Crystal structure and magnetic properties of substances with orbital degeneracy

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Exchange interaction in magnetic substances containing ions with orbital degeneracy is considered. It is shown that, among with spin ordering, superexchange also results in cooperative ordering of Jahn-Teller ion orbitals, which, generally speaking, occurs at a higher temperature and is accompanied by distortion of the lattice (which is a secondary effect here). Concrete studies are performed for substances with a perovskite structure ($KCuF_3$, $LaMnO_3$, MnF_3). The effective spin Hamiltonian is obtained for these substances and the properties of the ground state are investigated. The orbital and magnetic structures obtained in this way without taking into account interaction with the lattice are in accord with the structures observed experimentally. The approach employed also permits one to explain the strong anisotropy of the magnetic properties of these compounds and to obtain a reasonable estimate for the critical temperatures.

1. INTRODUCTION

When considering magnetic and crystallographic properties of transition-metal compounds, it is very important to take into account the d-level degeneracy. In the crystal field, the fivefold d-level splits (for example, in a field of cubic symmetry it splits into a threefold level t_{2g} and a twofold level e_g). A situation is then possible, for example, for the ions d^9—C^{2+}, d^4—Mn^{3+}, and Cr^{2+} in an octahedral environment, the ground state turns out to be degenerate with respect to the orbital angular momentum if cubic symmetry is preserved1). The class of compounds in which such a situation is encountered is quite large. These are compounds with the structure of perovskite ($LaMnO_3$, $KCuF_3$, $KCrF_3$, MnF_3), rutile ($CrCl_2$, CrF_2, CuF_2), or spinel, containing the ions Mn^{3+} and Cu^{2+}, and a number of other types of substances[1]. The study of such compounds is of great interest, since they usually undergo a lattice transition that leads to a lowering of the symmetry; the magnetic properties turn out to be more complicated and more interesting than in analogous substances without orbital degeneracy (more complicated magnetic structure, strong anisotropy); a low-frequency branch of the exciton type, connected with transitions between orbital states, can appear in the elementary-excitation spectrum and can interact with the magnons; this branch depends strongly on the temperature.

The properties of such compounds, particularly lattice transitions in them, are usually explained by starting from the Jahn-Teller effect[1-4]. Accordingly, at $T = 0$ the symmetrical arrangement of the ions, at which the orbital degeneracy is preserved, is unstable, and the lattice becomes deformed with the lowering of symmetry, so as to lift the degeneracy of the electronic state. Local deformations of the anion environment near the given transition-metal ion appear first; it is the elastic interaction of such local distortions which is assumed to be responsible for the cooperative deformation of the entire lattice, which occurs at $T < T_{orb}$. In this approach it is necessary to introduce many constants that describe the interaction of the deformations of different octahedra, and the values of these constants are usually unknown and it is quite difficult to predict the concrete type of the orbital ordering. In addition, the orbital ordering in this approach is not at all connected with the magnetic ordering.

In this paper we propose a different approach to the description of the properties of compounds containing ions with orbital degeneracy, the so-called Jahn-Teller ions (see also[5]). Our analysis is based on a natural generalization of ordinary superexchange, which is responsible for the magnetic properties of magnetic dielectrics, to include the case of orbital degeneracy. The reason for the appearance of ordering of localized spins in this approach is the fact that the reduction of the energy as a result of the virtual transitions of the d electron to a neighboring center depends on the mutual orientation of the spins at these centers. In complete analogy, in the case of orbital degeneracy the corresponding contribution to the energy depends not only on the magnetic structure, but also on the particular orbitals that are occupied at the neighboring centers. Thus, in our case the usual super-exchange leads in essence not only to magnetic ordering, but also to orbital ordering, thus determining uniquely both the magnetic and the orbital (and accordingly the crystal) structure of the ground state. The magnetic and orbital orderings turn out to be closely related in this case, although they occur generally speaking at different temperatures.

The possibility of ordering orbitals by superexchange was apparently first noted by Roth[6]; this phenomenon was subsequently investigated also by Pokrovskiĭ and Uĭmin[7]. They, however, considered only the simplest symmetrical model, without taking into account the real structure of the d-orbitals, and therefore no comparison with real substances was made.

In addition to describing the ordering of orbitals, our analysis has one more purpose. In the case of orbital degeneracy, the theoretical definition of magnetic structure becomes indeterminate: the well known Goodenough-Kanamori-Anderson rules[1,2,8] do not give an unambiguous answer in this case. From the generalized superexchange Hamiltonian obtained in this paper we can obtain the spin Hamiltonian given the type of orbital ordering, regardless of the cause of the ordering, and determine the magnetic structure. Conversely, knowledge of the magnetic structure can help in some cases to determine the concrete type of ordering of the orbitals.

2. FORMULATION OF MODEL AND QUALITATIVE STUDY

From the theoretical point of view, the model considered is two-level variant of the Hubbard model[9,10], with the intra-atomic exchange taken into account. We consider a crystal with a fixed lattice and with a doubly-degenerate level at each center with one electron per center. We take the Hamiltonian for the d-electrons in the form

$$H=\sum_{\substack{\langle i,j\rangle\\ \alpha,\beta,\sigma}} b_{i\,j}^{\alpha\beta}a_{i\alpha\sigma}^{+}a_{j\beta\sigma}+\frac{U}{2}\sum_{\substack{i,\sigma,\sigma'\\ \alpha,\beta}} n_{i\alpha\sigma}n_{i\beta\sigma'}(1-\delta_{\alpha\beta}\delta_{\sigma\sigma'}) \\ -J\sum_{i,\sigma,\sigma'} a_{i1\sigma}^{+}a_{i1\sigma'}a_{i2\sigma'}^{+}a_{i2\sigma}=H'+H_0+H_J. \tag{1}$$

The subscript i denotes here the number of the site, α and β are the numbers of the orbitals (α and β each assume two values, 1 and 2). The first term in (1) describes the transitions of the electron from center to center (the symbol $\langle i, j\rangle$ denotes summation over the nearest neighbors), the second term denotes Coulomb repulsion of the electrons by one center, and the third stands for the intra-atomic exchange (which leads, in particular, to the Hund rule).

In magnetic dielectrics, the relation between the parameters is usually $b \ll J < U$ ($U \approx 5$–10 eV, $J \approx 1$ eV, $b \approx 0.1$–0.2 eV). The initial state can therefore be assumed to be one with electrons localized on the centers, and the kinetic energy term H′ can be taken into account by perturbation theory in terms of b/U, changing over to the effective Hamiltonian. We shall frequently use also the ratio $J/U < 1$, although the results can be easily generalized to include all orders in J/U.

The state of an electron localized at the center i can be characterized in our case by two quantum numbers, the spin **s** and the number of the occupied orbitals. In the case of double degeneracy, it is convenient to describe the orbital state by means of the "pseudospin" operator $\boldsymbol{\tau}$ with properties that are exactly analogous to the properties of the usual spin operator 1/2. When a value $\tau^{\zeta} = +1/2$ corresponds to the occupied orbitals $|1\rangle$ (for example, $|d_{z^2}\rangle$), and $\tau^{\zeta} = -1/2$ corresponds to the orbital $|2\rangle = |d_{x^2-y^2}\rangle$. It is convenient to plot the orbital state on the $(\tau^{\zeta}, \tau^{\eta})$ plane. (In order not to confuse the axes in τ-space with the real axes x, y, and z of the crystal, they are designated η, ξ, ζ). The state characterized by the angle θ is

$$|\theta\rangle=\cos{}^1\!/_2\theta\,|d_{z^2}\rangle+\sin{}^1\!/_2\theta\,|d_{x^2-y^2}\rangle. \tag{2}$$

The angles $\theta = 0$, π, $\pi/3$, and $2\pi/3$ correspond to the orbitals d_{z^2}, $d_{x^2-y^2}$, $d_{z^2-y^2}$, and d_{y^2}, etc.

We shall explain the qualitative picture of the onset of orbital ordering together with spin ordering for two centers, using a simple model and taking in the Hamiltonian (1) the case $b_{11} = b_{22} = b$ and $b_{12} = 0$. For a pair of ions and an undegenerate level, the two possible situations are indicated in Fig. 1, which shows the increments to the energies of the corresponding states in second order in b/U, due to the virtual transitions of the electron to the neighboring center. The energy gain in the case of antiparallel spins (Fig. 1b) (jumps to the neighboring center at parallel spins are forbidden by the Pauli principle) is the cause of the antiferromagnetism in this case, and the corresponding exchange interaction is in fact the superexchange.

FIG. 1. Possible configurations for an ion pair in the degenerate case, and the corresponding energy increment: a–$\Delta E = 0$, b–$\Delta E = -b^2/U$.

FIG. 2. Possible configurations for a pair of ions in the case of double orbital degeneracy, and the corresponding energy increments: a–$\Delta E = 0$, b–$\Delta E = -b^2/U$, c–$\Delta E = -b^2/U$, d–$\Delta E = -b^2/(U-J)$.

The situation in the case of double degeneracy is shown in Fig. 2. Obviously, the same superexchange leads here, in addition to spin ordering, also to orbital ordering. The most convenient here is the configuration, d, i.e., the ordering is ferromagnetic in spin and "antiferromagnetic" (more accurately, singlet for two centers) with respect to the occupation of the orbitals.

3. DERIVATION OF THE EFFECTIVE HAMILTONIAN

The qualitative arguments advanced above can be rigorously proved by changing over from the Hamiltonian (1) to an effective Hamiltonian that depends on **s** and $\boldsymbol{\tau}$ and acts on the subspace of functions with singly-occupied centers. In this subspace, the operator $a_{i\alpha\sigma}^{+}a_{i\beta\sigma'}$ is set in correspondence, depending on the indices α, β and σ, σ', to the product τs in accordance with the following rules:

$$(\alpha=1,\ \beta=1)\to{}^1\!/_2+\tau^{\zeta},\quad (2{,}2)\to{}^1\!/_2-\tau^{\zeta},\quad (1{,}2)\to\tau^{+},\quad (2{,}1)\to\tau^{-}. \\ (\sigma=\uparrow,\sigma'=\uparrow)\to{}^1\!/_2+s^{z},\ (\downarrow,\downarrow)\to{}^1\!/_2-s^{z},\ (\uparrow,\downarrow)\to s^{+},\ (\downarrow,\uparrow)\to s^{-}. \tag{3}$$

Thus, for example, $a_{i1\uparrow}^{+}a_{i2\uparrow}=\tau_i^{+}(1/2+s_i^{z})$, $a_{i1\uparrow}^{+}a_{i2\downarrow}=\tau_i^{+}s_i^{+}$, $a_{i2\downarrow}^{+}a_{i2\uparrow}=(1/2-\tau^{\zeta})s_i^{-}$ etc. We have introduced here the standard notation: $\tau^{\pm}=\tau^{\eta}\pm i\tau^{\xi}$, $s^{\pm}=s^{x}\pm is^{y}$.

The transition to the effective Hamiltonian is carried out in the usual manner in second order in H′[8]. A certain difficulty is raised here by allowance for the term H_J, since a state with two electrons on a center, characterized by a pseudospin and spin of individual electrons, is not always an eigenstate for H_J. It is convenient to carry out expansion in terms of J/U; in this case we obtain

$$H_{\text{eff}}=-H'\frac{1}{H_0+H_J-E_0}H'=-H'\frac{1}{H_0-E_0}\Big(1-\frac{1}{H_0-E_0}H_J \\ +\frac{1}{H_0-E_0}H_J\frac{1}{H_0-E_0}H_J-\dots\Big)H'. \tag{4}$$

Substituting in (4) the expressions for H′, H_0, and H_J from (1) we obtain, after performing the corresponding commutations, an expression for H_{eff}, which contains products of groups of four and groups of eight Fermi operators; expressing them in terms of **s** and $\boldsymbol{\tau}$ in accordance with the rules (3), we obtain ultimately for the ion pair i, j, in the general case, at arbitrary values of the transition integrals b_{11}, b_{22}, $b_{12} = b_{21}$ (which we choose to be real), the effective Hamiltonian in the form

$$H_{\text{eff}}^{\langle ij\rangle}=\frac{2}{U}\Big\{\Big(\frac{1}{2}+2\mathbf{s}_i\mathbf{s}_j\Big)\Big[\frac{1}{4}(b_{11}^2+b_{22}^2+2b_{12}^2)\Big(1-\frac{J}{U}\Big) \\ +\tau_i^{\zeta}\tau_j^{\zeta}(b_{11}^2+b_{22}^2-2b_{12}^2)\Big(1+\frac{J}{U}\Big)+\frac{1}{2}\Big(\tau_i^{\zeta}+\tau_j^{\zeta}\Big)(b_{11}^2-b_{22}^2) \\ +2\tau_i^{\xi}\tau_j^{\xi}(b_{22}b_{11}-b_{12}^2)+2\tau_i^{\eta}\tau_j^{\eta}(b_{22}b_{11}+b_{12}^2)+(\tau_i^{\eta}+\tau_j^{\eta})\,b_{12}(b_{11}+b_{22})\Big(1-\frac{J}{2U}\Big) \\ +2(\tau_i^{\eta}\tau_j^{\zeta}+\tau_i^{\zeta}\tau_j^{\eta})\,b_{12}(b_{11}-b_{22})\Big(1+\frac{J}{2U}\Big)\Big]-\Big[\frac{1}{2}(\tau_i^{\zeta}+\tau_j^{\zeta})(b_{11}^2-b_{22}^2)$$

$$+(\tau_i^\eta+\tau_j^\eta)\,b_{12}(b_{11}+b_{22})\left(1-\frac{J}{2U}\right)-2\tau_i^\eta\tau_j^\eta(b_{11}b_{22}+b_{12}^2)\frac{J}{U}$$
$$-2\tau_i^\xi\tau_j^\xi(b_{11}b_{22}-b_{12}^2)\frac{J}{U}-(\tau_i^\eta\tau_j^\zeta+\tau_i^\zeta\tau_j^\eta)\,b_{12}(b_{11}-b_{22})\frac{J}{U}\Big]\Big\}. \quad (5)$$

The complete Hamiltonian of the crystal is a sum of expressions (5) over all pairs ⟨i, j⟩ of the nearest neighbors; generally speaking, the transition integrals $b_{ij}^{\alpha\beta}$ can be different for different pairs (see Sec. 4). Expression (5) has been out accurate to terms of order J/U; it can be derived also exactly, in all orders of J/U. The corresponding result is given below for the symmetrical model ($b_{11} = b_{22} = b$, $b_{12} = 0$). The complete effective Hamiltonian for this model is

$$H^s_{\text{eff}}=\frac{b^2}{U}\sum_{\langle i,j\rangle}\Big\{\left(\frac{1}{2}+2\mathbf{s}_i\mathbf{s}_j\right)\left(\frac{1}{2}+2\boldsymbol{\tau}_i\boldsymbol{\tau}_j\right)+\frac{J/U}{1-(J/U)^2}\Big[2(\boldsymbol{\tau}_i\boldsymbol{\tau}_j-\tau_i^\zeta\tau_j^\zeta)$$
$$-\left(\frac{1}{2}+2\mathbf{s}_i\mathbf{s}_j\right)\left(\frac{1}{2}-2\tau_i^\zeta\tau_j^\zeta\right)\Big]+\frac{(J/U)^2}{1-(J/U)^2}\Big[-\left(\frac{1}{2}-2\tau_i^\zeta\tau_j^\zeta\right) \quad (6)$$
$$+2\left(\frac{1}{2}+2\mathbf{s}_i\mathbf{s}_j\right)(\boldsymbol{\tau}_i\boldsymbol{\tau}_j-\tau_i^\zeta\tau_j^\zeta)\Big]\Big\}.$$

In the lowest order in J/U, this Hamiltonian was presented in[5] (formula (2) of[5] contains the wrong sign, and the second line of (2) should contain $(\boldsymbol{\tau}_i\cdot\boldsymbol{\tau}_j+JU^{-1}\tau_i^\zeta\tau_j^\zeta)$).

The properties of such a system at J = 0 were investigated in detail in[7]. In the self-consistent-field approximation (or for a corresponding Ising Hamiltonian), the ground state turns out to be strongly degenerate; if the quantum character is taken into account, however, it is more convenient to use complicated structures that are maximally "antiferromagnetic" both with respect to s and with respect to τ. The interatomic exchange (the terms with J in (6)) lifts the degeneracy even in the self-consistent field approximation, and leads, as can be easily verified, to a ground state that is ferromagnetic in the spin and antiferromagnetic in the pseudospin[5]. Such a state may turn out to be more convenient than the states considered in[7], at least at not too small J/U. Assuming that this ground state is realized, we can analyze in the self-consistent-field approximation all the properties of such a system, obtain the spectrum of the elementary excitations (spin waves, pseudospin excitations—in fact the exciton band, and also their possible bound states). It is also possible to investigate in this approximation the thermodynamic properties of the system; in particular, it turns out that when the temperature is increased, the spin ordering vanishes first (at $T_s \sim b^2J/U^2$), and then the orbital ordering, at $T_{\text{orb}} \sim b^2/U$. In view of the nonrealistic nature of the symmetrical model, and also because the properties of the ground state (6) for arbitrary J/U are not clear, we shall not present here these results, and proceed to study the real case of perovskites.

4. PROPERTIES OF PEROVSKITES WITH JAHN-TELLER IONS

In real cases, the transition integrals $b_{ij}^{\alpha\beta}$ depend both on the type of the orbitals α and β and on the mutual placement of the corresponding centers i and j. By way of a concrete application of the proposed general scheme, we consider compounds with perovskite structure. In these compounds (in the cubic phase), the magnetic ions form a simple cubic lattice, and the anions are located at the centers of the edges, so that only the 180° superexchange is significant. Choosing as the basis functions |1⟩ and |2⟩ the orbitals $|d_{z^2}\rangle$ and $|d_{x^2-y^2}\rangle$, we can, by starting from the explicit form of these d-functions[1], find the corresponding transition integrals $b_{ij}^{\alpha\beta}$.

For the functions $|d_{z^2}\rangle$ and $|d_{x^2-y^2}\rangle$ themselves, the corresponding values are listed in Table 2 of[8]. In the general case, for all the poles characterized by angles θ and θ' (see (2)), we have

$$b^z_{\theta\theta'}=2b\cos{}^1\!/_2\theta\cos{}^1\!/_2\theta',$$
$$b^x_{\theta\theta'}={}^1\!/_2 b[\cos{}^1\!/_2\theta\cos{}^1\!/_2\theta'+3\sin{}^1\!/_2\theta\sin{}^1\!/_2\theta'-\sqrt{3}\sin{}^1\!/_2(\theta+\theta')], \quad (7)$$
$$b^y_{\theta\theta'}={}^1\!/_2 b[\cos{}^1\!/_2\theta\cos{}^1\!/_2\theta'+3\sin{}^1\!/_2\theta\sin{}^1\!/_2\theta'+\sqrt{3}\sin{}^1\!/_2(\theta+\theta')].$$

The superscript denotes here the relative placement of the centers with respect to the axes z, x, and y, respectively; b = (1/6)Δ, where Δ is the distance between the levels e_g and t_{2g} in the cubic field. In particular, in accord with[8], we obtain from (7)

$$b^z_{d_{z^2}d_{z^2}}=2b,\; b^z_{d_{z^2}d_{x^2-y^2}}=0,\; b^{x,y}_{d_{z^2}d_{z^2}}={}^1\!/_2 b,\ldots$$

Using the explicit form of the quantities $b_{ij}^{\alpha\beta}$, we can obtain from (5) the effective Hamiltonian for perovskites. It takes the form

$$H_{\text{eff}}=\frac{b^2}{U}\sum_{\langle i,j\rangle_z}\Big\{8\mathbf{s}_i\mathbf{s}_j\Big[\tau_i^\zeta\tau_j^\zeta\left(1+\frac{J}{U}\right)+\tau_j^\zeta+\frac{1}{4}\left(1-\frac{J}{U}\right)\Big]$$
$$+2\Big[\tau_i^\zeta\tau_j^\zeta\left(1+\frac{J}{U}\right)-\tau_j^\zeta\Big]\Big\}+\frac{b^2}{U}\sum_{\langle i,j\rangle_x,\langle i,j\rangle_y}\Big\{2\mathbf{s}_i\mathbf{s}_j\Big[\tau_i^\zeta\tau_j^\zeta\left(1+\frac{J}{U}\right)-2\tau_j^\zeta$$
$$+\left(1-\frac{J}{U}\right)\pm\sqrt{3}\left(2+\frac{J}{U}\right)\tau_i^\eta\tau_j^\zeta\mp\sqrt{3}\left(2-\frac{J}{U}\right)\tau_j^\eta+3\tau_i^\eta\tau_j^\eta\Big] \quad (8)$$
$$+\frac{1}{2}\Big[\tau_i^\zeta\tau_j^\zeta\left(1+\frac{J}{U}\right)+2\tau_j^\zeta\pm\sqrt{3}\left(2+3\frac{J}{U}\right)\tau_i^\eta\tau_j^\zeta\pm\sqrt{3}\left(2-\frac{J}{U}\right)\tau_j^\eta$$
$$+3\left(1+2\frac{J}{U}\right)\tau_i^\eta\tau_j^\eta\Big]\Big\}.$$

In (8), the symbols $\langle i, j\rangle_x$, $\langle i, j\rangle_y$, and $\langle i, j\rangle_z$ denote summation over the nearest neighbors located along the corresponding axis; in the second sum, the upper sign corresponds to the pairs along the x axis and the lower to the pairs along the y axis. For the sake of brevity, the individual terms in (8) have been written out asymmetrically with respect to i and j, and the symmetry is restored upon summation.

It is seen that the Hamiltonian (8) is strongly anisotropic, both in the sense of the explicit dependence on τ^ζ and τ^η, and from the point of view that even for the operators s, which enter in (8) in the form of a scalar product, the values of the exchange integrals depend on the mutual placement of the corresponding pair of centers, namely, the exchange interaction along the c axis (in the [001] direction) differs from the corresponding value in a plane perpendicular to c. In addition, Eq. (8) contains terms of the "external field" type (linear in τ^ζ and τ^η).

The Hamiltonian (8) describes superexchange interaction in perovskites with Jahn-Teller ions. If the degenerate orbitals are ordered in a definite manner (by some arbitrary mechanism, say by the usual Jahn-Teller interaction with the lattice), then, substituting in (8) the corresponding mean values of the operators τ, we obtain the effective spin Hamiltonian, which determines the magnetic structure. We see, however, that the Hamiltonian (8) itself contains terms that lead to orbital ordering besides the spin ordering. We investigate the ground state of the system in the self-consistent-field approximation. Unlike in the symmetrical model considered in Sec. 3 and in[7], the Hamiltonian (8) exhibits, with respect to τ, not a Heisenberg-Hamiltonian behavior but an Ising behavior, even at J = 0. This is obvious for pairs of centers along the z axis; it is easy to verify that the terms corresponding to the interactions along the x and y axes are obtained from the corresponding terms along the z axis by rotation in τ-space through an angle $\theta = \pm 2\pi/3$, so that in the xy plane the interaction with respect to τ is of the Ising type. The self-consistent-field approximation is therefore satisfactory, at least for the determination of the pseudo-spin structure of the ground state.

We consider first the one-dimensional case. It is easy to verify by starting from (8), that the orbital structure at T = 0 corresponds to "τ-ferromagnetism," with all $\tau_l^\zeta = +1/2$ (the orbitals d_{z^2} are occupied); the spin Hamiltonian is in this case antiferromagnetic. This result can be applied to an analysis of the properties of one-dimensional antiferromagnets containing Cu^{2+} ions[11].

We shall seek the structure of the ground state of the perovskites in the following manner: we consider four very simple spin structures: 1) ferromagnetic, 2) two-sublattice antiferromagnetic, 3) a structure consisting of ferromagnetic filaments parallel to the c axis that are coupled with one another antiferromagnetically, and 4) a structure of ferromagnetic planes (001) that are antiferromagnetically coupled in the direction of the c axis. In each of these structures we consider the following type of τ-ordering: we assume that in the plane perpendicular to the c axis there are two τ sublattices characterized by the angles θ_1 and θ_2, and characterized in the neighboring plane by the angles θ_3 and θ_4. This is a rather general assumption, which includes, in particular, complete τ-ferromagnetism with angle $\theta = \theta_1 = \theta_2 = \theta_3 = \theta_4$, two-sublattice τ-antiferromagnetism ($\theta_1 = \pi + \theta_2$, $\theta_3 = \theta_2$, $\theta_4 = \theta_1$), ferromagnetic filaments ($\theta_1 = \theta_3$, $\theta_2 = \theta_4$), etc., and also canted structures. (The inclusion of structures that are canted in τ is necessary because (8) contains terms that are linear in τ). We do not consider here the more complicated types of s and τ ordering (helical structures etc.), since they arise in the Heisenberg model, as is well known, when account is taken of the interaction with the non-nearest neighbors, and the Hamiltonian (8) includes only the nearest interactions, albeit strongly anisotropic ones.

Under the assumptions made, we can write for each type of spin ordering the mean value of the Hamiltonian $\langle H_{eff} \rangle$ as a function of the angles θ_1, θ_2, θ_3, and θ_4, minimize it with respect to the angles, and then compare the energies of the corresponding most convenient states. The energies actually depend in this case on only one parameter J/U. This calculation yields the following results: out of all the possible structures, the most favored is the structure of type 4), consisting of planes perpendicular to the c axis that are ferromagnetic in the spin and are coupled antiferromagnetically (antiferromagnetic ordering of type A).

For this structure, the energy as a function of the angles θ_i takes the form

$$E_4 = \langle H_{\text{eff}} \rangle_4 = \frac{b^2}{U} N \left\{ -(\zeta_1 + \zeta_2 + \zeta_3 + \zeta_4) + \frac{1}{2}\left(1 + \frac{J}{U}\right) \times (\zeta_1\zeta_2 + \zeta_3\zeta_4 + 3\eta_1\eta_2 + 3\eta_3\eta_4) + \left(1 - \frac{J}{U}\right) \right\}, \qquad (9)$$

where $\eta_i = \sin\theta_i$ and $\zeta_i = \cos\theta_i$. Minimization of (9) with respect to θ leads to the following result: for all i we have $\cos\theta_i = 1/2\,(1 + J/U)$, $\theta_1 = -\theta_2$, $\theta_3 = -\theta_4$. Thus, in the plane perpendicular to the c axis, the orbital structure is characterized by an alternation of the angles $\pm\theta = \pm(\pi/3 + J/\sqrt{3}U)$, i.e., the occupied orbitals $d_{z^2-x^2}$ and $d_{z^2-y^2}$ actually alternate at small J/U. In the direction of the c axis, two equivalent structures corresponding to the same energy are possible: either two orbitals $d_{z^2-x^2}$ one on top of the other, as in Fig. 3b (i.e., we obtain chains that are ferromagnetic with respect to τ), or else we have $d_{z^2-y^2}$ on top of $d_{z^2-x^2}$, as in Fig. 3a (i.e., we obtain a two-sublattice canted antiferromagnetism with respect to the orbital state). The two equivalent types of orbital structures are shown in Fig. 3. The arrows in the figure show the displacements of the anions, if we are dealing with a hole orbital as in the ion $Cu^{2+}(d^9)$ in $KCuF_3$. Such a displacement of the negative ions must be the result of a secondary effect from the electrostatic interactions at the indicated ordering of the hole orbitals.

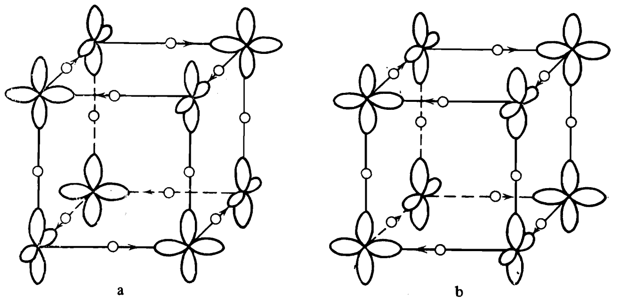

FIG. 3. Two equivalent types of ordering of singly-occupied orbitals in perovskites, obtained in the superexchange model. The figure shows the anion displacements produced for a hole orbital (Cu^{2+} ion).

The orbital and magnetic structures described above and shown in Fig. 3 were obtained by us without using the concepts of elastic interactions. This type of structure arises naturally as a result of superexchange when concrete account is taken of the characteristics of the d-orbitals, and subject to the only condition that J/U be small; it gives way to a pure ferromagnetic structure only at J/U $\gtrsim$ 0.7.

The obtained structure agrees well with that observed experimentally in MnF_3, $LaMnO_3$, $KCuF_3$ and $KCrF_3$[1]. The best agreement is observed in $KCuF_3$, a thoroughly investigated substance[12], in which the simplest situation is realized with completely occupied t_{2g} levels that make no contribution to the superexchange. The type of orbital ordering agrees exactly with that obtained theoretically. In addition, the presence of two types of crystalline and orbital structures, corresponding to the equivalent τ structures described above (Fig. 3), has been established in $KCuF_3$. Below $T_s \approx$ 20–40°K, the magnetic structure also agrees with the calculated one (ordering of type A). At higher temperatures (up to T_1 = 243°), considerable antiferromagnetic spin correlations along the z axis are preserved in $KCuF_3$, so that this substance is regarded as a good example of a one-dimensional antiferromagnet. Such a strong anisotropy of the magnetic properties is also explained by our approach.

It is clear from Fig. 3 that at the obtained type of orbital ordering the overlap of the occupied orbitals (of the hole type for Cu^{2+}) along the z axis is large, and this leads to a strong ($\sim b^2/U$) antiferromagnetic interaction in this direction; in the xy plane, on the other hand, the overlap of the occupied orbitals is zero, there are only transitions between occupied and empty orbitals, and this, in accordance with the Goodenough-Kanamori-Anderson rules[1,2,8], leads to a weak ($\sim b^2J/U^2$) ferromagnetic interaction.

These qualitative considerations can be easily confirmed by replacing in (8) the values of the operators τ by the mean values corresponding to the obtained type of τ-ordering. We obtain the spin Hamiltonian

$$H_s = \frac{9}{2}\frac{b^2}{U}\left(1-\frac{J}{U}\right)\sum_{\langle i,j\rangle_z} \mathbf{s}_i\mathbf{s}_j - \frac{15}{8}\frac{b^2J}{U^2}\sum_{\langle i,j\rangle_{x,y}} \mathbf{s}_i\mathbf{s}_j. \tag{10}$$

Usually $J/U \sim 0.1$–0.2; this value agrees well with the ratio T_S/T_1 of $KCuF_3$. Thus, it is precisely the described orbital ordering that causes the $KCuF_3$ crystal, the structure of which is close to cubic, to behave like a quasi-one-dimensional magnet.

A free analysis of the behavior of the system at $T \neq 0$ calls for a more detailed investigation, with simultaneous allowance for the variation of both $\langle s\rangle$ and $\langle\tau\rangle$, since, according to (8), the τ-ordering also vanishes at $T_{orb} \gtrsim b^2/U$. Accordingly, $T_S/T_{orb} \sim J/U \sim 0.1$. Actually, for example in $LaMnO_3$, we have $T_S = 100°$ K and $T_{orb} = 900°$ K, which again is in good agreement with the theoretical estimate.

5. ALLOWANCE FOR THE LOCAL JAHN-TELLER EFFECT

We now discuss the connection between the proposed superexchange orbital-ordering mechanism and the usual Jahn-Teller effect. The Jahn-Teller effect becomes manifest primarily in a local distortion of the anion environment of a given ion, which is possible also at low concentration of such ions (transition-element impurities in a nonmagnetic matrix[13]). In concentrated compounds, on the other hand, there can occur a cooperative ordering of the orbitals, which is usually attributed to the elastic interaction of the local deformations at different centers. The former effect (local deformations) is characterized by a rather large constant, and it is also possible that the local distortions due to the Jahn-Teller effect exist also above T_{orb}[3], and the superexchange considered above makes an appreciable contribution to the cooperative ordering; in this case, these two approaches complement rather than contradict each other.

From this point of view, we can understand also the properties of substances with Mn^{3+} and Cr^{2+}. The calculations of the local distortions near Jahn-Teller ions usually indicate[1] that both near Cu^{2+} and near Mn^{3+} the anion octahedron becomes elongated (one long axis and two short ones). It was found above that from the point of view of superexchange, the favored orbitals in perovskites are the singly-occupied ones of the type $d_{z^2-x^2}$ ($\theta = \pi/3$). For the Cu^{2+} ion (hole orbital), the local octahedron then becomes elongated; thus, the two factors, superexchange, and the local Jahn-Teller effect act in the same direction in this case. Indeed, in $KCuF_3$ we actually have $\theta \approx \pm 60°$[12]. On the other hand, for ions with d^4 structure (Mn^{3+}, Cr^{2+}), an orbital $d_{z^2-x^2}$ occupied by an electron would lead to a local oblate octahedron and to a pseudotetragonal deformation of the crystal with $c/a > 1$; in actual fact, however, $c/a < 1$ in $LaMnO_3$ and $KCrF_3$. The local Jahn-Teller effect, however, calls for the electron to occupy an orbital of the type d_x^2 ($\theta = \pm 120°$); the simultaneous action and competition of these two effects, the local Jahn-Teller effect and superexchange, can indeed explain the intermediate type of occupied orbital with $\theta \approx 90°$.

Mathematically, the local Jahn-Teller effect can be taken into account by adding to the energy, for each center, the quantity[1]

$$\Delta E_i = \frac{b^2}{U} g \cos 3\theta_i. \tag{11}$$

As a result of this factor, angles θ equal to $\pm\pi/3$ and π become more convenient at $g > 0$, and angles θ equal to $\pm 2\pi/3$ and 0 become more convenient at $g < 0$ (corresponding to the ions Mn^{3+} and Cr^{2+}). By adding (11) to expression (9) and minimizing with respect to θ_i, we now obtain for all values of i

$$\cos\theta_i = -\left\{\left(1+\frac{J}{U}\right) + \left[\left(1+\frac{J}{U}\right)^2 - 1 + (3g+1)^2\right]^{1/2}\right\} \Big/ 6g, \qquad \theta_1 = -\theta_2 = \pm\theta_3 = \mp\theta_4. \tag{12}$$

Thus, as before, the orbital structure (at least at not very small values of g) is of the type obtained in Sec. 4 above (canted antiferromagnetism in the (001) plane, equivalence of two structures in the c-axis direction), but the corresponding value of the angle θ at small J/U turns out to be as follows: when $g > -1/3$, as before, $\theta \approx \pm\pi/3$; when $g < -1/3$, the angle θ begins to decrease in larger negative g we obtain $\theta \to \pm 2\pi/3$. This calculation confirms the qualitative picture considered above, and demonstrates that this effect indeed can explain the situation in Mn^{3+} compounds. In MnF_3 we actually have $\theta \approx 97°$[2], corresponding to $g = -0.88$.

It can be verified that with such an occupation of the orbitals the spin interaction in a plane perpendicular to c will be ferromagnetic at $J/U \gtrsim 1/4$; this can be ensured by increasing the effective value of J through exchange with t_{2g} electrons.

6. CONCLUSION

It is clear from the foregoing analysis that the proposed superexchange mechanism of ordering of the orbitals describes well the structure and many properties of magnetic perovskites with Jahn-Teller ions, and, in particular, gives a reasonable estimate for the transition temperatures. On this basis, we can conclude that the superexchange is an appreciable part of the thermal interaction responsible for the orbital ordering. In any case, however, even if other factors play an important role, for example, the ordinary cooperative Jahn-Teller ordering, the magnetic structure is determined by the Hamiltonians (5) and (8) derived above, and the spin excitations are coupled with the orbital ones via the crossing terms in (8).

The foregoing analysis dealt specifically with perovskites; the scheme developed here can evidently be used to consider the properties of other classes of compounds, such as spinels[1], and also compounds of rare-earth metals ($DyVO_4$, $TbVO_4$[14], DySb[15]).

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[1)] We consider henceforth the doubly degenerate level e_g, for which the spin-orbit interaction is of no importance.

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