

Orbital ordering in CuGeO_3

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The combined effect of the ligand crystal field and the exchange interaction on the Cu^{2+} cation in CuGeO_3 is examined. It is shown that, if the magnitude of the exchange interaction exceeds the splitting of the energy levels of the $d_{x^2-y^2}$ and d_{xy} orbitals, then an alternate filling of the d orbitals along a chain (orbital ordering) is possible. This effect creates an antiferromagnetic interaction between Cu^{2+} pairs in 90° exchange and a doubling of the lattice period. A Jahn-Teller pseudoeffect causes singletization of the ground state of the antiferromagnetic chain of Cu^{2+} spins. © 1998 American Institute of Physics.
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In artificially synthesized single crystals of CuGeO_3 an anomalous reduction in the magnetic susceptibility has been observed¹ and, subsequently, an antiferromagnetic pairing of Cu^{2+} spins² at low temperatures, or the so-called spin-Peierls phase transition. The latter was first observed in organic compounds^{3,4} and described theoretically as a consequence of the interaction of a one-dimensional antiferromagnetic chain of spins $S=1/2$ with the three-dimensional system of lattice phonons.⁵ Not all features of the magnetic properties of CuGeO_3 can be understood at present.

The strong tetragonal crystal field of the oxygen octahedra stretched along the b_0 axis surrounding the Cu^{2+} cations leads to a doubling of the population of the d_{z^2} orbitals ($z\parallel b_0$ axis) by electrons, suppressing the exchange interaction along the b_0 axis of the crystal and imparting a quasi-one-dimensional exchange interaction along the c_0 axis. The observed⁶ exchange interaction along the c_0 axis is antiferromagnetic, which contradicts the conventional Goodenough-Kanamori rules for 90° indirect coupling. In the neighborhood of the transition temperature $T_{SP}=14$ K, there is a doubling of the lattice period of CuGeO_3 along the a_0 and c_0 axes.⁷ In doped $\text{CuGeO}_3:\text{Si}$ crystals the coexistence of a dimerized (singlet) phase and an antiferromagnetic phase has been observed at temperatures below T_{SP} .⁸ When a high pressure is applied to crystalline CuGeO_3 , the intrachain exchange constant decreases,⁹ while T_{SP} increases.¹⁰

An attempt¹¹ to explain the antiferromagnetic interaction in CuGeO_3 uses the concept¹² of the participation of neighboring nonmagnetic ions in indirect exchange in Cu-O-Cu dimers. In an examination of just the singly filled orbitals,¹¹ it was found that the deviation from quadratic symmetry and hybridization of oxygen atoms with neighboring Ge-O groups and with one another yield strong antiferromagnetic exchange of greater magnitude than the Cu-O-Cu ferromagnetic interaction. Here, unfortunately, the large potential contribution to the Cu-O-Cu interaction resulting from the interaction of filled and half-filled orbitals of neighboring Cu^{2+} was neglected.

In this paper we examine the combined effect on a Cu^{2+}

cation of the ligand crystal field and the exchange interaction with nearest neighbors in the chain. It is shown that when the exchange interaction energy is sufficiently high (larger than the splitting of the energy levels of the $d_{x^2-y^2}$ and d_{xy} orbitals), ordering of the $3d$ electron orbitals of neighboring Cu^{2+} cations becomes possible and this leads to an antiferromagnetic interaction in the chain with 90° indirect coupling and a doubling of the lattice period. By changing the energy of stabilizing the Jahn-Teller pseudoeffect acting on the energy levels of the $d_{x^2-y^2}$ and d_{xy} orbitals, the energy of the spin-orbit interaction may emerge as the reason for the alternating magnitude of the exchange interaction along a Cu^{2+} chain and singletization of the ground state.

1. EXCHANGE INTERACTIONS

The model of indirect-exchange interactions developed by Anderson,¹³ and subsequently by Zavadskii¹⁴ and Eremin,¹⁵ yields an analytic expression for the Goodenough-Kanamori rules for the interaction of an arbitrary pair of $3d$ cations.¹⁶ In this model the interaction of a pair of cations is represented by the sum of the interactions of all the $3d$ orbitals of the cations through the p orbitals of an intermediate ligand. Contributions of practical significance come from only two types of interactions: so-called kinetic and potential exchange. The kinetic exchange integral

$$I_{ij}^{1-1} = -\gamma^4(U_i + U_j) \quad (1)$$

describes the interaction of singly occupied $3d$ orbitals of the i -th and j -th neighboring cations, while the potential exchange integral

$$I_{ij}^{1-0(2-1)} = +\gamma^4 J^{\text{int}} \quad (2)$$

describes the interaction of an empty (or doubly occupied) orbital with one that is singly occupied. The signs in Eqs. (1) and (2) denote antiferromagnetic (−) and ferromagnetic (+) interactions. γ is the bond covalency parameter, given by the mixing coefficient of the atomic wave function of the ligand with the wave function of the cation; its magnitude depends

on the type of coupling (σ or π), the coupling geometry, and the ligand-cation distance. U is the energy of excitation of an electron from a ligand to a cation; its magnitude depends on the population of the $3d$ shell of the cation, the type of ligand, and the coordination. J^{int} is the intraatomic interaction integral; its value depends on the population of the $3d$ shell of the cation.

We neglect the other contributions to indirect exchange known from the literature, since they either are components of the exchange mechanisms discussed here or are associated with double excitation of the ligands. It is best to introduce extended couplings, such as Cu-O-Ge-O-Cu or Cu-O-O-Cu, only if the basic contributions indicated above are absent, since they correspond to higher orders in the small parameter for electron transport. The predictive adequacy of the contributions accounted for in Eqs. (1) and (2) has been verified¹⁶ for different lattices and cations.

Let us consider the exchange interaction in CuGeO₃. The strong tetragonal distortion of the coordination octahedra around the Cu²⁺ cations along the b_0 axis makes it so that the d_{z^2} orbitals are doubly occupied, so that there is no exchange interaction along the b_0 axis. (The interaction between doubly occupied and empty orbitals equals zero.) We have neglected the interaction along the a_0 axis (Cu-O-Ge-O-Cu). Thus, as a result of the tetragonal distortion, CuGeO₃ becomes quasi-one-dimensional magnetically. The electron hole in the copper cations is located in the $d_{x^2-y^2}$ orbitals. The indirect exchange couplings of two Cu²⁺ cations allowed by symmetry and the populations of the individual $3d$ orbitals are shown in Fig. 1. The total indirect exchange integral for such a pair of cations,

$$J(d_{x^2-y^2}, d_{x^2-y^2}) = +4bcJ^{\text{int}} \quad (3)$$

is ferromagnetic and confirms the predictions of the Goodenough-Kanamori rules for 90° coupling. Here $b = \gamma^2$ is the ligand-cation electron transport parameter with σ -coupling ($d_{x^2-y^2} - p_x$ or p_y) and c is the same parameter with π coupling ($d_{xy} - p_x$ or p_y). This means that, for sufficiently strong tetragonal distortion, the $d_{x^2-y^2}$ holes on neighboring Cu²⁺-cations cause the ferromagnetic interaction along the chain along the c_0 -axis. This is correct until the splitting of the $d_{x^2-y^2}$ and d_{xy} orbitals exceeds the energy of the exchange interaction.

2. ORDERED POPULATION OF THE d -ORBITALS OF NEIGHBORING CATIONS

Let us consider the energy of the $3d$ electrons when the coordination octahedron of the surrounding ligands is strongly distorted. Figure 2 shows a qualitative picture of the splitting of the energy levels of the Cu²⁺ ions in crystal fields with various symmetries. The cubic component Dq' of the crystal field for a plane square is considerably smaller than the splitting in an octahedron, if it means anything at all to speak of this for such a ligand configuration.

We are interested in the magnitude of the splitting E_d between the $d_{x^2-y^2}$ and d_{xy} orbitals. This splitting is suppressed by two effects: crystal fields with symmetries lower than tetragonal and the spin-orbit interaction which develops

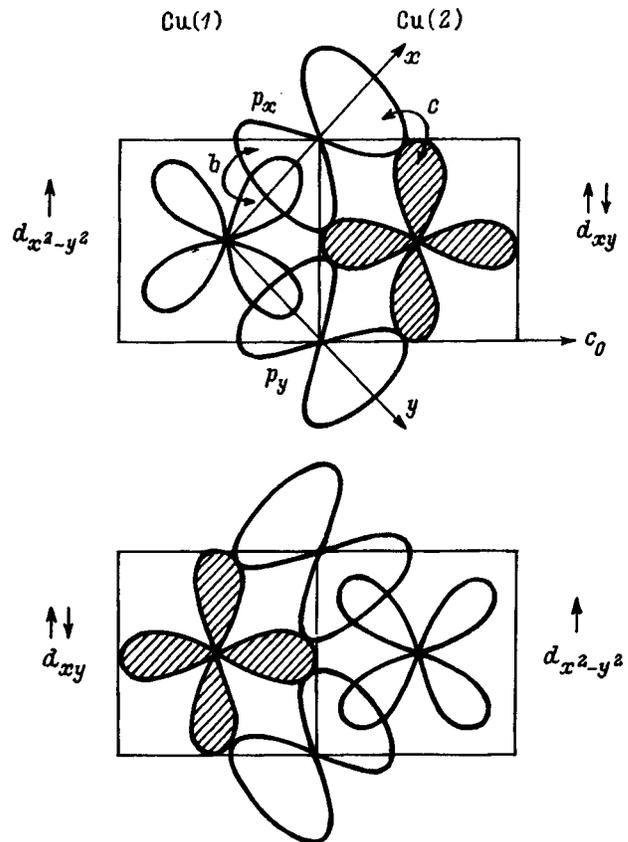


FIG. 1. A schematic representation of oblique exchange couplings of $3d$ orbitals of Cu²⁺(1) and Cu²⁺(2) cations in a CuGeO₃ structure with 90° exchange through intermediate p_x and p_y orbitals of the oxygens in the case where holes occupy the $d_{x^2-y^2}$ orbitals of both cations. The arrows on the d orbitals indicate their electron populations.

when the ion develops an orbital angular momentum owing to mixing of the $d_{x^2-y^2}$ and d_{xy} states. Let us assume that this splitting is small and that holes on neighboring Cu²⁺ cations can be in any of these orbitals. We shall calculate the exchange integrals for the possible cases. For the case when holes are placed in the $d_{x^2-y^2}$ orbitals of neighboring Cu²⁺ ions, we have already estimated the exchange integral (see

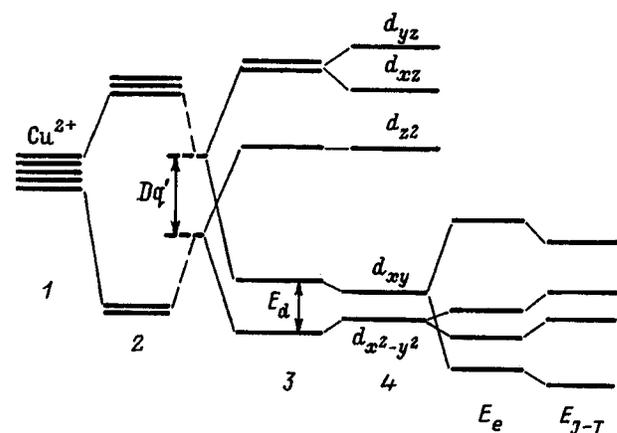


FIG. 2. A schematic diagram of the energy levels of the Cu²⁺ ion in the ligand fields of different symmetry as the octahedron is stretched tetragonally. The ion energy is determined by the $3d$ hole. (1) Free ion, (2) octahedron, (3) plane square, (4) rhombic distortion.

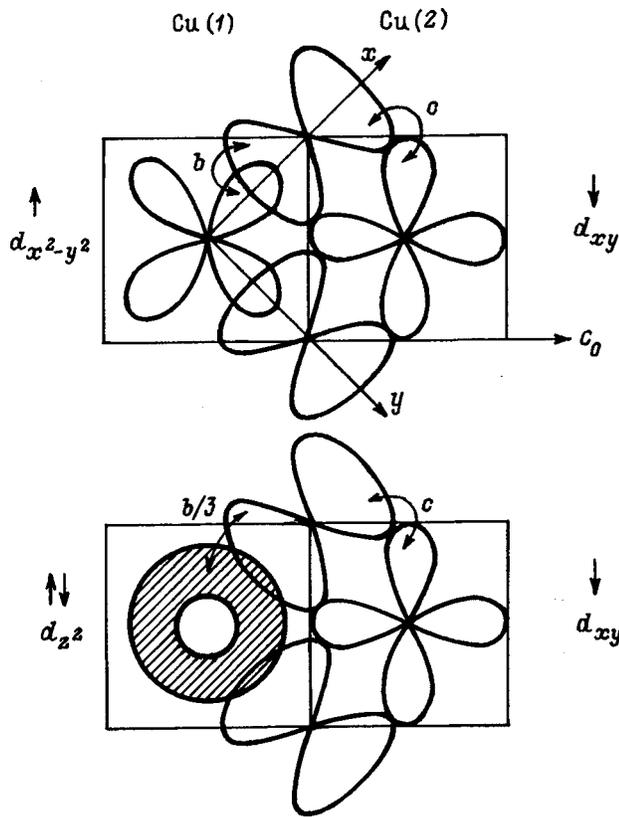


FIG. 3. A schematic representation of oblique exchange couplings of 3d orbitals of neighboring copper cations in a CuGeO₃ structure in the case where holes lie in the $d_{x^2-y^2}$ Cu(1) and d_{xy} Cu(2) orbitals (orbital ordering).

Eq. (3)) and it is positive. For the case when one hole is in the $d_{x^2-y^2}$ orbital of Cu(1) and the other, in the d_{xy} orbital of Cu(2), the oblique exchange couplings allowed by symmetry and the populations of the orbitals are shown schematically in Fig. 3. In this case, the cation-cation interaction integral is the sum of antiferromagnetic and ferromagnetic contributions,

$$J(d_{x^2-y^2}, d_{xy}) = -2bc \left(2U - \frac{1}{3} J^{\text{int}} \right). \quad (4)$$

For the case in which holes lie in the d_{xy} orbitals of neighboring Cu²⁺, we have

$$J(d_{xy}, d_{xy}) = + \frac{16}{3} bc J^{\text{int}}, \quad (5)$$

i.e., there is a ferromagnetic interaction.

The energy U of ligand-cation electronic excitation can be 2–6 eV for Cu²⁺.¹⁶ The intraatomic exchange integral for Cu²⁺, $J^{\text{int}} \sim 1$ eV. Thus, the interaction (4) is antiferromagnetic and its absolute magnitude exceeds the exchange terms (3) and (5). The system, as it tries to minimize its energy through the exchange interaction, chooses the antiferromagnetic ordering determined by the integral (4), i.e., in those cases where the energy E_e of the exchange interaction of a pair of neighboring cations is larger than the splitting E_d of the $d_{x^2-y^2}$ and d_{xy} orbitals in the crystal field, it is to be expected that holes in neighboring Cu²⁺ will occupy different 3d orbitals. For a linear Cu²⁺ chain, one expects alter-

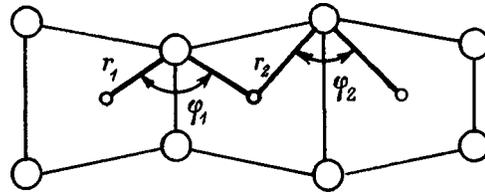


FIG. 4. A schematic representation of the distortions in the equatorial plane of the oxygen octahedra around Cu²⁺ in CuGeO₃ in the sP phase.

nating ($d_{x^2-y^2} - d_{xy} - d_{x^2-y^2} - d_{xy} - \dots$) splitting of the holes and we shall refer to this as the orbital ordering of neighboring cations. The phenomenon of orbital ordering is not new and has been examined theoretically before¹⁷ for the orbitally degenerate e_g level in perovskites. In the case of CuGeO₃, we expect pseudodegeneracy of the energy levels having $e_g(d_{x^2-y^2})$ and $t_{2g}(d_{xy})$ symmetry.

What does this imply? First, as noted above, orbital ordering leads to antiferromagnetic ordering of cation spins, with 90° oblique coupling, along chains along the c_0 axis in CuGeO₃, as has been observed experimentally.⁶ Second, orbital ordering leads to a doubling of the lattice period, which has been observed experimentally⁷ and is evident from the following reasons. The ordered placement of holes in the orbitals of neighboring cations corresponds to an alternation along the c_0 axis of $d_{x^2-y^2}$ orbitals with different populations ($d_{x^2-y^2}^\uparrow - d_{x^2-y^2}^\downarrow - d_{x^2-y^2}^\uparrow - d_{x^2-y^2}^\downarrow - \dots$). The electrons of a cation in which the $d_{x^2-y^2}$ orbital is singly populated shield the charge of the surrounding ligands less, so that the internuclear attractive forces shrink the Cu-O distance in the equatorial plane of the octahedron of this cation. The lattice period is doubled in the direction of the ordered disposition of the orbitals.

3. SINGLETIZATION OF THE GROUND STATE

When the splitting E_d is small enough, the energy levels of the $d_{x^2-y^2}$ and d_{xy} orbitals can be regarded as pseudodegenerate and the Jahn–Teller pseudoeffect must be invoked. When the stabilization energy of the Jahn–Teller pseudoeffect exceeds the spin-orbit interaction energy, it is more advantageous for the system to lower its symmetry to monoclinic. Probably these interactions manifest themselves through the distortion of the bases of the oxygen octahedra and shifts of the Cu²⁺ ions observed by neutron diffraction¹⁸ and illustrated schematically in Fig. 4. In this case, the geometric conditions for the oblique exchange coupling of a central Cu²⁺ ion to the left and right in a chain are different owing to the differences in the bond lengths and angles (r_1, φ_1 and r_2, φ_2). An alternation in the magnitudes of the exchange interactions sets in along the chain, leading to singletization of the ground state, as has been shown theoretically.¹⁹

In a system that has been stabilized by the Jahn-Teller effect, the dependence of the energy of a pair of Cu²⁺ cations on the interaction distance in an oblique Cu-O-Cu bond can be represented schematically by the curve shown in Fig. 5. For low-temperature lattice vibrations, the system is at a lo-

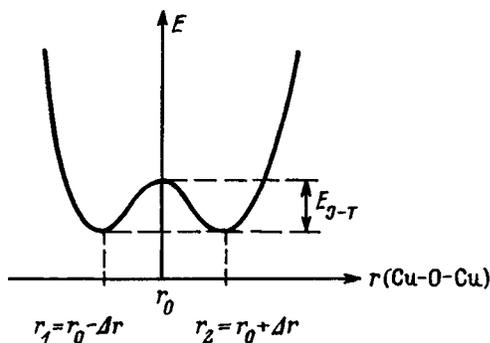


FIG. 5. The energy of a pair of Cu^{2+} cations as a function of the interaction distance in an oblique Cu-O-Cu bond in the equatorial plane of the octahedron. Δr is the change in the equilibrium distance r_0 when the lattice period is doubled. E_{J-T} is the stabilization energy for the Jahn-Teller effect.

cal minimum of the dimerized state. At high temperatures ($kT > E_{J-T}$), the amplitude of the vibrations of the coordination oxygen atoms exceeds Δr , and the base of the octahedron ceases to be distorted, since now the oxygen ions of which it is composed vibrate near the equilibrium distance r_0 . The lattice period is no longer doubled.

It is evident from Fig. 5 that at the temperature $kT_c = E_{J-T}$, the system undergoes a transition from an ordered dimerized state at low temperatures to a disordered state at high temperatures, i.e., the spin-Peierls transition is an order-disorder phase transition. As the phase transition temperature is reached, the chain becomes uniform and, consequently, the singlet state is destroyed.

4. EXAMPLES OF ORBITAL ORDERING

Researchers have encountered difficulties in interpreting the exchange interaction of Cu^{2+} cations with 90° oblique coupling even in studies of the properties of so-called exchange clusters, which consist of isolated copper dimers. In Cu(II) dihydroxo complexes, the oblique 90° exchange takes place through dihydroxo bridges.²⁰ Measurements showed that both the magnitude and sign of the exchange integral for a ground-state copper dimer vary, depending on the type of bridge. The exchange integral for the excited state of the dimer is ferromagnetic. Special exchange mechanisms have been developed to explain these results.¹²

Based on the concept of orbital ordering discussed above, however, it is possible to look at copper dimers from a new standpoint. As long as the energy of the exchange interaction is less than the splitting of the levels of the d_{xy} and $d_{x^2-y^2}$ orbitals, orbital ordering does not set in and ferromagnetic exchange (3) acts between a pair of copper cations. When the exchange energy is high enough, the dimer, minimizing its energy with respect to exchange, chooses a state of orbital ordering described by the antiferromagnetic exchange integral (4). In this case, the state corresponding to a $\text{Cu}(d_{x^2-y^2})\text{-Cu}(d_{xy})$ pair should be regarded as the ground state, while the state previously regarded as the ground state, $\text{Cu}(d_{x^2-y^2})\text{-Cu}(d_{x^2-y^2})$, should be regarded as excited. The change in the absolute magnitudes of the exchange integrals in the hydroxo complex series is caused by a change in the

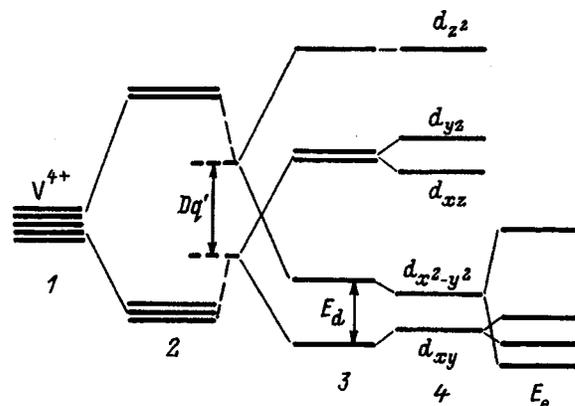


FIG. 6. A schematic diagram of the energy levels of the V^{4+} ion in fields of various symmetry as the octahedron is stretched tetragonally. The ion energy is determined by the $3d$ electron. (1) Free ion, (2) octahedron, (3) tetragonal compression, (4) rhombic distortion.

ligand-cation electron-transport parameters determined by the different composition and geometry of the ligands.

Another example of orbital ordering is $(\text{VO})_2\text{P}_2\text{O}_7$. The question of which model, dimerized or staircase chain, is better suited to describing this material has been discussed in the literature.^{21,22} We shall show that the concept of orbital ordering leads us to the conclusion that $(\text{VO})_2\text{P}_2\text{O}_7$ is best described by an ensemble of isolated dimers.

The vanadium cations in $(\text{VO})_2\text{P}_2\text{O}_7$ lie within coordination octahedra of surrounding oxygen atoms which are compressed along the a_0 axis. Along the a_0 axis, neighboring octahedra are bound by a shared oxygen atom, which allows $\text{V1}(d_{z^2})\text{-V2}(d_{z^2})$ oblique coupling. Isolated V^{4+} pairs lie along the b_0 axis. The octahedra of these neighboring V^{4+} have edges in common in the (b_0c_0) plane, giving rise to 90° exchange coupling along the b_0 axis. Along the c_0 axis the octahedra of neighboring V^{4+} are separated by layers containing phosphorus. The splitting of the energy levels of a V^{4+} ion in the compressed octahedron is illustrated schematically in Fig. 6. The absence of electrons in the d_{z^2} orbitals makes it possible to neglect exchange along the a_0 axis, i.e., $(\text{VO})_2\text{P}_2\text{O}_7$ should be regarded as an ensemble of isolated V^{4+} dimers. For sufficiently large splitting of the levels of the $d_{x^2-y^2}$ and d_{xy} orbitals, the electrons on both of the neighboring V^{4+} will lie in the d_{xy} orbitals. In this case, the 90° oblique interaction in the dimer leads to ferromagnetic exchange (5) and $(\text{VO})_2\text{P}_2\text{O}_7$ will be an ensemble of isolated ferromagnetic dimers. If, on the other hand, $E_e > E_d$, then we should expect orbital ordering in the dimer ($d_{x^2-y^2} - d_{xy}$), which leads to an antiferromagnetic interaction (4), as observed experimentally.²¹ The observed gap in the magnetic excitations²² is natural for isolated dimers, although the rhombic distortions which occur during orbital ordering will also make some contribution to this gap. It is appropriate to interpret the temperature dependence of the magnetic susceptibility of this material in terms of a model of isolated antiferromagnetic dimers, although the forms of this dependence are similar for isolated dimers, a chain, and a single staircase.

A new material, $\text{CaCuGe}_2\text{O}_6$, that has the properties of a

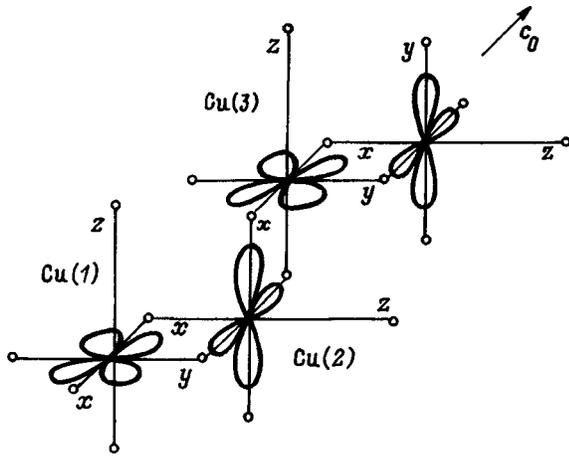


FIG. 7. Local axes of the oxygen octahedra around Cu^{2+} in $\text{CaCuGe}_2\text{O}_6$. The $3d$ orbitals, populated by holes, are shown schematically for the case of orbital ordering along a Cu^{2+} chain ($d_{xy}-d_{x^2-y^2}-d_{xy}-d_{x^2-y^2}-\dots$), leading to a model of ferromagnetically coupled antiferromagnetic dimers.

spin-Peierls system with $T_{SP} \approx 40$ K, has recently been synthesized.²³ Here the copper cations form zig-zag chains along the c_0 -axis. The local symmetry around the Cu^{2+} is shown schematically in Fig. 7. The sizes of the axes of the octahedra in $\text{CaCuGe}_2\text{O}_6$ are different, with $z > y > x$. Under the action of the tetragonal distortions of the octahedra when the exchange interaction is small, the holes in all the Cu^{2+} cations lie in the $d_{x^2-y^2}$ orbitals (see Fig. 2). In this case, the oblique exchange integral of neighboring cations is given by

$$J_{12} = J_{23} = +6bcJ^{\text{int}}, \quad (6)$$

i.e., it leads to a ferromagnetic chain. When $E_e > E_d$, the exchange interaction will also determine the distribution of the electrons among the $3d$ orbitals based on the minimum energy of a cation pair. We have two possible ways of distributing the holes among the $3d$ orbitals of neighboring cations: $d_{xy}-d_{x^2-y^2}$ and $d_{xy}-d_{xy}$. In the first version,

$$J_{12}(d_{xy}, d_{x^2-y^2}) = -2bc \left(2U - \frac{5}{3} J^{\text{int}} \right), \quad (7)$$

and

$$J_{23}(d_{x^2-y^2}, d_{xy}) = +2c(2b+c)J^{\text{int}}, \quad (8)$$

i.e., the Cu(1)-Cu(2) interaction integral is antiferromagnetic, while the Cu(2)-Cu(3) integral is ferromagnetic. $3d$ orbitals of copper, occupied by holes, are shown in Fig. 7 for this version. In the second version,

$$J_{12}(d_{xy}, d_{xy}) = J_{23}(d_{xy}, d_{xy}) = +2c \left(\frac{8}{3} b + c \right) J^{\text{int}}. \quad (9)$$

In order to evaluate the exchange integrals (6)–(9), we have to know the ligand-cation electron transport parameters for a given crystal. If, on the other hand, we are interested in the relative values of these integrals, rather than their absolute values, then we can use standard estimates of these parameters for other structures. Taking the values $b = 0.02$, $c = 0.01$, $U(\text{Cu}^{2+}) \approx 4$ eV, and $J^{\text{int}}(\text{Cu}^{2+}) \approx 1$ eV for the octahedral sites of the spinel structure,¹⁶ we obtain +14, -60,

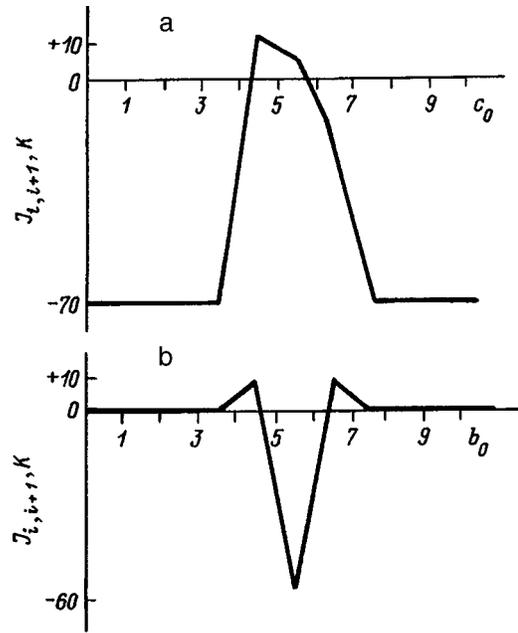


FIG. 8. Dependence of the Cu-Cu-exchange interaction on the cation number in a chain along the c_0 axis (a) and on the number of the chain along the b_0 axis (b) when the Si^{4+} dopant lies near sites 5 and 6.

+12, and +15 K, respectively, for the integrals (6)–(9). The total (left+right along the chain) exchange interaction of a copper cation will be greatest for the hole distribution described by the integrals (7) and (8) and shown in Fig. 7, $|-60| + 12 = 72$ K, compared to 28 and 30 K for the distributions (6) and (9). Thus, for an exchange interaction energy exceeding the splitting of the $d_{x^2-y^2}$ and d_{xy} orbitals, the Cu^{2+} chain in $\text{CaCuGe}_2\text{O}_6$ is a chain of antiferromagnetic dimers with a ferromagnetic interdimer interaction. Probably the intradimer interaction is ~ 5 times larger than the interdimer interaction.

The oblique coupling model is also useful for analyzing exchange interactions in crystals with different substitutions. In doped $\text{CuGeO}_3:\text{Si}$ crystals, because of differences in the ionic radii of Ge^{4+} and Si^{4+} , the initial local symmetry of neighboring oxygen octahedra may be distorted through distortion of the octahedron in the base plane and a reduction in the tetragonal stretching or compression of the octahedron. In the first case, the ordered filling of the d orbitals in Cu^{2+} is disrupted and ferromagnetic pairs develop at the end of the chains. Since the Si dopant touches four neighboring chains, small degrees of doping produce a substantial number of ferromagnetic centers in the crystal, which must cause a rise in the paramagnetic susceptibility as 0 K is approached. In the second case, there is a possibility of populating the d_{z^2} orbitals of the copper cations nearest the impurity with holes, and this leads to a change in the oblique exchange interactions. The perturbation of the pairwise exchange interactions owing to the presence of the Si^{4+} impurity is shown in Fig. 8. The Si^{4+} dopant is bound to the two nearest Cu^{2+} sites along the a_0 axis and to two along the b_0 axis. In Fig. 8 these sites are indicated by the numbers 5 and 6. The change in the interaction also affects the next neighbors in the lattice. As a result, we obtain a perturbation of the pairwise interaction

along the chain, illustrated qualitatively in Fig. 8a, which leads to a change in the sign of the exchange interaction near the substituted cation. The variation in the exchange along the b_0 axis illustrates the development of interchain interactions (Fig. 8b). It is evident that the chains closest to the impurity are coupled by strong antiferromagnetic exchange. The chains after them are coupled ferromagnetically and, at large distances, the interaction is zero. Clearly, with increasing concentration of substitute Si^{4+} cations, the quasi-one-dimensional CuGeO_3 is converted into a quasi-two-dimensional system whose magnetic structure depends on the relationship of the antiferromagnetic and ferromagnetic bonds. It is quite possible that the appearance of an antiferromagnetic phase at low temperatures⁸ is a consequence of these effects.

It has been shown therefore, that when the nature of the energy structure of the Cu^{2+} cation in the crystal field of crystalline CuGeO_3 is taken into account, ordered filling of the d orbitals along a chain of cations is possible when the exchange interaction energies of the cation pairs exceed the split in energy of the $d_{x^2-y^2}$ and d_{xy} orbitals. Orbital ordering produces an antiferromagnetic exchange interaction along a Cu^{2+} chain with 90° oblique coupling and a doubling of the lattice period.

When the Jahn-Teller stabilization energy exceeds the spin-orbit interaction energy, the reduction in symmetry of the base plane of the octahedron leads to an alternation in the angles and lengths of the exchange coupling in the Cu^{2+} chain, i.e., to alternation in the exchange interaction parameter and to a doubling of the lattice period.

$\text{CaCuGe}_2\text{O}_6$ can be represented by one-dimensional chains of antiferromagnetic dimers with a ferromagnetic interdimer coupling. The intradimer interaction is 5 times stronger than the interdimer coupling.

The entire analysis of exchange interactions in this paper has been done in terms of cubic symmetry. We assume that the nonorthogonality effects which arise with deviations from cubic symmetry are important for estimating the absolute magnitudes of the interactions, but can hardly affect the fundamental conclusions reached here.

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