

## Paramagnetic properties of XY-ordered Jahn-Teller crystals

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Unusual magnetic properties of paramagnetic XY-ordered systems with cooperative Jahn–Teller effect are discussed at a wide range of temperatures and external magnetic fields (and uniaxial pressures.) Magnetic nonlinearity and magnetic susceptibilities of the systems are reminiscent of that of the antiferromagnetically ordered materials, while only the structural phase transitions are under consideration.

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Crystals with cooperative Jahn–Teller effect are characterized by very unusual and interesting magnetic properties. Many unexpected combinations of magnetic and structural orderings take place in these systems as a result of the interactions between real spin variables and the lattice, mediated by the orbitally degenerate electronic states. This was discussed by Reinen and Friebel<sup>1</sup> and Kugel and Khomskii<sup>2</sup> for the case of transition metal compounds and by Kaplan and Vekhter<sup>3</sup> for rare earth compounds (see Refs. in 1–3). As was shown in Ref. 3, even in paramagnetic Jahn–Teller elastics, unusual magnetic properties are possible. This was discussed in Ref. 3 (see references therein) for different rare earth vanadates, phosphates, and arsenates. It was theoretically and experimentally demonstrated that the unusual behavior of the magnetic properties of the cooperative Jahn–Teller systems is caused by the electron correlation responsible for structural ordering. Similar effects in the transition metal Jahn–Teller crystals were not yet discussed and are the subject of this paper. However, it is clear that the higher (as a rule) crystal and local symmetries of these systems, and correspondingly richer variety of structural orderings related to different types of orbitally degenerate electron correlations, can lead to new types of behavior of the magnetic properties. Here, we analyze the magnetic properties of crystals with possible XY ordering due to the cooperative Jahn–Teller effect. The paramagnetic phase of transition metal ion compounds is under discussion. Since in the paramagnetic phase, the spin-orbital and exchange interactions play a minor role, these interactions are neglected (in the molecular field approximation, the contribution of magnetic interactions is zero in the paramagnetic crystal phase). It is well known that the XY type of ordering is found in different transition metal compounds with the orbital doublet or triplet ground electronic state of the Jahn–Teller transition metal ion (for example, the colossal magnetoresistance manganites,<sup>4</sup> the multiferroic magnetoelectrics,<sup>5</sup> the spinel vanadates,<sup>6</sup> and some other Jahn–Teller crystals with perovskite structure<sup>7</sup>). Our numerical calculations shown below are done for the ground doublet state with the excited triplet state. However, all analytical results remain valid for the ground triplet state after changing, in the Hamiltonian, the sign of the energy gap  $\Delta$  separating the ground doublet from the excited triplet.

The XY ordering in the crystals under discussion can be understood as an ordering in a two sublattice crystal, where one sublattice contains Jahn–Teller local octahedron distortions with elongation along the X axis, and the other sublattice

along the Y axis. This kind of Jahn–Teller ordering was discussed for the first time by Kanamori,<sup>8</sup> and, later, by Millis<sup>9</sup> and Kaplan and Zimmerman.<sup>10</sup> Here, we will follow the discussion from Refs. 10–12 where the regular quantum mechanical approach was developed.

The Hamiltonian of a crystal under discussion with the electronic structure of the Jahn–Teller ions consisting of the ground doublet state and the excited triplet state can be written as follows:

$$H = H_{\text{str}} + H_{\text{el-str}} + H_{\text{ph}} + H_{\text{el-ph}} + H_{\text{Zeem}} + H_{\text{cryst}}. \quad (1)$$

In Eq. (1) the first two terms describe the elastic energy of the crystal in the presence of the uniaxial pressures  $p_z$  and  $p_x$  and the electron-strain interaction, the third is related to the free phonons, and the last two terms are the Zeeman interaction in the magnetic field ( $H_z \neq 0$ ,  $H_x \neq 0$ ) and the crystal field describing the  $\Delta$  separation energy between the ground doublet and the excited triplet. The vibronic interaction

$$H_{\text{el-ph}} = - \sum_{m\kappa} (V_{m\kappa}^{E\theta} \sigma_{m\theta} + V_{m\kappa}^{E\varepsilon} \sigma_{m\varepsilon} + V_{m\kappa}^{T\theta} T_{m\theta} + V_{m\kappa}^{T\varepsilon} T_{m\varepsilon}) \quad (2a)$$

describes the interaction of the ground doublet and the excited triplet electronic states with the local doubly degenerate vibrations of the  $E_g(O_h)$  symmetry (it is accepted that the crystal symmetry is cubic), and the electronic operators are represented as

$$\sigma_{\theta} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & -1 \end{pmatrix}, \quad \sigma_{\varepsilon} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 \end{pmatrix},$$

$$T_{\theta} = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & -2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \quad T_{\varepsilon} = \frac{\sqrt{3}}{2} \begin{pmatrix} -1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (2b)$$

Using the canonical shift transformation or the displacement phonon operator method,<sup>3</sup> the intersite electron interaction can be obtained. In the case of a two sublattice crystal with possible *XY* ordering, it is convenient to present this electron correlation term in the following form:

$$\begin{aligned}
H_{\text{int}} = & - \sum_{mn} A_{mn}^{\text{I,II},E} \left[ \left( -\frac{1}{2} \sigma_{m\theta}^{\text{I}} + \frac{\sqrt{3}}{2} \sigma_{m\varepsilon}^{\text{I}} \right) \left( -\frac{1}{2} \sigma_{n\theta}^{\text{II}} - \frac{\sqrt{3}}{2} \sigma_{n\varepsilon}^{\text{II}} \right) \right. \\
& + \left. \left( \frac{1}{2} \sigma_{m\theta}^{\text{I}} - \frac{\sqrt{3}}{2} \sigma_{m\varepsilon}^{\text{I}} \right) \left( -\frac{1}{2} \sigma_{n\theta}^{\text{II}} + \frac{\sqrt{3}}{2} \sigma_{n\varepsilon}^{\text{II}} \right) \right] \\
& + A_{mn}^{\text{I,II},T} \left[ \left( -\frac{1}{2} T_{m\theta}^{\text{I}} + \frac{\sqrt{3}}{2} T_{m\varepsilon}^{\text{I}} \right) \left( -\frac{1}{2} T_{n\theta}^{\text{II}} - \frac{\sqrt{3}}{2} T_{n\varepsilon}^{\text{II}} \right) \right. \\
& + \left. \left( \frac{1}{2} T_{m\theta}^{\text{I}} - \frac{\sqrt{3}}{2} T_{m\varepsilon}^{\text{I}} \right) \left( -\frac{1}{2} T_{n\theta}^{\text{II}} + \frac{\sqrt{3}}{2} T_{n\varepsilon}^{\text{II}} \right) \right] + (\text{dyn}) \quad (3)
\end{aligned}$$

In the Hamiltonian [Eq. (3)], the electronic operators  $\sigma$  and  $T$  are defined on the doublet (*E*) and triplet (*T*) states, respectively; the operator combinations in the parentheses have the same symmetry as the Jahn–Teller octahedron *X* and *Y* elongations. The  $H_{\text{int}}$  contains other terms that describe the dynamics of the electron and the electron-phonon systems denoted by (dyn). However, these terms do not contribute to the Jahn–Teller molecular fields, therefore, we will calculate the thermodynamic properties of the crystal in the molecular field approximation, ignoring the dynamic vibronic coupling.

The  $A_{mn}^{\text{I,II},(E,T)}$  parameters describe the electron correlation caused by virtual phonon exchange and the electron-strain interaction between the *E* and *T* electrons on the crystal sites *m* and *n* belonging to the I and II sublattices, respectively.

In the molecular field approximation, the two sublattice Hamiltonians can be presented as<sup>10,11</sup>

$$\begin{aligned}
H_{\text{MF}}^{\text{I}} = & -A^{\text{I,II}}(0)(3L_{x\text{I}}^2 - 2)(3L_{y\text{II}}^2 - 2) - H_z L_{z\text{I}} - H_x L_{x\text{I}} \\
& - P_z(3L_{z\text{I}}^2 - 2) - P_x(3L_{x\text{I}}^2 - 2) - \Delta \tau_{\text{I}}, \\
H_{\text{MF}}^{\text{II}} = & -A^{\text{I,II}}(0)(3L_{x\text{I}}^2 - 2)(3L_{y\text{II}}^2 - 2) - H_z L_{z\text{II}} - H_x L_{x\text{II}} \\
& - P_z(3L_{z\text{II}}^2 - 2) - P_x(3L_{x\text{II}}^2 - 2) - \Delta \tau_{\text{II}}, \quad (4)
\end{aligned}$$

where

$$3L_x^2 - 2 = -\frac{1}{2} T_\theta + \frac{\sqrt{3}}{2} T_\varepsilon, \quad 3L_y^2 - 2 = -\frac{1}{2} T_\theta - \frac{\sqrt{3}}{2} T_\varepsilon,$$

$$\tau_{\text{I,II}} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}. \quad (5)$$

$P_{z,x} \equiv g_{0EP_{z,x}}(C_0 \Omega N)^{-1}$  and  $H_{z,x} \equiv g_{z,x} \beta h_{z,x} \cdot g_0 \cdot \beta$ , and  $L_{x,y,z}$  are the electron-strain interaction constant, Bohr's magneton, and orbital momentum projections for the triplet state electrons, respectively.  $C_0$ ,  $\Omega$ , and  $N$  are the module of elasticity, crystal cell volume, and number of atoms.  $p_{z,x}$  and  $h_{z,x}$  are the uniaxial stress and magnetic fields, inducing the tetragonal elongation of the octahedrons in the *z* and *x* directions (the energy gap  $\Delta$ , is, strictly speaking, renormalized to the difference in the energies of the Jahn–Teller stabilization for the doublet and triplet electrons). The validity of formulas (5) is the result of the isomorphism of the triplet electronic states and the eigenfunctions of the orbital moment  $L=1$ .<sup>13</sup>

The Hamiltonians [Eq. (4)] describe the possible ordering of octahedrons elongated along the *X* axis in one sublattice and the *Y* axis in the other. It is important to understand that each elongation of the octahedron along the *X* or *Y* axis is accompanied by octahedron contraction along *Z* direction, so that the initially octahedral crystal cell becomes tetragonally compressed as a result of the cooperative Jahn–Teller effect.

It is clear that virtual phonon exchange will create an unusual magnetic nonlinearity in this case of the structural transition. The mechanism of this nonlinearity is as follows: The external magnetic field changes the electronic states, modifying the virtual phonon exchange and the corresponding molecular field. This will additionally modify the electronic states and will respectively change the magnitude of the induced magnetic moment.

The sublattice order parameters and the corresponding free energy of the system were calculated<sup>12</sup> in the molecular field approximation using the Hamiltonians in Eq. (4). After that, the magnetic moments were found as derivatives of the free energy upon the external magnetic fields. The results of the calculations of the magnetic moments ( $M_i \sim L_i$ ,  $P_x=0$ ) in all three directions of the external magnetic fields can be presented as [ $A^{\text{I,II}}(0)=A^{\text{II,I}}(0)=A$ ]

$$\begin{aligned}
L_{z\text{I}} = L_{z\text{II}} = & \frac{2 \frac{g_z \beta H_z}{\sqrt{\frac{9}{4}(-A^2 \xi^2 + g^2 \beta^2 H_z^2)}} \exp\left(-\frac{\Delta - P_z + \frac{1}{2} A \eta}{kT}\right) \sinh \frac{\sqrt{\frac{9}{4}(-A^2 \eta^2 + g_z^2 \beta^2 H_z^2)}}{kT}}{2 + \exp\left(-\frac{\Delta}{kT}\right) \left[ \exp\left(-\frac{2P_z - A \eta}{kT}\right) + 2 \exp\left(-\frac{A \eta - 2P_z}{2kT}\right) \cosh \frac{\sqrt{\frac{9}{4}(-A^2 \eta^2 + g_z^2 \beta^2 H_z^2)}}{kT} \right]},
\end{aligned}$$

$$\begin{aligned}
\frac{M_x}{L_{xI}} &= \frac{4 \frac{g_x \beta H_x}{\sqrt{9P_z^2 + 4g_x^2 \beta^2 H_x^2}} \exp\left(-\frac{2\Delta + P_z - 2A\eta}{2kT}\right) \sinh \frac{\sqrt{9P_z^2 + 4g_x^2 \beta^2 H_x^2}}{2kT}}{2 + \exp\left(-\frac{\Delta}{kT}\right) \left[ \exp\left(-\frac{2A\eta - P_z}{kT}\right) + 2 \exp\left(-\frac{P_z - 2A\eta}{2kT}\right) \cosh \frac{\sqrt{9P_z^2 + 4g_x^2 \beta^2 H_x^2}}{2kT} \right]}, \\
\frac{M_x}{L_{xII}} &= \frac{4 \frac{g_x \beta H}{\sqrt{9(A\xi - P_z)^2 + 4g_x^2 \beta^2 H_x^2}} \left( \exp - \frac{2\Delta + A\xi + P_z}{2kT} \right) \sinh \frac{\sqrt{9(A\xi - P_z)^2 + 4g_x^2 \beta^2 H_x^2}}{2kT}}{2 + \exp\left(-\frac{\Delta}{kT}\right) \left[ \exp\left(\frac{A\xi + P_z}{kT}\right) + 2 \exp\left(-\frac{A\xi + P_z}{2kT}\right) \cosh \frac{\sqrt{9(A\xi - P_z)^2 + 4g_x^2 \beta^2 H_x^2}}{2kT} \right]}, \\
\xi &\equiv \overline{3L_x^2 - 2}, \quad \eta \equiv \overline{3L_y^2 - 2}. \tag{6}
\end{aligned}$$

Formulas (6) describe the behavior of the magnetic moments under external magnetic fields and uniaxial pressure. More importantly, they show the dependence of the magnetic moments on the magnitude of the electron correlation parameter  $A$ .

The results of the numerical calculations of the magnetic moments upon the external fields are shown in Figs. 1 and 2. In these numerical calculations, we assumed that  $P_z = P_x = 0$ .

In the case of the magnetic field directed along the  $x$  or  $y$  direction, the magnetic field induces an overturn of the sublattice of the Jahn–Teller distortions. In this case, the total magnetic moment of the crystal shows a sharp jump (Fig. 1). The reason for this is that the magnetic field supports the existing strain in one of the sublattices due to magnetostriction, and the magnetic moment operator commutes with the corresponding Jahn–Teller molecular field. However, in the second sublattice at small magnetic fields, the electronic states are not “favorable” for the magnetic moment. The situation changes dramatically at the “overturn” of a sublattice as a result of the metamagnetoelastic phase transition when the second sublattice contribution to the magnetic moment is

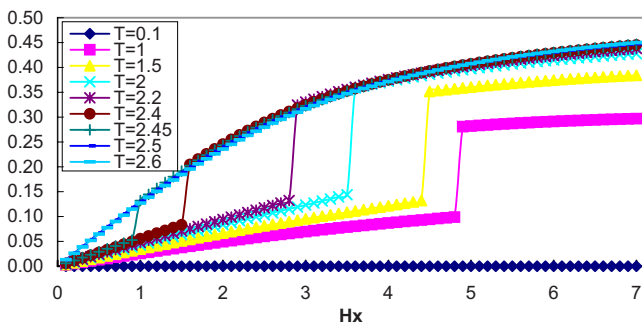


FIG. 1. (Color online) The dependence of the crystal magnetization  $M_x$  ( $x$  direction) on the magnetic field  $H_x$  applied in the  $x$  direction for  $A=2$  and  $\Delta=1$ . The magnetization increases with temperature. The discontinuities are marked by vertical lines.

sharply increased. The behavior shown in Fig. 1 describing the magnetic field dependence of the magnetic moment is similar to graphs typical for antiferromagnets. However, it should be mentioned once again that here we analyze the properties of paramagnetic systems.

The behavior of the magnetic moments and the magnetic susceptibility is completely different when the magnetic field is applied in the  $z$  direction,  $H_z$ . At this field orientation, the magnetostriction is responsible for the creation of the stress that supports the  $XY$  ordering in the crystal.

Both sublattices are equally compressed at temperatures below the structural phase transition. The operator of the  $M_z$ -magnetic moment commutes with the total crystal strain operator along the  $z$  direction. As a result of this, the crystal compression along the  $z$  direction enhances the  $z$ -magnetic moment. This mutual enhancement leads to the significantly nonlinear change in the magnetic moment with the field. Magnetic nonlinearity is especially strong near the critical

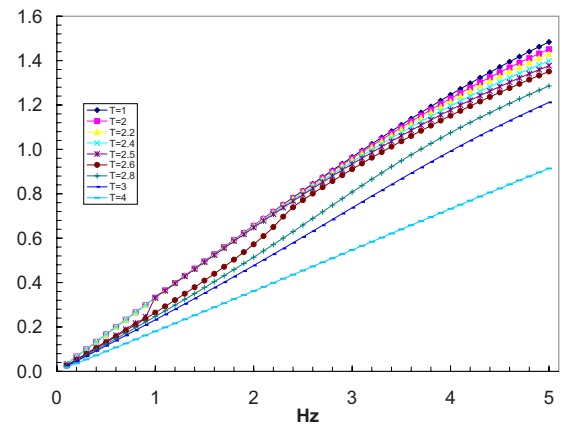


FIG. 2. (Color online) The dependence of the crystal magnetization  $M_z$  ( $z$ -direction) on the magnetic field  $H_z$  applied in the  $z$  direction for  $A=2$  and  $\Delta=1$ . The magnetization decreases with temperature.

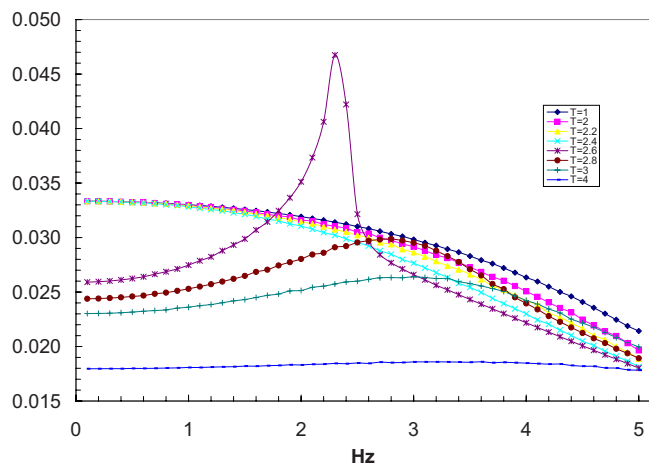


FIG. 3. (Color online) The magnetic susceptibility along  $z$  as a function of  $H_z$  at various temperatures. Note the peak at  $T=2.6$  and the rounded maxima above this temperature, while below, the susceptibility decreases monotonically with the field.

temperature. Below the critical temperature ( $T=2.6$  in units normalized to the crystal field gap  $\Delta$  see Fig. 3), the electron correlation is suppressed by the Jahn–Teller molecular field.

Above the critical temperature, the thermal fluctuations smear the correlation out.

One can easily obtain the magnetic susceptibility of the Jahn–Teller crystals from formulas (6). In the case of the  $z$  component of the magnetic susceptibility, the results of the calculations are shown in Fig. 3. The mutual enhancement of the Jahn–Teller distortion correlation and the magnetic moment is manifested in the  $H_z$ -magnetic field dependence of the magnetic susceptibility.

It is clearly seen that at the transition in the  $XY$ -ordered phase of the crystal, the magnetic susceptibility has a maximum that becomes significant at a critical temperature of  $T_s=2.6$ . Above the critical temperature the anomaly disappears.

In conclusion, we want to mention that the above discussed magnetic properties of the  $XY$ -ordered crystals could be observed in part in colossal magnetoresistance manganites. Moreover, it is well known that a lot of attention was devoted to the strange, from the first point of view, sharp changes in the magnetic moment behavior.<sup>14</sup> We think that these jumps could be at least partially related to the phenomena discussed above, and our results can be useful for the explanations of these and similar experimental observations.

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