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Spin-Orbit vs. Jahn-Teller Deformation in Chromium Spinels

JOHN B. GOODENOUGH
Lincoln Laboratory, Massachusetts Institute of Technology*
Lexington 73, Massachusetts, U.S.A.

It is pointed out that although tetrahedral-site Ni^{2+} may be stabilized by either spin-orbit or Jahn-Teller effects, each effect tends to quench the other so that it is possible to distinguish the dominant mechanism from the sign of the site deformations that occur. However, the fact that the two stabilizations are of comparable magnitude makes it possible for A-site Ni^{2+} in a spinel lattice to be stabilized by either one or the other mechanism, depending upon the number of A sites that are Ni^{2+} and the characters of the other cations in the structure. This fact is used to interpret the complex crystallographic properties of the system $NiCr_tFe_{2-t}O_4$ and the crystallographic anomaly of the system $Cu_{1-x}Ni_xCr_2O_4$. It is also pointed out that tetrahedral-site, low-spin-state Fe^{II} could have similar properties, which may be important for the interpretation of the system $Fe_{3-x}Cr_xO_4$.

1. The Hamiltonian for "localized", cation $3d$ electrons in spinels is

$$H=H_0+V_{el}+V_c+V_t+V_{LS}+V_\lambda+\Sigma_{ij}J_{ij}\,S_i\cdot S_j \qquad (1)$$

where H_0 is the one-electron approximation and V_{el} is the electrostatic correction to this approximation, V_c and V_t are the cubic and noncubic contributions to the crystal fields, and $V_{LS}=\lambda\,L\cdot S$ is the spin-orbit interaction given by Russell-Saunders coupling. These first five terms apply to a free-ion complex. In a solid, the cation complexes are coupled together, and it is necessary to consider the coupling interactions. V_λ is the energy required per critical cation to distort the lattice from cubic symmetry. The last term is the magnetic-exchange term, which is primarily responsible for the magnetic order on the magnetic-ion sublattice. Hyperfine splittings ($\sim 10^{-2}\ cm^{-1}$) are too small to compete with the effects listed in Eq. (1).

Several years ago, Dunitz and Orgel[1] pointed out that the sign of the tetragonal distortions that are observed in $Ni[Cr_2]O_4$ and $Cu[Cr_2]O_4$ may be attributed to a Jahn-Teller (J-T) effect at the A-site Ni^{2+} and Cu^{2+}. Prince[2] has verified that it is the A sites that are distorted in these compounds. Dunitz and Orgel used a simple one-electron model, in which V_{el} is assumed to be responsible only for Hund's highest multiplicity rule, to illustrate their point. Although this model is known to be inadequate, especially for the case of tetrahedral-site Ni^{2+}, nevertheless it does make transparent the essential physics of the problem. Therefore the one-electron model will also be used in this brief discussion. The Dunitz-Orgel argument was briefly as follows: In a cubic spinel, the ligand fields at an A site are purely cubic, and V_c splits the fivefold-degenerate orbital state into an upper, threefold-degenerate Γ_5 (d_{xy}, d_{yz}, d_{zx} atomic orbitals) and a lower, twofold-degenerate Γ_3 (d_{z^2}, $d_{x^2-y^2}$ atomic orbitals). With either one or two holes in the d shell, as is the case for Cu^{2+} and Ni^{2+}, the orbital ground state is degenerate. Jahn and Teller[3] have pointed out that if there are no other perturbations present to remove such a degeneracy, then the system will be stabilized by a spontaneous distortion of the interstice to some lower symmetry that introduces a V_t that removes the degeneracy. For a Cu^{2+} ion, the single d hole would be stabilized in a nondegenerate orbital (say d_{xy}), so that the interstice goes tetragonal ($c/a<1$). For a Ni^{2+} ion, two d holes would be ordered into d_{yz}, d_{zx}, so that the interstice goes tetragonal ($c/a>1$). If a large fraction of the A-site cations are J-T ions, then static, cooperative distortions of the interstices occur so as to minimize V_λ[4]. This introduces a macroscopic distortion of the structure that is a definite manifestation of J-T stabilization. (Since this mechanism is independent of spin, the magnetic-exchange

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interactions do not influence the problem.) In cubic symmetry either dynamic or disordered, local J-T stabilizations may be present. Dynamic (or quasistatic) stabilizations are possible because there is strong coupling between J-T electron ordering and the lattice vibrations[5].

About the same time Kanamori[6] concentrated attention on the spin-orbit coupling, which is always a significant perturbation if there are one or two holes in the three Γ_5 states, whose magnetic quantum numbers are $m=0, \pm 1$. He was able to show that the sign of the distortions that are observed below the Néel temperature in FeO and CoO can be attributed to the spin-orbit perturbation V_{LS}. Application of the Kanamori argument to the case of A-site Cu^{2+} or Ni^{2+} goes as follows: In order to optimize that contribution to the spin-orbit coupling that comes from the Γ_5 states, there should be a spontaneous distortion of the interstice to lower symmetry that orders the single Cu^{2+} hole into a twofold-degenerate state; the two holes of Ni^{2+}, one into a singlefold and the other into a twofold state. This calls for tetragonal $(c/a>1)$ Cu^{2+} sites and tetragonal $(c/a<1)$ Ni^{2+} sites. This is just opposite to the J-T distortion, which stabilizes an orbital singlet thereby tending to quench the orbital angular momentum.

There are several observations that follow from the above discussion. (1) Since the sign of the distortions that are associated with the J-T mechanism is opposite to those associated with V_{LS}, it follows that the two effects tend to exclude one another. It is for this reason that it is possible to distinguish the dominant mechanism that is operating in any given situation by the sign of the distortions that occur. (2) The fact that the distortion occurring in $Ni[Cr_2]O_4$ carries the sign of the J-T effect, but that in FeO the sign of V_{LS} (where octahedral-site Fe^{2+} is analogous to tetrahedral-site Ni^{2+}) suggests that for a free-ion complex of Ni^{2+} or Cu^{2+} with four tetrahedral O^{2-}, the stabilization associated with a deformation to $c/a<1$ is about equal to that for $c/a>1$. This deduction from experiment has been confirmed for the case of Ni^{2+} by Baltzer's detailed calculations, which are published in these Proceedings. (3) If this is so, then the sign of the distortion may be determined by the cooperative interactions that occur between complexes within a crystal, and it may be possible to induce a change in the sign of a given distortion by changing the character of the long-range phenomena. (4) For a spin-orbit deformation, there are two contributions to the stabilization, an increase in spin-orbit coupling $\alpha \boldsymbol{L}\cdot\boldsymbol{S}$ plus a deformation stabilization δ_t. For a J-T deformation, the two corresponding contributions give $2\delta_t \beta \boldsymbol{L}\cdot\boldsymbol{S}$, where $(\alpha+\beta)\approx\lambda$. The factor two enters the deformation stabilization because the total energy of the Γ_5 level is conserved through the perturbation. This gives the following criterion for the sign of the deformation:

$$\begin{array}{ll} \text{Spin-orbit} & \text{if } \lambda \boldsymbol{L}\cdot\boldsymbol{S} > \delta_t \\ \text{J-T} & \text{if } \lambda \boldsymbol{L}\cdot\boldsymbol{S} < \delta_t \end{array} \qquad (2)$$

The spin-orbit interaction is optimum if magnetic ordering aligns the spins parallel to the axis of the orbital-momentum vector. It is therefore most likely to dominate below a temperature at which the spins of the ions in question are ordered collinear. (However, if other J-T ions are simultaneously present to establish, through V_λ, a cooperative deformation stabilization with the sign of the spin-orbit effect, then the critical ions may participate in the cooperative effect even though there is no long-range ordering of the spins.) The deformation stabilization per J-T ion δ_t, on the other hand, depends upon the fraction of cations that are J-T ions.

2. These considerations lead to the speculation that it might be possible to induce the deformation found in $Ni[Cr_2]O_4$ to change from a J-T to a spin-orbit sign by simultaneously reducing the fraction of A sites that are Ni^{2+} and reducing the exchange-interaction ratio J_{BB}/J_{AB}. An appropriate system to study for this effect would be $NiCr_tFe_{2-t}O_4$. McGuire and Greenwald[7] have reported both magnetic and crystallographic measurements on this system. A plot of saturation magnetization *vs* composition shows that the inverse spinels $(t<1)$ have Néel-type magnetic order, but that for $1<t<2$, where Ni^{2+} are forced in a regular manner from the B to the A sites with increasing t, the magnetic order is not Néel-type. However, neutron-diffraction studies by Pickart and Nathans[8] have revealed that the A-site spins in a

sample with $t=1.5$ are collinear at 4.2°K. This suggests that anisotropy and magnetostrictive effects associated with strong spin-orbit coupling have forced the A-site spins to become collinear below some $T_t \leq T_c$. If this is so, then below T_t there should be a deformation with the sign of the spin-orbit coupling, which means that there should be a critical composition t_c such that $c/a<1$ is found for $t<t_c$, but $c/a>1$ for $t>t_c$. (Since molecular-field theory for *homogeneous* cation sublattices requires collinear spins just below T_c, a spin-orbit deformation might be anticipated at T_c. However, in these *heterogeneous* cation sublattices a $T_t<T_c$ is quite feasible.) Crystallographic measurements have revealed the anticipated sign reversal with $t_c \approx 1.8$, $T_t<T_c$, and a compositional range of orthogonal deformations where two, independent tetragonal distortions of opposite sign have their c axes at right angles. The width of this latter range is compatible with the chemical inhomogeneity that probably existed in the samples that were studied. It is also significant that spin-orbit distortions were observed with less than 25 percent of the A sites occupied by Ni^{2+}. This is possible, of course, because long-range coupling occurs via the magnetic-exchange term when spin-orbit coupling predominates.

Independent evidence that A-site Ni^{2+} may be stabilized by a tetragonal ($c/a<1$) distortion of its interstice comes from the systems $Cu_x{}^{2+}M_{1-x}^{2+}[Cr_2{}^{3+}]O_4$, which are tetragonal ($c/a<1$) for $x>0.5$ if M=Co, Mg, Zn, or Cd but for $x>0.1$ if M=Ni[9]. In this case the cooperative character of the spin-orbit distortions may be independent of any magnetic-ordering temperature because cooperating J-T distortions at the Cu^{2+} sites are independent of T_c. However, the spin-orbit contribution should be manifest by an anisotropy of the paramagnetic susceptibility for $T_c<T<T_t$.

In the system $CuFe_{2-x}Cr_xO_4$, any A-site Cu^{2+} spin-orbit distortions are masked by the cooperative J-T distortions at the B-site Cu^{2+}, which are also tetragonal ($c/a>1$). However, the small fraction of B-site ions that must be Cu^{2+} for $c/a>1$ may reflect spin-orbit effects at the A-site Cu^{2+}. With larger A-site, smaller B-site Cu^{2+} concentrations, cooperative spin-orbit ($c/a>1$) distortions at the A-site Cu^{2+} can only be induced by magnetic ordering that has collinear A-site spins. Ohnishi and Teranishi[10] found cubic spinels in this compositional range for $T>-150$°C. With A-site Cu^{2+} concentrations sufficiently large for J-T rather than spin-orbit stabilizations to predominate, any B-site Cu^{2+} would inhibit cooperative, static J-T distortions of an opposite sense at the A-site Cu^{2+} ions. The critical ratio of B-site to A-site Cu^{2+} in this system for tetragonal ($c/a<1$) distortions has not been determined, but it is probably $\lesssim 0.1$. This is to be contrasted to the systems $Cu_x{}^{2+}M_{1-x}^{2+}[Cr_2{}^{3+}]O_4$.

The system $Fe_{3-x}Cr_xO_4$ appears to have crystallographic properties that are analogous to those of $NiCr_tFe_{2-t}O_4$[11]. Room-temperature lattice parameters for this system do not obey Végard's law. There are four linear regions of a_0 *vs.* x: Region I ($0 \leq x \leq 0.3$) has $da_0/dx<0$; Region II ($0.3 \leq x \leq 0.7$) has $da_0/dx \approx 0$; Region III ($0.7 \leq x \leq 1.3$) has $da_0/dx>0$; and Region IV ($1.3 \leq x \leq 2.0$) has $da_0/dx<0$. At -183°C, the system was reported to be cubic in Regions I and II, increasingly tetragonal ($c/a>1$) throughout Region III, and orthorhombic through Region IV as a result of two independent tetragonal distortions of opposite sign and perpendicular c axes. The end member $FeCr_2O_4$ is not orthorhombic, but tetragonal ($c/a=0.967$). These results indicate that the ideal chemical formulae are $Fe^{3+}[Fe^{2+}Fe_{1-x}^{3+}Cr_x{}^{3+}]O_4$ for Region I; $Fe_{1-y}^{3+}Fe_y{}^{2+}[Fe_{1-y}^{2+}Fe_{1-x+y}^{3+}Cr_x{}^{3+}]O_4$ with $y<x-0.3$ for Region II and $y \approx x-0.3$ for Region III; and $Fe^{2+}[Fe_{2-x}^{3+}Cr_x{}^{3+}]O_4$ for Region IV. They also suggest that the sign of the distortion about an A-site divalent iron ion changes from $c/a>1$ to $c/a<1$ as all of its near-neighbor B-site ions become Cr^{3+}. Paramagnetic susceptibilities for $FeCr_2O_4$[12] give $C_{mol}=\mu_{eff}^2/8=2.22 \pm 0.05$, which is compatible with high-spin-state Fe^{2+} on the A sites and quenching of the orbital angular momentum. However, it should be noted that low-spin-state Fe^{II}, with only partially quenched angular momentum, could give a C_{mol} of nearly that magnitude as well as the observed anomaly at the tetragonal ($c/a<1$)$\rightleftarrows$cubic transition below which there would be further quenching of the momentum by static, J-T ordering. The sixth d electron on A-site, high-spin-state Fe^{2+} would occupy a twofold-degenerate Γ_3 (or E_g) state, which has quenched orbital momentum. The sign of the J-T effect associated with such a state is determined by anharmonic vibrational and higher-order coupling terms. Therefore if the A-site divalent iron is high-spin-state Fe^{2+}, the experiments suggest a sign reversal in the anharmonic vibrational and/or higher-order coupling terms as Cr^{3+} substitutes for B-site Fe^{3+}. If, on the other hand, the divalent A-site iron is in a low-spin state, then there is one Γ_5 hole among the unpaired electrons, which is analogous to A-site Cu^{2+} with one Γ_5 hole in the d shell, so that spin-orbit distortions would be tetragonal ($c/a>1$) and J-T distortions would be tetragonal ($c/a<1$).

It is to be noted that orthorhombic distortions due to two independent tetragonal distortions of opposite sign and perpendicular c axes occur in those spinels that have an A-site cation with two exclusive stabilization modes and a heterogeneous chemical composition. They do not appear to be characteristic of two types of J-T ion, one on the A-sites and the other on the B-sites, that are stabilized by distortions of an opposite sense. In this latter case, which is probably illustrated by $CuMn_2O_4$ (probable formula $Cu^{2+}[Mn_2^{3+}]O_4$), the opposing forces apparently stabilize dynamic J-T effects. Yet γMn_2O_3, which has $c/a=1.16$, apparently stabilizes spin-orbit coupling at the A-site Mn^{3+}, for spin-orbit stabilizations would be cooperative with the B-site J-T distortions. Cu^{2+} and Mn^{3+} are analogous ions except for the magnitude of S that influences by a factor of four the relative magnitudes of V_{LS} and V_{JT}.

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DISCUSSION

E. W. GORTER: Since you mentioned the dynamic Jahn-Teller effect, I should like to have your opinion on the question whether cubic spinels containing distorting ions in both lattice sites will have both distorted tetrahedral and octahedral sites. (This is not possible without additional non-tetragonal distrortion.)

J. B. GOODENOUGH: If the deformations on the two types of sites are in the same direction, then both types of sites can distort cooperatively. In this connection, it is interesting to note that in $CuFe_2O_4$ the critical fraction of B sites that must be Cu^{2+} for a cooperative distortion is only $f_c \approx 0.26$ whereas for Mn^{3+} ions the corresponding fraction is $f_c \approx 0.6$. The low value for $CuFe_2O_4$ may be due to the simultaneous existence of A-site Cu^{2+} which can distort compensatively with the B-site Cu^{2+} via spin-orbit stabilization.

However, if the distortions are of opposite sign, then one would expect either orthorhombic symmetry as a result of two independent, tetragonal distortions of opposite sign, but perpendicular c axes, or cubic symmetry with a dynamic Jahn-Teller stabilization that has electron configurations of neighboring sites correlated by the lattice vibrations.