volume of the unit cell is quadrupled in the low-symmetry ordered phase, then a phase transition directly into an ordered phase is impossible, and a sequence of two PT must take place. If, however, the space group C_w^4 ($Z=4$) established experimentally for RbCN below 110 K is correct, then the CN groups in this phase should be ordered relative to two equilibrium positions, and somewhere at low temperatures there should be a second PT into a fully ordered phase, in which the unit-cell volume should be least double the cell volume in the C_s^4 ($Z=4$) phase. It should be noted that an absence of a PT at low temperatures, by virtue of quantum tunneling effect, can likewise not be ruled out.

In our opinion, the PT in the RbCN crystal calls for a thorough experimental study. It is also of interest to obtain experimentally an answer to the question of the existence of a second PT in the CsCN crystal. If the CN groups in this crystal remain disorderd down to $T=0$, this may be evidence of strong tunneling of the C and N atoms relative to the "head-tail" states.

In conclusion, the authors are deeply grateful to V. G. Vaks and A. P. Levanvuk for a discussion of the results.

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Translated by J. G. Adashko

Polaron effects and exchange interaction in magnetic dielectrics with Jahn-Teller ions

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(Submitted 22 February 1980)
Zh. Eksp. Teor. Fiz. 79, 987–1005 (September 1980)

We consider the influence of electron-phonon interaction on the band width and on the values of the exchange integrals in magnets containing ions with orbital degeneracy (Jahn-Teller ions). The case of electrons on a doubly degenerate level, which interact with a nondegenerate phonon mode, is investigated in detail. The analysis is based on the Hubbard model with phonons taken into account. It is shown that a polaron narrowing of the bands takes place and depends, generally speaking, on the manner of occupation of the orbitals. Those terms of the effective exchange Hamiltonian which correspond to virtual transitions without a change in the orbital state are not significantly renormalized, while terms that include transitions between different orbitals acquire, on account of the phonons, exponential suppression factors that depend on the temperature. This leads to a strong decrease of the effective exchange integrals with temperature, as observed experimentally in a number of magnetic dielectrics with Cu^{2+}.

PACS numbers: 71.38. + i, 71.70.Gm

1. INTRODUCTION

An interesting special class of magnetic substances comprises compounds in which the state of the magnetic ions is characterized by orbital as well as spin degeneracy. The ions whose ground state turns out to be degenerate in a crystal field of sufficiently high symmetry are called Jahn-Teller (JT) ions (these include, e.g., the ions Cu^{2+}, Mn^{3+}, and Cr^{2+} in an octahedral surrounding). According to the Jahn-Teller theorem,[1] an atom configuration in which orbital degeneracy is realized is unstable. The symmetry of the indicated substances is therefore usually lowered and the degeneracy is lifted, corresponding in another context to ordering of the orbitals. For the case of double degeneracy, which is the one considered below, the orbital state can be characterized by a pseudospin $\tau = 1/2$ (thus, in the case of the e_g orbitals the state with $\tau = 1/2$ corresponds, e.g., to the orbital $d_{2z^2-x^2-y^2}$, while the state with $\tau^2 = -1/2$ corresponds to $d_{x^2-y^2}$). The exchange interaction in magnets with JT ions depends significantly on the type of ordering of the orbitals (the magnitude and even the sign of the exchange integral J_{ij} are determined by the value of the correlation function $\langle \tau_i \tau_j \rangle$, Ref. 2). In the same substances, there can occur also unique effects of strong influence of the electron-lattice (JT) interaction on the exchange, and in particular a temperature dependence of J_{ij}. Experiment has revealed in some Cu^{2+} compounds a fivefold decrease of the effective exchange integral with increasing T.[3-5]

The purpose of the present study was to examine the distinguishing features of exchange interaction in magnetic dielectrics with JT ions when account is taken of the influence of the lattice vibrations on the degenerate electronic states. The principal mechanism of the exchange interaction in magnetic dielectrics with ions of transition metals is superexchange.[6] A consistent description of the superexchange is possible within the framework of the Hubbard model.[7] In the case of one electron per center, in the absence of degeneracy, this mechanism leads to antiferromagnetism that is described by the Heisenberg Hamiltonian

$$H_{eff} = \frac{2t^2}{U} \sum_{\langle i,j \rangle} \mathbf{s}_i \mathbf{s}_j, \qquad (1)$$

where t is the integral of the transition of the electron from center to center, U is the Coulomb interaction of two electrons on one center, and the symbol $\langle i,j \rangle$ denotes summation over the nearest neighbors. In JT magnets, the exchange interaction can also be examined by starting from a generalization of the Hubbard model to include the case of degeneracy of the orbitals.[2] The corresponding exchange Hamiltonian then depends both on the spin operators s and on the pseudospin operators τ, i.e., it describes simultaneously both the spin and the orbital ordering. Its schematic form is

$$H_{eff} = \sum_{\langle i,j \rangle} \mathbf{s}_i \mathbf{s}_j (J_0 + J_{zz} \tau_i^z \tau_j^z + J_{zx} \tau_i^z \tau_j^x + J_{xx} \tau_i^x \tau_j^x) + H_\tau \qquad (2)$$

($J \approx t^2/U$; H_τ does not contain spin operators). Generally speaking, H_{eff} is strongly anisotropic in the variables τ. The magnitude and sign of the spin-exchange parameters is determined by the type of the orbital ordering. It should be noted that allowance for only the exchange mechanism of the orbital ordering leads to quite nontrivial types of orbital structures,[2] which, (e.g., in the case of $KCuF_3$ and K_2CuF_4), agree well with those obtained in experiment.

Besides the exchange interaction, however, a most important role is played in JT magnets also by the interaction between degenerate electronic states and the lattice. This is precisely the cause of the local JT effect—the lowering of the symmetry of the surrounding of an individual ion and of the cooperative JT effect—the lowering of the symmetry of the crystal as a whole as a result of the interaction of the local strains.[8] Usually it is this mechanism which is invoked to explain the cooperative ordering of the orbitals in concentrated systems. It is therefore most important to consider simultaneously the two interactions (superexchange and electron-phonon) within the framework of a unified model, for the purpose of clarifying the influence of the phonons on the electronic properties of the corresponding compounds, and particularly on the magnitude of the effective exchange integrals.

This paper contains such an analysis and shows that when account is taken of the electron-phonon interaction in the degenerate Hubbard model, two effects arise: 1) the effective pseudospin interaction of the type $\tau_i \tau_j$, due to superexchange,[2] is supplemented by the JT interaction[8]; more importantly, 2) the electron-lattice interaction leads to a renormalization of the exchange integrals. This renormalization depends, generally speaking, on the concrete characteristics of the electron-lattice interaction (degeneracy of the corresponding phonon modes, dispersion of phonons and of electron-phonon interaction constants) as well as on the temperature. In essence, these effects in the JT systems are close analogs of the polaron effects, in particular, the modification of the exchange integrals is analogous to the polar on suppression of the off-diagonal matrix elements.

The actual analysis was carried out in this paper for a model with a nondegenerate phonon mode. In this case our result reduces schematically to the fact that in the exchange Hamiltonian (2)

$$J_{zz} \to J_{zz}, \quad J_{zx} \to \exp\left(-2\lambda^2 \operatorname{cth} \frac{\hbar\omega}{2T}\right) J_{zx},$$

$$J_{xx} \to \exp\left(-4\lambda^2 \operatorname{cth} \frac{\hbar\omega}{2T}\right) J_{xx}, \qquad (3)$$

i.e., the exchange integrals are renormalized and acquire small factors (similar to the Ham suppression factors known in the theory of the JT effect, see Ref. 8). The net result is that the effective "magnetic" exchange integral decreases and becomes also strongly dependent on the temperature (more accurate relations are given in the text below).

The plan of the exposition is the following. In Sec. 2 we analyze the influence of the electron-phonon interaction within the framework of the nondegenerate Hubbard model. This analysis, which is simpler than in the degenerate case, illustrates the main features of the employed method and the character of the results. It is also of independent interest, since divergent views have been published on this question. In Sec. 3, the effect of the electron-phonon interaction are considered by starting from the degenerate Hubbard model in the case $T = 0$; we investigate both the case of local phonons, when their dispersion can be neglected, and the general case of arbitrary dependences of the phonon frequency $\omega_{\mathbf{k}}$ and of the electron-phonon interaction $g(\mathbf{k})$ on the wave vector. In Sec. 4 we study the case of nonzero temperatures and in Sec. 5, finally, we summarize the main results and compare them with the real situation in compounds with JT ions.

2. POLARON EFFECTS IN THE NONDEGENERATE HUBBARD MODEL

We consider first the role of the electron-phonon interaction in the case of a nondegenerate Hubbard model with one electron per center. When the phonons are taken into account, the Hamiltonian takes the form

$$H=H_1+H_0+H_{ph}+H_{el-ph}=t\sum_{\langle i,j\rangle,\sigma}a_{i\sigma}{}^+a_{j\sigma}+{}^1/_2\,U\sum_{i,\sigma}n_{i\sigma}n_{i-\sigma}+\sum_{\mathbf{k}}\hbar\omega_{\mathbf{k}}b_{\mathbf{k}}{}^+b_{\mathbf{k}}+\sum_{i,\mathbf{k},\sigma}g_i(\mathbf{k})\,(b_{-\mathbf{k}}^++b_{\mathbf{k}})\,n_{i\sigma}. \tag{4}$$

Here $a_{i\sigma}^+, a_{i\sigma}$ are the operators of the creation and annihilation of electrons at the site i, with spin projection $\sigma, n_{i\sigma}=a_{i\sigma}^+a_{i\sigma}, b_{\mathrm{k}}^+$ and b_{k} are the phonon operators, t is the integral of the transition of the electrons between neighboring centers, U is the energy of the Coulomb repulsion of two electrons at one center, and $g_i(\mathbf{k})$ is the electron-phonon interaction constant. The last term in (4) describes in fact the polaron effects—the change of the lattice configuration and of the energy of the states with changing number of electrons on the ion.

In this section we confine ourselves to the simplest case of constant ω and g, when the electron-phonon interaction can be written in the form $\Sigma g(b_i^++b_i)n_{i\sigma}$, where b_i^+ and b_i are operators corresponding to localized vibrations. The generalizations to the case of an arbitrary dispersion law is quite simple; we shall discuss this question in the analysis of the degenerate Hubbard model. The corresponding problem was considered in a number of papers[9-11]; it was found that the result depends substantially on the ratio of the energy parameters of the model (the Coulomb repulsion U, the phonon energy $\hbar\omega$, the polaron-shift energy $E_B=g^2/\hbar\omega$). However, even in the simplest (and most realistic case $U\gg\hbar\omega$ and $U\gg E_B$ there are discrepancies in the results; nor has a single convenient expression been obtained for the exchange integrals with account taken of the polaron effects.

To assess the role of the electron-phonon interaction, we carry out first, following Ref. 9, a canonical transformation of the Hamiltonian (4), which eliminates from the Hamiltonian the terms linear in the phonons:

$$\tilde{H}=e^{-\hat{S}}He^{\hat{S}},\quad \hat{S}=\sum_i\hat{S}_i=-\sum_{i,\sigma}\frac{g}{\hbar\omega}n_{i\sigma}(b_i{}^+-b_i). \tag{5}$$

The transformation (5) is equivalent to the phonon-operator shift transformation

$$\tilde{b}_i=b_i-\frac{g}{\hbar\omega}\sum_\sigma n_{i\sigma}.$$

The transformed Hamiltonian, apart from an inessential constant, is of the form

$$\tilde{H}=t\sum_{\langle i,j\rangle,\sigma}e^{-\hat{S}}a_{i\sigma}^+a_{j\sigma}e^{\hat{S}}+{}^1/_2\sum_{i,\sigma}(U-2E_B)\,n_{i\sigma}n_{i-\sigma}+\sum_i\hbar\omega b_i{}^+b_i=\tilde{H}_1+\tilde{H}_0+H_{ph}. \tag{6}$$

It is seen that the transformation of the single-center terms reduces to a renormalization of the Coulomb interaction. As for the first term, which describes electron transitions from center to center, allowance for the electron-phonon interaction leads here to a change in the transition matrix element $\tilde{t}=t\exp(-E_B/\hbar\omega)$ (polaron narrowing of the band).[9]

We consider in greater detail the change of the exchange integrals under the influence of the interaction with the phonons. In the absence of phonons, the Hubbard Hamiltonian reduces at $t\ll U$, in second-order perturbation theory in t/U, to the Heisenberg antiferromagnetic Hamiltonian (1). The derivation of the effective exchange Hamiltonian H_{eff} in the presence of phonons is carried out in fact in similar fashion. The matrix elements should satisfy the condition

$$\langle\alpha_a|H_{eff}|\alpha_b\rangle=\left\langle\alpha_a\left|\tilde{H}_1\frac{1}{E_0-\tilde{H}_0-H_{ph}}\tilde{H}_1\right|\alpha_b\right\rangle, \tag{7}$$

where $|\alpha_a\rangle$, $|\alpha_b\rangle$ are two arbitrary wave functions of the 2^N-fold spin-degenerate ground state of the Hamiltonian $\tilde{H}_0'=\tilde{H}_0+H_{ph}$, and correspond to one electron per center and to the absence of phonons, while E_0 is the energy of the ground state of the Hamiltonian $\tilde{H}_0'$ (hereafter assumed to be zero). After simple transformations we obtain

$$\langle\alpha_a|H_{eff}|\alpha_b\rangle=-t^2\sum_{\langle i,j\rangle}\langle\alpha_a|a_{j\sigma}{}^+a_{i\sigma}\exp[\lambda(b_j{}^+-b_j)-\lambda(b_i{}^+-b_i)]\times\frac{1}{\tilde{H}_0'}\exp[-\lambda(b_j{}^+-b_j)+\lambda(b_i{}^+-b_i)]a_{i\sigma'}^+a_{j\sigma'}|\alpha_b\rangle, \tag{8}$$

where $\lambda=g/\hbar\omega$ and

$$e^{\lambda(b^+-b)}|0\rangle=e^{-\lambda^2/2}e^{\lambda b^+}e^{-\lambda b}|0\rangle=\sum_{n=0}^{\infty}e^{-\lambda^2/2}\frac{\lambda^n}{(n!)^{1/2}}|n\rangle \tag{9}$$

($|n\rangle$ is a state with n phonons). In the derivation of (8) and (9) we used the equalities

$$ae^{Aa^+a}=e^Aa,\ e^{Aa^+a}a^+=a^+e^A,\ e^{A+B}=e^Ae^Be^{1/2[B,A]}. \tag{10}$$

(A is a function of the phonon operators). Hence

$$H_{eff}=J\sum_{\substack{\langle i,j\rangle\\ \sigma,\sigma'}}a_{j\sigma}{}^+a_{j\sigma'}(a_{i\sigma'}^+a_{i\sigma}-\delta_{\sigma\sigma'}), \tag{11}$$

$$J=t^2\sum_{m,n=0}^{\infty}e^{-2\lambda^2}\frac{1}{U-2E_B+\hbar\omega(m+n)}\frac{\lambda^{2(m+n)}}{m!\,n!}. \tag{12}$$

The sum in (11) contains the same combinations of the electron operators as in the case of the usual Hubbard model without phonons.[6] On going over to spin operators (using the formulas $a_\uparrow^+a_\uparrow=\frac{1}{2}+s^z, a_\downarrow^+a_\downarrow=\frac{1}{2}-s^z$, $a_\uparrow^+a_\downarrow=s^+, a_\downarrow^+a_\uparrow=s^-$) we obtain from (11), apart from the constants, the antiferromagnetic Heisenberg Hamiltonian

$$H_{eff}=2J\sum_{\langle i,j\rangle}\mathbf{s}_i\mathbf{s}_j. \tag{13}$$

Using the identity

$$\frac{1}{a}=\int_0^\infty e^{-ax}\,dx, \tag{14}$$

we can transform J into a more compact form:

$$J=t^2\int_0^\infty dx\exp\{-(U-2E_B)x-2\lambda^2(1-e^{-\hbar\omega x})\}. \tag{15}$$

This form is valid at $U > 2E_B$, when the denominator in (12) does not take on negative values. It is seen that at large U, when the main contribution to the integral is made by the region near $x=0$ and it suffices to retain the first two terms of the expansion $e^{-\hbar\omega x} = 1 - \hbar\omega x$, the expression in the curly brackets of (15) is equal simply to $-Ux$ [we recall that $\lambda^2 = E_B/\hbar\omega = g^2/(\hbar\omega)^2$]. This means that in this limit the exchange interaction is practically not renormalized, $J = t^2/U$.

From (15) we obtain also the next corrections to this result. At large $U (U \gg E_B, \hbar\omega)$ we get

$$J = \frac{t^2}{U}\left(1 + \frac{2E_B\hbar\omega}{U^2}\right). \tag{16}$$

On the other hand, in the case of $U \ll \hbar\omega$ (which can be realized for the so called excitonic polarons[10]) we can neglect the exponential in the curly brackets of (15); we then obtain

$$J = t^2 e^{-2\lambda^2}/(U - 2E_B). \tag{17}$$

These results agree with those obtained in Ref. 9, but differ somewhat from those given in Ref. 11, where $J = t^2/(U - 2E_B)$ was obtained in the limit $\hbar\omega \ll U$; this is apparently due to the insufficiently correct procedure of averaging over the phonon states in Ref. 11.

The results can be easily understood also from the qualitative point of view. The process of the virtual transition of an electron between neighboring centers, a process responsible for the exchange interaction, can proceed in two ways: in the first, the lattice in the intermediate state (wherein there are two electrons on one center and a hole on the neighboring one) manages to relax to a new electronic state; in the second, virtual rapid transition proceeds in accord with the Franck-Condon principle for a frozen lattice.

In the first case, which is realized at $U \ll \hbar\omega$, the energy increment due to the phonons can be expressed in the form

$$E_{ph} = \hbar\omega\langle b^+\rangle\langle b\rangle + gn(\langle b^+\rangle + \langle b\rangle). \tag{18}$$

The mean values $\langle b^+\rangle, \langle b\rangle$ are obtained from the condition that the energy be a minimum,

$$\langle b^+\rangle = \langle b\rangle = -gn/\hbar\omega. \tag{19}$$

Therefore in accord with (18) $E_{ph} = -g^2n^2/\hbar\omega = -E_B n^2$ and the energy difference between the intermediate state (Fig. 1b) and the ground state (Fig. 1a) amounts to

$$E_{\text{exc}} - E_0 = (U - 4E_B) - (-2E_B) = U - 2E_B.$$

The matrix element of the transition acquires in this case an additional factor $\tilde{t} = te^{-\lambda^2}$, due to the fact that the lattice deformation is different in the initial and intermediate states (the analog of the polaron narrowing of the band). Therefore in this case the exchange integral is equal to

$$J = t^2 e^{-2\lambda^2}/(U - 2E_B).$$

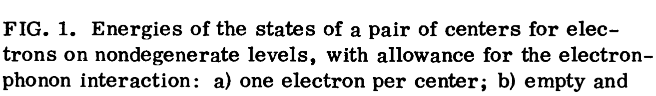

FIG. 1. Energies of the states of a pair of centers for electrons on nondegenerate levels, with allowance for the electron-phonon interaction: a) one electron per center; b) empty and doubly occupied centers in electron transitions with complete restructuring of the lattice; b′) the same in transitions in a frozen lattice (in accord with the Franck-Condon principle).

In the second case (fixed lattice) the phonon mean values are at all time equal to the initial ones for $n=1$, $\langle b^+\rangle = \langle b\rangle = -g/\hbar\omega$ [see (19)]. Then the phonon energy in the intermediate state, given by (18) with the same $\langle b\rangle$, is equal to $E_{ph} = E_B$ for an empty center ($n=0$) and $E_{ph} = U - 3E_B$ for a doubly occupied center ($n=2$), see Fig. 1b′; the matrix element t, on the other hand, is not renormalized. As a result we have

$$J = t^2/(E_{\text{exc}} - E_0) = t^2/U.$$

3. DEGENERATE HUBBARD MODEL WITH PHOTONS. T=0

a) When considering the Hubbard model in the case of degeneracy of the electronic states it is necessary in principle to take into account the same type of interaction with the phonons as in the absence of degeneracy. This interaction does not have any distinguishing features in the degenerate case; just as in Sec. 2, it can be shown, e.g., that at $U \gg E_B$ and $U \gg \hbar\omega$ it does not lead to a renormalization of the exchange integrals. However, in the presence of degeneracy, one other interaction that is typical of this case appears, namely the interaction with that phonon mode which leads to lifting of the degeneracy. It is precisely this interaction which is responsible for the JT effect, and, as will be shown below, determines the specifics of the degenerate case.

We consider for simplicity the interaction between electrons on doubly degenerate orbitals and a nondegenerate phonon mode. The Hamiltonian of the model is of the form

$$H = \sum_{\substack{\langle i,j\rangle \\ \alpha,\alpha',\sigma}} t_{ij}^{\alpha\alpha'} a_{i\alpha\sigma}^{+} a_{j\alpha'\sigma} + {}^1/_2 \sum_{\substack{i,\alpha,\alpha' \\ \sigma,\sigma'}} U_{\alpha\alpha'} n_{i\alpha\sigma} n_{i\alpha'\sigma'} (1 - \delta_{\alpha\alpha'}\delta_{\sigma\sigma'})$$
$$+ \sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}} b_{\mathbf{k}}^{+} b_{\mathbf{k}} + N^{-1/2} \sum_{i,\mathbf{k},\sigma} g(\mathbf{k}) e^{i\mathbf{k}\mathbf{R}_i} (b_{\mathbf{k}} + b_{-\mathbf{k}}^{+})(n_{i1\sigma} - n_{i2\sigma}), \tag{20}$$

where, in contrast to (4), the transition integrals $t_{ij}^{\alpha\alpha'}$, the Coulomb interaction $U_{\alpha\alpha'}$, as well as the electron operators depend on the orbital indices α and α', which take on values 1 and 2. The last term describes the electron-phonon interaction that lifts the degeneracy. This is precisely the interaction that is taken into account when the cooperative JT effect is considered [in this case it is frequently written down directly in the pseudospin representation, $g\tau^z(b^+ + b)$, Ref. 8].

The specifics of the considered case and the character of the results can be qualitatively explained with a simple scheme, in analogy with the procedure used in Sec. 2. The increment to the energy due to the phonons [analogous to (18)] can be written in the case of double degeneracy in the form

$$E_{ph} = \hbar\omega\langle b^+\rangle\langle b\rangle + g(n_1 - n_2)(\langle b^+\rangle + \langle b\rangle),$$

where n_1 and n_2 are the average numbers of electrons on the orbitals 1 and 2, respectively. The energy-minimum condition yields

$$\langle b^+\rangle = \langle b\rangle = -\frac{g}{\hbar\omega}(n_1 - n_2). \tag{21}$$

From this we get for the energy of the equilibrium states (reached in slow virtual processes)

$$E_{ph}=-E_B(n_1-n_2)^2,\quad E_B=g^2/\hbar\omega. \tag{22}$$

The energy difference between the ground state of the pair of centers and the nearest excited states now depends therefore on the character of occupation of the orbitals (see Fig. 2). In the case of two electrons on two orbitals (Fig. 2b), this difference is $E^{b}_{exc}-E_0=U_2+2E_B$, while for two electrons on one orbital (Fig. 2c) we have $E^{c}_{exc}-E_0=U_1-2E_B$. We see thus that interaction with the phonons leads to different renormalizations of the individual terms of the Coulomb interaction (this result will be derived rigorously below).

On the other hand, if the virtual transitions proceed in accord with the Franck-Condon principle, then, using the same reasoning as in Sec. 2, we can verify that the energies of the intermediate states take on the values indicated on Figs. 2b′ and 2c′, and the energy differences of the excited and ground states are equal to $E^{b'}_{exc}-E_0=U_2+4E_B$ and $E^{c'}_{exc}-E_0=U_1$.

However, the main distinguishing feature of the degenerate case is not the indicated modification of the Coulomb interaction, but the dependence of the exchange integrals on the occupation of some particular orbitals. It can be shown that an exponential suppression of certain matrix elements is possible even in the case of transitions that occur in a fixed lattice.

In the degenerate case, for virtual transitions, the initial and final states of the center do not necessarily coincide. Some terms of H_{eff} contain the operators τ_i^z and describe transitions in which the lattice point i returns to the initial state with the same deformation, and for these terms the situation is the same as in the absence of degeneracy. In our case, however, there are also transitions into another orbital state, with a different deformation (these terms contain the operators τ_i^x); for these transitions, even at $U\gg\hbar\omega$, suppression factors appear on account of the overlap of the different oscillator functions of the initial and final states (the Ham suppression factors). It is the strong dependence of these factors on the temperature which leads to the decrease of the exchange integrals with temperature.

We proceed now to a successive analysis of the effects indicated above.

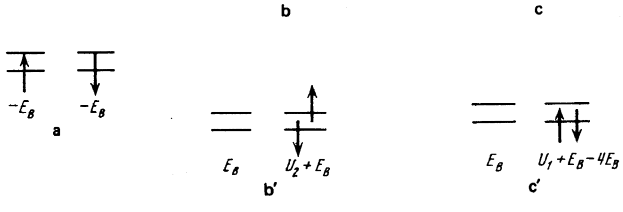

FIG. 2. Energies of states of pair of centers in twofold orbital degeneracy with allowance for the electron-phonon interaction: a) one electron per center; b),c) possible states in transitions with complete restructuring of lattice; b′),c′) the same for transition in a frozen lattice.

b) We investigate first the case when there is no dispersion, $\omega_k=\omega$, $g(k)=g$ the analysis procedure is the same as in Sec. 2. We carry out first a canonical transformation that eliminates from (20) the terms linear in the phonon operators. These transformations take the form (5), where the matrix $\hat{S}$ is given by

$$\hat{S}=\sum_i \hat{S}_i=-\sum_{i,\sigma}\frac{g}{\hbar\omega}(n_{i1\sigma}-n_{i2\sigma})(b_i^+-b_i). \tag{23}$$

As a result of the transformation, the single-center part of the Hamiltonian (20) takes the form

$$\tilde{H}_0'=\sum_{i,\alpha}(U_1-2E_B)n_{i\alpha\uparrow}n_{i\alpha\downarrow}+\sum_{i,\sigma,\sigma'}(U_2+2E_B)n_{i1\sigma}n_{i2\sigma'}+\sum_i\hbar\omega b_i^+b_i. \tag{24}$$

We have used here the notation $U_{11}=U_{22}=U_1$, $U_{12}=U_2$. Thus, allowance for the phonons in H_0 was reduced, as would follow from the qualitative arguments presented above, to a Coulomb-interaction renormalization that depends on the type of the occupation of the orbitals.

We examine now the transformation of the first term of the Hamiltonian (20), namely H_1, which describes the transitions of electrons from one center to another. We obtain the Hamiltonian matrix element

$$\tilde{H}_1=e^{-\hat{S}}H_1e^{\hat{S}},$$

corresponding to electron transition between eigenstates of the initial Hamiltonian H in the presence of one electron per center:

$$M=\langle 0|a_{i\alpha\sigma}\tilde{H}_1a_{j\beta\sigma}^+|0\rangle, \tag{25}$$

where $|0\rangle$ is the vacuum state, in which there are neither electrons nor phonons, i.e., $a_{i\alpha\sigma}|0\rangle=0$, $b_i|0\rangle=0$. The nonzero matrix elements in (25) are the following:

$$M=\langle 0|a_{i\alpha\sigma}e^{-\hat{S}}a^+_{i\alpha\sigma}a_{j\beta\sigma}e^{\hat{S}}a_{j\beta\sigma}|0\rangle. \tag{26}$$

Using expression (23) for the matrix $\hat{S}$ and taking (10) into account, we obtain, after carrying out the corresponding commutations,

$$M=\langle 0|\exp\left\{-\frac{g}{\hbar\omega}(b_i^+-b_i)(-1)^\alpha\right\}\exp\left\{-\frac{g}{\hbar\omega}(b_j^+-b_j)(-1)^\beta\right\}|0\rangle. \tag{27}$$

Using again the last identity of (10), we arrive at the result

$$M=e^{-\lambda^2},\quad \lambda=g/\hbar\omega. \tag{28}$$

It can thus be assumed that within the limits of the considered aggregate of matrix elements the effective transition integral (width of the band) is renormalized in the following manner:

$$\tilde{t}_{ij}^{\alpha\beta}=t_{ij}^{\alpha\beta}e^{-\lambda^2}. \tag{29}$$

The fact that the renormalization (29) does not depend on the type of the orbitals α and β is a consequence of the absence of dispersion. As will be shown below, in the case of an arbitrary dispersion law the different $t_{ij}^{\alpha\beta}$ are differently renormalized.

We consider now the exchange interaction. Just as in the preceding section, we construct an effective Hamiltonian in second order of perturbation theory in t/U [see (7)]. The only difference from (7) is the increase of the multiplicity of the degeneracy of the states $|\alpha_a\rangle$ and $|\alpha_b\rangle$: now these are two arbitrary functions of the 4^N-fold degenerate ground state of the Hamiltonian $\tilde{H}_0'=\tilde{H}_0+H_{ph}$. Using (9) and (10) we can obtain, in analogy with (8)–(12), the following expression for the effective Hamiltonian:

$$\langle\alpha_a|H_{eff}|\alpha_b\rangle=-\langle\alpha_a|\tilde{H}_1\frac{1}{\tilde{H}_0'}\tilde{H}_1|\alpha_b\rangle$$

$$=\sum t_{ij}^{\alpha\beta}t_{ij}^{\alpha'\beta'}\langle\alpha_a|\overset{+}{a}_{j\beta'\sigma'}a_{i\alpha'\sigma'}\overset{+}{a}_{i\alpha\sigma}a_{j\beta\sigma}|\alpha_b\rangle\sum_{m,n=0}^{\infty}\frac{e^{-2\lambda^2}}{U_{1,2}+\hbar\omega(m+n)}$$

$$\times\frac{[(-1)^{\alpha+\alpha'}\lambda^2]^n}{n!}\frac{[(-1)^{\beta+\beta'}\lambda^2]^m}{m!},\qquad(30)$$

where $U_{1,2}=U_1-2E_B$ or U_2+2E_B, depending on the type of the intermediate state, and the summation is over all the spin and orbital indices i and j of the nearest neighbors.

The matrix elements of the electron operators take the same form as in the case of the absence of phonons,[2] and only their coefficients are renormalized. As indicated above, it is convenient to change from the electron operators to the operators of the spin s and pseudospin τ. The electron-operator products $a^+_{i\alpha\sigma}a_{i\beta\sigma'}$ are set in correspondence with the products τs in accordance with the standard rules:

$$(\alpha=1,\ \beta=1)\to{}^1/_2+\tau^z,\quad(2,2)\to{}^1/_2-\tau^z,\quad(1,2)\to\tau^+,\ (2,1)\to\tau^-,\qquad(31)$$

$$(\sigma=\uparrow,\ \sigma'=\uparrow)\to{}^1/_2+s^z,\quad(\downarrow,\downarrow)={}^1/_2-s^z,\quad(\uparrow,\downarrow)\to s^+,\quad(\downarrow,\uparrow)\to s^-.\qquad(32)$$

Thus, for example,

$$\overset{+}{a}_{i1\downarrow}a_{i2\downarrow}\to\tau_i^+({}^1/_2-s_i^z),\qquad\overset{+}{a}_{i1\uparrow}a_{i2\downarrow}\to\tau_i^+s_i^+,\text{etc.}$$

We have used here the same symbols for the axes in the s and τ spaces; to prevent misunderstandings, however, it must be borne in mind that the axes in τ space are in no way connected with the axes x, y, and z of the crystal.

The obtained two-spin Hamiltonian has a rather complicated form (if the relation between the transition integrals $t_{ij}^{\alpha\beta}$ is not spelled out concretely)

$$H_{eff}=\sum_{\langle i,j\rangle}({}^1/_2-2\mathbf{s}_i\mathbf{s}_j)\{S_1^{(1)}[(t^{12})^2({}^1/_4-\tau_i^z\tau_j^z)$$

$$+((t^{11})^2+(t^{22})^2)({}^1/_4+\tau_i^z\tau_j^z)+((t^{11})^2-(t^{22})^2)\tau_i^z]$$

$$+2S_2^{(2)}[(t^{12})^2(\tau_i^x\tau_j^x-\tau_i^y\tau_j^y)+t^{11}t^{22}(\tau_i^x\tau_j^x+\tau_i^y\tau_j^y)]$$

$$+(S_3^{(1)}+S_3^{(2)})[2t^{12}(t^{11}-t^{22})\tau_i^z\tau_j^x+t^{12}(t^{11}+t^{22})\tau_i^x]\}$$

$$-\sum_{\langle i,j\rangle}\{S_1^{(2)}[2(t^{12})^2({}^1/_4+\tau_i^z\tau_j^z)+((t^{11})^2+(t^{22})^2)({}^1/_4-\tau_i^z\tau_j^z)]$$

$$+2S_2^{(2)}[(t^{12})^2(\tau_i^x\tau_j^x-\tau_i^y\tau_j^y)+t^{11}t^{22}(\tau^x\tau^x+\tau^y\tau^y)]-4S_3^{(2)}t^{12}(t^{11}-t^{22})\tau_i^x\tau_j^z\}.\qquad(33)$$

In (33), $S_p^{(q)}$ are various types of the sums over m and n in (30); the superscript in the parentheses shows whether the corresponding sum contains U_1 or U_2.

Equation (30) contains three types of sums over the phonon occupation numbers m and n. Using again the identity (14), we can reduce these sums to the form (for each $U_{1,2}$)

$$\int_0^\infty\exp\{-\tilde{U}_1x\pm2\lambda^2(e^{-\hbar\omega x}\mp1)\}dx=S_{1,2}^{(1)},$$

$$\int_0^\infty\exp\{-\tilde{U}_1x-2\lambda^2\}dx=e^{2\lambda^2}/\tilde{U}_1=S_3^{(1)},\qquad(34)$$

where the upper signs pertain to S_1, and the lower to S_2. Similar expressions for $S_1^{(2)}, S_2^{(2)}, S_3^{(2)}$ are obtained by replacing $\tilde{U}_1=U_1-2E_B$ by $\tilde{U}_2=U_2+2E_B$.

We consider the most frequently realized case $U\gg E_B,\hbar\omega$. At the indicated relations between the parameters we have

$$S_1^{(1)}=\frac{1}{U_1}+O\left(\frac{1}{U_1^3}\right),\quad S_1^{(2)}=\frac{1}{U_2}\left(1-\frac{4E_B}{U_2}\right)+O\left(\frac{1}{U_2^3}\right),$$

$$S_2^{(1)}=\frac{e^{-4\lambda^2}}{U_1}\left[1+\frac{4E_B}{U_1}+O\left(\frac{1}{U_1^2}\right)\right],\quad S_2^{(2)}=\frac{e^{-4\lambda^2}}{U_2}\left[1+O\left(\frac{1}{U_2^2}\right)\right].\qquad(35)$$

The values of $S_3^{(1)}, S_3^{(2)}$ are given in (34). It is thus seen from (33)–(35) that, in accord with the qualitative reasoning presented above, the coefficients of the terms that contain τ^z and do not alter the original state remain practically unrenormalized, whereas the coefficients of the terms with τ^x and τ^y undergo a substantial renormalization ($\sim e^{-4\lambda^2}$). For the crossing terms of the type $\tau^z\tau^x$ the situation is intermediate—the suppression factor is proportional to $e^{-2\lambda^2}$.

c) We consider now the possible change of the situation for an arbitrary phonon dispersion law $\omega_{\mathbf{k}}$ and electron-phonon interaction $g(\mathbf{k})$ [see (20)]. The analysis procedure is not changed fundamentally in this case. At first, using the canonical transformation (5) with a matrix $\hat{S}$ now given by

$$\hat{S}=\sum_i\hat{S}_i=-N^{-1/2}\sum_{i,\mathbf{k},\sigma}\frac{g(\mathbf{k})}{\hbar\omega_{\mathbf{k}}}(n_{i1\sigma}-n_{i2\sigma})(b_{\mathbf{k}}^+e^{-i\mathbf{k}\mathbf{R}_i}-b_{\mathbf{k}}e^{i\mathbf{k}\mathbf{R}_i}),\qquad(36)$$

we obtain a Hamiltonian similar to (23), with

$$E_B=\frac{1}{N}\sum_{\mathbf{k}}\frac{g^2(\mathbf{k})}{\hbar\omega_{\mathbf{k}}}$$

and a phonon term of the type

$$\sum_{\mathbf{k}}\hbar\omega_{\mathbf{k}}b_{\mathbf{k}}^+b_{\mathbf{k}},$$

to which, however, there is added an additional term

$$H_{\mathrm{JT}}=\sum_{i\neq j,\mathbf{k},\sigma}\frac{g^2(\mathbf{k})}{\hbar\omega_{\mathbf{k}}}(n_{i1\sigma}-n_{i2\sigma})(n_{j1\sigma}-n_{j2\sigma})\cos\mathbf{k}(\mathbf{R}_i-\mathbf{R}_j).\qquad(37)$$

In the language of τ operators, (37) can be written in the form

$$H_{\mathrm{JT}}=\sum_{i\neq j}A_{ij}\tau_i^z\tau_j^z.\qquad(38)$$

This is the usual form of the interaction Hamiltonian considered when the cooperative JT effect is described.[8]

Thus, allowance for phonons with arbitrary dispersion law within the framework of the degenerate Hubbard model enables us to describe not only the superexchange, but also the ordinary JT interaction. The polaron narrowing of the band is given by the expressions

$$\tilde{t}_{ij}^{\alpha\alpha}=t_{ij}^{\alpha\alpha}\exp\left\{-\frac{2}{N}\sum_{\mathbf{k}}\lambda_{\mathbf{k}}^2\sin^2\frac{1}{2}\mathbf{k}(\mathbf{R}_i-\mathbf{R}_j)\right\},$$

$$\tilde{t}_{ij}^{12}=t_{ij}^{12}\exp\left\{-\frac{2}{N}\sum_{\mathbf{k}}\lambda_{\mathbf{k}}^2\cos^2\frac{1}{2}\mathbf{k}(\mathbf{R}_i-\mathbf{R}_j)\right\},\qquad,(39)$$

where $\lambda_{\mathbf{k}}=g(\mathbf{k})/\hbar\omega_{\mathbf{k}}$. In the absence of dispersion ($\lambda_{\mathbf{k}}=\lambda$) the $t_{ij}^{\alpha\beta}$ renormalization does not depend on the orbital indices α and β, see (28). In the opposite limiting case, $\lambda_{\mathbf{k}}^2=\lambda^2\delta(\mathbf{k})$, we have

$$\tilde{t}_{ij}{}^{\alpha\alpha}=t_{ij}{}^{\alpha\alpha}, \quad \tilde{t}_{ij}{}^{12}=t_{ij}{}^{12}e^{-2\lambda^2}. \tag{40}$$

The integrals of the transitions between identical orbitals are not renormalized [the transitions take place in fact between identical states of a uniformly deformed ($k=0$) crystal]; the $t_{ij}^{\alpha\beta}$ for different α and β are strongly suppressed, since the corresponding transitions are accompanied by a change in the type of the uniform deformation.

The different character of the renormalization of $t_{ij}^{\alpha\alpha}$ and of t_{ij}^{12} leads to the appearance of additional singularities in the effective exchange Hamiltonian compared with (33). The obtained effective Hamiltonian differs from (33) in the following: the Hamiltonian terms that have previously contained the phonon coefficients $S_{1,2}^{(1,2)}$ now contain $S_{1,2}^{(1,2)}$ as the coefficients of $(t^{12})^2$, while the transition integrals $(t^{11})^2, (t^{22})^2, t^{11}t^{22}$ have different coefficients $\Sigma_{1,2}^{(1,2)}$. On the other hand, the terms with $S_3^{(1,2)}$ remain unchanged. For the coefficients themselves, we obtain in place of (34) the expressions

$$S_{1,2}^{(1)}=\int\limits_0^\infty \exp\left\{-\tilde{U}_1x\pm\frac{2}{N}\sum_{\mathbf{k}}\lambda_{\mathbf{k}}{}^2(e^{-\hbar\omega_{\mathbf{k}}x}\mp 1)(1+\cos\mathbf{k}(\mathbf{R}_i-\mathbf{R}_j))\right\}dx,$$

$$S_3{}^{(1)}=(U_1-2E_B)^{-1}\exp\left(-\frac{2}{N}\sum_{\mathbf{k}}\lambda_{\mathbf{k}}{}^2\right), \tag{41}$$

where again the upper signs pertain to S_1 and the lower to S_2; $\Sigma_1^{(1)}$ and $\Sigma_2^{(1)}$ differ respectively from $S_1^{(1)}$ and $S_2^{(1)}$ in that there is a minus sign in front of $\cos\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_j)$.

In the absence of dispersion $\Sigma = S$ and these expressions go over into those considered above. In the opposite limiting case, when only the components with $k=0$ differ from zero, i.e.,

$$\frac{1}{N}\sum_{\mathbf{k}} f(\mathbf{k})=f(0),$$

we have

$$S_{1,2}^{(1)}=\int\limits_0^\infty \exp\{-\tilde{U}_1x\pm 4\lambda^2(e^{-\hbar\omega x}\mp 1)\}\,dx, \tag{42}$$

$$\Sigma_{1,2}^{(1)}=\int\limits_0^\infty \exp\{-\tilde{U}_1x\}\,dx=\frac{1}{U_1-2E_B}, \quad S_3^{(1)}=e^{-2\lambda^2}/(U_1-2E_B),$$

where $\omega=\omega(0), g=g(0), \lambda=g^2/\hbar\omega$.

The expressions for $S_1^{(1)}, S_2^{(1)}$ are equal, apart from the coefficient of λ^2, to the analogous expressions in the case of absence of dispersion (34). Therefore at $U\gg E_B$, just as in (34), S_1 and Σ_1 are hardly renormalized, while S_2 has an exponential factor ($e^{-8\lambda^2}$). A new element is here the absence of renormalization of the coefficient Σ_2 of the Hamiltonian terms corresponding to the change of the orbital state, which do not have the combinations of t^{11} and t^{22} as factors [in analogy with the band width, see Eq. (40)]

The modification of the exchange interaction on account of the JT effect was also considered by Vekhter and Kaplan[12]; the idea of our approach is quite close to that of theirs, although the actual results do differ. In fact, our paper and Ref. 12 consider different initial systems: in our case orbital and magnetic ordering can coexist (a situation realized in a number of compounds of transition metals), whereas in the case considered in Ref. 12 these types of ordering compete with each other and are mutually incompatible (as is the case in a number of rare-earth compounds).

4. DEGENERATE HUBBARD MODEL WITH PHONONS. FINITE TEMPERATURES

a) We investigate first the temperature dependence of the band width with allowance for the polaron effects. It is necessary in fact to obtain the temperature mean value of those matrix elements of the Hamiltonian $\tilde{H}_1$ which correspond to transitions between the eigenstates of the initial Hamiltonian H (or, equivalently, $\tilde{H}$) in the presence of one electron per center.

We assume that the electronic states with doubly occupied and empty lattice points lie high enough in energy, and carry out the averaging only over the phonon occupation numbers. In the preceding section, in the calculation of the band width, we have considered matrix elements of the type $M=\langle 0|a_{i\alpha\sigma}\tilde{H}_1a_{i\beta\sigma}^+|0\rangle$, where $|0\rangle$ is a state in which there are no electrons on the sites i and j. At $T\neq 0$, if we regard $\hat{A}=a_{i\alpha\sigma}\tilde{H}_1a_{j\beta\sigma}^+$ as an operator whose temperature mean value is taken, the temperature-averaged expression for the matrix element of the transition takes in the case of dispersion the form

$$\langle M\rangle_T=\frac{\mathrm{Sp}\,\hat{A}e^{-\tilde{H}/T}}{\mathrm{Sp}\,e^{-\tilde{H}/T}}$$

$$=\sum_{\{n_l\}}\langle\{n_l\},0|a_{i\alpha\sigma}\tilde{H}_1a_{j\beta\sigma}^+e^{-\tilde{H}/T}|0,\{n_l\}\rangle \Big/ \sum_{\{n_l\}}\langle\{n_l\},0|e^{-\tilde{H}/T}|0,\{n_l\}\rangle, \tag{43}$$

$|0,\{n_l\}\rangle$ is a state in which there are no electrons in sites i and j, but at the arbitrary site l there are excited n_l local phonons, with n_l running through values from zero to infinity.

With this definition, the density matrix contains in fact only the phonon part of the Hamiltonian, inasmuch as $\langle\alpha|e^{-\tilde{H}/T}|\alpha\rangle=1$, where $|\alpha\rangle$ is a certain electronic state, and

$$e^{-\tilde{H}_0/T}|0,\ \{n_l\}\rangle=e^{-E_0/T}|0,\ \{n_l\}\rangle, \tag{44}$$

i.e., the electronic part of the Hamiltonian produces in the numerator and the denominator identical factors that cancel out, therefore

$$\langle M\rangle_T=t_{ij}^{\alpha\beta}\sum_{m,\,n=0}^{\infty}e^{-\hbar\omega\,(m+n)/T}\langle\{m,n\},0|a_{i\alpha\sigma}e^{-\hat{S}}a_{i\alpha\sigma}^+$$

$$\times\, a_{j\beta\sigma}e^{\hat{S}}a_{j\beta\sigma}^+|0,\{m,n\}\rangle \Big/ \Big(\sum_{n=0}^{\infty}e^{-\hbar\omega n/T}\Big)^2. \tag{45}$$

Here $|0,\{m,n\}\rangle$ is a two-center state in which there are no electrons but there are m phonons on the site i and n phonons on the site j, i.e., the band-width problem was reduced to the single-center problem.

Carrying out the corresponding commutations and representing the wave function as a product of the electronic and phonon functions, we obtain

$$\langle M\rangle_T=t_{ij}{}^{\alpha\beta}\sum_{m,n=0}^{\infty}e^{-\hbar\omega(m+n)/T}\langle n|\exp[-(-1)^\alpha\lambda(b_i{}^+-b_i)]|n\rangle$$

$$\times\langle m|\exp[-(-1)^\beta\lambda(b_j{}^+-b_j)]|m\rangle(1-e^{-\hbar\omega/T})^2$$

$$=t_{ij}{}^{\alpha\beta}\left\{(1-e^{-\hbar\omega/T})\,\mathrm{Sp}\left[\exp[\pm\lambda(b^+-b)]\exp\left(-\frac{\hbar\omega b^+b}{T}\right)\right]\right\}^2. \tag{46}$$

The phonon mean values that enter in (46) and be easily calculated (see the Appendix), and are equal to

$$\mathrm{Sp}\left[\exp(\pm\lambda(b^{+}-b))\exp\left(-\frac{\hbar\omega b^{+}b}{T}\right)\right]=(1-e^{-\hbar\omega/T})^{-1}\exp\left(-{}^{1}/{}_{2}\lambda^{2}\operatorname{cth}\frac{\hbar\omega}{2T}\right). \tag{47}$$

From this we obtain directly an expression for the effective width of the band:

$$\tilde{t}_{ij}{}^{\alpha\beta}=\langle M\rangle_{T}=t_{ij}{}^{\alpha\beta}\exp\left(-\lambda^{2}\operatorname{cth}\frac{\hbar\omega}{2T}\right). \tag{48}$$

This result can be generalized also to include the case of an arbitrary phonon dispersion law. Expressions similar to (39) are obtained, but with the temperature factor $\coth(\hbar\omega/2T)$ in the argument of the exponential

$$\tilde{t}_{ij}{}^{\alpha\beta}=t_{ij}{}^{\alpha\beta}\exp\left\{-\frac{1}{N}\sum_{\mathbf{k}}\lambda_{\mathbf{k}}{}^{2}[1-(-1)^{\alpha+\beta}\cos\mathbf{k}(\mathbf{R}_{i}-\mathbf{R}_{j})]\operatorname{cth}\frac{\hbar\omega_{\mathbf{k}}}{2T}\right\}. \tag{49}$$

A temperature dependence of the type (48) and (49) is typical of polaron band narrowing[13] and is not peculiar to JT systems. For example, just as for ordinary polarons, in the limit of high temperatures, $T>\hbar\omega$, the argument of the exponential increases linearly with temperature:

$$t_{ij}{}^{\alpha\beta}=t_{ij}{}^{\alpha\beta}\exp\left\{-\frac{E_{B}}{\hbar\omega}\frac{2T}{\hbar\omega}\right\}.$$

A distinguishing feature of JT systems is the different character of the renormalization of $t^{\alpha\alpha}$ and t^{12} [see (41)]. This distinguishing feature is retained also at $T\neq 0$.

b) We proceed now to consider the temperature dependence of the exchange integrals. The problem is to find the temperature mean value of the effective Hamiltonian obtained in second order of perturbation theory in t/U. In this case, as above, we assume that the nearest excited electronic state lies high enough in energy, and we take the trace only over the phonon states. According to the definition of the effective Hamiltonian, we can write

$$\langle H_{eff}\rangle_{T}=\mathrm{Sp}\left\{\tilde{H}_{1}\frac{1}{E_{0}-\tilde{H}_{0}'}\tilde{H}_{1}e^{-\tilde{H}/T}\right\}\Big/\mathrm{Sp}\,e^{-\tilde{H}/T}. \tag{50}$$

We begin, as before, with the case of no dispersion. If we take out from under the trace sign all the electronic operators, then the general form of the temperature-dependent coefficient in $\langle H_{\text{eff}}\rangle_{T}$ becomes

$$J_{ij}(T)=-t_{ij}{}^{\alpha\beta}t_{ij}^{\alpha'\beta'}\sum_{\{n_{l}\}}\exp\left\{-\hbar\omega\sum_{l}\frac{n_{l}}{T}\right\}$$
$$\times\langle\{n_{l}\}|\exp\{-(-1)^{\beta'}B_{j}+(-1)^{\alpha'}B_{i}\}\frac{1}{\tilde{U}+\hbar\omega\sum_{m}b_{m}{}^{+}b_{m}-E_{0}}$$
$$\times\exp\{-(-1)^{\alpha}B_{i}+(-1)^{\beta}B_{j}\}|\{n_{l}\}\rangle\Big/\sum_{\{n_{l}\}}\exp\left\{-\hbar\omega\sum_{l}\frac{n_{l}}{T}\right\}. \tag{51}$$

Here $B_{i}=\lambda(b_{i}^{+}-b_{i})$, $|\{n_{l}\}\rangle$, as above, is the phonon state in which n_{l} phonons are excited on any arbitrarily taken site l; the energy of this state, which enters in the denominator of (51) is equal to $E_{0}=\sum_{l}\hbar\omega n_{l}$.

Since the expression in the denominator of (51) need not necessarily be positive, it is convenient in the calculation of the sums over the phonon terms to employ not the Laplace transformation (14), but the Fourier integral

$$\frac{1}{a}=\frac{i}{2}\int_{-\infty}^{+\infty}\operatorname{sign}xe^{iax}\,dx.$$

We then obtain

$$J_{ij}(T)=t_{ij}^{\alpha\beta}t_{ij}^{\alpha'\beta'}(1-e^{-\hbar\omega/T})^{2}\frac{i}{2}\int_{-\infty}^{+\infty}dx\operatorname{sign}xe^{i\tilde{U}x}$$
$$\times\sum_{n_{i},n_{j}=0}^{\infty}\exp\frac{-\hbar\omega(n_{i}+n_{j})}{T}\langle n_{i},n_{j}|\exp(\pm B_{i}\pm B_{j}) \tag{52}$$
$$\times\exp[i\hbar\omega(b_{i}{}^{+}b_{i}-n_{i})x]\exp[i\hbar\omega(b_{j}{}^{+}b_{j}-n_{j})]\exp(\pm B_{i}\pm B_{j})|n_{j},n_{i}\rangle.$$

It turns out that when account is taken of the signs of B_{i} and B_{j}, only three variants of terms are possible [these terms actually constitute a generalization, to finite temperature, of the coefficients S_{1}, S_{2}, and S_{3} in the exchange Hamiltonian (34)]

$$S_{1,2}=\frac{i}{2}\int_{-\infty}^{\infty}dx\operatorname{sign}xe^{i\tilde{U}x}C_{1,2}^{2}(x),\quad S_{3}=\frac{i}{2}\int_{-\infty}^{\infty}dx\operatorname{sign}xe^{i\tilde{U}x}C_{1}(x)C_{2}(x); \tag{53}$$

$$C_{1,2}(x)=(1-e^{-\hbar\omega/T})\sum_{n=0}^{\infty}\langle n|e^{-B}\exp(i\hbar\omega xb^{+}b)e^{\pm B}|n\rangle e^{-\hbar\omega n(1/T+ix)}. \tag{54}$$

Calculating the phonon mean values (see the Appendix), we obtain ultimately

$$C_{1,2}(x)=\exp\left\{-\lambda^{2}(1\mp e^{i\hbar\omega x})\left[1+\frac{1\mp e^{-i\hbar\omega x}}{e^{\hbar\omega/T}-1}\right]\right\}. \tag{55}$$

The upper signs in (54) and (55) pertain to C_{1}, and the lower to C_{2}. At $U\gg E_{B}$, using the asymptotic expression for Fourier integrals,[14] we obtain, accurate to terms of first order in E_{B}/U,

$$S_{1}{}^{(1)}=\frac{1}{U_{1}},\quad S_{1}{}^{(2)}=\frac{1}{U_{2}}\left(1+\frac{4E_{B}}{U_{2}}\right),$$
$$S_{2}{}^{(1)}=\frac{1}{U_{1}}\exp\left(-4\lambda^{2}\operatorname{cth}\frac{\hbar\omega}{2T}\right)\left[1-\frac{4E_{B}}{U_{1}}\left(1-\frac{1}{e^{\hbar\omega/T}-1}\right)\right],$$
$$S_{2}{}^{(2)}=\exp\left(-4\lambda^{2}\operatorname{cth}\frac{\hbar\omega}{2T}\right)\left(1+\frac{4E_{B}}{U_{2}}\frac{1}{e^{\hbar\omega/T}-1}\right)\frac{1}{U_{2}}. \tag{56}$$

The corresponding integrals for S_{3} can be calculated exactly:

$$S_{3}{}^{(1)}=\frac{1}{U_{1}-2E_{B}}\exp\left(-2\lambda^{2}\operatorname{cth}\frac{\hbar\omega}{2T}\right),\quad S_{3}{}^{(2)}=\frac{1}{U_{2}+2E_{B}}\exp\left(-2\lambda^{2}\operatorname{cth}\frac{\hbar\omega}{2T}\right). \tag{57}$$

It is seen that the coefficients of the terms with $\tau_{i}^{z}\tau_{j}^{z}$ in the exchange Hamiltonian (33) ($\propto S_{1}$) remain practically unchanged with increasing temperature, while in the terms corresponding to the change of the orbital state (proportional to S_{2} or S_{3}), the argument of the exponential in the suppression factor acquires the factor $\coth(\hbar\omega/2T)$. At high temperatures ($T\gg\hbar\omega$) these exchange integrals decrease with temperature like $\exp(-\lambda^{2}T/\hbar\omega)$.

Similar results can be obtained also when account is taken of dispersion: the Hamiltonian terms containing exponential factors of the type $e^{-c\lambda^{2}}$ decrease additionally with increasing temperature in analogy with (56) and (57).

5. DISCUSSION OF RESULTS

Thus, it was shown above that the exchange interaction in magnetic dielectrics with JT ions are substantially renormalized when account is taken of the interaction with phonons, an interaction peculiar to these systems. The principal effect is here of the same physical nature as the phenomenon well known in polaron physics and in the JT effect, that of the suppression of the off-diagonal matrix elements as a result of non-orthogonality of the corresponding lattice states. In the absence of dispersion, when the problem actually reduces to the one-center problem, allowance for the electron-phonon interaction leads simply to the fact that in all the expressions, e.g., in exchange interaction (33), the diagonal operators τ^z are not renormalized, while the off-diagonal operators τ^x, τ^y or τ^+, τ^- acquire a small factor $\tau^x \to e^{-2\lambda^2}\tau^x$. On the other hand, when the dispersion is taken into account, no such simple connection is obtained, and both the band width and the exchange interaction are modified in a more complicated manner.

The true "magnetic" exchange integral (the total coefficient of the term $\mathbf{s}_i \cdot \mathbf{s}_j$) obtained by averaging (34) over the corresponding orbital state, is decreased by the JT interaction even at $T=0$. Of greater interest, however, is the noticeable change of the exchange integrals with temperature, which takes place here at $T \approx \hbar\omega_D$. This should be reflected in the magnetic properties of the corresponding systems. Generally speaking, the temperature dependence of the exchange integrals is also the result of the variation of the orbital ordering [of the correlation functions $\langle\tau_i\tau_j\rangle$ in (34)] with temperature. The corresponding change is appreciable at temperatures of the order of the temperature of the cooperative JT ordering $T \approx T_c \approx E_B$, and is relatively slow (the correlation functions decrease like E_B/T at high temperatures). The sign of this effect, generally speaking, is not definite and depends on the concrete details of the orbital ordering in the particular compound. On the other hand, the mechanism considered in the present article produces a much stronger temperature dependence and, as a rule, weakens the exchange interaction with temperature, particularly strongly at $T \sim \hbar\omega_D$. Inasmuch as $\lambda^2 = E_B/\hbar\omega = V_{JT}/\hbar\omega$, the polaron effect is most significant particularly at $V_{JT} > \hbar\omega_D$ in the temperature region $T \sim \hbar\omega_D < T_c \approx E_B$, i.e., at temperatures lower than those at which the first mechanism is effective.

The JT stabilization energy E_B can be estimated from the temperature of the cooperative JT transition in concentrated systems or, e.g., from the EPR spectra: at a temperature $T \simeq E_B$ the character of the spectrum changes. These estimates yield, in typical cases, values $E_B \approx 300$–500 K for the Cu^{2+} ion. At the same time, the characteristic values of the phonon frequencies are $\hbar\omega_D \lesssim 300$ K, so that $\lambda \simeq E_B/\hbar\omega_D \approx 1 \div 2$.

A strong decrease of the exchange integral (by a factor of five with rise from liquid-nitrogen to room temperature) was experimentally observed[3,5] in $K_2CuCl_4 \cdot 2H_2O$; a similar although weaker change was observed also in $(C_3H_7NH_3)_2CuCl_4$ and K_2CuF_4 (see Ref. 4). It is interesting that these effects are observed almost exclusively in systems with JT ions, although the specifics of the JT effect have so far not been invoked to explain them. The explanation given in Ref. 4 does not seem convincing to us; it reduces in fact to allowance for the thermal expansion of the lattice (on account of the excitation of the optical phonons), which is patently insufficient for such a strong $J(T)$.

The concrete character of the change of the exchange integral with temperature depends on the type of the orbital ordering for the given pair of ions, and can be different for different pairs; as the final result, the exchange integrals, say for the nearest and non-nearest neighbors, can vary differently with temperature, leading to changes in both sign of the internal field and the very type of magnetic ordering. This mechanism differs from Kittel's exchange-inversion mechanism usually considered in these cases.[15]

The foregoing analysis was carried out for the case of a nondegenerate phonon mode. Actually in JT systems, e.g., on the basis of 3d ions (Cu^{2+}, Mn^{3+}) one frequently encounters a situation wherein the degenerate electronic states interact with the doubly degenerate phonon mode E_g. In this case the electron-phonon interaction acquires the form $g[\tau^z(b_1^+ + b_1) + \tau^x(b_2^+ + b_2)]$, rather than the one contained in (20). Although an exact analysis cannot be carried out in this case (cf. Ref. 8), the main conclusions should qualitatively remain in force: the diagonal matrix elements remain unchanged and the off-diagonal elements acquire small factors of the type $e^{-c\lambda^2}$. Such factors appear more readily both at the operators τ^x (they are nondiagonal with respect to the interaction $\tau^z(b_1^+ + b_1)$, and at τ^z [on account of the $\tau^x(b_2^+ + b_2)$ interaction]. As a result, the answer should be even more symmetrical than (33), and, roughly speaking, the entire part of the exchange integral in which the orbital operators τ are contained acquires a common small factor $\sim e^{-c\lambda^2}$, which in turn decreases with temperature.

APPENDIX

According to (46), it is necessary to calcuate the following trace:

$$\mathrm{Sp}\left(\exp[-\lambda(b^+ - b)]\exp\left[-\frac{\hbar\omega b^+ b}{T}\right]\right)$$

$$= \sum_{n=0}^{\infty}\int_{-\infty}^{\infty} \psi_n^2(p)\, e^{2^{1/2} i\lambda p}\, e^{-\hbar\omega n/T}\, dp. \tag{A.1}$$

Here $\psi_n(p)$ is the eigenfunction of the harmonic oscillator,

$$\psi_n(p) = (\pi^{1/2} n! 2^n)^{-1/2} e^{-p^2/2} H_n(p), \tag{A.2}$$

where $H_n(p)$ is a Hermite polynomial. In (8.1) we used the standard representation of b^+ and b in terms of dimensionless coordinates and momenta:

$$b^+ = (q - ip)/2^{1/2}, \quad b = (q + ip)/2^{1/2}. \tag{A.3}$$

Using for the calculation of the sum over n the known expression[16]

$$\sum_{n=0}^{\infty} \frac{H_n^2(p)}{n!\, 2^n} w^n = \exp\left(-\frac{2p^2 w}{1+w}\right)\frac{1}{(1-w^2)^{1/2}}, \quad |w| < 1, \tag{A.4}$$

we obtain, after simple operations, the relation (47).

Similarly, the expression for $C_1(x)$ in (54) can be rewritten in the form

$$C_1(x)=(1-e^{-\hbar\omega/T})\sum_{m,n=0}^{\infty}\langle n|e^{-B}|m\rangle\langle m|e^{B}|n\rangle$$

$$\times\exp\left[-\hbar\omega n\left(\frac{1}{T}+ix\right)+i\hbar\omega mx\right]. \qquad (A.5)$$

Using now, just as in the calculation of the width of the band, the representation of the matrix elements $\langle n|e^{\pm B}|m\rangle$ in terms of the eigenfunctions $\psi_n(p)$ of the harmonic oscillator, we get

$$C_1(x)=(1-e^{-\hbar\omega/T})\sum_{m,n=0}^{\infty}\int_{-\infty}^{\infty}dp\int_{-\infty}^{\infty}dp'\,\psi_n(p)\,e^{-2^{1/2}i\lambda p}\,\psi_m(p)\,\psi_m(p')$$

$$\times e^{2^{1/2}i\lambda p'}\,\psi_n(p')\exp\left\{-\hbar\omega n\left(\frac{1}{T}+ix\right)+i\hbar\omega mx\right\}. \qquad (A.6)$$

Using the following relation for the sum over Hermite polynomials[16]

$$\sum_{n=0}^{\infty}\frac{w^n}{n!\,2^n}H_n(p)H_n(p')=(1-w^2)^{-1/2}\exp\left[\frac{2pp'w-(p^2+p'^2)w^2}{1-w^2}\right] \qquad (A.7)$$

and carrying out the corresponding integrations, we obtain (55) and analogously (56).

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Translated by J. G. Adashko