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The Jahn-Teller effect and magnetism: transition metal compounds

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The properties of magnetic insulators containing orbitally degenerate transition metal ions (Jahn-Teller ions) are discussed. The Jahn-Teller effect in these insulators causes structural phase transitions, lowers the lattice symmetry, and gives rise to an orbital ordering. Various interactions responsible for these effects are discussed: the electron-lattice, quadrupole-quadrupole, and exchange interactions. The mutual effects of the orbital ordering and the magnetic properties of corresponding compounds are discussed. The exchange interaction in the cases of twofold and threefold orbital degeneracy is discussed. The effect of a magnetic field on the orbital and magnetic structure and the temperature dependence of the exchange interaction are studied. The properties of several representative compounds containing Jahn-Teller ions are discussed.

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1. INTRODUCTION

At first glance, the two phenomena in the title of this review do not seem to have all that much in common. The "Jahn-Teller effect" is the name applied to several phenomena which occur in systems which have a degenerate electronic state. This degeneracy makes the symmetric configuration of atoms unstable, gives rise to a specific and strong electron-vibrational (vibron) interaction, causes structural phase transitions in several cases which lower the symmetry of the crystal, etc. Magnetism, on the other hand, deals primarily with the properties which result from the electron spins, and although the lattice is important in several effects it is usually not a decisive factor.

It nevertheless turns out that there is a large and distinctive class of magnetic materials in which the Jahn-Teller effect plays an extremely important role, largely determining not only the structural properties but also the magnetic properties. In turn, the exchange

interaction, of obvious importance to magnetism, may substantially affect the lattice in such systems, inducing structural transitions. The intimate relationship between the structural and magnetic properties distinguishes this class of materials and makes it particularly interesting. These questions are the subject of this review.

Specifically, this review will deal with materials in which the ground state of the magnetic ions in the symmetric configuration has an orbital degeneracy in addition to the Kramers (spin) degeneracy. This is by no means an exotic situation: A simple analysis shows that the materials of this class may outnumber ordinary, "classical" magnetic materials within the larger class of magnetic insulators.

For the most part, the review will deal with the properties of transition metal compounds. Many rare earth compounds exhibit similar effects, but they are manifested in different ways because of the strong spin-or-

TABLE I. Some examples of ordinary and Jahn-Teller magnetic materials.

	Crystal structure	Magnetic structure
Perovskites		
Ordinary: KNiF ₃	Cubic (the magnetic ions form a simple cubic lattice)	Two-sublattice antiferromagnet with antiparallel spins of nearest neighbors (of the G type) ²
JT: KCuF ₃	With tetragonal distortions ($c/a < 1$); doubling of the period in the basis plane	Ferromagnetic planes coupled antiferromagnetically (of the A type). ³ KCuF ₃ is an example of a quasi-one-dimensional antiferromagnet (the exchange integral along the c axis is much larger than that in the basis plane)
KCrF ₃	With orthorhombic distortions	
LaMnO ₃	The same (transition to the cubic phase at $T_c = 900$ K)	
Stratified compounds with a square lattice of transition ions ("two-dimensional perovskites")		
Ordinary: K ₂ NiF ₄	Two-dimensional perovskite (perovskite-like square lattice in a layer)	Quasi-two-dimensional antiferromagnet
JT: K ₂ CuF ₄ Rb ₂ CrCl ₄ (C ₂ H ₅ NH ₃) ₂ CuCl ₄	Distorted two-dimensional perovskites with a doubling of the period in the layer	Quasi-two-dimensional ferromagnets (weak ferromagnetic or antiferromagnetic interaction between layers)
Spinel		
Ordinary: NiFe ₂ O ₄	Cubic	Neel spin configuration
JT: CuFe ₂ O ₄	Tetragonal, $c/a = 1.06$; transition to a cubic phase at $T_c = 633$ K	The same
Mn ₃ O ₄	Tetragonal, $c/a = 1.16$, $T_c = 1143$ K	Yafet-Kittel configuration (a more complicated spin structure is possible). The magnetic structures are significantly related to an exchange between ions in tetrahedral (A) and octahedral (B) sites and have no special properties for spinels with e_g ions.
Rutile		
Ordinary: NiF ₂	Tetragonal (magnetic ions forming a volume-centered lattice)	Two-sublattice antiferromagnet with antiparallel spins of nearest neighbors
JT: CrF ₂	With monoclinic distortions	The same
CrCl ₂	With orthorhombic distortions	Antiferromagnet with alternating (110) ferromagnetic planes
CuF ₂	With monoclinic distortions	Magnetic lattice is doubled in comparison with the crystal lattice
Garnets		
Ordinary: Ca ₃ Fe ₂ Ge ₂ O ₁₂	Cubic (Fe ³⁺ ions in octahedral surroundings form a bcc lattice)	Two-sublattice antiferromagnet with antiparallel spins of nearest neighbors
JT: Ca ₃ Mn ₂ Ge ₂ O ₁₂ (Mn ³⁺ Jahn-Teller ion)	With tetragonal distortions, $c/a = 1.003$; transition to the cubic phase at $T_c = 400$ K (Ref. 85)	Complex noncollinear structure with moments lying on a cone whose axis is the c axis ⁸⁴

*The experimental data are taken primarily from Refs. 2-4.

bit interaction. The properties of rare earth compounds exhibiting a Jahn-Teller effect are discussed in detail in the review by Gehring and Gehring.¹

Compounds which contain ions having an orbital degeneracy ("Jahn-Teller ions") are found among magnetic insulators of essentially all classes. Their properties are significantly different from those of the corresponding materials containing "ordinary" ions: Their crystal structures are distorted; they frequently exhibit structural phase transitions; the magnetic structure is also more complicated in most cases; and they frequently exhibit an anomalously pronounced magnetic anisotropy and magnetostriction. Some representative compounds are listed in Table I, where their properties

are compared with those of ordinary magnetic materials.

We first notice that the symmetry is typically lower for materials containing Jahn-Teller ions, and structural transitions occur. Such effects, which occur in concentrated Jahn-Teller systems, result from an interaction between the Jahn-Teller ions and are collectively referred to as the "cooperative Jahn-Teller effect." The transitions which result from the cooperative effect are unique among the many and varied structural transitions which occur in solids, for the following reason: These transitions seem to constitute essentially the only case in which the elementary, microscopic nature of the transition is known precisely (another case might be transitions involving the excitation of space-charge waves). In the case of the cooperative effect it is possible, with knowledge of nothing more than the chemical composition of the crystal (i.e., the nature of the ions in it), to unambiguously predict a structural transition in the crystal which lowers the symmetry. For most transitions of other types, e.g., for ferroelectrics, such predictions are not possible at present.

It is also clear from Table I (which gives a far from exhaustive list of Jahn-Teller magnetic materials), that in nearly all cases the Jahn-Teller systems have unusual magnetic properties in addition to their lower crystal symmetry. Perhaps the clearest example is the compound KCuF₃, in which the magnetic properties are definitely of a quasi-one-dimensional nature, while the crystal lattice remains nearly cubic. Another interesting observation is that ferromagnetic ordering occurs more frequently in compounds containing Jahn-Teller ions (compare K₂CuF₄ and K₂NiF₄, for example). Our purpose in this review will be to explain these and other distinctive features of these materials.

2. JAHN-TELLER IONS IN CRYSTALS

To describe the state of an electron in a d level ($l = 2$) in a transition metal ion we need to specify, in addition to the spin, the orbital quantum number: $l^z = -2, -1, \dots, +2$. In a solid, the fivefold-degenerate d level is split by the crystal field, but the orbital degeneracy is not lifted completely in the crystal symmetry is sufficiently high. In a field of cubic symmetry (for example, in octahedral surroundings, Fig. 1a), the one-electron d level splits into a threefold-degenerate level (t_{2g}) and a two-fold-degenerate level (e_g) [in tetrahedral surroundings (Fig. 1b) there is an inversion of terms, and the e_g levels lie below t_{2g}]. In a multielectron ion these levels are systematically filled by electrons with parallel spins in accordance with Hund's rule; it is obvious, however, that orbital degeneracy may remain.¹⁾ If the

¹⁾We will use the single-electron model everywhere in this review, and we will not switch to the complete systematics of many-electron terms which is customarily used. Although this approach is not always completely rigorous, it does yield a clear qualitative interpretation of these phenomena, and in a study of the Jahn-Teller effect it is very convenient: Knowing nothing more than the number of d electrons in the ion we are frequently in a position not simply to analyze the stability of the original symmetric configuration but also to predict the type of distortion in several cases.

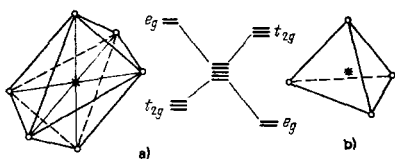


FIG. 1. Splitting of the d level of an ion. a—In octahedral surroundings; b—in tetrahedral surroundings.

spin-orbit interaction is ignored, for example, only the ions with d^3 , d^5 , and d^8 configurations would have a non-degenerate state in an octahedron; all other ions would have an orbital degeneracy (twofold if there is a single electron or hole in an e_g level or threefold if there are one or two electrons or holes in a t_{2g} level). It has been established (see Ref. 5, for example) that the orbital angular momentum is completely frozen for e_g levels: The e_g states have real wave functions $d_{z^2-x^2-y^2}$ (we will use the designation d_{z^2} below) and $d_{x^2-y^2}$, which correspond to the states $|l^z=0\rangle$ and $(1/\sqrt{2})(|l^z=+2\rangle + |l^z=-2\rangle)$. For them, the spin-orbit interaction is inconsequential. The corresponding ions with the configurations (in octahedral surroundings) d^4 (Cr^{2+} , Mn^{3+}) and d^9 (Cu^{2+} , Ag^{2+}) or (in tetrahedral surroundings) d^1 (Ti^{3+} , V^{4+}) and d^6 (Fe^{2+} , Ni^{3+}) are usually called "Jahn-Teller ions" (in the narrow sense of the term). Many anomalous properties are also exhibited by compounds containing these ions: structural phase transitions and a lowering of the lattice symmetry, nontrivial magnetic structures, an exchange with an anomalous temperature dependence, etc. (Table I). In contrast, the spin-orbit interaction may lift the degeneracy for ions in which the t_{2g} shell is partially filled [the wave functions of this shell are d_{xy} , d_{xz} , d_{yz} ; alternatively, they may be characterized by an effective angular momentum $l_{\text{eff}} = 1$ with the eigenfunctions $|l^z=0\rangle = d_{xy}$, $|l^z=\pm 1\rangle = (\mp 1/\sqrt{2}) \times (d_{xz} \pm id_{yz})$]. Again, however, these ions and the corresponding magnetic materials retain many anomalous properties, which are ultimately due to this partial filling of the initial t_{2g} states. In the first place, several magnetic compounds of this type also undergo structural transitions of a purely Jahn-Teller nature, with the result that the spin-orbit interaction again becomes ineffective. Even if the spin-orbit interaction is predominant, however, these materials exhibit several unusual properties: The magnetic ordering is frequently accompanied by significant lattice distortions; they exhibit a giant magnetostriction (one or two orders of magnitude stronger than the ordinary magnetostriction); the magnetic anisotropy is extremely strong; etc. Among the materials of this type are compounds which contain such important ions as Fe^{2+} and Co^{2+} (there are many others). Below, we will focus on Jahn-Teller systems with a twofold degeneracy; because of the special nature of systems with t_{2g} electrons, we will consider these systems separately in Section 5 (we will also be touching briefly on certain aspects of t_{2g} systems in the following sections).

The difference in the roles played by the spin-orbit interaction—the difference which is responsible for the difference between the properties of t_{2g} and e_g ions—also causes differences between transition metal compounds and rare earth compounds. In rare earth com-

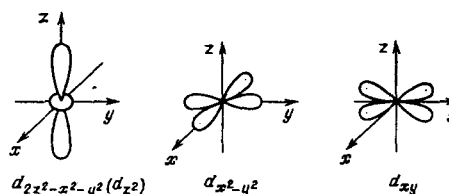


FIG. 2. Distribution of the electron density for the $e_g(d_{z^2}, d_{x^2-y^2})$ and $t_{2g}(d_{xy}, d_{xz}, d_{yz})$ orbitals. The d_{yz} and d_{xz} orbitals have the same shape as the d_{xy} orbital, with an appropriate change in axes.

pounds the exceedingly strong LS coupling keeps the orbital and spin states of an ion interrelated in all situations, and the only good quantum number is the total angular momentum J . Correspondingly, the magnetic ordering in these compounds is usually accompanied by a lattice distortion (there are exceptional cases), or the magnetic ordering and the orbital (Jahn-Teller) ordering turn out to be mutually exclusive.⁶ In compounds of transition metals, in contrast, especially those with a twofold degeneracy (e_g), these transitions occur at different temperatures, and the relationship between the magnetic ordering and the orbital ordering is more complicated.

The specific form of the wave functions of the e_g and t_{2g} electrons, given above, may also help explain the very nature of the level splitting by a crystal field. The electron density distribution in these wave functions is shown in Fig. 2. It is obvious from simple electrostatic considerations that the repulsion of the electron cloud from the negatively charged ligand ions in octahedral surroundings is stronger for the e_g orbitals (which are pointed directly at these ions), and for this reason the energy of the e_g levels is higher than that of the t_{2g} levels in this case. In tetrahedral surroundings we find the opposite situation. It is also clear that if the ideal cubic symmetry is preserved (in the absence of octahedral distortions) the e_g levels themselves and also the t_{2g} levels will have identical energies. This qualitative picture will be helpful below.

3. THE JAHN-TELLER EFFECT FOR ISOLATED CENTERS AND THE COOPERATIVE JAHN-TELLER EFFECT

A fairly extensive literature has been built up on the various aspects of the interaction of electrons with the lattice in the case of a level degeneracy (see, for example, Refs. 1, 5, and 7-10). The history of this question actually begins with the papers in Ref. 11. In these papers a theorem is proved according to which any configuration of atoms or ions (except a linear chain) in which there is a degenerate electron ground state is unstable with respect to deformations which lower the symmetry of the configuration (the degeneracy here is understood to be a degeneracy other than the Kramers degeneracy). It is clear from no more than the formulation of this theorem that the interaction of electrons with ion vibrations in Jahn-Teller systems should have some peculiarities. The entire range of phenomena which result from the degeneracy of the

ground term are referred to as the "Jahn-Teller effect." In this section of the review we will give only a simplified qualitative description of the Jahn-Teller effect; all the details can be found in the cited literature.

a) *The Jahn-Teller effect for an isolated center.* We first consider the Jahn-Teller effect for an isolated center, e.g., a Jahn-Teller impurity in a crystal. We assume that the ground state is twofold-degenerate in the symmetric phase. The lowering of the symmetry, characterized by a deformation δ , causes a splitting of the electronic levels which is linear in δ , while the decrease in elastic energy is $\sim \delta^2$. As a result, the symmetric configuration is always unstable, and there is a lifting of the degeneracy, accompanied by a lowering of the symmetry. As we will see below, the physical reason for these events is an interaction between the electrons of the degenerate level and the deformation of the surroundings or, equivalently, an interaction with the vibrations of the ligands surrounding the given ion. In the simplest case the energy of the system may be written as

$$E(\delta) = \frac{C}{2} \delta^2 \pm g\delta, \quad (1)$$

where the parameter δ is a measure of the deformation, C is the elastic modulus, g is the constant of the interaction of the electronic subsystem with the deformation δ , and the second term in (1) describes the change in the energy of the electronic levels. The equilibrium configuration is found by minimizing (1); it corresponds to $\delta_{\pm} = \pm g/C$.

What does the wave function of the system look like? If there are no distortions, the wave function in the adiabatic approximation can be written as the product of an electronic wave function $\psi_{1,2}(r)$ (a superposition of two degenerate states) and a nuclear wave function $\varphi(R)$: $\Phi_{1,2}(R, r) = \varphi(R) \psi_{1,2}(r)$. The nuclear wave function describes the state of the surrounding ions with the equilibrium position corresponding to the symmetric configuration ($\delta=0$), with small oscillations about this equilibrium position.

The electron-lattice interaction lifts the degeneracy, and the new equilibrium position corresponds to a deformation $\delta_{\pm} = \pm g/C$. At the position δ_{+} the lower level is level 1, say, while in position δ_{-} the lower level is level 2. Corresponding to the different electronic wave functions ψ_1 and ψ_2 are different nuclear wave functions, φ_1 and φ_2 , with the equilibrium positions δ_{\pm} :

$$\Phi_1(R, r) = \varphi_1(R) \psi_1(r), \quad \Phi_2(R, r) = \varphi_2(R) \psi_2(r); \quad (2)$$

here Φ_1 and Φ_2 are the wave functions of two equivalent

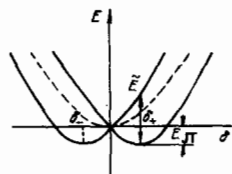


FIG. 3. Schematic deformation dependence of the energy for the case of twofold degeneracy. Here E_{JT} is the lowering of the energy due to the Jahn-Teller effect.

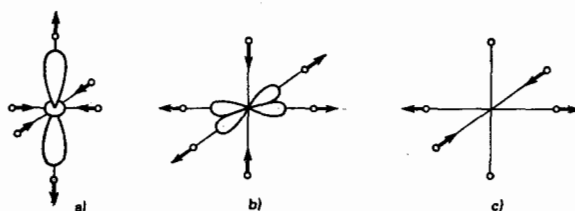


FIG. 4. Displacements of anions: a—corresponding to the filled d_{z^2} orbital; b—corresponding to the filled $d_{x^2-y^2}$ orbital (the Q_2 vibrational mode); c—the Q_2 vibrational mode (which stabilizes a certain superposition of the d_{z^2} and $d_{x^2-y^2}$ orbitals).

ground states of the system, with corresponding energies

$$E_{JT} = \frac{C}{2} (\delta_{\pm})^2 \mp g\delta_{\pm} = -\frac{g^2}{2C}. \quad (3)$$

The wave functions Φ_1 and Φ_2 are called "vibron functions." Figure 3 shows the δ dependence of the energy for these two types of deformations; the energy minima correspond to the functions Φ_1 and Φ_2 , and the excited states $\varphi_2\psi_1$ and $\varphi_1\psi_2$ correspond to the energy \bar{E} , indicated in this figure.²⁾

As a specific example we consider the case of ions for which there is a single electron in the e_g level and which are in octahedral surroundings. The charge distribution corresponding to the degenerate orbitals $d_{2z^2-x^2-y^2}$ (d_{z^2}) and $d_{x^2-y^2}$ is shown schematically in Fig. 4; the circles here represent negatively charged ligands (O^{2-} or F^- ions, for example). Figure 4 helps explain the nature of the Jahn-Teller distortions: If the d_{z^2} orbital is filled, conditions will favor a stretching of the octahedron along the z axis because of Coulomb repulsion (as indicated by the arrows in Fig. 4). The deformation corresponding to the orbital $d_{x^2-y^2}$, in contrast, tends to flatten the octahedron. These two possibilities are equivalent in the harmonic approximation, as was found above. When the anharmonicity of the lattice is taken into account, one possibility may prove preferred; just which will depend on the parameters. Experiments show that the stretching ($c/a > 1$) is usually preferred (specifically, for the Cu^{2+} , Cr^{2+} , and Mn^{3+} ions).

In a real cubic crystal there is yet another sort of latitude: Even if we know that the octahedron will be stretched, the particular axis along which the stretching occurs may be any of the three crystal axes, x , y , z . Experimentally, it is observed that this random orientation does in fact occur for impurities. For each impurity, the orientation is determined primarily by the local stresses which are always present in real

²⁾Strictly speaking, the Jahn-Teller effect does not imply a lifting of the degeneracy for an isolated center. It corresponds rather to simply an instability of the symmetric state. As is clear from Eq. (3) and Fig. 3, the deformations δ_{\pm} are equivalent, and the twofold degeneracy is preserved, but for new electronic-vibronic (vibron) states, rather than for purely electronic states. Thermal and quantum transitions can occur between the states Φ_1 and Φ_2 ; these transitions are the essence of the so-called dynamic Jahn-Teller effect (more on this below).

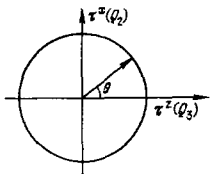


FIG. 5. Description of the Jahn-Teller distortion and of the orbital ordering in the plane of the variables τ^x , τ^y or of the variables Q_2 , Q_3 . The angle θ characterizes an arbitrary linear superposition of e_g orbitals. The orbitals $d_{x^2-y^2}$, d_{xz} , and d_{yz} and, correspondingly, octahedra stretched along the z , x , and y axes correspond to the angles $\theta = 0$, $(2\pi/3)$, $(4\pi/3)$. The orbitals $d_{x^2-y^2}$, d_{yz} , d_{xz} and the correspondingly compressed octahedra correspond to the angles π , $-\pi/3$, $+\pi/3$. For the case of a hole orbital (for example, for the Cu^{2+} ion in octahedral surroundings) the signs of the deformations are opposite to that of the electronic deformation. In other words, the angle θ in the Q_2 , Q_3 plane is replaced by $\pi - \theta$.

crystals.³⁾ The axes of the deformed octahedra can be oriented by a uniaxial external pressure.

In a mathematical description of the e_g levels, some fictitious spin or pseudospin $\tau = 1/2$ may be associated with the two wave functions $d_{x^2-y^2}$ and d_{z^2} , in such a manner that the wave function $d_{x^2-y^2}$ corresponds to the value $\tau^z = 1/2$, while d_{z^2} corresponds to $\tau^z = -1/2$. An arbitrary superposition of wave functions is then characterized by the angle θ in the (τ^x, τ^y) plane (Fig. 5). The Hamiltonian of the interaction of the electrons with the vibrations may be written¹³

$$H_{\text{int}} = -g(Q_3\tau^x + Q_2\tau^y). \quad (4)$$

Here Q_3 is the coordinate of the normal vibration mode indicated by the arrows in Figs. 4a and 4b, while Q_2 corresponds to another vibrational mode, which may also lift the degeneracy; it is shown in Fig. 4c. The ion vibrations in the mode Q_3 are of the form $2z^2 - x^2 - y^2$, while those in the Q_2 mode are of the form $x^2 - y^2$. The total Hamiltonian for an e_g center which is interacting with the vibrations is

$$H = \frac{C}{2}(Q_2^2 + Q_3^2) - g(Q_3\tau^x + Q_2\tau^y) + H_{\text{anhar}}. \quad (5)$$

If the anharmonic terms are ignored, the ground state is degenerate in the angle θ , and the energy surface, in contrast with that in Fig. 3, has the axisymmetric ("sombbrero") form in Fig. 6. When the anharmonicity is taken into account [it generates terms $\sim \cos 3\theta$ in the Hamiltonian in (5)], the preferred states become, for example, the three states $d_{x^2-y^2}$, d_{xz} , d_{yz} , which correspond to the angles $0, \pm 2\pi/3$ (Ref. 13). Tunneling and thermal transitions can occur from one minimum to another (there may be a reorientation of the long axes of the octahedron). If there is a high probability for such transitions, we may speak of a "dynamic" Jahn-Teller effect, while if they go slowly, i.e., if the system is "frozen" in one state, then we are dealing with a "sta-

³⁾At a sufficiently high impurity concentration there may even be a state of a "Jahn-Teller glass," in which (by analogy with spin glasses) the axes of the octahedra are oriented in a random manner, but the reorientation of each octahedron leads to changes in the system as a whole.¹²

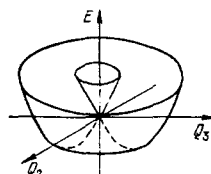


FIG. 6. The energy surface for the e_g terms which are interacting with twofold-degenerate E_g vibrations. Anharmonic effects produce a "ripple" (three minima) at the bottom of the "channel."

tic" Jahn-Teller effect.⁴⁾ In the static case, a deformation of the lattice can be observed near the center; in the dynamic case, the deformations are averaged out, and the picture remains spherically symmetric. In the latter case, however, the wave function of the system is of a vibron nature, leading to several important consequences, primarily a decrease in many of the matrix elements (the appearance of so-called Ham suppression factors⁹).

If, for example, some operator (the angular momentum operator L , say) has nonvanishing off-diagonal matrix elements which in the absence of a Jahn-Teller effect would be of the form $\langle \Phi_i | \hat{L} | \Phi_j \rangle = \langle \psi_i | \hat{L} | \psi_j \rangle \langle \varphi_0 | \varphi_0 \rangle = \langle \psi_i | \hat{L} | \psi_j \rangle$, now, according to (2), the different electronic wave functions ψ_i correspond to different nuclear wave functions φ_i (different equilibrium positions); i.e.,

$$\langle \Phi_i | \hat{L} | \Phi_j \rangle = \langle \psi_i | \hat{L} | \psi_j \rangle u, \quad (6)$$

where (for $i \neq j$)

$$u = \langle \varphi_i(R) | \varphi_j(R) \rangle = e^{-3E_{JT}/2\hbar\omega} < 1,$$

and E_{JT} is the energy lowering caused by the Jahn-Teller effect. In particular, the appearance of the suppression factors u reduces the multiplet splitting of the terms caused by the spin-orbit interaction: $LS \rightarrow uLS$.

In addition to weakening the spin-orbit interaction, the Jahn-Teller effect causes other changes in the magnetic properties of the ions. For example, it may give rise to an important anisotropy of the g -factors (for Cu^{2+} , for example, we usually find $g_{\parallel} \approx 2.4$ and $g_{\perp} \approx 2.08$).

It should be emphasized that for isolated centers the difference between the static and dynamic Jahn-Teller effects is not a fundamental one: A given system with a characteristic transition time $\tau \sim \hbar/\omega$ may exhibit the characteristics of a dynamic Jahn-Teller effect in certain experiments, where there is an averaging over long time intervals (in NMR, for example), while it may exhibit the characteristics of a static effect in other experiments, where the scale time is short (optical absorption, for example). In the discussion below, of concentrated systems, we will be dealing primarily with the static case.

b) The interaction of Jahn-Teller ions in concentrated systems. Let us consider in more detail the Jahn-Teller effect in materials which have a high concentration

⁴⁾Generally speaking, the terminology has not yet been finally established here; these terms are sometimes applied to slightly different situations.



FIG. 7. "Antiferro" orbital ordering due to an interaction of Jahn-Teller ions with the lattice. The displacement of the cation (the common vertex of the two octahedra) indicated by the arrow stabilizes the d_{x2} and d_{x2-y2} orbitals, respectively, at the neighboring centers.

of Jahn-Teller ions; some examples of such compounds were given in the Introduction. It is easy to see that in this case the Jahn-Teller distortions and the corresponding filling of the orbitals of different centers are not independent: An interaction between them arises and makes these distortions cooperative, leading to phase transitions. We should point out here that the cooperative Jahn-Teller effect can be characterized from several points of view. First, there is a lowering of the symmetry, and there is a distortion of the lattice, accompanied by a simultaneous ordering of orbitals. Finally, the Jahn-Teller effect and the filling of one of the orbitals are accompanied by a change in the space-charge distribution—more precisely, by the appearance of a quadrupole moment at the center.

We may distinguish among three types of interactions between Jahn-Teller ions, which may be called "electronic-vibrational," "quadrupole," and "exchange" interactions.

The electronic-vibrational interaction results from the deformation of the surroundings of a given ion. The deformations caused by different cations in the crystal interact with each other. In the simplest case (Fig. 7), an ion lying halfway between two Jahn-Teller ions belongs to the surroundings of both of these ions simultaneously, and its displacement due to the Jahn-Teller effect at cation 1 thus implies some deformation of the surroundings of cation 2; this deformation leads to a corresponding filling of orbitals (in the case in Fig. 7, the d_{x2} orbital will be filled at center 1 and the d_{x2-y2} orbital will be filled at center 2). It may be said that in a crystal the vibrations which are important for the Jahn-Teller effect transform from local vibrations into phonons, which propagate throughout the crystal and carry the interaction between Jahn-Teller ions.

For a description of this interaction it is convenient to use the pseudospin representation which was introduced above for a discussion of isolated centers. In a crystal we find,¹³ instead of (5),

$$H = \sum_{\mathbf{k}, s} \frac{\hbar \omega_{\mathbf{k}s}}{2} (p_{\mathbf{k}s}^* p_{\mathbf{k}s} + q_{\mathbf{k}s}^* q_{\mathbf{k}s}) - \frac{1}{\sqrt{N}} \sum_{\mathbf{k}, s, j} e^{i\mathbf{k}\mathbf{R}_j} (g_{\mathbf{k}s}^{(j)} q_{\mathbf{k}s} \tau_j^z + g_{\mathbf{k}s}^{(x)} q_{\mathbf{k}s} \tau_j^x) - \sum_j \frac{1}{N} (g_0^{(x)} \tau_j^x \epsilon^x + g_0^{(z)} \tau_j^z \epsilon^z) + \frac{C}{2} [(\epsilon^x)^2 + (\epsilon^z)^2]; \quad (7)$$

here $\omega_{\mathbf{k}s}$ is the frequency of a phonon with wave vector \mathbf{k} and polarization s , $q_{\mathbf{k}s}$ and $p_{\mathbf{k}s}$ are the corresponding

coordinate and momentum, and τ_j is the pseudospin of the j -th center. The term corresponding to the interaction with a homogeneous deformation ϵ (phonons with $\mathbf{k}=0$) has been singled out explicitly in (7); this term is characterized by the constant g_0 . It turns out to be extremely useful to single out this term in several cases, e.g., in a study of the behavior of the elastic moduli (Section 9).

Phonons can be eliminated from Hamiltonian (7), and as a result we find an interaction directly between pseudospins (between Jahn-Teller states). We will not reproduce the corresponding derivation here^{1,13}; it is quite simple, but it leans heavily on the particular features of the given system (on the lattice structure, the nature of the degenerate electronic levels, and the nature of the phonons with which these levels are interacting). The resulting Hamiltonian may be written schematically in a form which is similar to that of the Heisenberg (or Ising) Hamiltonian for pseudospins,

$$H = \sum_{i,j} (J_{ij}^z \tau_i^z \tau_j^z + J_{ij}^x \tau_i^x \tau_j^x), \quad (8)$$

where the "exchange" constants are expressed in terms of the parameters of Hamiltonian (7) by

$$J_{ij}^z = -\frac{(g_0^z)^2}{C} - \sum_{\mathbf{k}, s} \frac{g_{\mathbf{k}s}^{(z)} g_{\mathbf{k}s}^{(z)}}{\omega_{\mathbf{k}s}} e^{i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)} \quad (9)$$

with a corresponding expression⁵⁾ for J_{ij}^x .

In other cases, in which only a single nondegenerate vibrational mode is coupled with Jahn-Teller levels, the effective Hamiltonian which is found may contain only the τ^x components; i.e., it may correspond to the Ising interaction. This is the situation, for example, in the orthovanadates of rare earth metals,¹ MeVO_4 .

Another form of the interaction, which can also lead to an orbital ordering, is the direct quadrupole-quadrupole interaction. We have already mentioned that the Jahn-Teller effect is accompanied by the appearance of a quadrupole moment, because of the d electrons. The interaction of the quadrupole moments is described in the standard way,

$$H_{qu} = \frac{1}{2} \sum_{i,j} \frac{D_{\alpha\beta}}{6} \frac{D_{\gamma\delta}}{6} \frac{\partial^2}{\partial x_{\alpha}^i \partial x_{\beta}^i} \frac{\partial^2}{\partial x_{\gamma}^j \partial x_{\delta}^j} \left(\frac{1}{R_{ij}} \right). \quad (10)$$

We know that the quadrupole moment of an atom or ion can be expressed in terms of its orbital angular momentum,

$$D_{\alpha\beta} = \frac{3D}{2L(L-1)} \left(\hat{L}_{\alpha} \hat{L}_{\beta} + \hat{L}_{\beta} \hat{L}_{\alpha} - \frac{2}{3} \hat{L}^2 \delta_{\alpha\beta} \right). \quad (11)$$

In the case of e_g orbitals (for which the matrix elements of the orbital angular momentum are zero) it turns out that the quadrupole moment can be expressed in terms of the same pseudospins⁵ τ , so that the interaction (10) takes a form similar to that of (8). In the case of the t_{2g} orbitals, in contrast, an effective orbital angular momentum $l_{\text{eff}} = 1$ (we will omit the "eff" below)

⁵⁾Strictly speaking, since the operators τ^x and τ^z do not commute the transformation from Hamiltonian (7) to the pseudospin Hamiltonian (8) is not exact. In this case the phonons are not completely separated, and there are several special consequences¹ (see also Section 7).

appears in (10), and the interaction (10) can be expressed in terms of the product of invariants of the type $(I_x^2 - 2/3), (I_x^2 - I_y^2)$, etc.^{5,14} On the other hand, the interaction for the t_{2g} orbitals and the interaction induced by phonons can also be expressed in terms of these invariants, but with different constants.¹⁵

Let us examine these pseudospin Hamiltonians.

First, we note that they are anisotropic: In general, the terms $\tau_i^x \tau_j^x$ and $\tau_i^y \tau_j^y$ enter with different constants. There may also be terms of the form $\tau_i^x \tau_j^y$. More interesting, however, is that while the form of the interaction Hamiltonian (e.g., $S_i S_j + \lambda S_i^x S_j^x$) in ordinary spin systems is the same for any adjacent pairs of spins, in the present case the very form of the interaction strongly depends on the mutual positions of the centers. For example, while the electron-lattice interaction is of the form $\tau_i^x \tau_j^x$ for a pair of spins arranged along the z axis, this interaction takes the following form for the same pair of spins if arranged along the x axis:

$$\left(-\frac{1}{2}\tau_i^x + \frac{\sqrt{3}}{2}\tau_i^y\right)\left(-\frac{1}{2}\tau_j^x + \frac{\sqrt{3}}{2}\tau_j^y\right).$$

The interaction between orbitals is thus anisotropic even to the extent that its very form depends on the radius vector which connects the given pair. The reason for this circumstance can easily be explained in qualitative terms. For example, while the d_{z^2} orbitals (which correspond to τ^x) overlap markedly for a pair arranged along the z axis and give rise to a strong interaction, the corresponding role for a pair arranged along the x axis is played by the $d_{x^2-y^2}$ orbitals, which are characterized in the (τ^x, τ^y) plane by the angle $\theta = 2\pi/3$. They correspond to the combination $(-\tau^x/2 + \sqrt{3}\tau^y/2)$.

We thus see that when the exchange of phonons and the quadrupole interaction are taken into account the system comes to be described by a pseudospin Hamiltonian which is of the form of an anisotropic Heisenberg Hamiltonian. The interaction may turn out to be either ferromagnetic or antiferromagnetic. For example, if long-wave acoustic phonons are predominant in an interaction which is caused by lattice vibrations, or even if simply a uniform deformation [specified by the constant g_0 in (7)] is predominant, we find a "ferromagnetic" Hamiltonian. If, on the other hand, an interaction through optical modes is stronger, we find an "antiferromagnetic" Hamiltonian. Correspondingly, the orbital (and quadrupole) ordering may turn out to be either "ferro" or "antiferro." As we will see below, there are also some more complicated situations: "skewed

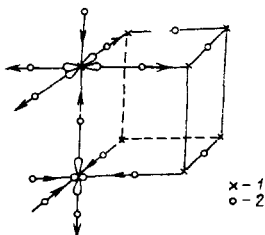


FIG. 8. The perovskite structure, in which "antiferro" deformations and orbital ordering are favored. 1—Jahn-Teller ions; 2—anions; arrows—possible displacements of the anions during Jahn-Teller ordering (cf. Fig. 13).

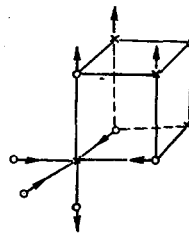


FIG. 9. The spinel structure, in which "ferro" deformations are favored. The notation is the same as in Fig. 8. Shown here is the part of the unit cell which contains Jahn-Teller ions in octahedra (B) sites.

antiferromagnetism" (KCuF_3 , MnF_3 ; Refs. 13 and 16), structures with a tripled period (CsCuCl_3 ; Ref. 17), and incommensurate structures [$\text{K}_2\text{PbCu}(\text{NO}_2)_6$; Ref. 18].

In order to derive a specific explanation for the type of ordering from first principles it is necessary to know the phonon characteristics of the crystal; this problem runs into considerable difficulties. The general tendencies, on the other hand, can be seen from some crude, qualitative arguments. For example, in a perovskite lattice, in which the octahedra surrounding the Jahn-Teller ions have a common vertex (Fig. 8), we would naturally expect an "antiferro" ordering (cf. Fig. 7). In a spinel lattice, in contrast, we would expect on the basis of purely geometric considerations that a stretching of the octahedron near the ion A, for example, would be accompanied by a similar stretching near all the cations (Fig. 9), which would lead to a tetragonal distortion of the "ferro" type. A d_{z^2} orbital would be filled at each site.

Up to this point we have been talking about two types of interactions which are of essentially the same nature and which are caused by a direct Coulomb interaction (either by a direct quadrupole interaction or through anions). In Jahn-Teller systems, however, there is also an exchange interaction, which also leads to an ordering of orbitals.¹⁹ Furthermore, this interaction may make the governing contribution to the ordering energy. In contrast with the direct interactions, which do not depend on the spin and which are expressed exclusively in terms of pseudospins (the spins can come into play only as a result of spin-orbit coupling), the exchange interaction also depends on the spins, and it leads simultaneously to an orbital degeneracy and a spin degeneracy.

4. THE EXCHANGE INTERACTION IN JAHN-TELLER SYSTEMS

a) Superexchange and the Hubbard model. Before describing the exchange interaction in the degenerate case we shall briefly review some basic concepts regarding exchange in magnetic insulators which we shall draw on in the discussion below.

The primary mechanism for the exchange interaction in transition metal compounds, where the direct overlap of d orbitals of adjacent ions is slight, is indirect Kramers—Anderson exchange, or "superexchange," as it is more commonly called.²⁰⁻²² The essence of this



FIG. 10. Scheme for superexchange in the nondegenerate case. Shown here is the energy increase due to virtual transitions of an electron to a neighboring center. An antiparallel orientation of the spins is seen to be preferred from the energy standpoint.

effect is that the overlap is an overlap not of the atomic d wave functions but of their superposition with the s and p wave functions of the ligands. Figure 10 shows the essential features of superexchange for the case of a single electron in a nondegenerate level. The two most important factors are (1) the energy increase which results from virtual transitions of electrons from center to center and which is determined by the effective transition integral t , and (2) the Coulomb repulsion of electrons at a common center, U . The usual relation between these parameters in magnetic insulators is $t \ll U$. We see that in case a) hops of electrons are forbidden by the Pauli principle, while in case b) they are allowed, and there is an energy increase of $-2t^2/U$, which corresponds to a preferred antiferromagnetic state. The effective exchange Hamiltonian is of the Heisenberg form,

$$H_{\text{Heis}} = \frac{2t^2}{U} \sum_{\langle i, j \rangle} S_i S_j, \quad (12)$$

where $\langle i, j \rangle$ indicates a summation over nearest neighbors. In oxides, we find $t \sim 0.1-0.3$ eV in practice, and U is of the order of the ionization energy, reduced for screening effects (i.e., ~ 5 eV). We thus have a well-defined perturbation theory in the parameter $t/U \leq 0.1$.

The approach to the superexchange problem which we have just outlined was proposed by Anderson, and it is analogous to that used in constructing the Hubbard model.²⁴ The Hubbard model is used to describe the behavior of materials having narrow band gaps and is based on the existence of a strong intraatomic interaction of electrons. In the original formulation of Ref. 24, the crystal was assumed to have a fixed lattice, and the d electrons were approximated by strongly coupled nondegenerate s states.

In the Hubbard model, the most important of the various types of electron-electron interactions is taken into account: the Coulomb repulsion of electrons at a common center. The corresponding Hamiltonian is

$$H_{\text{Hubb}} = H_1 + H_0 = t \sum_{i, j, \sigma} a_{i\sigma}^\dagger a_{j\sigma} + \frac{U}{2} \sum_{i, \sigma} n_{i\sigma} n_{i-\sigma}, \quad n_{i\sigma} = a_{i\sigma}^\dagger a_{i\sigma}, \quad (13)$$

where $a_{i\sigma}^\dagger$ is the operator which creates an electron with a spin σ in a state with a Wannier function centered at the i -th atom, H_1 describes the ordinary band energy, and H_0 describes the Coulomb repulsion of the electrons.

Let us examine the properties of the Hubbard model in the case in which there is a single electron at the center, and we have $U \gg t$. The H_0 ground state is a state with localized electrons (there is one electron at



FIG. 11. Various possible types of overlay of e_g orbitals at neighboring centers. a—the overlap of single filled orbitals, which leads to a strong antiferromagnetic exchange interaction; b—the overlap of filled orbitals is zero. A filled orbital and an empty orbital (dashed line) overlap, and the exchange is accordingly ferromagnetic.

each of the N centers) which is 2^N -fold degenerate in the spins. The degeneracy is lifted in second-order perturbation theory, and the corresponding energy increase is determined by the effective Hamiltonian

$$H_{\text{eff}} = H_1 \frac{1}{E_0 - H_0} H_1 = -\frac{t^2}{U} \sum_{\langle i, j \rangle} a_{i\sigma}^\dagger a_{j\sigma} a_{j\sigma}^\dagger a_{i\sigma}. \quad (14)$$

Qualitatively, the picture is the same as that in Fig. 10, and the ground state is antiferromagnetic. If the electron operators are expressed in terms of the spin operators by the standard expressions,

$$\begin{aligned} a_{i\uparrow}^\dagger a_{i\uparrow} &= n_{i\uparrow} = \frac{1}{2} + S_i^z, & a_{i\uparrow}^\dagger a_{i\downarrow} &= S_i^+ = S_i^x + iS_i^y, \\ a_{i\downarrow}^\dagger a_{i\downarrow} &= n_{i\downarrow} = \frac{1}{2} - S_i^z, & a_{i\downarrow}^\dagger a_{i\uparrow} &= S_i^- = S_i^x - iS_i^y, \end{aligned} \quad (15)$$

the effective Hamiltonian in (14) can be put in the Heisenberg form in (12). The Anderson picture of superexchange is thus described completely by the Hubbard model in the limit $t \ll U$.

For real materials it is necessary to consider the presence of other levels and the particular symmetry of the corresponding wave functions [this symmetry determines the magnitude of the overlap integral t in Eqs. (13) and (14)]. There may be a situation in which orbitals containing single electrons overlap strongly for adjacent ions [Fig. 11(a)]; in this case the exchange is antiferromagnetic and is described accurately by (12). However, there may also be cases of a zero overlap of filled orbitals (Fig. 11b) but a large overlap of a filled orbital at one center with a vacant orbital at an adjacent center. In order to lift the spin degeneracy in this case it is necessary to consider the intraatomic exchange interaction $J_H S_1 S_2$ (here the subscripts 1 and 2 designate the orbital at one ion, and $J_H > 0$), which leads to Hund's rule (configurations with parallel spins are preferred). In this case the spin degeneracy is lifted in the next order of perturbation theory, and it is of a ferromagnetic nature [Figs. 12(c) and 12(d)], with an exchange integral $J \sim (t^2/U)J_H/U$ (in practice, $J_H \sim 0.5-1$ eV $< U$).

These arguments explain the empirical Goodenough-

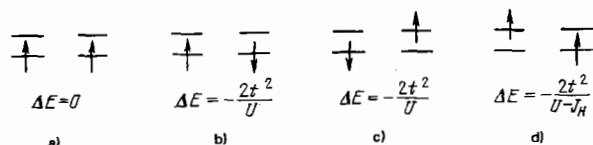


FIG. 12. Superexchange in the case of twofold-degenerate orbitals. Shown here is the energy increase if only diagonal transitions are possible ($t_{11} = t_{22} = t$, $t_{12} = 0$). Intraatomic (Hund) exchange is also taken into account.

Kanamori-Anderson rules which were established earlier.² The general features of these rules may be summarized as follows:

- 1) If half of the filled orbitals overlap at adjacent centers, the exchange is antiferromagnetic and comparatively strong.
- 2) If a vacant orbital and a filled orbital overlap, the exchange is ferromagnetic and weaker (by a factor J_H/U , i.e., by nearly an order of magnitude).

These rules are significantly more detailed in their complete formulation (see Refs. 2, 21, and 23, for example). For example, the particular values of the angles in the cation-anion-cation trio in which the exchange occurs turn out to be important. For our purposes, however, it will be sufficient to use these simpler versions of the rules, whose origin was explained above.

b) *Superexchange in the case of orbital degeneracy.* Up to this point we have been talking about a nondegenerate ground state, in which case we know precisely which states are filled and which are vacant. The situation changes significantly when we consider an orbital degeneracy. In this case the Goodenough-Kanamori-Anderson rules no longer tell us the nature of the exchange; the magnitude and even the sign of the exchange interaction are not determined, and they depend on the filling of the orbitals. Antiferromagnetism in the nondegenerate case was a consequence of the Pauli principle, but if each atom has, say, two states of identical energy then the restrictions imposed by the Pauli principle are generally removed. Even in this case, however, it can be shown that the same exchange mechanism lifts the degeneracy, simultaneously causing an ordering of both the spins and the orbitals,^{19, 27-29} as can be seen clearly from Fig. 12. Comparison of the energies of the four possible configurations shows that when we take intraatomic exchange into account (a consequence of this exchange is Hund's rule) in the simple model in which an electron may undergo only diagonal transitions ($t_{11} = t_{22}, t_{12} = 0$), configuration d) turns out to be the most favorable. Specifically, the order is ferromagnetic in terms of the spin but antiferromagnetic (i.e., there is an alternation of states 1 and 2) in terms of the filling of orbitals.

The degenerate case can be described mathematically by the same pseudospin operators τ which were introduced in the study of the Jahn-Teller effect, if we begin from the Hubbard model as generalized to the degenerate case:

$$H = H_0 + H_1, \quad H_1 = \sum_{(i,j)} t_{ij}^{\alpha\beta} a_{i\alpha}^\dagger a_{j\beta}, \quad (16)$$

$$H_0 = \frac{1}{2} \sum_{\alpha\beta} U_{\alpha\beta} n_{i\alpha} n_{i\beta} + (1 - \delta_{\alpha\beta} \delta_{\sigma\sigma'}) \sum_{\alpha \neq \beta} J_{\alpha\beta} (a_{i\alpha}^\dagger a_{i\alpha\sigma'} a_{i\beta\sigma}^\dagger a_{i\beta\sigma} + a_{i\alpha\sigma}^\dagger a_{i\beta\sigma} a_{i\alpha\sigma'}^\dagger a_{i\beta\sigma'}).$$

Here α and β designate the orbitals, and the summation runs over all indices (unless otherwise specified). We have also incorporated the intraatomic (Hund) exchange here [the last term in (16)].

Again, as in the nondegenerate case, by lifting the

degeneracy (4^N -fold here) in second-order perturbation theory, and transforming to the spin and pseudospin operators S and τ by rules analogous to (15) [$a_{1,2}^\dagger a_{1,2} = (1/2) \pm \tau^\pm, a_{1,2}^\dagger a_{2,1} = \tau^\pm$; Ref. 19], we find an effective Hamiltonian which depends on the two types of spin variables S and τ . In the simplest case, corresponding to Fig. 12, this Hamiltonian is

$$H = \sum_{(i,j)} (J_1 S_i S_j + J_2 \tau_i \tau_j + 4J_3 S_i S_j \tau_i \tau_j), \quad (17)$$

where

$$J_1 = \frac{2t^2}{U} \left(1 - \frac{J_H}{U}\right), \quad J_2 = J_3 = \frac{2t^2}{U} \left(1 + \frac{J_H}{U}\right).$$

The absence of terms of the type $S\tau$ from (17) corresponds to the absence of a spin-orbit interaction, which is present in the case of the e_g orbitals.

c) *Superexchange ordering of orbitals in some specific materials.* In real materials we must take into account the fact that the transition integrals $t_{ij}^{\alpha\beta}$ depend on the nature of the orbitals α and β and also on the mutual arrangement of the centers i and j , since the electron density distribution is not spherically symmetric. A detailed derivation of the exchange interaction for the case of the e_g terms can be found in Refs. 19 and 29, and one for the t_{2g} terms can be found in Ref. 14.

When the actual relation between transition integrals is taken into account (see Ref. 30, for example), the Hamiltonian becomes highly anisotropic in terms of the τ variables (Ref. 19). As an example, the Hamiltonian for perovskites (with e_g ions at the sites of a simple cubic lattice) is

$$H_{\text{eff}} = \frac{t^2}{U} \sum_{(i,j)_x} \left\{ 8S_i S_j \left[\tau_i^\pm \tau_j^\mp \left(1 + \frac{J_H}{U}\right) + \tau_i^\pm + \frac{1}{4} \left(1 - \frac{J_H}{U}\right) \right] \right. \\ \left. + 2 \left[\tau_i^\pm \tau_j^\mp \left(1 + \frac{J_H}{U}\right) - \tau_i^\pm \right] \right\} + \frac{t^2}{U} \sum_{(i,j)_{x,y}} \left\{ 2S_i S_j \left[\tau_i^\pm \tau_j^\mp \left(1 + \frac{J_H}{U}\right) \right. \right. \\ \left. \left. - 2\tau_j^\pm + \left(1 - \frac{J_H}{U}\right) \pm 2\sqrt{3} \left(1 + \frac{J_H}{U}\right) \tau_i^\pm \tau_j^\mp \mp 2\sqrt{3} \tau_j^\pm \right. \right. \\ \left. \left. + 3 \left(1 + \frac{J_H}{U}\right) \tau_i^\pm \tau_j^\mp \right] + \frac{1}{2} \left[\tau_i^\pm \tau_j^\mp \left(1 + \frac{J_H}{U}\right) \right. \right. \\ \left. \left. - 2\tau_j^\pm \pm 2\sqrt{3} \left(1 + \frac{J_H}{U}\right) \tau_i^\pm \tau_j^\mp \pm 2\sqrt{3} \tau_j^\pm + 3 \left(1 + \frac{J_H}{U}\right) \tau_i^\pm \tau_j^\mp \right] \right\}. \quad (18)$$

Here $\langle i, j \rangle_{x,y,z}$ denotes a summation over the nearest neighbors which are arranged along the corresponding axis, and $t = 10Dq/6$ ($10Dq$ is the distance between the e_g and t_{2g} levels in the cubic field). It has been assumed for simplicity in (18) that the Coulomb repulsion does not depend on the particular orbital ($U_{11} = U_{22} = U_{12} = U$).

Because of the complicated nature of (18), the ground state for this Hamiltonian may not be that which would follow from Fig. 12. For example, for a simple cubic lattice of ions having a single electron or hole in a two-fold-degenerate e_g level we would find the orbital structure shown in Fig. 13. This structure is characteristic of perovskites in which the Cu^{2+} ions form a simple cubic lattice (KCuF_3 , for example). The structure corresponding to the ground state consists of (001) planes which are ferromagnetic in terms of the spin; the spins in adjacent planes are in opposite directions. The ordering of the orbitals characteristically has an

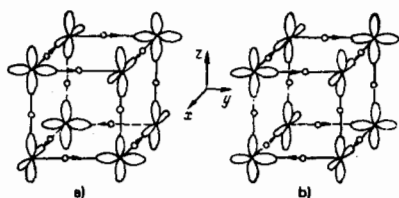


FIG. 13. Orbital ordering in a perovskite of the KCuF_3 type caused by the superexchange mechanism.¹⁹ a, b—Two equivalent types of ordering; both are actually observed¹⁶ in KCuF_3 .

alternation of $d_{x^2-y^2}$ and d_{z^2} states [this type of ordering corresponds to a skewed τ -antiferromagnetism with an alternation of $\pm\pi/3$ sites in the (τ^x, τ^y) or (Q_3, Q_2) plane; Fig. 5]. There may be two types of ordering, which are equivalent (which correspond to the same energy), as shown in Fig. 13. In practice, KCuF_3 crystals of both types occur during growth,¹⁶ and crystals of this sort frequently contain stacking faults.³¹ This type of filling of the orbitals leads to a strong antiferromagnetic interaction along the z axis (half of the filled orbitals overlap strongly) and a relatively weak ferromagnetic interaction in the (x, y) plane. It is for this reason that the KCuF_3 crystal, with a nearly cubic structure, behaves as if it were a quasi-one-dimensional magnetic material.¹⁶ It should be noted that the orbital structure for perovskites with Mn^{3+} and Cr^{2+} ions (such ions have a single electron in an e_g level and three in a t_{2g} level) differs slightly from that shown in Fig. 13 (angles θ of approximately $\pi/2$ alternate). Eremin and Kalinenkov³² have shown that an interaction between the electrons in the e_g and t_{2g} levels can give rise to a structure of this type in the same model.

The structure in Fig. 13 was found by considering only the exchange interaction; in this case, the exchange interaction by itself gives a correct description of both the orbital and magnetic orderings. If, on the other hand, we know the orbital structure (a structure caused, for example, by direct interactions) from independent considerations, then by substituting the corresponding average values $\langle \tau \rangle$ into the resulting Hamiltonian of the type (18) we find the effective spin Hamiltonian. This sort of analysis, for two-dimensional ferromagnets of the type K_2CuF_4 , for example, has revealed that the orbital structure which had been proposed previously³³ for these ferromagnets (and which has in fact been identified in monographs^{2,38} as the single case in which the Cu^{2+} ion is surrounded by a flattened, rather than stretched, octahedron) is incompatible with the ferromagnetism observed in K_2CuF_4 . An alternative structure proposed in Ref. 34 on the basis of theoretical arguments, which has alternating octahedra which are stretched out along the x and y axes, was subsequently confirmed experimentally by different methods.³⁵⁻³⁷ It may therefore be stated, in particular, that in all known cases, without exception, the Jahn-Teller ion Cu^{2+} in octahedral surroundings causes a deformation of the stretching type (the $d_{x^2-y^2}$ hole orbital is stabilized).

The exchange mechanism for the ordering of orbitals thus acts along with the direct mechanisms (the Jahn-

Teller and quadrupole mechanisms), and in some cases it is capable of giving the correct orbital structure by itself. In this mechanism, the change in the lattice structure (the structural transition) is a secondary effect; here we may speak in terms of a "Jahn-Teller ordering without a Jahn-Teller interaction." Actually, of course, all three mechanisms act jointly, and it is quite difficult to determine just which will be predominant in each specific case. Some help may be obtained by studying pairs of Jahn-Teller impurity ions,³⁹ for which the different mechanisms give rise to different types of ground states. Direct ultrasonic methods may also be useful; they may be able to distinguish the effect of an interaction with a homogeneous deformation from the background of all other interactions (see Ref. 40 and Section 9 below). In general, however, the question remains open.

The tendency toward an "antiferro" orbital ordering, which was illustrated above for a model (Fig. 12) and also for the real case of KCuF_3 (Fig. 13) (and which is important, in particular, if neighboring octahedra have a common vertex), is responsible for the appearance of a ferromagnetic exchange interaction for certain pairs of ions. This circumstance explains the effectiveness of Jahn-Teller ions for the appearance of ferromagnetism. A related effect (mentioned earlier) is the frequent appearance of ferromagnetic ordering in Jahn-Teller magnetic materials (Table I). Furthermore, it is apparently not by chance that the long search for ferromagnetism due to double exchange⁴¹ in magnetic insulators with impurities has yielded only two cases in which this mechanism is believed to operate, $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ and $\text{Mn}_{1-x}\text{Li}_x\text{Se}$ (Ref. 2), and in both these materials we find the Jahn-Teller ion Mn^{3+} . The peculiar properties of this ion probably play an important role in the ferromagnetism of these systems.

We will point out again that the exchange interaction described in this section, which occurs in Jahn-Teller magnetic materials and which is of the form of (17) and (18), incorporates spin and orbital variables simultaneously. As a result, there is an unusual interaction between these two subsystems, and there is also the possibility that, say, the magnetic field will affect the orbital structure, etc. These questions will be discussed below, but we will first consider how the situation changes in the case of a threefold degeneracy (t_{2g} ions).

5. IONS WITH A THREEFOLD ORBITAL DEGENERACY (t_{2g} IONS)

A rather large number of ions have a partially filled t_{2g} level in a symmetric configuration. In octahedral surroundings, these are ions in the states $d^1(\text{Ti}^{3+}, \text{V}^{4+})$, $d^2(\text{Ti}^{2+}, \text{V}^{3+}, \text{Cr}^{4+})$, $d^6(\text{Fe}^{2+})$, $d^7(\text{Co}^{2+})$. States in tetrahedral surroundings are also common. As mentioned in Section 2, these states may be characterized by an effective angular momentum $l=1$, and for them the spin-orbit interaction is in principle important. It is easy to see that the degeneracy can be lifted in two ways in this case, by a spin-orbit mechanism and by a Jahn-Teller mechanism. In a sense, these two mechanisms are mutually exclusive; the situation here is similar to that

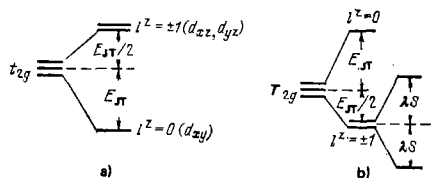


FIG. 14. Two types of splitting of the t_{2g} one-electron level. a—Lifting of degeneracy “in the Jahn-Teller channel.” $c/a < 1$. The d_{xy} orbital ($|l^z = 0\rangle$) is stabilized; b—lifting of degeneracy due to the spin-orbit interaction. $c/a > 1$. The deformation stabilizes the twofold-degenerate state d_{xz}, d_{yz} or $|l^z = \pm 1\rangle$. This state is then split by the spin-orbit interaction.

for certain rare earth ions, e.g., Tm^{3+} in $TmVO_4$ (Ref. 6).

Let us examine the case of a single electron in a t_{2g} level (d^1 ion or a d^6 ion, which is equivalent); the analysis for a single hole (d^2 or d^7) is analogous. When an octahedron near such an ion is compressed, the t_{2g} level splits as shown in Fig. 14(a). A nondegenerate level with a d_{xy} wave function (which corresponds to $|l^z = 0\rangle$) moves downward, by an energy E_{JT} , while two other levels, with d_{yz} and d_{xz} wave functions (or $|l^z = \pm 1\rangle$) remain degenerate and move upward by an energy $\Delta E = E_{JT}/2$. Such a deformation is favorable from the standpoint of the Jahn-Teller energy, but in this case the ground state does not have an angular momentum ($l^z = 0$), and the spin-orbit interaction in it is correspondingly ineffective: $\langle l^z = 0 | \lambda \mathbf{L} \cdot \mathbf{S} | l^z = 0 \rangle = 0$.

We now assume that a tetragonal deformation of the other sign, corresponding to a stretching of the octahedron, has occurred. In this case there is an inversion of terms [Fig. 14(b)], and the lowest term turns out to be the doublet $|l^z = \pm 1\rangle$. We see that the energy of the term also decreases (this is an energy increase due to the Jahn-Teller effect), but the decrease is half that in the first case, and from the standpoint of the Jahn-Teller effect compressions ($c/a < 1$) are more favorable. In return, the ground state now has an unfrozen orbital angular momentum, and this state is split further by the spin-orbit interaction, with an additional energy increase λS [the spin is parallel or antiparallel to the orbital angular momentum, depending on the sign of λ ; the spin becomes oriented along the deformation (z) axis; i.e., a spin anisotropy arises].

It is thus obvious that in the ordered phase the Jahn-Teller and spin-orbit interaction mechanisms stabilize deformations of opposite types (for one t_{2g} electron, $c/a < 1$ or $c/a > 1$, respectively). The result depends on the relationship between the energy of the Jahn-Teller stabilization, E_{JT} , and the energy of the spin-orbit interaction, $\lambda \langle S \rangle$. Generally speaking, these energies are comparable in magnitude in crystals of 3d elements, and in practice transitions are observed by both the Jahn-Teller and spin-orbit mechanisms.

A Jahn-Teller transition (if this is the dominant interaction) is a purely structural transition, and the magnetic ordering occurs at some other (lower) temperature. This is the situation in the spinels $NiCr_2O_4$ (Ref. 42), $NiRh_2O_4$, and $CuRh_2O_4$ (Ref. 43) [the Ni^{2+} and

Cu^{2+} ions in these spinels are in tetrahedral surroundings (A sites) and have a threefold orbital degeneracy]. On the other hand, the transitions determined by the spin-orbit increase in the energy occur simultaneously with the magnetic ordering. It is simple to see that if the spins become ordered, along the z axis, for example, then the ls interaction will automatically stabilize the orbitals $|l^z = \pm 1\rangle$, and the corresponding lattice deformation will occur (and, vice versa, if the corresponding ordering of orbitals occurred first, there would be a simultaneous spin ordering). In this case, therefore, the lattice deformation occurs at the Curie point (or at the Néel point) and has the external manifestations of simply a magnetostrictive effect. We wish to emphasize, however, that this deformation differs in nature from magnetostriction, say for nondegenerate ions such as Ni^{2+} or Fe^{3+} ; here the deformation is due to the initial degeneracy in a symmetric configuration. The corresponding deformations are roughly an order of magnitude greater than in the nondegenerate case. The nature of the deformations (the direction of the symmetry axes of the low-temperature phase) is unambiguously related to the spin ordering direction. In CoO and $KCoF_3$, for example, where the spins are directed along the $[001]$ axis at $T < T_N$, a tetragonal deformation with $c/a < 1$ occurs (the Co^{2+} ion with the d^7 configuration has a single hole in a t_{2g} shell; according to the arguments above, in this case the Jahn-Teller effect would stabilize the hole orbital $|d_{xy}\rangle = |l^z = 0\rangle$ in the case $c/a > 1$ and the orbital $|l^z = \pm 1\rangle$ in the case of a compression, $c/a < 1$). In the compound FeO , in contrast, the spins are directed along the $[111]$ axis in the ordered phase; correspondingly, a trigonal distortion of the lattice occurs in this crystal at $T < T_N$. (For the t_{2g} levels, in contrast with e_g , the splitting of terms occurs not only in an interaction with the E_g vibrations corresponding to a tetragonal or orthorhombic distortion but also in an interaction with the trigonal vibrations T_{2g} ; it is easy to see that the quantization axis for the angular momentum in these cases is in fact the $[111]$ direction.⁶⁾)

It is also clear from a comparison of the energy increases that the spin-orbit interaction becomes progressively more effective as the spin S of the corresponding ion increases. In general, this tendency is confirmed by experiment: For the Fe^{2+} ion ($S = 2$) and for the Co^{2+} ion ($S = 3/2$) in octahedral surroundings, the

⁶⁾ We might add that the Jahn-Teller interaction is itself probably the reason why the spins in CoO or $KCoF_3$ are oriented along the $[100]$ axis, while those in FeO and $KFeF_3$ are along the $[111]$ axis. The interaction constants for the interaction of t_{2g} electrons with E_g and T_{2g} vibrations are generally different. There are corresponding differences in the energy increase due to the Jahn-Teller effect in the cases of tetragonal and trigonal deformations (even when the deformation has the “spin-orbit” sign). Accordingly, if, for the Co^{2+} ion, for example, the interaction with the E_g mode is stronger, a tetragonal distortion will be preferred, and the spins will accordingly be directed along the $[001]$ axis. For the Fe^{2+} ion the situation is apparently the opposite, so that the easy axis is the $[111]$ axis. For t_{2g} ions, therefore, the Jahn-Teller interaction apparently determines not only the magnitude but also the sign of the anisotropy constants.

spin-orbit interaction is more frequently the governing interaction, while for the Cu^{2+} ion ($S=1/2$) and the Ni^{2+} ion ($S=1$) in tetrahedral surroundings the ordering is usually a Jahn-Teller ordering.

Let us examine in slightly more detail how the discussion of Sections 3 and 4 would be modified for t_{2g} electrons. The threefold-degenerate t_{2g} electrons interact with the E_g vibrations (the Q_2 and Q_3 modes) and the T_{2g} vibrations (vibrations of the type xy , yz , and xz). The corresponding electron operators, which replace the pseudospin operators τ , are constructed from the orbital angular momentum $l=1$: The combinations $(l^x)^2 - (l^y)^2$ and $(l^x)^2 - 2/3$ interact with the E_g vibrations, while the combinations $(l^x l^y + l^y l^x)$, $(l^x l^z + l^z l^x)$, $(l^y l^z + l^z l^y)$ interact with the T_{2g} vibrations. These combinations embody corresponding representations of the symmetry group of the crystal; they are actually the same as the corresponding components of the quadrupole-moment tensor.

Eliminating phonons, we again find a direct interaction between the electronic states of different ions, which may be described schematically by

$$H_{\text{IT}} = \sum_{i,j} \left[J_{ij}^E \left\{ \left[(l_i^x)^2 - \frac{2}{3} \right] \left[(l_j^x)^2 - \frac{2}{3} \right] + [(l_i^x)^2 - (l_i^y)^2] [(l_j^x)^2 - (l_j^y)^2] \right\} + J_{ij}^T \{ (l_i^x l_j^y + l_j^x l_i^y) (l_i^y l_j^z + l_j^y l_i^z) + \dots \} \right]. \quad (19)$$

The direct quadrupole-quadrupole interaction is of the same form.

Although the problem of the ordering of interacting quadrupoles is not fundamentally different from the dipole-ordering problem, the technical details are much more complicated: There may be many different types of ordering, and extensive calculations are usually required to choose among the various possibilities. The choice is frequently ambiguous. Some results along this line are reported in Refs. 14 and 45-47. An extremely closely related problem is that of so-called biquadratic exchange.^{48,49} For the most part, the work on this problem has been limited so far to an examination of very simple models with (spatially) isotropic exchange and with simple types of ordering. In reality, however, the situation is not always this simple: In addition to the simple "ferro" ordering, which is observed in the spinel NiCr_2O_4 or CuRh_2O_4 , for example,^{42,43} cases arise in which the orbital ordering is quite complicated. In the compound $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, for example (which would be described better as $\text{Ca}_{1/4}\text{Cu}_{3/4}\text{TiO}_3$, to show that this compound is an ordinary perovskite in which one-fourth of the ions are at

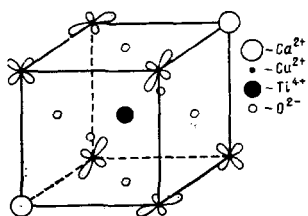


FIG. 15. Orbital structure of the substitutional perovskite $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ with the t_{2g} ions Cu^{2+} in tetrahedral surroundings.⁵⁰

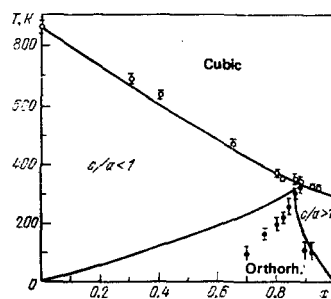


FIG. 16. Phase diagram of the system $\text{Ni}_x\text{Cu}_{1-x}\text{Cr}_2\text{O}_4$ (Ref. 15). Points—experimental data; curves—theoretical.

tetragonal sites—these are the nonmagnetic Ca^{2+} ions—and three-fourths are Cu^{2+} ions with a single hole in a t_{2g} level), the ordering shown in Fig. 15 is observed⁵⁰: There are three types of Cu^{2+} ions, at which the orbitals d_{xy} , d_{yz} , and d_{zx} , respectively, are filled.

There is also an interesting situation in the mixed crystals of the types $\text{Ni}_x\text{Cu}_{1-x}\text{Cr}_2\text{O}_4$ and $\text{Ni}_x\text{Fe}_{1-x}\text{Cr}_2\text{O}_4$ (Refs. 15, 51, and 52). At $x=0$ these crystals have a tetragonal symmetry with $c/a < 1$ because of the Jahn-Teller effect at Cu^{2+} and Fe^{2+} ions at A sites. At the other end ($x=1$) the symmetry is again tetragonal, but in this case we have $c/a > 1$. At intermediate concentrations there is an orthorhombic phase (Fig. 16), which may be thought of as caused by two simultaneous deformations: a tetragonal stretching along the z axis and a compression along the perpendicular axis. The qualitative reason for this result is as follows: If we place a Jahn-Teller impurity ion with a ground state corresponding to a flattened octahedron (a flat disk) in a NiCr_2O_4 crystal with $c/a > 1$ (with a structure as if constructed from stretched small cylinders), this impurity will naturally assume a position with its short axis perpendicular to the z axis of the matrix. At a finite concentration of such centers, their axes will also become ordered at a certain temperature, leading to the formation of an orthorhombic phase. A theory derived for this phenomenon by Kataoka and Kanamori¹⁵ gives a good description of the experimental situation.⁷¹

The exchange interaction in magnetic materials with t_{2g} electrons can also be put in a form corresponding to (19), by replacing the pseudospins τ by combinations of the type $[(l^x)^2 - 2/3]$, $[(l^x)^2 - (l^y)^2]$, and $(l^x l^y + l^y l^x)$, etc.⁵ For a perovskite crystal, for example, we find the following for a pair of ions arranged along the z axis, when we take into account the specific form of the t_{2g} functions¹⁴:

$$(H_{ij})_{\text{ex}} = \frac{t^2}{2U} \left[\left(\frac{1}{2} + 2S_i S_j \right) \{ (l_i^x)^2 (l_j^x)^2 + l_i^x l_j^x + [(l_i^x)^2 - (l_i^y)^2] [(l_j^x)^2 - (l_j^y)^2] + (l_i^x l_j^y + l_j^x l_i^y) (l_i^y l_j^z + l_j^y l_i^z) \} - \{ (l_i^x)^2 + (l_j^x)^2 \} \right]; \quad (20)$$

(here we have omitted terms which result from intra-atomic exchange, J_H).

⁷¹A similar situation is encountered in the case of spin ordering. For example, in mixed crystals containing ions with different types of anisotropies, an intermediate phase is observed in which the two types of spin orbiting coexist (see Ref. 53 regarding a study of $\text{Co}_{1-x}\text{Fe}_x\text{Cl}_2$).

Analysis of the orbital and magnetic ordering on the basis of the corresponding Hamiltonian for crystals with a cubic magnetic lattice shows that (as for the direct Jahn-Teller interaction) there may be some rather complicated structures, which are frequently degenerate in the lowest-order approximations. It is not possible to identify unambiguously the type of joint orbital and spin ordering here, but the general qualitative conclusion is the same as for the case of e_g ions: In a cubic lattice there is a tendency toward an "antiferromagnetic" ordering of orbitals (in qualitative accordance with the situation in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$).

Nevertheless, even though an unambiguous conclusion regarding the orbital structure has not yet been reached in this approach, it may prove extremely useful for analyzing magnetic ordering: If, on the basis of independent considerations, we know the type of structural ordering, we can then find an effective spin Hamiltonian. A study of this type carried out for $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ by Lacroix⁵⁰ has yielded a description of the rather complex magnetic structure observed in this compound (this is apparently the case, but the single-ion anisotropy was handled incorrectly in Ref. 50). The exchange interaction of a pair of ions is given in this case by the two following expressions.⁵⁰ First, if the same orbital, m , is filled at the ions i and j , the exchange interaction is given by

$$J_{ij} = -\frac{2(t_{ij}^{mm})^2}{U_1} + \frac{2J_H}{U_2(U_2 - J_H)} \sum_{m' \neq m} (t_{ij}^{mm'})^2, \quad (21)$$

where U_1 is the repulsion of the electrons in one orbital, U_2 is that in different orbitals, and J_H is the Hund intraatomic exchange. If, on the other hand, different orbitals are filled at the corresponding ions, the exchange integral is

$$J_{ij} = -\frac{2(t_{ij}^{m'm'})^2}{U_1} - \frac{J_H}{U_2(U_2 - J_H)} \left(\sum_{m'' \neq m'} (t_{ij}^{m'm''})^2 + \sum_{m'' \neq m} (t_{ij}^{m''m})^2 \right). \quad (22)$$

Actually, the same expressions apply to the case of e_g electrons.

In writing out the expression for the exchange interaction in the (l, s) basis above [see (19) and (20)], we separated the spin and orbital variables. This approach is convenient when the initial state is degenerate, and when we are interested in the orbital ordering itself in addition to the spin ordering. When spin-orbit coupling is taken into account, especially if the nature of the deformation (i.e., the symmetry of the low-temperature phase) is already known, another approach can be taken. A transformation can be made to operators representing the total angular momentum, projected onto the lowest-lying multiplet (in particular, this is the procedure which is always used in the case of the rare earths). In this case we can introduce an effective spin \tilde{S} (for a Co^{2+} ion in an octahedron, for example, $\tilde{S} = 1/2$) and write the exchange interaction in terms of it. In general, this interaction is anisotropic and also contains invariants of higher orders.^{54,57} This is, in fact, the physical origin of the biquadratic exchange which we mentioned earlier.

As we also mentioned earlier, the basic distinction between the t_{2g} and e_g ions lies in the important role

played by the spin-orbit interaction in the former case. Aside from the fact that the spin-orbit interaction may impose its own type of orbital ordering, which differs from that caused by the Jahn-Teller effect and which occurs at the same time as the magnetic ordering, it strongly affects the magnetic anisotropy and the magnetostriction. If spin-orbit coupling is dominant, and the crystal is, say, a tetragonal crystal at a temperature below T_N , the spins are parallel to the angular momentum l , i.e., directed along the deformation axis. To turn the spins away from this direction will require either breaking the spin-orbit coupling (i.e., an energy lowering $\sim \lambda S$) or reorienting the deformation axis. Each of these processes requires a substantial expenditure of energy, and, as a result, the magnetic anisotropy of these materials is high (a particularly well-known example is the Co^{2+} ion).

However, even in those cases in which the Jahn-Teller interaction is "overpowering" and the ordering proceeds by that route, we can expect a significant anisotropy. In this case the ground state is an orbital singlet, and the magnetic anisotropy results from an admixture of excited states in which the angular momentum is not frozen. The standard approach⁵ here is to use a perturbation theory in λ/Δ (λ is the spin-orbit interaction constant, and Δ is the distance to the nearest excited levels); this approach yields a single-ion-anisotropy term

$$\sum_{\mu, \nu} D_{\mu\nu} S^\mu S^\nu, \quad D_{\mu\nu} = -\lambda^2 \sum_{n \neq 0} \frac{\langle n | L^\mu | 0 \rangle \langle 0 | L^\nu | n \rangle}{E_n - E_0}, \quad (23)$$

in the spin Hamiltonian, where the summation runs over the intermediate states $|n\rangle$ with energies E_n .

Ordinarily we would have $E_n - E_0 \approx 10Dq \approx 1$ eV, but in the case of systems with t_{2g} electrons and with a Jahn-Teller orbital ordering the excited states are $|l' = \pm 1\rangle$ states, which are separated from the $|l' = 0\rangle$ ground state by an amount $E_{JT} \ll 10Dq$. Correspondingly, the constants of the single-ion anisotropy for these materials should be much larger than those for nondegenerate ions. (In real systems with $3d$ ions we have $E_{JT} \sim \lambda$, so that it is not legitimate to use a perturbation theory in λ ; the complete secular equation must be solved in the basis of t_{2g} states. For an estimate, however, this approach shows that the anisotropy in t_{2g} systems with a Jahn-Teller ordering is generally comparable in magnitude to that in the case of IS ordering.)

Similar arguments show that the magnetostriction constants are also large in this case. A lattice deformation strongly affects the orbital state of the t_{2g} ions, and because of the spin-orbit interaction this effect is transferred to the spin subsystem. For ions of the Co^{2+} type this situation is quite familiar experimentally. We may thus say that the pronounced anisotropy and magnetostriction of transition metal ions with t_{2g} electrons actually stem from the orbital degeneracy.

6. STRUCTURAL PHASE TRANSITIONS IN MATERIALS HAVING AN ORBITAL DEGENERACY

The discussion above has dealt primarily with the forms taken by the orbital (Jahn-Teller) and exchange

interactions in Jahn-Teller magnetic materials and with the particular ground-state structures to which these interactions lead.

As the temperature is raised, the orbital ordering changes and may disappear. A transition to a disordered phase is simultaneously a structural phase transition to a phase with a higher symmetry, in which the orbital degeneracy is not lifted. In several materials (e.g., KCuF_3) such transitions do not occur. Apparently, the Jahn-Teller interaction in such materials is so strong that the lattice is distorted over the entire temperature range in which there is a crystalline phase. In other cases, these transitions are in fact observed; they may be either first-order or second-order transitions, and they sometimes involve intermediate phases (in particular, phases with incommensurable structures).

The structural phase transitions which result from the cooperative Jahn-Teller effect are the subject of an extensive independent literature, including several reviews.^{1,8,55,56} We will accordingly just skim over these questions lightly, singling out some points which are important to the primary subject of this review (the interrelationship between the Jahn-Teller effect and the magnetic properties) and noting some new results which we find particularly clear-cut and pertinent.

The cooperative Jahn-Teller transitions are conveniently described in pseudospin terms: Both the direct Jahn-Teller interaction, (8), and the exchange interaction, (18), give rise, in pseudospin terms, to an effective Hamiltonian of the Ising or Heisenberg type (in some cases, in an external field). The statistical properties of such systems have been studied thoroughly and can be used directly to describe the orbital degeneracy in Jahn-Teller systems. Some different cases arise here, and we will consider them in the subsections which follow.

a) *Ferrodistortion ordering (crystals with the spinel structure)*. In crystals having the spinel structure and containing Jahn-Teller ions the orbital ordering is usually "ferromagnetic": The crystals become tetragonal without any change in the unit cell. The best-known examples are the manganese ferrite spinels, for which we usually find a ratio $c/a \approx 1.10-1.15$ (Ref. 2). It can be shown that the transition in this case, with the anharmonicity taken into account, is a first-order transition¹³ (for t_{2g} ions, this is also true in the harmonic case). Figure 17 compares the theoretical and experi-

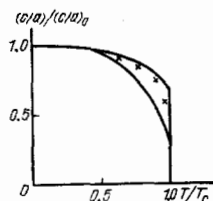


FIG. 17. Temperature dependence of the Jahn-Teller deformation c/a in spinels. Points—experimental data⁵⁸ for CuFe_2O_4 ; curves—theoretical,¹³ for various values of the anisotropy constants.

mental temperature dependences of the ratio c/a for the ferrite CuFe_2O_4 (Refs. 13 and 58).

In ferrite spinels with e_g ions the orbital (structural) ordering usually occurs at temperatures higher than that at which the magnetic ordering occurs; for Mn_3O_4 , for example, we have $T_{JT} = 1443$ K and $T_N = 43$ K (Ref. 59). In contrast, in spinels containing t_{2g} ions there may be different situations, as discussed in Section 5: In some cases the spin-orbit interaction causes orbital ordering to occur along with magnetic ordering, and there are also materials in which the structural transition due to the cooperative Jahn-Teller effect occurs at a higher temperature. The system $\text{NiCr}_x\text{Fe}_{2-x}\text{O}_4$ has some interesting properties²: In the concentration range $x \approx 1.2-1.8$ in this system, in a phase which is already ordered in S, a further lowering of the temperature apparently causes an additional lowering of the lattice symmetry, accompanied by a change in the spin configuration.

b) *Antiferrodistortion ordering (crystals with the perovskite structure)*. More peculiar from the standpoint of the orbital structure is the situation in perovskites with e_g ions (KCuF_3 , KCrF_3 , LaMnO_3 , MnF_3 , etc.). They have an "antiferro" orbital ordering (the reasons for this ordering were discussed in a qualitative way in Section 4). In terms of the pseudospins τ this type of ordering corresponds to a skewed rather than ordinary antiferromagnetism (the situation is quite rare for ordinary spins). In KCuF_3 at $T=0$, for example, there is an alternation of states with angles of the order of $\pm 60^\circ$ [in the (τ^x, τ^y) plane; see Fig. 13] (Ref. 16). The corresponding angles in MnF_3 are 97° (Ref. 13).

In principle, this skewed antiferromagnetism could result directly from a Hamiltonian of the type in (8) or (18) which is bilinear in τ . As we have already mentioned, the corresponding exchange with respect to τ is highly anisotropic and may give rise to a structure of this sort. A direct calculation¹⁹ with the exchange Hamiltonian in (18) does in fact predict a structure for KCuF_3 which corresponds precisely to the experimental structure (Fig. 13).

Another factor which skews the pseudospins is a local anisotropy. Anharmonic effects give rise to terms of the type $g\tau^3 \cos 3\theta$ in the Hamiltonian (more precisely, in the free energy). As a result, local minima appear in the energy, depending on the sign of g , at the angles $\theta = 0, \pm 2\pi/3$ or $\pm \pi/3, \pi$. An antiferromagnetic interaction in τ combined with an anisotropy can lead to the observed structures; for example, the skewed structure for MnF_3 (angles $\theta \approx \pm 97^\circ$) may be thought of as the result of a competition between an interaction between centers (which would give rise to angles θ of, for example, $\pm 90^\circ$) and an anisotropy (which would give rise to, say, $\pm 120^\circ$).

In this case we see an interesting effect as the temperature is raised: The structure changes in a way which corresponds to a "straightening" of the skewed τ -sublattices, and the angles θ approach $\pm \pi/2$. A phase transition in the cubic modification can go as a second-order transition from a purely "antiferromagnetic"

structure, despite the nominal presence of the cubic invariant $g\tau^3 \cos 3\theta$ in the free energy. For a two-sublattice structure of the type observed in MnF_3 and KCuF_3 , the free energy may be written as

$$F = A\tau^2 + A'\tau^2 \cos 2\theta - c\tau^3 \cos 3\theta + B\tau^4, \quad (24)$$

[τ is the orbital order parameter of the sublattice, and θ is the angle in the (τ^x, τ^y) plane]. The parameter A' here is proportional to the interaction of Jahn-Teller centers, while c is proportional to the local anisotropy constant.

Minimization of (24) with respect to the angle θ yields the temperature dependence of θ . At values of θ near $\pi/2$, $\theta = (\pi/2) - \varphi$, we find $\varphi = -(3c/4A')\tau$. Substituting this expression back into (24), we finally find

$$F = (A - A')\tau^2 + \left(B - \frac{27}{8} \frac{c^2}{A'}\right)\tau^4. \quad (25)$$

In other words, for a two-sublattice structure with an alternation of θ and $-\theta$ the cubic term in the free energy disappears, but the coefficient of the fourth-degree term is renormalized. If $B - (27c^2/8A') > 0$, the phase transition is a second-order transition, and at the transition point the angles are $\theta = \pm\pi/2$. A corresponding problem has been studied by Kanamori,¹³ who concluded that the transition is always a second-order transition in perovskites containing Jahn-Teller ions. It can be seen, however, that with a sufficiently strong anisotropy (a large value of c^2/A') the transition may remain a first-order transition.⁹⁾ In the case of a ferrodistor-tion (in the preceding subsection) there is no cancellation of the contributions of the different sublattices, and the cubic term remains in the free energy. The transition is therefore a first-order transition. The situation is the same in the case of a tripling of the period, with $\theta_n = (2\pi/3)_n$ (see the following subsection).

c) Phases with a tripling of the period and incommensurable structures. In addition to the relatively simple "ferro" and "antiferro" types of orbital ordering, more-complicated structures are also found in systems with a cooperative Jahn-Teller effect. Aside from the compound $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, which was mentioned in Section 5, two systems with an orbital ordering of the helicoidal type have been identified and studied in some detail: CsCuCl_3 and $\text{K}_2\text{PbCu}(\text{NO}_3)_6$.

The compound CsCuCl_3 is apparently the sole insulator in which a structural transition accompanied by helicoidal displacements of atoms occurs. The Jahn-Teller ions in this case are at the centers of octahedra which have a common face and which form chains along the z axis (Fig. 18). At $T_c = 423$ K in CsCuCl_3 , a first-order transition occurs, accompanied by a tripling of the period; local deformations (stretching) of the octahedra occur upon this transition. All three axes of the octahedra become the long axes in the crystal in succession. As a result, helicoidal displacements with a wave vector $q = (0, 0, 2\pi/3)$ occur. The transition is accompanied by singularities in the electrical conductivity.

⁹⁾ See Ref. 60 for a more detailed study of the mathematically equivalent problem for another physical system: a system with charge density waves.

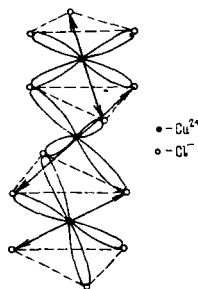


FIG. 18. Orbital ordering in the low-temperature phase of CsCuCl_3 . A chain of CuCl_6 octahedra having a common face is shown. The arrows show the axes along which the octahedra are stretched.

ity, the dielectric function, and several other properties.¹⁷ A low-frequency absorption mode with a frequency $\omega_0 = 17-18 \text{ cm}^{-1}$ has been observed in the low-temperature phase⁶¹ and interpreted as phase oscillations of a superstructure.

Anharmonicity apparently plays an important role in forming the structure observed in CsCuCl_3 , as in the compounds discussed in the preceding subsection.^{17,62} Specifically, terms $\sim \cos 3\theta$, which give rise to the skewed sublattices in the systems of the MnF_3 type, lead to a tripling of the period in the CsCuCl_3 crystal with its quasi-one-dimensional structure. The interaction between the centers along the chain, on the other hand, is apparently an "antiferro" interaction and would give rise to an alternation of the distortions in adjacent octahedra. Since there are two octahedra in the unit cell in the original, undistorted CsCuCl_3 lattice (the CsNiCl_3 structure), this superstructure (and the interaction maximum itself) would correspond to $q = 0$. This conclusion is supported by results from a study of the diffuse scattering of neutrons¹⁷ at $T > 423$ K. A maximum was observed there at $q = 0$. Curiously, the structure of the low-temperature phase could, in principle, be changed by applying a uniaxial pressure at certain angles in the basis plane.⁶²

There are indications of yet two more phase transitions in CsCuCl_3 above 423 K (Refs. 64 and 65). At present, the nature of these transitions is not clear; they are probably caused by a cooperative Jahn-Teller effect, and the intermediate phases correspond to either an incommensurable superstructure or a phase with an alternation of distortions ($q = 0$). Structural transitions which appear to be analogous to those observed in CsCuCl_3 are also observed in CsCrCl_3 and RbCrCl_3 , which contain the Jahn-Teller ion Cr^{2+} (Ref. 63).

An example of a compound with a cooperative Jahn-Teller effect in which there is an incommensurable structure is $\text{K}_2\text{PbCu}(\text{NO}_3)_6$ (Refs. 18 and 66). As the temperature is lowered in this compound two successive transitions occur, at $T_1 = 230$ K and at $T_c = 273$ K. Both are first-order transitions, although the lower-temperature one is apparently an approximately second-order transition. Neutron and x-ray studies have shown that the intermediate phase has an incommensurable superstructure with a wave vector $q = (0.416, 0.430, 0)$. The low-temperature phase is commensur-

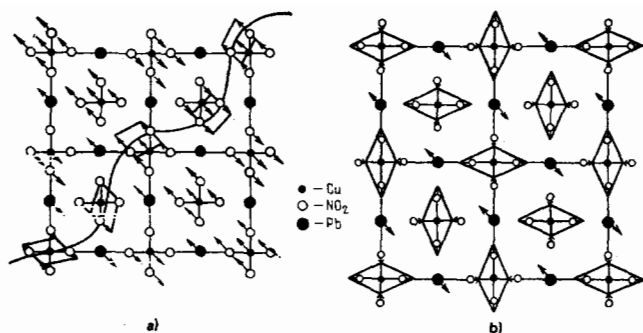


FIG. 19. Orbital structure in $K_2PbCu(NO_2)_6$ (Ref. 18). The (001) plane is shown. a—Incommensurable phase ($q = (0.416, 0.430, 0)$); b—commensurable phase.

able, with $q = (0.5, 0.5, 0.5)$, and the orbital ordering is similar to that observed in $KCuF_3$. In the basis plane there is an alternation of octahedra which are elongated along the x and y axes (Fig. 19a). In pseudospin terms, this phase also corresponds to a skewed antiferromagnetism, with sublattice angles of $\pm 2\pi/3$; the incommensurable phase, on the other hand (Fig. 19b), is described as a "fan" structure⁶⁶: The vector τ changes continuously from $+2\pi/3$ to $-2\pi/3$. Actually, the anharmonicity should apparently render such a superstructure inhomogeneous; the commensurable domains with $\theta \approx \pm 2\pi/3$ will be separated by comparatively narrow "walls" within which the intermediate directions of τ are traversed rapidly.⁶⁷

In another compound of the same class, $Cs_2PbCu(NO_2)_6$, we find not two but three successive transitions,⁶⁸ at $T_c = 112-114^\circ C$, $23-34^\circ C$, and between $-2^\circ C$ and $+12^\circ C$ (these are the hysteresis intervals). The wave vector of the superstructure takes on the respective values $q = (0.5, 0.5, 0)$, $(0.5, 0.5, 0.25-0.2)$ and $(0.5, 0.5, 0.5)$ as the temperature is lowered; the intermediate phase has a somewhat uncertain superstructure, which is believed by Mori *et al.*⁶⁸ probably to be incommensurable.

In general, we should say that crystals exhibiting a cooperative Jahn-Teller effect also exhibit a wide variety of structural phase transitions, including essentially all types of such transitions which are observed in any insulators.⁶⁹ These crystals constitute a special case, on the other hand, in that the elementary nature of the transition is understood very well; these materials are thus extremely promising for a study of the general aspects of structural phase transitions.

7. TEMPERATURE DEPENDENCE OF THE MAGNETIC PROPERTIES OF JAHN-TELLER SYSTEMS

a) *Change in the orbital structure and the exchange interaction.* As was shown in Section 4, the nature of the exchange interaction in a magnetic material containing Jahn-Teller ions depends strongly on the nature of the orbital ordering. Correspondingly, a change in the orbital structure (in particular, upon a change in the temperature) should also affect the exchange interaction (another mechanism for the temperature dependence of the exchange integrals will be discussed in the

following subsection). The modification of the exchange can be analyzed by working from a Hamiltonian like that in (17) [in specific systems, the Hamiltonian is much more complicated, but the structure remains the same; see (18), for example]. Separating the spin and orbital degrees of freedom, we can find the spin exchange by replacing the pseudospin operators in (17) by their average values (the correlation functions):

$$J_S = J_1 + 4J_2 \langle \tau_i \tau_j \rangle. \quad (26)$$

Just how J_S varies with the temperature depends on the details of the orbital ordering. In general, the only point that is clear is that the corresponding change is most pronounced near a structural transition. On the whole, however, the change is quite slow (the correlation functions for the τ variables fall off in proportion to T_{JT}/T at $T > T_{JT}$). We will offer only a qualitative discussion of the possible nature of the exchange in the disordered phase.

Even at temperatures above the temperature for cooperative Jahn-Teller ordering the Jahn-Teller effect continues to affect the physical properties of the corresponding materials. Various limiting cases are possible. One possibility is that the high-temperature phase contains local distortions near Jahn-Teller centers, but that these centers are distributed at random through the crystal (and they fluctuate over time). Another limiting case is that in which there are no distortions in the disordered phase. In the first of these cases the cooperative Jahn-Teller transition is an order-disorder transition, while in the second it is a displacement transition. From the standpoint of the static properties, these pictures are essentially the same; the differences may be seen primarily in the dynamic characteristics. In both cases the exchange interaction is determined by the correlation functions $\langle \tau_i \tau_j \rangle$. If there are no correlations between centers, the exchange interaction will be antiferromagnetic, even though the local distortions are conserved. If, however, the correlations are retained, in particular if they are of the same nature as in, say, the basis plane of perovskites of the $KCuF_3$ type (Fig. 20), the exchange may be ferromagnetic (despite the fact that the low-temperature phase is antiferromagnetic). Similar arguments were advanced by Goodenough² in an effort to explain the ferromagnetic sign of the Curie-Weiss temperature in the high-temperature susceptibility of $LaMnO_3$ and related compounds. At sufficiently high

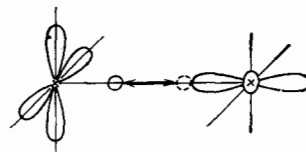


FIG. 20. Diagram illustrating the possibility of ferromagnetic correlations of neighboring centers due to the dynamic Jahn-Teller effect. Orthogonal orbitals are stabilized during slow vibrations of the anion between the Jahn-Teller centers (cf. Fig. 11b). Shown here are the filled orbitals for the case in which the anion is near the Jahn-Teller center at the left. In the opposite phase of the vibration, the orbitals exchange places.

temperatures, however, dynamic correlations of this sort should disappear, and the exchange should become antiferromagnetic, according to (17).

b) Suppression of the exchange interaction by the Jahn-Teller effect. In addition to the changes in the effective exchange integrals due to the modification of the orbital structure with changing temperature, there is yet another mechanism which operates in Jahn-Teller magnetic materials. It transforms the exchange interaction, giving it a temperature dependence which is usually far more significant than that caused by the change in the orbital structure. This mechanism, in contrast with that discussed in subsection a, is related only weakly to the intercenter correlations and is essentially a single-particle mechanism. It is of the same nature as the suppression of off-diagonal matrix elements which is well known in the theory of the Jahn-Teller effect (Section 3). The interaction of degenerate electronic states with phonons, particularly with a phonon mode which lifts the degeneracy, gives rise to a temperature-dependent renormalization of the coefficients in the effective exchange Hamiltonian, i.e., gives rise to a strong temperature dependence of the exchange, which is a distinctive property of Jahn-Teller ions.

Much experimental information has now been accumulated on the temperature dependence of the exchange integrals in magnetic materials containing Jahn-Teller ions, especially Cu^{2+} ions (see Ref. 70 and the bibliography there). The most remarkable material in this regard is the Heisenberg ferromagnet $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$, in which the Cu^{2+} ions form a bcc lattice. According to ESR data,^{71,72} the exchange integral for nearest neighbors decreases by a factor of about five as the temperature is raised from 77 to 300 K (Fig. 21). Corresponding results are found from an NMR study.⁷³ A significant temperature dependence of J is also observed (from the exchange narrowing of ESR lines) in stratified compounds containing ferromagnetic planes formed by Cu^{2+} ions [for example, K_2CuF_4 (Ref. 74) and $(\text{C}_6\text{H}_{2n+1}\text{NH}_3)_2\text{CuCl}_4$ (Ref. 75)] and in certain other copper compounds.⁷⁰ This effect is usually attributed to a phonon modulation of the exchange interaction,⁷⁰ which reduces to an increase in the distance between magnetic ions because of thermal expansion. This mechanism actually plays some role in shaping the temperature dependence of the exchange integrals, and it is probably a governing factor for compounds which contain ions having no orbital degeneracy, Mn^{2+} , for example. For Jahn-Teller systems, however, this mechanism is ap-

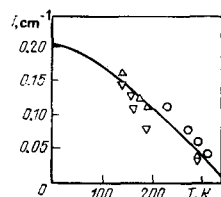


FIG. 21. Temperature dependence of the exchange integrals in $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$ according to ESR data. Δ —From Ref. 71; \circ —from Ref. 72.

parently insufficient. For $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$, for example, we have $\Delta J/J \approx 3.5 \cdot 10^{-3} \text{ K}^{-1}$ near room temperature, while the thermal expansion for this material is^{72,75} $\Delta l/l \approx 8 \cdot 10^{-5} \text{ K}^{-1}$.

In Jahn-Teller magnetic materials, however, there is another, distinctive, mechanism, which modifies the exchange and gives it a temperature dependence.^{75,76} The simplest way to explain this mechanism is to speak in pseudospin terms, as we did in Sections 2 and 3. For simplicity we consider a twofold-degenerate system which is interacting with a nondegenerate phonon mode (for the time being we will assume that the phonons are local):

$$H_{\text{int}} = \sum_{i,k} g_{ik} \tau_i^x (b_k^\dagger + b_{-k}). \quad (27)$$

An interaction of this type is known (see Ref. 1 and Section 3 of the present paper) to make the new states mixed electron-phonon states (or pseudospin-phonon states), and as a result the off-diagonal matrix elements of the various operators decrease [see (6)]. In particular, the operator τ^x is a nondiagonal operator; it acquires an exponential factor $\tau^x \rightarrow e^{-E_{JT}/\hbar\omega} \tau^x$, where ω is a characteristic phonon frequency. The corresponding suppression factors depend on the temperature, falling off sharply (as $e^{-E_{JT}/(\hbar\omega)^2}$) for $T \gg \omega$. Recalling that the complete exchange Hamiltonian also contains the operators τ^x and τ^y in the degenerate case [see (18)], we clearly see that when we take the interaction with the lattice into account the "nondiagonal" part of this Hamiltonian (the terms containing τ^x) will be modified and will acquire a temperature dependence. In other words, in the complete Hamiltonian, which may be written

$$H_{IJ} = \left(\frac{1}{2} + 2S_I S_J \right) (J_0 + J_{xx} \tau_i^x \tau_j^x + J_{yy} \tau_i^y \tau_j^y + J_{zz} \tau_i^z \tau_j^z), \quad (28)$$

the exchange constants J_0 and J_{xx} are not renormalized, while J_{yy} and J_{zz} acquire some small coefficients.

The same result is found⁷⁶ through a complete analysis of this problem carried out (instead of by working directly from the pseudospin representation) by using the initial degenerate model of Hubbard, (16), to which an appropriate electron-phonon interaction is added.⁹⁾ For local phonons we find in this case

$$J_{xx} \rightarrow \exp\left(-2\zeta^2 \coth \frac{\hbar\omega}{2T}\right) J_{xx}, \quad J_{yy} \rightarrow \exp\left(-4\zeta^2 \coth \frac{\hbar\omega}{2T}\right) J_{yy}, \quad (29)$$

in accordance with the discussion above. Here $\zeta = g^2/(\hbar\omega)^2 = E_{JT}/\hbar\omega$. When the phonon dispersion and the electron-phonon interaction are taken into account, some complications arise,⁷⁶ but they do not change the

⁹⁾ In contrast with the nondegenerate Hubbard model, in which the interaction with phonons affects the exchange substantially only if $\omega > U$ (Refs. 76–78), there is also an effect at small values of ω in the present case. The reason is that in the presence of a degeneracy the structural changes of the phonon subsystem which lead to the appearance of suppression factors occur not only in the intermediate state (as in the nondegenerate case) but also in situations in which the initial and final states of the exchange are themselves different. This situation is described by the operators τ^x , which change the orbital configuration of the ion.

overall qualitative picture, and we will not discuss them here.

In practice there are frequent cases in which degenerate electronic states interact with degenerate phonons. The interaction is then of the form in (5), and as a result we find not only the operators τ^x (which are nondiagonal with respect to the interaction $\tau^x Q_3$) but also operators τ^y (which are nondiagonal with respect to the interaction $\tau^x Q_2$). The corresponding suppression factors have been calculated numerically (see Ref. 9, for example). Their qualitative behavior is roughly the same as in an interaction with a nondegenerate mode, (29); the only difference is in the numerical coefficient in the argument of the exponential function. As a result, the entire part of the interaction in these systems which depends on the operators τ will decrease exponentially.

It can be seen from expressions such as (29) that the suppression of the exchange will be particularly marked at $T \approx \hbar \omega_D$ if $E_{JT} > \hbar \omega$. Analyzing the structure of the exchange Hamiltonian in (18), we also note the following: In this general form the exchange contains a large antiferromagnetic part $\sim t^2/U$, which does not depend on the orbital structure, and terms which contain the operators τ ; only these terms fall off with the temperature. It is clear that if the resultant exchange for a given pair of ions is antiferromagnetic then the change in this exchange as a function of the temperature will not be very pronounced—of order of unity (the terms containing τ decrease, but the constant part remains the same). The effect may be much stronger if the orbital structure of the ground state is such that, in the leading order in t/U , the terms containing τ completely cancel the constant term in the exchange integral, so that the resultant exchange becomes a relatively weak ferromagnetic exchange. This is the situation in $K_2CuCl_4 \cdot 2H_2O$ and K_2CuF_4 and also in the basis plane of $KCuF_3$. In this case the decrease in the terms containing τ in the exchange leads to an "unbalance," and the ferromagnetic exchange falls off significantly (here we are essentially seeing the tendency, mentioned above, toward a restoration of a strong antiferromagnetic exchange at high temperatures, when all the orbitals are filled equiprobably.¹⁰) In fact, the most noticeable change in the exchange interaction as a function of the temperature is usually observed in precisely those compounds containing Jahn-Teller ions in which the exchange is primarily ferromagnetic.

Up to this point we have been discussing the modifications of the exchange in materials containing e_g ions. In compounds containing t_{2g} ions the situation is similar in principle, but there are some important distinctions. If the primary interaction is one of t_{2g} electrons with E_g vibrations (the t-E problem; tetragonal and orthorhombic distortions), the diagonal operators $[(I^x)^2 - 2/3]$

and $[(I^y)^2 - (I^z)^2]$ are not suppressed, while the operators $(I^x I^y + I^y I^x)$, $(I^y I^z + I^z I^y)$, $(I^x I^z + I^z I^x)$, which also appear in the exchange Hamiltonian, decrease. In an interaction with trigonal vibrations we find the opposite situation. A more important point, however, is that the operator 1 (the orbital angular momentum) itself and, correspondingly, the spin-orbit interaction are suppressed exponentially in both these cases.⁹ Accordingly, as mentioned in Section 5, the spin-orbit interaction imposes its own type of ordering and opposes the Jahn-Teller ordering; in turn, the Jahn-Teller effect weakens the spin-orbit interaction (a similar situation in rare earth compounds was discussed in Ref. 6). The joint effects of all these factors have not been studied in detail; it is clear at a qualitative level that in cases in which the Jahn-Teller effect is predominant the temperature dependence of the exchange interaction may be stronger than when the ordering results from the spin-orbit interaction. Since the exchange in t_{2g} systems, however, is usually antiferromagnetic (i.e., the orbital terms cancel the constant antiferromagnetic contribution to the exchange very rarely), the effect of the temperature in these compounds should be less apparent than in systems with e_g ions.

To conclude this section we should state that it is really somewhat arbitrary to make a distinction between these two mechanisms (of subsections a and b) for the temperature dependence of the exchange integrals in Jahn-Teller systems. As we will see, the vibron ("polaron") suppression of exchange which we discussed above, may be ascribed, instead of to the exchange integral $J - \tilde{J}(T)$, to an average of the nondiagonal operators $\tau^x [\langle \tau^x \rangle - \exp(-\xi^2 \text{cth} \hbar \omega / 2T) \langle \tau^x \rangle]$. From this standpoint, the results of subsection b may also be treated as an effective attenuation of the orbital correlations $\langle \tau_i \tau_j \rangle \approx \langle \tau_i \rangle \langle \tau_j \rangle$, by analogy with subsection a (when the phonon dispersion is taken into account, this distinction is not always appropriate, but the general approach remains valid). We may say that the mechanism discussed in subsection a actually results from a change in the orbital ordering in the approximation of a self-consistent field, while the results of subsection b reduce to incorporating the effect of fluctuations in the electron-phonon (or pseudospin-phonon) system.

8. EFFECT OF A MAGNETIC FIELD ON JAHN-TELLER SYSTEMS

It has been shown in the preceding sections that the orbital structure and the magnetic order depend on each other in magnetic materials which contain ions having an orbitally degenerate ground state. This interrelation leads to some quite nontrivial orbital and magnetic structures (Section 4), which have been observed experimentally.

The existence of two order parameters—spin and orbital—may strongly affect the behavior of the corresponding materials in a magnetic field. If we perturb the filling of orbitals in some manner (by applying pressure, for example), we can change the structure of the spin system. On the other hand, a magnetic field acting on the spins simultaneously affects the orbital

¹⁰ Therefore, because of this effect, the exchange interaction may change sign upon a change in the temperature. This would be a new exchange-inversion mechanism, different from the ordinary Kittel mechanism,⁷⁹ which involves a thermal expansion (see also Ref. 49).

structure, and the parameters of the spin system also change. As a result, the dependence of the magnetic moment on the magnetic field becomes nonlinear even in the case of an isotropic exchange interaction of the type $S_i S_j$, and this circumstance distinguishes Jahn-Teller systems from ordinary Heisenberg magnetic materials. As the magnetic field is increased, abrupt transitions may also occur between different types of magnetic structures and, correspondingly, between different types of orbital structures. This circumstance actually means that there may be a metamagnetism (i.e., a highly nonlinear, even abrupt, change in the magnetic moment as a function of the magnetic field) in the case of an isotropic exchange interaction.¹⁰² Metamagnetism is usually thought of as a consequence of a pronounced anisotropy of the exchange interaction.⁸⁰⁻⁸² In the isotropic case, metamagnetic behavior may be exhibited in systems having an exchange interaction which includes terms which are biquadratic in the spin^{48,49} or in models of a similar nature, such as those of Ref. 83, for example, where the incorporation of the spin-lattice interaction in a chain of classical spins leads to biquadratic terms in the spin Hamiltonian. In Jahn-Teller magnetic materials, metamagnetism is possible even with $S = 1/2$, in which case there are no biquadratic terms or terms of higher order.

The mechanisms for the occurrence of a nonlinearity and for the metamagnetic behavior in this case can be understood easily¹⁰² from the simple model discussed in Section 4, with the Hamiltonian in (17). The complete "orbital" exchange J_τ is clearly

$$J_\tau = J_2 + 4J_3 \langle S_i S_j \rangle, \quad (30)$$

i.e., depends on the spin correlation function. The magnetic field H changes the spin structure and thereby affects J_τ . For $J_3 > J_2 > 0$, for example, the ground state is antiferromagnetic in terms of the spin, $\langle S_i S_j \rangle = -1/4$, and we have $J_\tau = J_2 - J_3 < 0$; in other words, an orbitally ferromagnetic state is produced. As the field is increased, the inclination of the spins causes the correlation function $\langle S_i S_j \rangle$ to increase, and a field is eventually reached [when $\langle S_i S_j \rangle > J_2/4J_3$] at which J_τ changes sign, i.e., at which the τ ordering gives way to an antiferromagnetic ordering. In turn, the actual spin exchange is [see (20)]

$$J_s = J_1 + 4J_3 \langle \tau_i \tau_j \rangle,$$

and a change with the field in the orbital structure characterized by $\langle \tau_i \tau_j \rangle$ leads to a dependence of J_s on the magnetic field, i.e., to a nonlinear dependence of the magnetization on the field. In the particular case discussed above, the transition from a "ferro" to an "antiferro" τ ordering leads to a decrease in J_s with the field (the correlation function $\langle \tau_i \tau_j \rangle$ becomes negative), and this effect causes the metamagnetism.

Let us illustrate these arguments for the particular system⁸⁴ described in Section 4: a perovskite structure in which ions having a single electron or hole in a two-fold-degenerate e_g level form a simple cubic lattice. We recall that the ground state of such a system with $H=0$ corresponds to a magnetic structure consisting of ferromagnetic planes perpendicular to one of the axes,

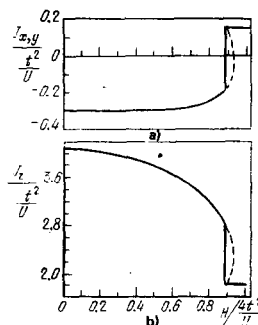


FIG. 22. Dependence of the exchange integrals on the magnetic field in systems of the perovskite type containing Jahn-Teller ions.⁸⁴

say the z axis, coupled in an antiferromagnetic manner. The orbital structure typically has an alternation of $d_{x^2-x^2}$ and $d_{x^2-y^2}$ orbitals (Fig. 13).

When the spin structure is changed by the magnetic field, the minimum energy naturally corresponds to some other orbital configuration, but at the same time the parameters of the effective spin Hamiltonian change, and the system does not behave in the magnetic field as it would if it were described by a Heisenberg model with constant coefficients. The corresponding problem was studied in Ref. 84 for the case in which the field H is parallel to the z axis and there is no anisotropy of the exchange interaction. In the limit $H \rightarrow 0$ the spins become aligned perpendicular to H , and as the field is increased they begin to incline progressively more, forming an angle with H which is determined by the minimum energy. The effective exchange integrals in the (x, y) plane and along the z axis change as shown in Figs. 22a and 22b. Generally speaking, there may be an abrupt change in the sign of the spin interaction, from ferromagnetic to antiferromagnetic, so that in a certain field the stratified spin structure transforms into an ordinary two-sublattice antiferromagnet (in which, of course, the sublattices are skewed because of the magnetic field).

It is simple to explain the appearance of a two-sublattice antiferromagnetic structure in a qualitative way. As mentioned earlier, there is an alternation of filled $d_{x^2-x^2}$ and $d_{x^2-y^2}$ orbitals in systems of the $KCuF_3$ type at $H=0$ (Fig. 13), so that the overlap of filled orbitals is zero in the (x, y) plane; the only overlap is of filled orbitals with empty orbitals, so that we have a ferromagnetic exchange $\sim t^2 J_H / U^2$. The magnetic field changes the orbital structure as well as the spin structure; an overlap between modified filled orbitals appears along the x and y axes. As a result, the magnetic field causes an "antiferromagnetic rigidity" along the directions perpendicular to H . The changes in the orbital structure and, correspondingly, in the crystalline structure which are required here are comparatively slight.

With a further increase in the field, the angle between the sublattices becomes progressively smaller, until saturation magnetization is reached at a certain field. Figure 23 shows the behavior of the magnetic moment of the system as the field is increased; this behavior is similar to that which is observed in typical metamagnets.

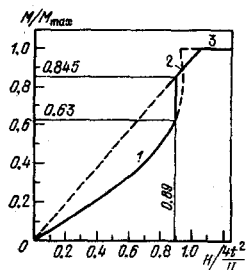


FIG. 23. Field dependence of the magnetic moment in perovskites containing e_g ions. $J_H/U=0.1$. 1—Stratified spin structure; 2—two-sublattice antiferromagnet; 3—ferromagnet.

In the description above we assumed that the g factors remained constant. If we allow for possible virtual transitions to higher-lying levels, however, for which the spin-orbit interaction is important, then the g -factors turn out to depend on the filling of the orbitals, even in the case of e_g states. Consequently, the g -factors may also change upon a change in the magnetic field. The corresponding interaction is described by terms proportional to $S^i \tau^i H$ at the i -th site. Incorporating this interaction does not change the situation described above in a qualitative way, but it does lead to some numerical corrections.⁸⁴

We note, however, that these aspects of the behavior of a system described by a superexchange Hamiltonian may occur only at fields $H/g\mu_B \sim t^2/U$. For a transition temperature $T_c \sim 100$ K ($T_c \sim t^2/U$), the typical field values are $\sim 10^6$ Oe ($\mu_B = 0.67 \cdot 10^{-4}$ deg/Oe); in other words, for ordinary transition metal compounds the fields required are not feasible experimentally. There is the hope that with $T \neq 0$ (in particular, with $T \sim T_N$) the necessary fields will be considerably weaker, while the situation will not be fundamentally different. At realistic field values it might be possible to observe effects due to the nonlinear dependence of the magnetic moment on the field. Incidentally, if the superexchange occurs through two or more intermediate ions, instead of through a single such ion, the characteristic critical temperatures and, correspondingly, the fields will be much lower. This is apparently the case for the garnet $\text{Ca}_3\text{Mn}_2\text{Ge}_3\text{O}_{12}$, with Mn^{3+} ions at octahedral interstitial positions forming a bcc lattice. This material shows indications of a cooperative Jahn-Teller transition at

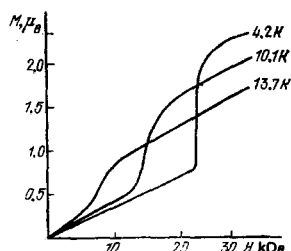


FIG. 24. Metamagnetic behavior of the garnet $\text{Ca}_3\text{Mn}_2\text{Ge}_3\text{O}_{12}$ containing the Jahn-Teller ion Mn^{3+} (Ref. 87). These are the magnetization isotherms for the case in which the field is directed along the [111] axis. $T_N = 13.85$ K.

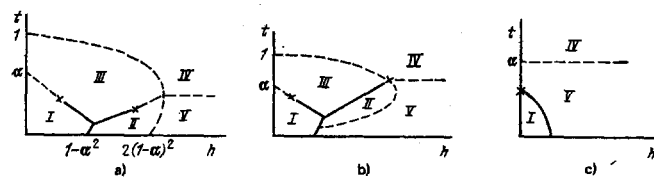


FIG. 25. Phase diagram of the two-spin Heisenberg model in (17) for various values of the parameter $\alpha = J_3/J_1$ (Ref. 88). $J_2=0$, $t=T/2zJ_1$, $h=H/2\sqrt{2}zJ_1$, and z is the number of nearest neighbors. a— $0 < \alpha < 1/12$; b— $1/3 < \alpha < 1$; c— $\alpha > 1$. The first-order transitions are indicated by solid lines and second-order transitions by dashed lines. \times —Tricritical points. I—Phase which is ferromagnetic with respect to τ and antiferromagnetic with respect to S ; II—phase which is antiferromagnetic with respect to both τ and S ; III—phase which is paramagnetic with respect to τ and antiferromagnetic with respect to S ; IV—phase which is paramagnetic with respect to both τ and S ; V—phase which is antiferromagnetic with respect to τ and paramagnetic with respect to S .

~ 400 K (Ref. 85). Neutron-diffraction measurements⁸⁶ have shown that its magnetic structure is extremely unusual, a structure not ordinarily found in garnets; this structure is evidently also a consequence of cooperative Jahn-Teller ordering. A study of this compound in a magnetic field has revealed a metamagnetic behavior⁸⁷ (Fig. 24). The magnetic anisotropy of $\text{Ca}_3\text{Mn}_2\text{Ge}_3\text{O}_{12}$ is slight and could hardly explain the unusual observed behavior; the metamagnetism of this compound may possibly be caused by the mechanism discussed above.

The unusual behavior of Jahn-Teller magnetic materials in an external field can also have a strong effect on the thermodynamic properties of the corresponding materials, particularly as represented on a phase diagram. A detailed analysis of the model in (17) has shown⁸⁸ that lines of first-order and second-order phase transitions, tricritical points, points at which several phases coexist, etc., are observed on a temperature vs magnetic field phase diagram (Fig. 25). The first-order transition in the field at low temperatures is the metamagnetic transition discussed above; interestingly, the transitions remain first-order transitions even above the triple point on the diagram. Some general theoretical models of this sort will be discussed further in Section 10.

Up to this point we have been discussing the effect of a magnetic field on Jahn-Teller magnetic materials. There are also other ways to perturb the orbital and spin structures of these materials. For example, the imposition of a uniaxial pressure P gives rise to terms of the type $A\tau^i P$ in the Hamiltonian; in other words, a uniaxial pressure affects the τ system in much the same way that a magnetic field affects the spin system.

A change in the orbital structure caused by a uniaxial compression could in principle lead to a modification of the spin ordering, but in materials exhibiting a symmetric cubic phase (spinel and perovskites) the primary effect is simply a reorientation of the distortion axis (a particular type of domain becomes preferential), while the nature of the orbital and magnetic ordering remains the same. The situation may not be this trivial in crystals exhibiting a lower initial symmetry

(see Ref. 62 and subsection 6c).

The Jahn-Teller magnetic materials discussed above had a "frozen" orbital angular momentum (e_g ions). In the case of t_{2g} ions, on the other hand, the indirect effect discussed above is accompanied by a direct effect of the magnetic field on the orbital angular momentum l , i.e., on the orbital structure. A linear relationship between l and the field H also occurs by virtue of the spin-orbit interaction. Correspondingly, with a spin-orbit ordering mechanism (Section 5) the orientation of the spins by the magnetic field involves some orientation of the resulting lattice distortions; i.e., the sample is again transformed into a single-domain sample in the simplest cases. Actually, the corresponding phenomena are closely related to the problem of the magnetic anisotropy in compounds with t_{2g} ions, which was discussed in Section 5.

On the other hand, when the ordering in a system with t_{2g} ions goes by the Jahn-Teller mechanism, and the ground state is an orbital singlet with a frozen angular momentum, the situation is slightly more complicated. The most important difference is that the magnetic field, by changing the spin structure, can shift the "balance" between the Jahn-Teller and spin-orbit energies. In spinels with a Yafet-Kittel triangular spin ordering, for example, a tetragonal distortion accompanied by the filling of states with angular momenta $l = \pm 1$ is unfavorable; in NiCr_2O_4 , for example, the ordering results from the Jahn-Teller effect ($C/a = 1$, $l^z = 0$). The magnetic field, by lining up the spins in a parallel arrangement, can in principle produce a favorable structure with $l^z = \pm 1$ (spin-orbit ordering; $c/a < 1$). This is apparently the nature of the additional temperature-induced transition to a phase with $c/a < 1$ in $\text{Fe}_{1-x}\text{Cr}_x\text{Ni}_2\text{O}_4$ (Ref. 2). It would be interesting to see how a magnetic field affects this transition.

9. METHODS FOR STUDYING ORBITAL ORDERING

The effect of orbital ordering on the magnetic properties is the basic subject of this review. In the present section we will consider some other, "nonmagnetic" manifestations of the cooperative Jahn-Teller effect which are widely studied experimentally and which serve as a basis for determining the orbital structure of the ordered phase. These questions are already the subject of an extensive literature (see the reviews in Refs. 1, 8, and 69), and we will discuss them only briefly here. To make the discussion more concrete we will illustrate the various methods primarily for a single case: the nontrivial orbital structure of K_2CuF_4 (Section 4).

We begin by noting that the symmetry and distortion of the low-temperature phase of a crystal can be studied by direct methods (x-ray and neutron methods). These results yield the orbital filling directly. For e_g ions, for example, the deformation of the octahedron near the Jahn-Teller ion determines the angle θ in the (Q_2, Q_3) plane or in the (τ^x, τ^y) plane¹³:

$$\tan \theta = \frac{Q_2}{Q_3} = \frac{\sqrt{3}(l-s)}{2m-l-s}, \quad (31)$$

where l , m , and s are respectively the long, intermediate,

and short axes of the octahedron. Equation (31) then gives the ground-state wave function $|\psi\rangle = \cos\theta/2 |d_{x^2-y^2}\rangle + \sin\theta/2 |d_{xy}\rangle$ [we recall that for the Cu^{2+} ion, which has a hole instead of an electron in the e_g level, the angles θ in the (Q_2, Q_3) plane must be replaced by $\pi - \theta$]. Analysis of the experimental data shows that for typical e_g ions the octahedra are usually not flattened but instead stretched; this is always the case for the Cu^{2+} ion, and the situation is apparently the same in compounds containing Mn^{3+} and Cr^{2+} , although in these latter cases the deformation may incorporate a substantial orthorhombic component, described by Q_2 . In Ref. 90 it is asserted that Mn^{3+} ions in orthoferrites and in manganates of the LaMnO_3 type are characterized by a $d_{x^2-y^2}$ wave function, but those results are very dubious, apparently a consequence of errors in the theoretical interpretation of the experiment. In Mn^{3+} compounds the angle θ actually lies in the range $\pi/2 \leq \theta \leq 2\pi/3$ ($\theta = 2\pi/3$ in spinels and $\theta \approx 97^\circ$ in MnF_3). For Cu^{2+} the angle θ (in the τ plane) is usually near $\pi/3$; i.e., in practice the hole fills a $d_{x^2-y^2}$ orbital.

The nature of the orbital filling can also be seen in many other properties of a crystal. It strongly affects the ESR and NMR spectra, particularly the NMR of diamagnetic anions (because of the covalent admixture of cation wave functions). Manifestations of the Jahn-Teller effect in ESR are well known.⁵ An example of the use of the NMR method to analyze the orbital structure of K_2CuF_4 is described in Ref. 36.

Optical spectroscopy is a powerful tool for studying term splitting and structural transitions.^{1,89} This is primarily direct ligand spectroscopy, which yields the positions of the electronic energy levels and their changes during transitions; this type of spectroscopy is widely used to study Jahn-Teller compounds.^{1,92} Light scattering yields some important information about structural transitions. Since both electronic and lattice characteristics change in the course of the cooperative Jahn-Teller effect, the transition can be seen in both electron Raman scattering and scattering by phonons. Analysis of the corresponding data also yields the type of orbital ordering; an example of this approach is Ref. 94, where Raman scattering in K_2CuF_4 confirmed a structure which had been inferred indirectly. Orbital ordering is also manifested in the optical properties; in particular, it gives rise to a dichroism (see Ref. 37 for a corresponding study of K_2CuF_4).

Finally, some important information can be obtained by studying phonon characteristics, especially through ultrasonic measurements. This method is particularly effective when a structural phase transition actually occurs in a system, but it also yields some information in the ordered phase itself. Which particular modulus softens near a transition is determined by the original degeneracy and by the type of deformation during the transition. For a deformation with E_g symmetry, for example, the elastic modulus $C_{11} - C_{12}$ softens, while the C_{44} modulus softens in a T_g deformation.⁴⁰ The temperature dependence of the corresponding modulus is given by the following expression^{40,55} (if the macroscopic deformation can be used as an order parameter,

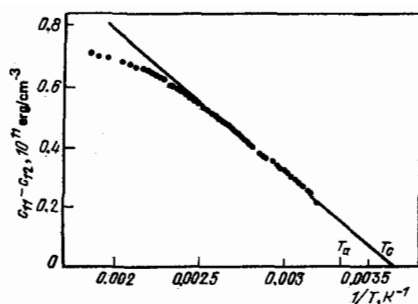


FIG. 26. Softening of the elastic moduli accompanying a Jahn-Teller structural transition in NiCr_2O_4 (Ref. 111). T_0 —Point of first-order phase transition.

i.e., for ferroelastic transitions—and most of the cooperative Jahn-Teller transitions fall in this category):

$$C(T) = C_0 \frac{T - [T_0 + (g^2/a'C_0)]}{T - T_0}, \quad (32)$$

where C_0 is the initial elastic modulus, T_0 is the temperature of the transition caused by any mechanism other than an interaction with a uniform deformation, g is the constant of the interaction with a uniform deformation of the corresponding symmetry, and $a' = a'(T - T_0)$ is the coefficient of the quadratic term in the Landau expansion of the free energy.

Interestingly, by using (32) we can determine from the corresponding experimental data the relative role played in the transition by the interaction with a uniform deformation [see (8)] and the relative roles played by all other interactions (including the Jahn-Teller interaction with short-wave phonons, the direct quadrupole interaction, and the exchange interaction). An analysis of this type for the Jahn-Teller transition in NiCr_2O_4 , for example, has shown^{96,111} that the interaction with a uniform deformation plays a leading role in this compound (Fig. 26). So far we have no corresponding data for perovskites, in which we could expect stronger interactions of a different type.

10. SOME OTHER THEORETICAL QUESTIONS

In addition to the specific questions discussed above, several related theoretical problems arise in research on the cooperative Jahn-Teller effect and on the magnetic properties of materials having an orbital degeneracy. These problems are also of interest in their own right, and we will discuss a few of them briefly here.

Several problems arise in the analysis of a purely Jahn-Teller system. In our discussion of the structural transitions which result from the cooperative Jahn-Teller effect we actually used an approximation corresponding to the approximation of a self-consistent field. There was almost no mention of fluctuation effects, in particular, above the transition. It is clear, however, that even an isolated Jahn-Teller center in such a system has an important and distinctive property: With a sufficiently strong interaction, the wave functions of this center are vibron wave functions, and local distortions near the Jahn-Teller centers may have to be considered in the high-temperature symmetric phase. The

transition will be of the nature of an order-disorder transition; if these local effects are ignored, on the other hand, the transition is more nearly a displacement transition. In practice, the distortions at $T > T_{JT}$ are dynamic; i.e., the actual situation lies somewhere between these two limiting cases. Only a few papers^{47,91,96,97} have been devoted to a theoretical analysis of the role played by vibron effects in the cooperative Jahn-Teller effect, and this question also requires further experimental study.

In materials exhibiting a cooperative Jahn-Teller effect the situation is more complicated than for other structural transitions in cases in which the degenerate electron mode interacts with a degenerate phonon mode. For example, the interaction in the case of twofold degeneracy is frequently of the form in (4) or (7); i.e., it depends simultaneously on the operators τ^x and τ^y . In such cases the phonon coordinates do not separate upon a canonical transformation corresponding to a displacement transformation for the phonon operators, because the operators τ^x and τ^y do not commute; the result is a very complicated dynamic situation (there is an analogous situation in the case of a pseudodegeneracy, which is quite common in rare earth compounds^{1,89}). The analysis of this case and of its consequences has been the subject of many papers (see Refs. 98 and 101, for example).

At this point we leave the purely Jahn-Teller situation to consider some problems and results for situations in which there are interacting spin and orbital subsystems. As was mentioned earlier, the degenerate Hubbard model (Section 4) is the mathematical model for this case. In addition to the results which were discussed above and which already have some specific applications, there are some other results available for this model.

The properties of the exchange interaction which are characteristic of orbital degeneracy have been studied on the basis of symmetry considerations in a series of papers.^{99,100} In particular, the possible appearance of a phase with a "frozen" (or greatly reduced) spin has been studied, and the possibility of piezomagnetism has been pointed out.

The properties of the degenerate Hubbard model were studied in Refs. 103–105 for an arbitrary (in particular, fractional) number of electrons at a center. This case may be pertinent to Jahn-Teller systems with impurities and also to materials in which there is an appreciable overlap of the d levels of adjacent centers (the examples usually cited are the systems $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$, $\text{Co}_{1-x}\text{Ni}_x\text{S}_2$, and $\text{CoS}_{2-x}\text{Se}_x$; Refs. 105, 106). It turns out that in this case the orbital and magnetic structures change as the bands are filled¹⁰³; in particular, it is possible to derive an exact result¹⁰⁷ which is analogous to Nagaoka's result¹⁰⁸ for the nondegenerate case. According to Ref. 108, the ground state of a degenerate system having only a single extra electron (above $n = 1$) turns out to be ferromagnetic in terms of spins and orbitals. The thermodynamics at high temperatures has also been studied for the degenerate Hubbard model.¹⁰⁹ Essentially all the results derived for the nondegener-

ate Hubbard model can be generalized to the degenerate case (although this has not yet been done systematically). It should be noted, however, that essentially all the work which has been carried out in this direction has dealt with the very simple symmetric version of the model, in which the transition matrix elements t_{ij} are identical for all ion pairs i, j and in which $t_{11} = t_{22}$. As we saw above, however, the corresponding anisotropy in a real situation is extremely pronounced, so that the results of these studies are hardly directly applicable to specific systems.

Orbital degeneracy plays an important role in cases other than that of highly localized electrons, as in magnetic insulators. This degeneracy may also be important in the intermediate range of the parameters $t \sim U$; it may be manifested in a Mott insulator-metal transition. There has been essentially no study along this line; the only really detailed discussion of this question has been in the papers in Ref. 110. Specific calculations were carried out there for the properties of V_2O_3 in both the insulator and metal phases. It was shown, in particular, that below the insulator-metal transition in V_2O_3 there is, in addition to a magnetic ordering, an "antiferro" orbital ordering. Only if this orbital ordering is taken into account can the structure of the low-temperature phase be described correctly. It is clear from this result and also from general considerations that in real materials (in particular, in transition metal compounds which undergo insulator-metal transitions) the degeneracy of electronic levels should play an important role. These questions clearly deserve further study (all that we have so far are the qualitative and semiphenomenological discussions in Refs. 112 and 113).

It is not, however, only in the case $n \neq 1$ or $t \sim U$ that theoretical problems arise for such systems. Even in the simplest case of strong coupling and a single electron per center the situation is far from completely clear. As was shown in Section 8, the problem reduces to a "two-spin" problem in this case, in which there are spins S and τ at each site which have a bilinear and quaternary interaction and, frequently, a peculiar anisotropy. Correspondingly, models of the types which are widely used for purely theoretical purposes in the phase-transition problem naturally arise here. For example, the two-spin model with the Hamiltonian

$$H = \sum_{i,j} (J_1 S_i S_j + J_2 \tau_i \tau_j + J_3 S_i S_j \tau_i \tau_j) \quad (33)$$

becomes the same as the Ashkin-Teller model¹¹⁴ when the variables S and τ are the Ising variables. Several interesting results have now been established for the Ashkin-Teller model (see Ref. 115, for example). If, on the other hand, one or both of the variables S and τ are Heisenberg variables, the situation is even more complicated. An analysis has been carried out for this case^{116,117} in the approximation of a selfconsistent field and in the constant-coupling approximation. The phase diagram for this model for the case of a magnetic field $H \sum_i S_i^z$ was studied in Ref. 88 (see Section 8 of the present review). It is also a simple matter to derive an exact solution for the two-spin Ising model in a magnetic field in the one-dimensional case^{118,119} and also for

the model in (33) for the case of a one-dimensional chain of classical spins S and τ (Ref. 118). The one-dimensional Heisenberg model of the type in (33) has also been solved exactly for the symmetric interaction.¹²⁰

A distinctive feature of all these two-spin models is the presence of three order parameters: S , τ , and $\eta = S\tau$, with the kinematic coupling $S\tau\eta = \text{const}$. In the Ising version these three parameters are all equivalent, and there is the corresponding possibility of a strong degeneracy. For Heisenberg spins, in contrast, the parameter η is not equivalent to S and τ , so that this case has some distinctive features.^{88,118}

Yet another curious spin model which arises in a natural way in a study of Jahn-Teller magnetic materials is the model incorporating the anisotropy of the exchange for different pairs of ions. As was shown in Section 4, the τ exchange is different for pairs lying along the x , y , and z axes. In the simplest case, the situation can be described by a Hamiltonian of the type

$$H = J \left(\sum_{\langle i,j \rangle_x} \tau_i^x \tau_j^x + \sum_{\langle i,j \rangle_y} \tau_i^y \tau_j^y + \sum_{\langle i,j \rangle_z} \tau_i^z \tau_j^z \right), \quad (34)$$

where $\langle i,j \rangle_{x,y,z}$ denotes the i, j pairs which are arranged along the x , y , and z axes, respectively. Although the interaction within each pair is a sort of Ising interaction, the overall symmetry is considerably more complicated. The "cubic" model¹²¹ in (34) has much in common with the real dipole-dipole interaction, and its properties, even its ground-state structure, are not yet clear. Pairs arranged along the z axis, for example, would like to align their spins along z ($\langle \tau^z \rangle \neq 0$), while pairs arranged along the x axis would like to rotate their spins around the axis.¹²² This situation can be described by the classical model of a lattice of magnetic needles ("compasses"). In contrast with a one-dimensional system, the properties of two-dimensional and three-dimensional systems are not understood even qualitatively. In a one-dimensional chain of this type, a situation of this sort is understandable: All the needles line up head to tail and become ordered along the direction of the chain. For a square two-dimensional lattice, on the other hand, the nature of the ordering (i.e., the direction of the arrows) is not clear even in the classical case. We might note in this connection that the Bogolyubov inequality has been used to prove a theorem¹²³ that ordering is not possible in the three-dimensional case for a system with a purely dipole-dipole interaction. In the one-dimensional case, on the other hand, this is not proved. The situation here is opposite that in the usual spin models,¹²⁴ where there is no ordering in the one-dimensional case.

Finally, the model describing the orbital ordering which allows for an anisotropy with respect to the angle θ in the (τ^x, τ^y) plane has some distinctive properties. The Hamiltonian for this model can be written in the form

$$H = \sum_{\langle i,j \rangle} J_{ij} (\tau_i^x \tau_j^x + \tau_i^y \tau_j^y) + H_{\text{anis}}, \quad H_{\text{anis}} = g \sum_i \cos 3\theta_i. \quad (35)$$

With $g=0$, this becomes the model of plane rotors (the XY or, here, the XZ model, but an interaction of the

Heisenberg type can also be treated), and at large values of g this model becomes the Potts model with three states per site.¹²⁵ The model in (35) may be thought of as a quantum generalization of the Potts model.

All these models, which are of theoretical interest in their own right, arise naturally in the theory of Jahn-Teller magnetic materials. The actual properties of these materials will exhibit the various characteristic features of each of these models in some form or other.

11. CONCLUSION

We have seen that the orbital degeneracy which is common in magnetic insulators has extremely important effects on the entire range of properties, including magnetic properties, of these materials. This is the justification for singling out magnetic materials containing Jahn-Teller ions as a special class. A study of these materials is of much interest in itself, because of the rich variety of properties. The situation combines effects stemming from structural changes (with all the distinctive features characteristic of structural phase transitions) and nontrivial magnetic properties. We have seen that the analysis of the distinctive magnetic properties of Jahn-Teller compounds and the application of the corresponding models permit a slightly new approach to, and a better understanding of, such "classical" magnetic phenomena as magnetic anisotropy and magnetostriction.

A quite attractive aspect of the study of Jahn-Teller magnetic materials, especially those containing transition metals, is that graphic qualitative concepts—regarding the nature of the orbital wave functions, the corresponding electrostatic interaction, and overlap—work very well here. These materials are apparently unique in the sense that with knowledge of nothing more than the chemical composition of the compound (the nature of the transition ions in it) it is usually possible to predict the presence and nature of a lowering of the symmetry and the associated features in the magnetic behavior.

The topics discussed in this review do not exhaust the manifestations of the Jahn-Teller effect in transition metal compounds. In essentially all systems which contain Jahn-Teller ions (or in which such ions appear) these ions have many physical consequences. The Jahn-Teller effect influences both the conductivities of the corresponding materials (see Ref. 126, for example) and resonance phenomena. Specifically, the interaction with the lattice, which is strong for Jahn-Teller ions, is apparently responsible for that firming up of domain walls which leads to the photomagnetic effect¹²⁷ in chromium chalcogenide spinels. We could cite many other examples.

Orbital degeneracy undoubtedly affects the properties of metallic systems also; in addition to the papers which we cited in Section 10, we might also mention the ideas of Thalmeier and Falicon¹²⁸ regarding a possible role of orbital degeneracy in transition metals. In this connection we note that the splitting of the threefold-degenerate t_{2g} states lies at the basis of the theory pro-

posed by Labbé and Fiedel¹²⁹ for structural transitions in compounds of the V_3Si and Nb_3Sn type. In general, the Jahn-Teller band effect and the associated structural transitions in metals and alloys now constitute a rather large independent field of research.¹³⁰

Returning to the Jahn-Teller magnetic insulators, we might say that we now have a rather clear picture of their static properties (their orbital and crystalline structures, the type of magnetic ordering, the particular features of magnetic anisotropy and magnetostriction, and the response to an external magnetic field). The primary need at this point would seem to be a study of the dynamic characteristics (by means of neutron scattering, the scattering of light, ultrasonic measurements, etc.). Studies of this type may reveal some interesting new effects in this unusual class of compounds.

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