Elastic Anomalies in Jahn-Teller Crystals with Competing Structural Orderings

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Abstract. Crystals of transition metal compounds with perovskite and spinel structures are characterized by several competing electron interactions responsible for different structural and magnetic orderings. The shape of the acoustic anomaly temperature dependences allows to distinguish between them and to estimate the difference between the structural and magnetic transition critical temperatures.

1. Introduction
The interest to the crystals of the transition metal compounds with perovskite and spinel structures permanently continues to grow for a significant period of time [1]. It is related to a range of surprising discoveries of unusual properties of these materials. The anomalous properties of perovskite and spinel structure crystals are the direct consequence of the electronic orbital degeneracy or pseudo-degeneracy of the transition metal ions. The corresponding electronic states are very sensitive to the local distortions (Jahn-Teller effect [2, 3]) and to their correlation through the crystal phonons (cooperative Jahn-Teller effect [4]). This leads to the different structural transitions and the corresponding property anomalies [5, 6]. On another hand the magnetic intersite interaction in case of the local electronic orbital degeneracy results in the possibility of different unusual magnetic structures (for example, because of the electron exchange at orbital degeneracy [7]). The combination of the mentioned above interactions in Jahn-Teller
perovskite and spinel crystals causes the unordinary richness of their properties.
The real situation in these systems under discussion becomes even more interesting and complicated as the detail of the crystal structure - types of the connection between different octahedrons and tetrahedrons – could significantly affect the relative magnitude of the virtual phonon exchange responsible for the structural transitions and the magnitude of the exchange interaction at orbital degeneracy. It is often not easy to understand the primary reason of the type of structural ordering in these crystals and to attribute it to a specific virtual phonon interaction type or to an exchange magnetic interaction with the followed magnetostriction. Very often the resulting structural and magnetic orderings are the same on average (thermodynamically).
It is clear that the development of the experimental approach to the fundamental problem of the driving force in the material transformation process becomes extremely important for understanding and correct description of the phase transitions and crystal properties.
Below it is shown that such an approach could be developed basing on the analysis of the acoustical anomaly temperature dependences. The results are applicable to the Jahn-Teller crystals containing the ions with triple orbital degenerate electronic states [8-11] and in part to the MnV$_2$O$_4$ crystals the properties of which are getting a lot of attention nowadays [10, 12,13].

2. Microscopic model
We are considering a crystal with the Jahn-Teller ions in at least one of the crystal sublattices. The ground electronic state of the ions is an orbital triplet. While in this case two different types of Jahn-Teller local vibrations – e-symmetry and t-symmetry - are active in the Jahn-Teller effect, we will take into account only the e-vibrations as the interaction with them in the perovskites and spinels as a rule is the strongest. The double degeneracy of the local and corresponding crystal vibrations is responsible for the high level of degeneracy of the ordered crystal structure state caused by virtual phonon exchange. As a result many different types of packing of the tetragonally distorted structural crystal units are possible.
The most typical types of ordering in the crystals under discussion are so called ZZ-type and XY-type of orderings. In case of ZZ-type of ordering the Jahn-Teller structural units are distorted tetragonally along the c(z)-crystal axis, and all distortions are parallel, As a result of that at $T<T_s$ the
crystal transfers from the paradistortive cubic state to a tetragonal crystal state with the elongation along the c(z)-axis and contraction in the plane perpendicular to OZ. If the XY-ordering takes place the Jahn-Teller structural units again are distorted tetragonally but at T<Ts the crystal is divided in two sublattices. In both sublattices the Jahn-Teller structural units are elongated in the ab-plane of the crystal, however in one of the sublattices the elongations are parallel to the a(x)-axis, and in the another one – along the b(y)-axis. It is clear that in this case once again there is a structural transition from the cubic to the tetragonal phase. However this time in the tetragonal state the crystal is compressed along the c(z)-axis. In other words ZZ-ordering leads to a tetragonal crystal strain with c/a>1, and XY-ordering causes the strain with c/a<1. It is completely clear that if the magnitudes of the corresponding interaction constants are close the orderings compete. This is what often happens in perovskite and spinel crystal structures. Moreover, sometimes the magnetic interaction constants defining the magnetic phase transition critical temperature are also pretty close to the virtual phonon exchange constants. In this situation it is not easy to determine the major driving force of the phase transformation. But the analysis of the magnitude and of the character of acoustic anomalies helps to shed some light on the question.

The Hamiltonian of the crystal could be written as

\[ H = H_{el} + H_{ph} + H_{el-ph} + H_{str} + H_{el-str} + H_{magn} \]

(1)

where the first two terms describe the electronic states and the free phonons of the crystal, the electron-phonon interaction is typical for the T-e-Jahn-Teller problem

\[ H_{el-ph} = \sum_{mk} [V^\theta_{mk} (3L^2_{zm} - 2) + V^e_{mk} (L^2_{zm} - L^2_{ym})](b_k + b_k^+) \]

(2)

with \( V^\theta,e_{mk} \) as the electron-phonon constants, \( L_{z,x} \) - projections of the orbital electronic moment operators defined on the ground triplet state, and \( b_k, b_k^+ \) - phonon operators.

The magnetic interactions in the crystals under discussion are described in the simplest way reflecting the cubic symmetry of the high temperature crystal phase
The depending upon the homogeneous strain part of the Hamiltonian can be presented as

\[ H_{magn} = -\beta \sum_m (g_x L_x H_x + g_y L_y H_y + g_z L_z H_z) \]  

(3)

From formula (6) it is clear that the orbital state ordering leads to the simultaneous strain of the crystal. Both of them are the result of the cooperative Jahn-Teller effect.

The crystal modulus is easily found from (6) as
After the standard canonical transformation of the Hamiltonian (1) eliminating the linear term of the electron-phonon interaction [4], the virtual phonon exchange electron correlation is described as

\[
\frac{1}{C} \equiv \left( \frac{\partial U_\theta}{\partial P_\theta} \right)_{P_\theta = 0} = \frac{1}{C_0 \Omega} + g_0 \sqrt{\frac{N}{C_0 \Omega}} \left( 3L_z^2 - 2 \right)
\]

or

\[
\frac{C}{C_0} = \frac{1}{1 + g_0 \sqrt{C_0 \Omega 2N} \left( \frac{\partial (3L_z^2 - 2)}{\partial P_\theta} \right)}
\]

After the standard canonical transformation of the Hamiltonian (1) eliminating the linear term of the electron-phonon interaction [4], the virtual phonon exchange electron correlation is described as

\[
H_{\text{zt}} = -\sum_{m,n} \left[ \frac{V_{mk}^\theta V_{nk}^\theta}{\hbar \omega_\kappa} (3L_{zm}^2 - 2)(3L_{zn}^2 - 2) + \frac{V_{mk}^\varepsilon V_{nk}^\varepsilon}{\hbar \omega_\kappa} (L_{zm}^2 - L_{zn}^2)(L_{zn}^2 - L_{zm}^2) + 2 \frac{V_{mk}^\theta V_{nk}^\varepsilon}{\hbar \omega_\kappa} (3L_{zm}^2 - 2)(L_{zn}^2 - L_{zm}^2) \right]
\]

Due to the vibronic reduction the magnetic terms of (1) become relatively complicated. For example, the z-component of the Zeeman interaction looks like that

\[
\tilde{H}_{\text{Zeem}} = -g_\beta H_z \sum_m \left[ \cos 2g_m^\varepsilon L_{zm} - \sin 2g_m^\varepsilon \tau_m \right]
\]

where

\[
g_{m,\varepsilon}^\theta = i \sum_\kappa \left( \frac{V_{mk}^{\theta,\varepsilon}}{\hbar \omega_\kappa} b_\kappa - \frac{V_{mk}^{\theta,\varepsilon}}{\hbar \omega_\kappa} b_\kappa^+ \right)
\]

and the electronic operator \( \tau \) is represented by the matrix

\[
\tau_m = \begin{pmatrix}
0 & 1 & 0 \\
1 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\]
It is accepted that the magnetic ordering along z-direction is taking place in the crystals under discussion (the magnetic molecular field \( J \gamma^2 \mathbf{L}_z \) and the external magnetic field \( H_z \) are the largest, \( \gamma = \cos 2g \) is the vibronic reduction factor).

The transformed electron correlation Hamiltonian (9) evidently (its first term) contains the ZZ-interaction. But using some transformation of the electronic operators entering (9) it could be shown that the XY-interaction is present too in the form

\[
H_{\text{int}}^{xy} = -2 \sum_{mn} A_{mn}^{xy} (3L_{xm}^2 - 2)(3L_{yn}^2 - 2)
\]

(13)

where

\[
A_{mn}^{xy} = 2 \sum_\kappa \frac{|V^\kappa|^2 - |V^\gamma|^2}{\hbar \omega_\kappa} e^{i\kappa(m-n)}
\]

(14)

In the following analysis it is accepted that both – ZZ- and XY-interactions are present together with the magnetic interactions in the crystal in agreement with possible real situation.

For a two sublattice crystal the Hamiltonian in the molecular field approximation is written as follows

\[
H_i^I = -A_{i,II}^I (0)(3L_{zII}^2 - 2)(3L_{ymII}^2 - 2) - B_{i,II}^I (0)(3L_{zII}^2 - 2)(3L_{zII}^2 - 2) - h_z^I \gamma L_{zII} - P_z (3L_{zII}^2 - 2)
\]

\[
H_i^{II} = -A_{i,II}^{II} (0)(3L_{zII}^2 - 2)(3L_{ymII}^2 - 2) - B_{i,II}^{II} (0)(3L_{zII}^2 - 2)(3L_{zII}^2 - 2) - h_z^{II} \gamma L_{zII} - P_z (3L_{zII}^2 - 2)
\]

(15)

\[
h_z^{I,II} = g_z \beta \gamma H_z + J(0)\gamma^2 L_{zI,II}
\]

(16)

\[
P_z = \frac{g_0^E}{\sqrt{C_{0,E}} \Omega N}
\]

(17)
Formulae (15)-(17) allow the calculation of the ordering parameters for the ZZ- or XY-ordering or for a magnetic ordering in the crystal. The corresponding ordering parameters are defined as $3L_{zz}^2 - 2 = 3L_{zz}^2 - 2 = z$, $3L_{zz}^2 - 2 = 3L_{zz}^2 - x$, and $L_{zz}^2 = L_{zz}^2 = L_{zz}$. These parameters define correspondingly the strain in the sublattices and in the total crystal and the crystal magnetization [14].

The detailed analysis of the physics picture described by the developed above microscopic model was discussed in detail earlier [14]. That’s why here we only are briefly reminding that the ZZ- and the XY-virtual phonon exchange interactions are competing trying to establish tetragonal $c/a>1$ and $c/a<1$ crystal distortion. Naturally, the result depends upon the relative magnitude of the interactions. However the role of the magnetic (internal or external) interaction in this situation becomes important and sometimes even crucial. Really, the magnetic interaction as it was shown in [14] are supporting the $c/a<1$ tetragonal crystal strain due to the crystal magnetostriction. In other words the magnetic interaction is leading to the magnetic moments parallel to the $c(z)$-axis and is supporting the XY-type of structural ordering and counteracts the ZZ-ordering. In the crystal where $B>A$ (ZZ-ordering overcomes the XY-ordering), the magnetic ordering that happens below the structural phase transition can change the structure of the crystal replacing the $c/a>1$ at $T_N<T<T_s$ with the $c/a<1$ at $T<T_N$. Therefore a new type of the structural ordering of the tetragonal-tetragonal type takes place.

Of course, in this situation it is not clear in advance why this structural ordering to the state with $c/a<1$ takes place: because of the big magnetic interaction or because of the significant XY-interaction, or because of the combination of all these interactions.

The acoustic anomaly measurements as it is explained by the following below calculation results could shed some light on this type of questions. Plus, we hope that these calculations are helping to understand some other experimental results that before were looking contradictory.

3. **Numerical calculation analysis.**

The calculations of the order parameters, strains and magnetic moments were done for different combinations of the intersite electron interaction constants $A$, $B$, and $J$. For simplicity here only the results for one of these parameters equal to zero is discussed. We will concentrate our attention on the temperature dependence of the elastic modulus.
On the Fig.1 and 2 it is accepted that the XY-ordering only takes place (B=0). It is seen that the increase of the magnetic interaction shifts the minimum of the temperature dependence of the modulus of elasticity to higher temperature. At the same time the magnetic interaction are decreasing the relative magnitude of the acoustic anomaly. The last becomes really small when J>>A what is typical for the magnetic phase transitions accompanied by small crystal structure changes caused by magnetostriction.

Figure 1. Temperature dependence of the modulus of elasticity at the XY-ordering for different magnitudes of the magnetic interaction J

As it is seen from the Fig.1 at the big enough magnetic interaction the acoustic anomaly is not only small, but it is additionally smeared out.
The increase of the electron-strain interaction constant is increasing the magnitude of the elastic anomaly (the minimum on $C(T)$ is dipper) as always at the cooperative Jahn-Teller effect.

Figure 2. The same that on the Fig.1, but at the bigger electron-strain interaction constant

Figure 3. Temperature dependence of the modulus of elasticity at the ZZ-type of structural ordering at the different magnitudes of the magnetic interactions
On the Fig. 3 the temperature dependence of the modulus of elasticity is completely different from the presented on the Figs. 1 and 2. If at the big enough magnetic interactions a typical smearing out and magnitude decrease of the acoustic anomaly takes place, at the magnetic interactions of the order of the B magnitude – $J=1, 2$ – two critical temperatures could be observed with a plato between them. At the low temperatures there is a sharp decrease of the modulus of elasticity followed by a slow increase with the temperature typically for the structural transition. However at higher temperatures the magnetic interactions prevail, they are smearing out the anomaly changing or inducing the tetragonal-tetragonal structural transition.

Figure 4. The same that on the Fig. 3 but at the larger electron-strain interaction constant.
On the Fig. 4 the C(T) behavior is similar to observed on the Fig. 3. However due to bigger electron-strain interaction constant the minimum of C(T) is dipper and the plato between the two phase transitions is located near C=0. It means that the acoustic attenuation at this temperature interval is huge and the signal at the measurements is impossible to observe.

Figure 5. Influence of the external magnetic field on C(T) at the XY-type of ordering for different magnetic interaction constants J.

On the Fig. 5 the temperature dependence of the modulus of elasticity is shown in the presence of the external magnetic field. The field is accelerating the decrease and the smearing out of the anomaly.
Figure 6. External magnetic field influence of the acoustic anomaly in case of the ZZ-type of structural ordering at the different magnitudes of the magnetic interaction J.

On the Fig.6 the influence of the external field on $C(T)$ is demonstrated. The magnetic field is decreasing the ZZ-ordering critical temperature and increasing the width of the plato where the modulus of the elasticity is near its minimum. On the contrary to the Fig.4 at $J=1$ the plato already disappeared and the anomaly is significantly smeared out. For example, the comparison of the calculations and ultrasonic measurements [15] in MnV2O4 crystal allows concluding that in that crystal XY-interaction is larger than ZZ-interaction and the virtual phonon exchange of the XY-type is close in magnitude to the magnetic interaction.
Conclusions.
In perovskite and spinel structure crystals with competing virtual phonon exchange interactions and magnetic interactions the analysis of the temperature dependences of the modulus of elasticity can help to explain the driving force of the crystal transformations and crystal properties.

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