

MAGNETOELASTIC PROPERTIES OF JAHN-TELLER CRYSTALS WITH COLOSSAL MAGNETORESISTANCE

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Key words: Structural phase transition, virtual phonon exchange, magnetostriction.

Abstract: The cooperative Jahn-Teller effect in the low doped $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ crystals with colossal magnetoresistance is considered. Experimentally observed magnetoelastic properties like metamagnetoelasticity and magnetic field induced structural phase transitions are explained on the basis of the developed microscopic approach. It is proposed that the presence of an excited electronic orbital triplet, located relatively close to the ground Mn^{3+} -electronic state, is fundamentally important for the understanding the experimental magnetic and magnetoelastic data. The existence of the excited triplet state separated by a small energy gap from the ground doublet is in agreement with the Tanabe-Sugano theoretical energy diagrams and is supported by the infrared absorption and Raman scattering measurements. Numerous calculations of the temperature and external magnetic field dependence of different crystal characteristics are made. Those calculations are in qualitative agreement with the experimental results.

1. Introduction

The comparison of the phenomenon of colossal magnetoresistance with high- T_c superconductivity demonstrates a striking similarity. In both types of compounds the ground electronic state is doubly degenerate or pseudodegenerate and is related mostly to the d-electrons. Both groups of crystals are characterized by perovskite, or similar, structure. There is no doubt that for both phenomena the electron-phonon interaction plays an important role. Both colossal magnetoresistance manganites and high- T_c superconductors demonstrate various types of phase transitions: magnetic, structural, charge ordering and others. It is our feeling that these similarities are reflecting the basic fact that both groups of compounds are Jahn-Teller crystals. In other words both types of compounds contain a sublattice of typical Jahn-Teller ions: it is Cu^{2+} -ion in the high- T_c systems and Mn^{3+} -ion in the manganites. Even the strategies of the study of both phenomena are similar: while the basic phenomenon related to the electrical conductivity is still not completely understood, a large effort has been made to analyse other properties of the crystals. This research direction is aimed not only at the different compound properties themselves but also toward the understanding of the tight connection between the conductivity and the electron-phonon, magnetic and dielectric material properties.

In this manuscript we are going to focus on the magnetoelastic properties of some colossal magnetoresistance compounds. The central interaction under discussion is the electron correlation caused by virtual phonon exchange. This is just the interaction that most of the published articles are lacking and without which, we think, the complete understanding of both high- T_c superconductivity and colossal magnetoresistance is impossible.

2. Hamiltonian

Magnetoelastic anomalous properties are typical for the Jahn-Teller crystals [1]. Among these properties are giant static and dynamic magnetostriction [1,2], matamagnetoelasticity [3] and magnetic field induced structural phase transitions [4]. At the same time, the authors of [5] measured experimentally the metamagnetoelastic behaviour (the sharp change of the crystal elastic strain with the external magnetic field) and the magnetic field induced structural phase transitions in low doped colossal magnetoresistance $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ compounds. In such a situation, it is natural to attempt to explain the experimental data in the framework of the cooperative Jahn-Teller effect theory that earlier was successfully applied in

a similar situation to the rare earth compounds with zircon structure [6,7]. However, this approach is facing serious difficulties in the case of the manganites with the perovskite structure.

The external magnetic field can influence the crystal lattice due to the electron-phonon interaction only by affecting directly the electron orbital variables or the real Mn^{3+} spins. However the "spin channel" can work only in combination with the superexchange or spin-orbital interactions. And the above mentioned direct interaction is possible only if the electron orbital moment is not completely quenched (the same is true for the spin-orbital interaction). Analysis shows that the superexchange is of small importance in the magnetoelastic phenomena under discussion. The external magnetic field could overturn one of the orbital sublattices if the spins are coupled antiferromagnetically and the orbitals are ordered in a "ferro-type" structure. However this is not the case in the manganites where the superexchange contributes to the "antiferro-type" ordering of orbitals and ferromagnetic ordering of spins in the (ab)-crystal plane. At the same time the ground electronic orbital doublet of the Mn^{3+} -ion with the local cubic symmetry surrounding is characterized by zero spin-orbital and zero magnetic field-orbital interaction.

To solve the problem we suggest that in the colossal magnetoresistance perovskites the first excited energy level of Mn^{3+} -ion is an orbital triplet separated by a small gap from the ground doublet. In this case the magnetic field can directly interact with the non-zero orbital moment and drastically change the crystal structure through the coupling of the electronic triplet with the lattice (we accept that the spin-orbital contribution does not change the general results).

The idea of a triplet state located closely to the ground electronic doublet can be supported theoretically and experimentally. Analysis of the Sugano-Tanabe diagrams for the transition metal ion energy levels in different crystal fields just shows that in the case of the Mn^{3+} -ions in the octahedral surrounding the ${}^3T_{1g}$ -triplet can be located very close to the ground 5E_g -state [8]. Matsumoto, in [9], had discussed the observation in the infrared absorption experiments of a low lying triplet state. Similar observations were made by Tsushima for $YAlO_3: Mn^{3+}$ [10]. Recently Cooper [11] had reported on an observation of a T-symmetry level in $(Bi, Ca)MnO_3$.

The Hamiltonian of a manganite crystal with the electronic structure of the Mn^{3+} cations consisting of the ground doublet state and excited triplet state can be written as follows

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

In (1) the first two terms describe the elastic energy of the crystal and the electron-strain interaction, the third one is related to the free phonons, and the last three terms are

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

$$H_{Zeem} = -g\beta H_z \sum_m L_{zm}^{eff}; \quad L_{zm}^{eff} = L_{zm}(t) + L_{zm}(t-e); \quad (3)$$

$$H_{cryst} = -\Delta \sum_m \tau_m. \quad (4)$$

The z-projection of the orbital moment, L_{zm}^{eff} , contains contributions from the triplet t-state, $L_{zm}(t)$, and from the mixing of the triplet (t) and doublet (e) states, $L_{zm}(t-e)$ ($L_{zm}(e)=0$ for the octahedral symmetry).

In the electron-phonon interaction (2) only the interactions of the doublet (the first two terms in (2)) and of the triplet (the last two terms in (2)) with the doubly degenerate phonons are considered. It is taken into account that the E_g -vibrations do not mix the triplet and doublet electronic states.

Choosing the quantization axis along the z-axis (the direction of the magnetic field), the matrices of the σ , T and τ operators on the basis of the five lowest electronic states can be written as

$$\sigma_{\theta} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & -1 \end{pmatrix}; \quad \sigma_{\varepsilon} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 \end{pmatrix}. \quad (5)$$

$$T_{\theta} = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & -2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}; \quad T_{\varepsilon} = \frac{\sqrt{3}}{2} \begin{pmatrix} -1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}. \quad (6),$$

$$L_z(t) = \begin{pmatrix} 0 & -i & 0 & 0 & 0 \\ i & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}; \quad L_z(t-e) = \alpha \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -i & 0 \\ 0 & 0 & i & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (8),$$

$$\tau_1 = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}.$$

The parameter α in (8) depends upon the ratio of the Zeeman energy and the gap between the doublet and the triplet states. The oxygen octahedron tilts can contribute significantly to the value of α .

In the Hamiltonian (1) the real spin variables are not considered and correspondingly the double exchange and superexchange interactions are not considered either. However we assume, that the contribution of these interactions to the intrinsic magnetic field, acting on the orbitals, can be included by renormalizing the external magnetic field value H_z .

3. Electron Correlations Caused By Virtual Phonon Exchange

The Hamiltonian (2) is a typical starting point for the description of the cooperative Jahn-Teller systems with structural phase transitions. It will be shown below that the Hamiltonian describes the electron correlation that can lead to the antiferrodistortive ordering in the (ab)-plane ((ab) \perp z) of the

tetragonally elongated octahedron as is observed experimentally in the manganites.

The central interaction in cooperative Jahn-Teller crystals is the electron-electron correlation caused by virtual phonon exchange. The virtual phonon exchange in its turn is the result of the electron-phonon interaction and the phonon dispersion of the crystal lattice. The operator of the electron-electron interaction can be obtained by the canonical transformation of Hamiltonian [1,7] or by the displacement phonon operator method [6]. In any case, the transformed Hamiltonian has a complicated form due primarily to the non-adiabatic $e \otimes E$ -interaction of the electrons and phonons. However neglecting the terms responsible for the electron-phonon dynamics of the crystal (only the thermodynamic properties are under consideration), the electron interaction term can be expressed as

$$\begin{aligned} \tilde{H}_{\text{int}} = & - \sum_{\substack{mnk \\ m \neq n}} \left[\frac{V_{mk}^{E*} V_{nk}^E}{\hbar \omega_k} (\sigma_{m\theta} \sigma_{n\theta} + \sigma_{m\epsilon} \sigma_{n\epsilon}) + \frac{V_{mk}^{T*} V_{nk}^T}{\hbar \omega_k} (T_{m\theta} T_{n\theta} + T_{m\epsilon} T_{n\epsilon}) \right] - \\ & - \Delta E_{JT}^T \left(\sum_m 1_m + \frac{\Delta E_{JT}^E}{\Delta E_{JT}^T} \sum_m \tau_{2m} \right); \end{aligned} \quad (9)$$

$$\tau_{2m} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}; \quad \Delta E_{JT}^{E,T} = \sum_{mk} \frac{|V_{mk}^{E,T}|^2}{\hbar \omega_k} \quad (10)$$

In the Hamiltonian (9) the last two terms describe the Jahn-Teller stabilization energy ("polaronic" energy) caused by the triplet and doublet states. The first two terms are related to the virtual phonon exchange between the electrons in the doublet (the first term) and the triplet states. The $(\theta\epsilon)$ -terms in (9) are omitted as they do not contribute to the Jahn-Teller molecular field (MF) (the thermodynamic properties in the MF

approximation will be considered). The $\sigma_\theta T_\theta$ and $\sigma_\epsilon T_\epsilon$ product operators are zeros at the chosen basis.

In general in the case of conducting Jahn-Teller systems one more electron correlation term caused by virtual phonon exchange should be taken into account. It is the electron interaction through the totally symmetrical phonons ("breathing" modes). This term, as it was discussed in [12], can be responsible for the charge ordering processes. However this kind of phase transitions is probably less important for the low doped manganites and is not considered in this manuscript.

It is important to mention that the structural phase transition in manganites, caused by the cooperative Jahn-Teller effect, takes place at the temperatures higher than the magnetic transition temperatures. That means that the interaction (9) is bigger than the double- or superexchange interactions.

The structural ordering due to the cooperative Jahn-Teller effect in manganites leads to a two sublattice crystals with the octahedron elongations along the x- and y-axes in each of the sublattices. That is why it is convenient to rewrite the electron interaction terms in the following form:

$$\begin{aligned}
 H_{\text{int}} = & - \sum_{\substack{n,n \\ \alpha, \alpha' \neq I, II}} A_{mn}^{\alpha, \alpha', E} \left[\left(-\frac{1}{2} \sigma_{mz}^\alpha + \frac{\sqrt{3}}{2} \sigma_{mx}^\alpha \right) \left(-\frac{1}{2} \sigma_{nz}^{\alpha'} - \sigma_{nx}^{\alpha'} \right) + \right. \\
 & \left. + \left(-\frac{1}{2} \sigma_{mz}^\alpha - \frac{\sqrt{3}}{2} \sigma_{mx}^\alpha \right) \left(-\frac{1}{2} \sigma_{nz}^{\alpha'} + \frac{\sqrt{3}}{2} \sigma_{nx}^{\alpha'} \right) \right] - \\
 & - \sum_{\substack{mn \\ \alpha, \alpha' \neq I, II}} A_{mn}^{\alpha, \alpha', T} \left[\left(-\frac{1}{2} T_{m\theta}^\alpha + \frac{\sqrt{3}}{2} T_{m\epsilon}^\alpha \right) \left(-\frac{1}{2} T_{n\theta}^{\alpha'} - \frac{\sqrt{3}}{2} T_{n\epsilon}^{\alpha'} \right) + \right. \\
 & \left. + \left(-\frac{1}{2} T_{m\theta}^\alpha - \frac{\sqrt{3}}{2} T_{m\epsilon}^\alpha \right) \left(-\frac{1}{2} T_{n\theta}^{\alpha'} + \frac{\sqrt{3}}{2} T_{n\epsilon}^{\alpha'} \right) \right] \quad (11)
 \end{aligned}$$

In the Hamiltonian (11) the α, α' subscripts number the sublattices, and the operators in the parentheses have the symmetry of the local tetragonal distortions of octahedra along the x- and y-axes, for example

$$\begin{aligned}
-\frac{1}{2}T_{\theta} + \frac{\sqrt{3}}{2}T_e &= 3L_x^2 - 2 \\
-\frac{1}{2}T_{\theta} - \frac{\sqrt{3}}{2}T_e &= 3L_y^2 - 2,
\end{aligned} \tag{12}$$

where

$$L_x = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -i & 0 & 0 \\ 0 & i & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \quad L_y = \begin{pmatrix} 0 & 0 & i & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ -i & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}. \tag{13}$$

4. Structural Phase Transition And Magneto-Acoustical Properties

As it was mentioned before and can be clearly seen from (11), both electronic states – the doublet and the triplet – contribute to the electron correlation. If the gap between the ground and first excited states is of the order of the critical temperature it is not easy to find out which of the contributions is of more importance for the structural transition. Additionally the tilts of the oxygen octahedra can mix significantly the doublet and triplet states.

However, aiming to elucidate the role of the triplet electronic state, its contribution only will be taken into account in the calculations. Besides that in the Zeeman interaction (3) for simplicity we will ignore the contribution to the orbital moment caused by the mixture of the ground and the excited states by the magnetic field.

Within these approximations the sublattice MF Hamiltonians are

$$\begin{aligned}
H_{MF}^I &= -A^{T,II}(0) \overline{(3L_{xI}^2 - 2)(3L_{yII}^2 - 2)} - g\beta H_z L_{zI} - \tilde{\Delta}\tau_{II}, \\
H_{MF}^{II} &= -A^{T,II}(0) \overline{(3L_{yII}^2 - 2)(3L_{xI}^2 - 2)} - g\beta H_z L_{zII} - \tilde{\Delta}\tau_{III}.
\end{aligned} \tag{14}$$

($\tilde{\Delta}$ is the energy gap renormalized due to the different Jahn-Teller stabilization energies for the doublet and triplet states). The set of the self-consistent transcendental equations for the sublattice order parameters $x=3L_x^2-2$ and $y=3L_y^2-2$ looks like that:

$$x = \frac{e^{-\frac{\Delta}{kT}} [e^{\frac{Ay}{kT}} (\cosh \frac{B_y}{kT} + \frac{9Ay}{2B_y} \sinh \frac{B_y}{kT}) - e^{-\frac{Ay}{kT}}]}{2 + e^{-\frac{\Delta}{kT}} (e^{\frac{Ay}{kT}} + 2e^{\frac{2Ay}{kT}} \cosh \frac{B_y}{kT})};$$

$$y = \frac{e^{-\frac{\Delta}{kT}} [e^{\frac{Ax}{kT}} (\cosh \frac{B_x}{kT} + \frac{9Ax}{2B_x} \sinh \frac{B_x}{kT}) - e^{-\frac{Ax}{kT}}]}{2 + e^{-\frac{\Delta}{kT}} (e^{\frac{Ax}{kT}} + 2e^{\frac{2Ax}{kT}} \cosh \frac{B_x}{kT})} \quad (15)$$

$$B_{x(y)} \equiv \sqrt{\frac{9}{4} A^2 x^2 (y^2) + g^2 \beta^2 H_z^2}; \quad A \equiv A(0).$$

It is easy to see that the equations in (15) can be transformed one into another by the $x \rightarrow y$ interchange. This is the result of the symmetry of the crystal and remains unchanged even at $H_z \neq 0$, when the crystal becomes uniaxial, but the symmetry in the ab -plane is preserved. In this case $x=y=x_0$ is always a solution of the set (15) that becomes a single equation

$$x_0 = \frac{e^{-\frac{\Delta}{kT}} [e^{\frac{Ax_0}{kT}} (\cosh \frac{B}{kT} + \frac{9Ax_0}{2B} \sinh \frac{B}{kT}) - e^{-\frac{Ax_0}{kT}}]}{2 + e^{-\frac{\Delta}{kT}} (e^{\frac{Ax_0}{kT}} + 2e^{\frac{2Ax_0}{kT}} \cosh \frac{B}{kT})} \quad (16)$$

The set of equations (15) in the absence of the magnetic field, $H_z=0$, describes an antiferrodistortive structural phase transition, at which the octahedron elongations alternate in the ab-plane,

$$x = \frac{2e^{-\frac{\Delta}{kT}} \left(e^{\frac{2Ay}{kT}} - e^{-\frac{Ay}{kT}} \right)}{2 + e^{-\frac{\Delta}{kT}} \left(e^{\frac{2Ay}{kT}} + 2e^{-\frac{Ay}{kT}} \right)};$$

$$y = \frac{2e^{-\frac{\Delta}{kT}} \left(e^{\frac{2Ax}{kT}} - e^{-\frac{Ax}{kT}} \right)}{2 + e^{-\frac{\Delta}{kT}} \left(e^{\frac{2Ax}{kT}} + 2e^{-\frac{Ax}{kT}} \right)}. \quad (17)$$

As a result of this first order structural phase transitions, the crystal becomes compressed along the z-axis and elongated in the ab-plane ($c/a < 1$).

The magnetic field H_z reduces (at small fields) the sublattice order parameters x and y and increases the critical temperature of the structural phase transition. The latter is the result of the magnetic field's support of the tetragonal crystal deformation at the temperatures near $T_s(H_z=0)$. As can be seen from (16), at $H_z \gg A$

$$x_0 = \frac{e^{-\frac{\Delta}{kT}} \left(\cosh \frac{g\beta H_z}{kT} - 1 \right)}{2 + e^{-\frac{\Delta}{kT}} \left(\cosh \frac{g\beta H_z}{kT} + 1 \right)}. \quad (18)$$

and at $H_z \rightarrow \infty$ $x=y=x_0 \rightarrow 0.5$. In other words, if the magnetic field is not zero, the tetragonal strain of the crystal is always not zero, even at $kT \gg A$.

Numerical analysis confirms that equations (15), (16) describe the magnetic field induced structural transition accompanied by sharp changes in crystal cell parameters, that is in agreement with the experiment. However this huge magnetostriction is not the result of an overturn of a crystal distortion sublattice as the magnetic field equally reduces and supports both sublattices.

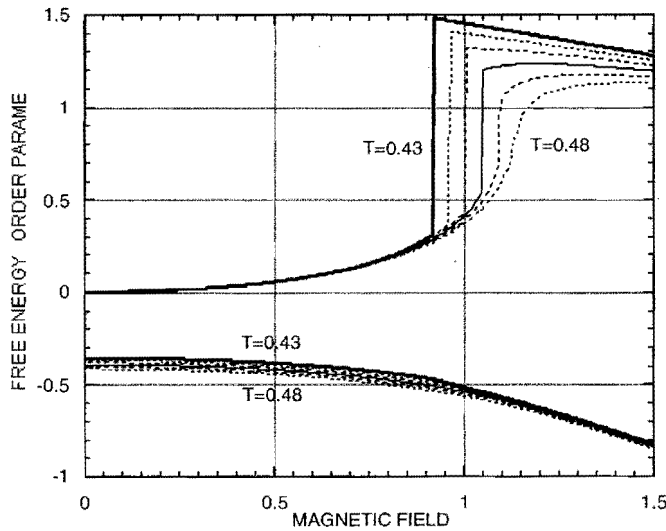


Figure 1. Order parameter, (upper part in figure,) and free energy, as a function of the reduced magnetic field at various temperatures. The curves with the bigger order parameter correspond to lower temperature. T and H are normalized to the energy gap Δ .

The results of the calculations of some temperature and magnetic field dependences for the order parameters and free energies are shown on Fig.1 and Fig.2 for parameters $A/\Delta=0.6$. At $g\beta Hz/\Delta > 1.1$ the structural phase transition is smeared out.

5. Conclusions

The cooperative Jahn-Teller effect theory allows the description of the structural phase transitions and of the magnetoelastic properties of colossal magnetoresistance manganites. The basic electron interaction at this approach is the virtual phonon exchange. The theory accepts that the electronic structure of the Mn^{3+} cations contains a low lying triplet excited state. While there are some indications that this can be true, the solid experimental confirmation should be demonstrated.

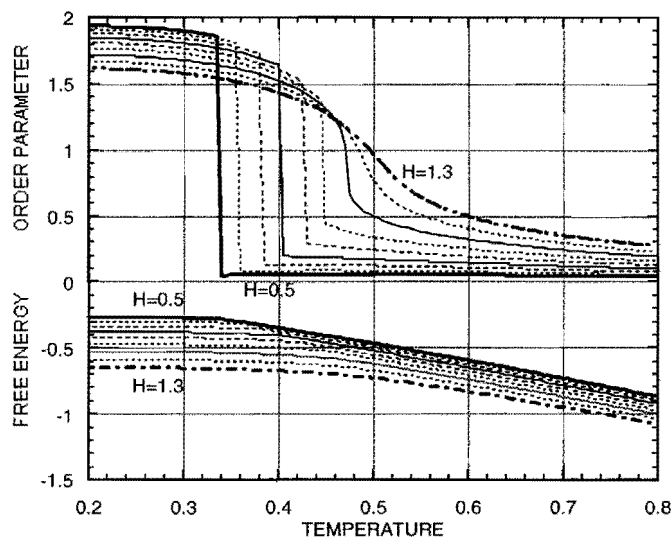


Figure 2. Order parameter, (upper part in figure,) and free energy, as a function of the reduced temperature at various magnetic fields. At lower temperatures the smaller order parameter curves correspond to bigger magnetic fields. T and H are normalized to the energy gap Δ .

In the more detailed theory the double exchange and superexchange interactions should be taken into account. At the same time the virtual phonon exchange can significantly affect the conductivity of the crystals with the electron orbital degeneracy.

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