nearest neighbours of V^{2+} ion is active. The influence of local oscillations of the exchange complex on the energy of the superexchange is not examined in this work. The operator $V_j(r_3, r_4)$ is described in the approximation of point ions. For numerical estimations, we used the linear dispersion law for phonon frequencies. For definiteness, we consider that exchange-coupled pair is spaced along the direction [100]. The integration over the phonon variable is carried out within the first Brillouin zone. The maximal wavevector is determined by expression $q_m^3 = 2\pi^2 N/V$, where N is the number of atoms in an elementary cell, V is the volume of an elementary cell. For $KMgF_3$, $q_m \approx \pi/R$, where R is the distance between a vanadium ion replacing the magnesium one, and the nearest fluorine ion ($R \approx 1 \text{ \AA}$). For the sound velocities and the crystal density, we used the values given in [21]: $C_l \approx 6.93 \cdot 10^5 \text{ cm} \cdot \text{s}^{-1}$ and $C_t \approx 4.05 \cdot 10^5 \text{ cm} \cdot \text{s}^{-1}$ for longitudinal and transverse speeds, correspondingly, $\rho \approx 3.15 \text{ g} \cdot \text{cm}^{-3}$.

The matrix elements of the crystal potential appropriated to a totally symmetric oscillations of the nearest neighbours of vanadium ions were calculated using the Slater one-electron functions. For integrals of overlapping the values $S \approx 0.075$ and $T \approx -0.0018$ were used (In accord with [18]). The expansion of $V_j(r_3, r_4)$ over the electron coordinates was carried out up to the members of the sixth order. In the longwave approximation, the energy of a superexchange through phonons determined by Eq.(7) add up to $\approx 1.75 \text{ K}$ (ferromagnetics). For the given system, the energy of the Coulomb superexchange was calculated in the work [18], it was $\approx -7.2 \text{ K}$ (antiferromagnetics), that is nearly twice as large as the experimental value -3.2 K [18]. The value of interaction obtained in our experiment results in a shift of exchange energy to the experimental value. In the order of magnitude, the superexchange through phonons is comparable with the Coulomb superexchange.

Thus, even for paramagnetic ions with the frozen orbital moment, the interaction in question can take a significant effect on a size of a total exchange. For ions

with a degenerate ground state, the similar interaction will result in occurrence of an additional contribution to a total exchange and will not be reduced to vibron reduction of EI of the Jahn – Teller ions [22].

4. Temperature dependence of spin-spin interactions

For a long time, the modulation of an exchange integral by thermal vibrations of a lattice was considered as the only source of the temperature dependence of exchange interactions. Following [23] we expand the exchange integral

$$\langle I(R_{12}) \rangle \approx I(R) \langle z-R \rangle + \frac{I'(R)}{2R} \langle (x^2 + y^2) \rangle + \frac{1}{2} I''(R) \langle (z-R)^2 \rangle, \quad (8)$$

where $\vec{R}_{12} = \vec{u} + \vec{R}$, \vec{R} is the zero-temperature equilibrium vector connecting a pair of magnetic ions, the axis OZ is directed along \vec{R} , the vector $\vec{u} = \{z-R, x, y\}$ corresponds to the relative ion displacement from the equilibrium position, the angular brackets means the averaging over the phonon variables,

$$\langle z-R \rangle = R \left(\exp \int_0^T \alpha_L(T) dT - 1 \right) \approx R \int_0^T \alpha_L(T) dT, \quad (9)$$

where $\alpha_L(T)$ is the temperature-dependent coefficient of the linear expansion.

To estimate $\alpha_L(T)$, it is possible to use independent experiments. The physical sense of the $I(R)$ change with the account of inharmonicity, is reduced to decreasing the exchange integral with growing R as a result of increasing interionic distance. Except for the anharmonic

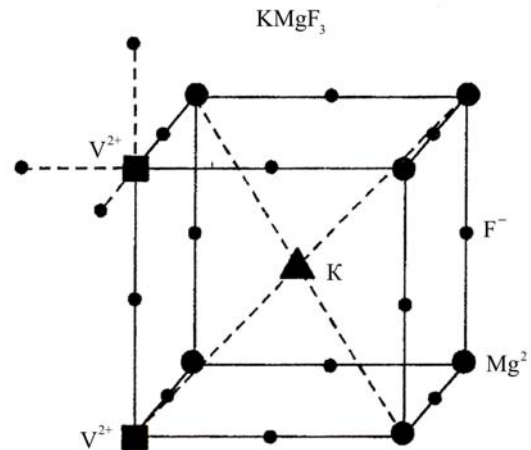


Fig. 1. Crystalline structure of $KMgF_3: V^{2+}$.

contribution, Eq. (8) contains the harmonic component that reduces the increase of an exchange interaction with a rise in temperature. We assume that:

$$\begin{aligned} \langle x^2 \rangle &= \langle y^2 \rangle = \langle (z-R)^2 \rangle = \\ &= \frac{\hbar}{M} \sum (\lambda_{\mathbf{q}} \mathbf{e}_{\mathbf{q},s}) (2n_{\mathbf{q}} + 1) \left(1 - e^{i\mathbf{q}R_0} \right) \omega_{\mathbf{q},s}^{-1}, \end{aligned} \quad (10)$$

where M is a mass of a crystal, $\lambda_{\mathbf{q}}$ is the unit vector in the direction \mathbf{q} , $\mathbf{e}_{\mathbf{q},s}$ is a polarization vector, $n_{\mathbf{q}}$ is the mean number of phonons with the momentum \mathbf{q} , $\omega_{\mathbf{q},s}$ is the phonon frequency with the momentum \mathbf{q} and the polarization s .

For the linear dispersion law, we obtain:

$$\langle x^2 \rangle = \frac{\hbar}{2\pi^2 \rho_0 v_s} \int_0^{k_D} (2n_k + 1) \left(1 - (kR)^{-1} \sin kR \right) k dk, \quad (11)$$

where $n_k = (\exp(\hbar v_s k / k_0 T) - 1)^{-1}$, ρ_0 is the density of a crystal, k_D is the maximal wavevector of phonons, v_s is the sound velocity. The Debye temperature is defined as $\theta_D = \hbar v_s k_D / k_0$, where k_0 is the Boltzmann constant.

Let's consider two limiting cases:

$$\langle x^2 \rangle \approx \frac{k_D k_0 T}{\pi^2 \rho_0 v_s^2} \left(1 - \frac{Si k_D R}{k_D R} \right), \quad T \gg \theta_D, \quad (12)$$

$$\langle x^2 \rangle = \frac{\hbar R^2}{12\pi^2 \rho_0 v_s^5} \left(\frac{k_0}{\hbar} \right)^4 T^4 \int_0^{\theta_D/T} (2n_x + 1) k^3 dk, \quad (13)$$

$T \ll \theta_D$.

In the majority of crystals, the melting temperature changes in the limits from 1000 to 2000 K. At the same time, θ_D changes from 300 to 800 K. Therefore the limiting case (12) practically never can be valid, which basically casts doubt on the validity of the linear approximation (12). However, the numerical calculations show that this approximation is valid even at $T < \theta_D$. So, for KMnF_3 at $T = 300$ K, the linear approximation (12) is accurate up to 6%. At these rough approximations made when writing Eq. (12), this accuracy is quite sufficient. At $T < 100$ K, the main contribution in (11) is given by zero phonons, and the temperature changes $\langle x^2 \rangle$ can be mainly neglected. When the exchange integral decreases exponentially with increasing the interionic distance, the contribution of harmonic terms results in the increase of exchange interaction when decreasing the temperature. Otherwise, the accounting for the inharmonicity results in the reduction of a total exchange. In the most cases, the inharmonic contribution surpasses the harmonic one at least by the order of magnitude.

In the work by Shrivastava [19], the temperature dependence of a superexchange turned out by other way, namely as a result of the account of the contribution of

the orbital-lattice interaction in energy of a superexchange. After substitution the operator of the orbital-lattice interaction in the expression for energy of a superexchange derived by Huang and Orbach [18], Shrivastava obtained:

$$J_f \approx -\frac{4}{9} \left(\frac{54}{5} \pi \right) \Delta_D^{-1} \left[a_4 |r^2 (Y_2^1 - Y_2^{-1})| a_3 \right] - \quad (14)$$

$$\langle a_3 | r^2 (Y_2^1 - Y_2^{-1}) | a_3 \rangle (T + S^2) \Big] \langle Q^2 \rangle,$$

$$V_5(r) = (54\pi/5)^{1/2} r^2 (Y_2^1 - Y_2^{-1}),$$

$$S = \langle a_3 | a_1 \rangle, \quad T = \langle a_3 | a_4 \rangle, \quad (15)$$

where a_3, a_4 are the d_{xz} -orbitals of the first and second cations, Δ_D is the power difference appropriated to carry a charge between cations.

Using the numerical values of the matrix elements of the operator V_5 given in [19]

$$\langle a_3 | r^2 (Y_2^1 - Y_2^{-1}) | a_3 \rangle \approx -2.2 \text{ a.u.},$$

$$\langle a_4 | r^2 (Y_2^1 - Y_2^{-1}) | a_3 \rangle \approx 0.32 \text{ a.u.},$$

for an interatomic separation between the nearest neighbours of the complex XY_6 of $R_0 = 3.78$ a.u., $S = 0.0757$, $T = -0.0018$, $\Delta_D = 0.568$ a.u., we have got

$$I_f \approx -109 \langle Q^2 \rangle \text{ (erg)}. \quad (16)$$

To estimate the efficiency of the interaction (16) in comparison with the traditional mechanism of modulation of the Coulomb superexchange by oscillations of the lattice, we shall calculate the contribution of harmonic terms for the pair of V^{2+} ions in KMgF_3 .

For the even normal coordinates, the following expression is valid

$$\begin{aligned} \langle Q^2 \rangle &= \frac{\hbar}{8\pi^2 \rho_0 v_0} \times \\ &\times \int_0^{k_D} (2n_k + 1) \left(1 - (2kR_0)^{-1} \sin 2kR_0 \right) k dk. \end{aligned} \quad (17)$$

By comparing Eqs (17) and (11) with the accounting that, for the V^{2+} ions in KMgF_3 , $R = 2R_0$, we derived

$$\langle x^2 \rangle = 4 \langle Q^2 \rangle. \quad (18)$$

Having taken the experimentally determined value of the exchange interaction $J(R) = -4.4$ K [17] and believing, for the pair of V^{2+} ions in KMgF_3 [23, 24],

$$\left(\frac{d \ln I}{d \ln R} \right)_{\bar{R}=\bar{R}_0} \cong -12, \quad (19)$$

we have got the expression for the contribution of harmonic phonons, which is determined by Eq. (8)

$$J_{hr} = \left[\frac{J'(R)}{R} + J''(R) \right] \frac{\langle (z-R)^2 \rangle}{2} \approx -107 \langle Q^2 \rangle \text{ (erg)}. \quad (20)$$

I. e. in this case, the both methods give practically the identical values.

In the work [19], the comparison of Eqs (16) and (20) was not carried out, therefore the author of this works made, in our opinion, erroneous conclusions about magnitude of the relative contribution J_{ph} determined by Eq. (14) into a total exchange. Actually, the antiferromagnetic phonon contribution is suppressed by the ferromagnetic one caused by the account of inharmonic terms as, in crystals of the KMgF_3 type, they exceed J_{hr} by an order [23].

There exist situations, in which the phenomenological approach consisting in expansion of the exchange energy on a small displacement is obviously unacceptable. So, in the systems with the close located levels (Debye energy exceeds the splitting energy of levels inherent to an isolated ion in a crystal field), the adiabatic approximation admitting expansion (8) does not valid. One of the characteristic examples of a similar situation is Cu^{2+} ion in the strong cubic field and in the weak field of a lower symmetry (Figs 4a, b). Such system are characterized by these two close located levels. The distance between these levels for solid salts can be from 300 to 800 K [25]. The consistent microscopic theory must be used for the description of the temperature dependence of EI in such systems. It means that the orbital-lattice interaction should be included into the initial Hamiltonian and, having founded the decision of the appropriate Schrödinger equation, a phonon contribution into the energy of singlet and triplet states of an exchange-coupled pair must be determined. Thus, for the systems with close located levels, the exponential temperature dependence of a singlet-triplet splitting both the shallow centers in crystals with a complex zone of conductivity, and then for paramagnetic ions [11] was predicted.

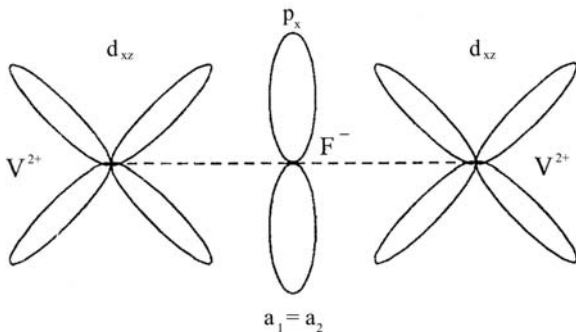


Fig. 2. Electronic orbitals of an exchange-coupled pair of $V^{2+} - F^- - V^{2+}$ (ionic configuration).

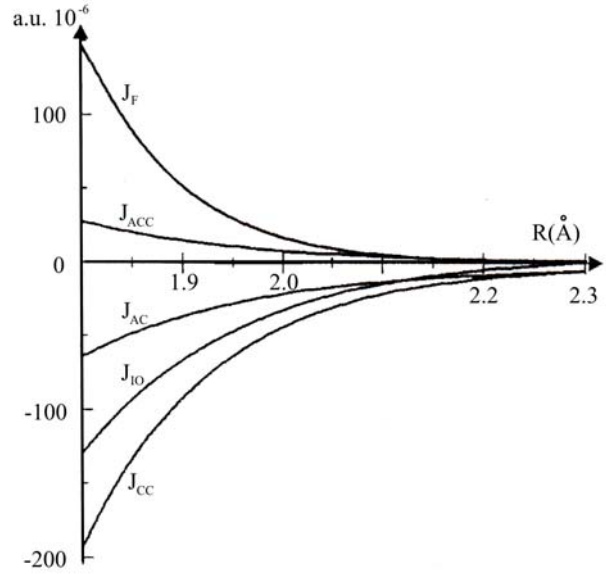


Fig. 3. dependences on the distance between ions V^{2+} and F^- of the various contributions to an exchange energy for an exchange-coupled pair $V^{2+} - F^- - V^{2+}$ in KMgF_3 . $J_{ph} = 9/2 J_0^{ph}$ corresponds to the superexchange through phonons (J_0^{ph} is determine from Eq. (7) in the text of our paper), J_{ACC} , J_{AC} , J_{IO} , J_{CC} are the various configurations contributions to the exchange energy have been calculated in the work [18].

One of the most interesting examples that can not be explained on the basis of the traditional phenomenological approach is the temperature dependence of an exchange energy of Cu^{2+} pair ions in the crystal $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$.

The EPR spectrum of Cu^{2+} ions in the temperature interval from 77 up to 295 K was investigated in the works [26, 27]. Susceptibility data taken around the helium temperature indicate that the approximate equality $J/k \approx 0.30$ K is valid [28]. The measured data on the low-temperature thermodynamic behaviour (specific-heat data) has been analyzed by Wood and Dalton [29]. Thus, the authors of [26] came to the conclusion that at all the temperatures the nearest environment of Cu^{2+} ions keeps the configuration shown in Fig. 4a, i.e., the degeneracy of the basic state 2D is removed by the tetragonal crystal field. It was especially emphasized that the EPR spectrum of Cu^{2+} ions does not have the features characteristic for Jahn-Teller systems, and its temperature changes can be caused only by anomalous strong dependence of the exchange energy of Cu^{2+} pair ions on the temperature (see Fig. 5).

As seen from Fig. 4a, the spatial configuration of the system consisting of the copper cation and intermediate anions participating in the superexchange is extremely

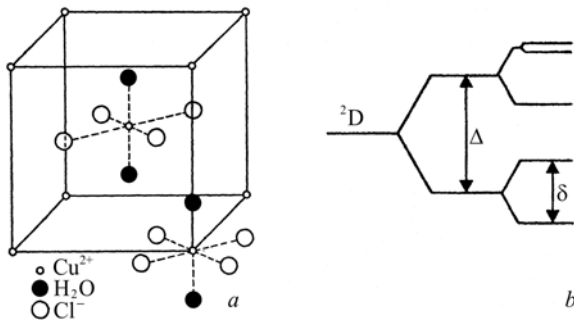


Fig. 4. Exchange-coupled pair of ions Cu^{2+} in $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$. Spatial arrangement (a), energy levels splitting of the ion Cu^{2+} in a crystalline field (b).

difficult. Any of the known scheme of 90° or 180° exchanges can not be applied for this system. Therefore, the microscopic calculations of the superexchange energy for this system are not performed up to now. At present, the only question that can be discussed is as follows: what known mechanisms of an exchange can give even qualitative explanation of observed temperature changes of the singlet-triplet splitting energy. The effects caused by thermal expansion of the crystal can explain no more than 6% of observed reduction of the exchange energy. There are no bases to use for an explanation of this effect the low-temperature dependence of EI caused by the contribution of odd vibrations, as was made by Shrivastava in [27]. The contribution of the phonon mechanism investigated by Shrivastava, as was shown above, at best can be comparable by the order of its magnitude with that arising as a result of accounting for the inharmonicity. Besides, the dependence proposed by Shrivastava in [30]

$$J \approx J_0 - J_1 T^6 \int_0^{600/T} x^5 (e^x - 1)^{-1} dx, \quad (21)$$

where $J_0 = 0.276$, $J_1 = 3.5 \cdot 10^{-16}$, is not so good approximation to describe the experimental curve $J(T)$ (see Fig. 5), as informed in [30]. The exchange (21) tends to zero at about $T = 207$ K. The corresponded experimental results give for this temperature 340 K [26].

The strong temperature dependence EI of Cu^{2+} ions can arise in two limiting cases: for strong and weak coupling. Let's consider these opposite cases separately.

5. Temperature dependence of exchange interaction for Jan-Teller ions (strong coupling)

One of the plausible reasons of a strong temperature dependence of EI caused by the Jan-Teller nature of the interacting centers was considered in the works by Kugel and Khomski [31], when in the case of a degenerate

orbitals, the exchange Hamiltonian can be written down as

$$\hat{\mathbf{H}}_{ij} = \left(\frac{1}{2} + 2\bar{S}_i \bar{S}_j \right) \cdot (I_0 + I_{ZZ} \bar{\tau}_i^Z \bar{\tau}_j^Z + I_{ZX} \bar{\tau}_i^Z \bar{\tau}_j^X + I_{XX} \bar{\tau}_i^X \bar{\tau}_j^X), \quad (22)$$

where \bar{S}_i, \bar{S}_j are spin-operators of the first and second centers, $\bar{\tau}_i, \bar{\tau}_j$ are pseudospin operators.

As is known, in systems with a strong electron-phonon interaction, the suppression of off-diagonal matrix elements of the operators $\bar{\tau}_i^x$ and $\bar{\tau}_i^y$ occurs. In the operator (22), the constants I_0 and I_{zz} are not renormalized, I_{xz} and I_{xy} get the small multipliers $\exp(-E_{JT} kT / (\hbar \omega)^2)$. The reduction of an exchange will be especially strong when the following conditions are performed: $T \geq \hbar \omega_D / k$, $E_{JT} > \hbar \omega_D$. In [31], the opportunity to apply the similar mechanism to the crystal $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$ was not checked.

The first of the above-stated conditions ($T \geq \hbar \omega_D$) is not valid, since the Debye temperature is 700 K, and the strong temperature dependence of EI begins (as it has been already shown at 77 and 300 K) exchange splitting goes to zero [26]. As to the second condition ($E_{JT} > \hbar \omega_D$), the invariance of a spatial configuration at all the temperatures shown in Fig. 4a (as reported in

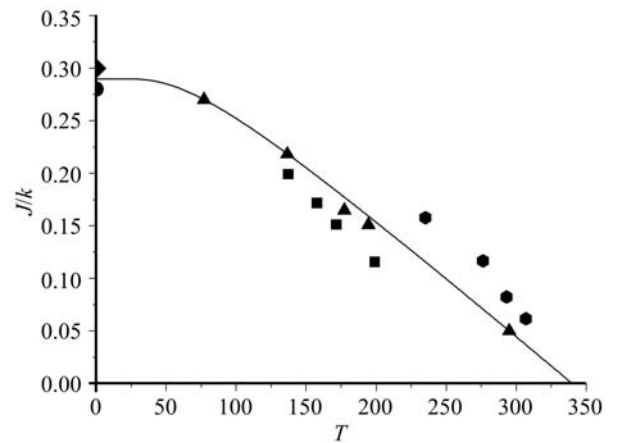


Fig. 5. Temperature dependence of the exchange energy of ions Cu^{2+} in $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$. The curve (1) corresponds to the experimental one obtained in the work [26] for $77 \leq T \leq 395$ K, and, completely coincided with it the theoretical dependence defined Eq. (23). The theoretical dependence are normalized such that the exchange energy $J(T)$ at $T = 77$ K is 0.27 K and at $T = 295$ K $J_\Sigma = 0.05$ K in accordance with experimentally-observed those in the work [26]. 7 35 GHz EPR width, ! – 65 GHz EPR widths [26]; μ EPR line shift [27]; \cdot T – susceptibility [28], 4 – specific-heat data [29].

[26]) offers a plausible assumption of the presence of two closely located levels in the system (Fig. 4a), appearing as a result of the removal of a degeneration 2D -term of Cu^{2+} ion by the tetragonal crystal field. I.e., just the opposite conditions are carried out.

Let's consider an explanation of the phenomenon observed in $K_2CuCl_4 \cdot 2H_2O$ on the basis of the "resonant" mechanism resulted in the exponential temperature dependence of an exchange splitting in systems with closely located levels.

6. The temperature dependence of the superexchange caused by phonons

Qualitatively new temperature effects can appear in systems with the closely spaced electron levels $\delta < k_0 \theta$ (where θ is the Debye temperature, δ is the power splitting of two close located levels), for which the expression (3) will result in the occurrence of following temperature dependence of the EI

$$I_{\Sigma} \approx I_0 - I_1(e^x - 1)^{-1}, \quad (23)$$

where $x = \delta / k_0 T$. We assume that I_0 and I_1 do not depend on the temperature.

The accurate reproduction of an experimental curve described by the temperature dependence of the EI between Cu^{2+} ions in K_2CuCl_4 [26] can be achieved at the following choice of parameters appropriated to the temperature dependence of the exchange energy in the crystal $K_2CuCl_4 \cdot 2H_2O$: $I_0 \cong 0.29$ K, $I_1 \cong 0.220$ K, $\delta \approx 192$ K.

7. Conclusion

The theoretical consideration of the influence of an electron-phonon interaction on the energy spectrum of the exchange-coupled pairs of deep PCs in crystals is carried out in this work. Using the example of the exchange-coupled pair of the ions of $V^{2+} - F^{-} - V^{2+}$ in $KMgF_3$ it is shown that the phonon contribution to a superexchange plays a considerable role in a total exchange interaction of PCs even for those with frozen orbital moment. The energy term describing a polaron contribution to an exchange interaction of similar centers corresponds to the ionic configuration of the concerned system.

When providing the description of an interaction of PCs with the close located energy levels, the additional "resonant" term caused by the orbital-lattice interaction appears in the exchange energy of the system by a complete analogy with the resonance fluorescence theory of phonons. At a rather low temperatures ($T < \theta$), the temperature dependence corresponding to the "resonant" part of the exchange interaction can be described by an exponential function like $\exp(-\theta/T)$. The occurrence of the similar terms can be reduced to

the anomalously strong temperature dependence of the total superexchange, including a change of a sign of this exchange interaction when the temperature rises. The exchange pair of the copper ions in the crystal $K_2CuCl_4 \cdot 2H_2O$ is considered as an example of similar systems. The examination of the similar interaction is extremely utterly for the Anderson theory of the high-temperature superconductivity (HTSC) concerned with the consideration of exchange interactions between magnetic ions [32], and also in the mechanisms of HTSC, resulting from the formation of spin polarons and bipolarons in the crystals with the magnetic ordering analyzed by Mott [33]. The energy of the exchange interaction enters into the above-listed mechanisms as a phenomenological parameter. With the noticeable temperature dependence of given parameter (for example, the resonant mechanism of an exchange interaction analyzed in the our work), the HTSC mechanisms of such type gain additional peculiarities and will be considered in the original research.

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