Volume contraction at the Jahn-Teller transition of LaMnO$_3$

T. Maitra,$^1$ P. Thalmeier,$^2$ and T. Chatterji$^3$

$^1$Max-Planck-Institute for the Physics of Complex Systems, Nöthnitzer Str. 38, 01187 Dresden, Germany
$^2$Max-Planck-Institute for the Chemical Physics of Solids, Nöthnitzer Str.40, 01187 Dresden, Germany
$^3$Institute Laue-Langevin, BP 156, 38042 Grenoble Cedex 9, France

We have studied the volume collapse of LaMnO$_3$ at the Jahn-Teller (JT) transition temperature $T_{JT} = 750$ K which has recently been found in high temperature powder x-ray and neutron diffraction experiments. We construct a model Hamiltonian involving the pseudospin of Mn$^{3+}$ $e_g$ states, the staggered JT distortion and the volume strain coordinate. We show that the anharmonic coupling between these primary and secondary order parameters leads to the first order JT phase transition associated with a comparatively large reduction of the unit cell volume of $\Delta V/V \approx 10^{-2}$. We explain the temperature dependence of JT distortions and volume strain and discuss the volume change as function of the anharmonic coupling constant. A continuous change to a second order transition as function of model parameters is obtained. This behaviour is also observed under Ba doping.

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I. INTRODUCTION

The parent compound of colossal magnetoresistive manganites, LaMnO$_3$ has drawn a lot of attention because of its various states of spin and orbital order under variation of temperature $T$. This compound undergoes a structural phase transition at $T_{JT} = 750$ K associated with an orbital order-disorder transition $\text{[4]}$. It has been observed that in the low temperature phase the orbital ordering is of C type with alternate arrangement of $d_{3z^2-r^2}$ and $d_{3y^2-r^2}$ orbitals in the $ab$-plane while the planes are stacked along the $c$-axis $\text{[5]}$. On further lowering the temperature LaMnO$_3$ undergoes a magnetic transition to an A-type antiferromagnetic phase at the temperature $T_N \approx 145$ K where the spins are aligned parallel to each other in the $ab$-plane and antiparallel along the $c$-axis $\text{[6, 7]}$.

In a recent experiment T. Chatterji et al. $\text{[8]}$ have investigated in detail the Jahn-Teller transition in LaMnO$_3$ using high temperature x-ray and neutron diffraction on powder samples. They observed that the unit cell volume of LaMnO$_3$ decreases with increasing temperature in a narrow temperature range below $T_{JT}$ and then undergoes a sudden collapse at $T_{JT}$. It was argued that this striking volume collapse is caused by the orbital order-disorder transition. In the orbitally ordered phase the packing of MnO$_6$ octahedra needs more space than in the disordered phase. The authors compared this unusual phenomenon to the melting of ice which is accompanied by a similar volume collapse. They also observed that with very small doping of Ba the first order like transition becomes second order $\text{[4]}$. The above mentioned experimental observation of the volume contraction at the Jahn-Teller transition temperature in LaMnO$_3$ has motivated us to study the effect from a microscopic model for LaMnO$_3$. In addition to the usual Jahn-Teller interaction terms we include the coupling between volume strain and the Jahn-Teller distortions. This allows us to explain both the observed volume contraction and the first order transitions in the temperature dependence of Jahn-Teller distortions $Q_2$ and $Q_3$ within the same context.

II. PSEUDO SPIN MODEL FOR THE JT-TRANSITION IN LaMnO$_3$

In LaMnO$_3$ the Mn$^{3+}$ ion in each MnO$_6$ octahedra is in its $t_{2g}^{1}e_{g}^{1}$ state, the degenerate $e_g$ orbital is singly occupied and hence JT-active. The local JT-distortions around each Mn$^{3+}$ ion interact with each other cooperatively and give rise to the observed orbital ordering. Several theoretical investigations have been reported in the past to study the cooperative JT-phenomena in 3d- compounds like MnF$_3$, KCuF$_3$, LaMnO$_3$ and others. Among the first few attempts to study such systems is the approach of Kanamori $\text{[10]}$. He started from a microscopic Hamiltonian with the couplings of JT- electrons to uniform bulk distortions as well as to all vibrational modes.

In this model two possible ordered phases are considered, the ‘ferroorbital’ phase where the local distortions together with the orbitals of JT-ions align in the same direction and the the ‘antiferroorbital’ case where they align in opposite directions leading to a staggered order. Kanamori’s theory was successfully applied to some spinel-type JT-crystals with ferroorbital order to explain the bulk tetragonal distortion and the nature of the structural transition $\text{[11]}$. The theory of this type of ordering was further developed by Pytte $\text{[12]}$ for more than one JT-ion in an unit cell. A review of JT phase transitions was given by Sturge $\text{[13]}$. In addition it was predicted that the structural phase transition for the antiferro-orbitally ordered state should be of second order even in the presence of higher order terms in the JT- energy and anharmonic terms in the JT distortions $\text{[10]}$. But the observed phase transitions in most of these antiferroorbitally ordered compounds are in fact first order like. Later on Kataoka $\text{[14]}$ showed that for large higher order JT interactions and if both ferro- and antiferro- distortions are
taken into account the transition may still be of first order. We will now use a similar model, supplemented by the effect of the volume strain, to the present case of LaMnO$_3$. As in [10, 12], we start from a microscopic model Hamiltonian with the usual first order JT-terms coupling the electronic states to the $\Gamma_3$ ($E_g$) type JT-distortions. Since the fully symmetric $\Gamma_1$ ($A_{1g}$) volume strain can always couple to the square of the JT order parameter, irrespective whether it is of ferro- or antiferro-type, one has to expect a corresponding third order anharmonic term in the lattice energy. It has two consequences: Firstly it induces a spontaneous volume strain $Q_0$ below $T_{JT}$ as secondary order parameter in addition to the primary staggered JT order parameter $Q_s$. Secondly, if the coupling term is large enough compared to the energy of the JT distortion, it can also lead to a first order JT transition. Since in LaMnO$_3$ we indeed observe a large volume strain below $T_{JT}$ and the transition is of first order, despite having a pure staggered order parameter, we conclude that this term which couples volume and JT- strains is more important than the higher order terms in the JT energy itself introduced in [10, 12, 14].

Our model Hamiltonian is then given by

$$H = \frac{1}{2} C_T (Q_s^2 + Q_3^2) - g_0 \sum_i (Q_2 \sigma_{x_i} + Q_3 \sigma_{z_i}) + \frac{1}{2} C_B Q_0^2 - \gamma_1 Q_0 (Q_2^2 + Q_3^2) - \gamma_0 Q_0^3$$

(1)

Here the first term is the elastic energy of JT distortions with $C_{ij} = \Omega e_{ij}$ where $\Omega$ is the unit cell volume and for the ferro- distortive case $e_{ij}$ are the bulk elastic constants. Thus $C_T/\Omega = e_{11}-e_{12}$ is the elastic constant of $\Gamma_3$ symmetry distortions ($Q_2,Q_3$). In the ferro- distortive case they are related to the cartesian elastic strain components $e_{ii}$ by $(Q_2,Q_3) = 1/\sqrt{2}(e_{11}-e_{22},1/\sqrt{2}(2e_{33}-e_{22}-e_{11}))$. The second term in Eq. (1) represents the first order JT-coupling to the distortions with $g_0$ being the coupling constant. The third term gives the energy due to volume change where the bulk modulus $C_B = 1/3(C_{11}+2C_{12})$ and $Q_0$ is the volume strain given by $Q_0 = e_{11} + e_{22} + e_{33}$. Here we assume that $Q_0(T) = (V(T)-V_0(T))/V_0(T_{JT})$ is the dimensionless volume change caused by the JT ordering in addition to the already present background volume variation of $V_0(T)$. The coupling between volume strain and the JT-distortions is given by the fourth term with a coupling strength $\gamma_1$. The last term represents the anharmonic energy due to the volume change. Furthermore $\sigma_x$ and $\sigma_z$ are pseudo spin Pauli matrices within the subspace of $e_{1g}$ states. The experimental observations [11] show that the Mn-O bond lengths alternate between short and long in the $xy$-plane and are the same along $z$-axis which suggests that pure staggered orbital order is realised in LaMnO$_3$ without any admixture of ferrodistortion. The pure staggered order is of C-type corresponding to wave vector $Q = (\pi,\pi,0)$. To study this case we divide the lattice into two sublattices A and B and the staggered order requires that distortions in A and B have equal magnitude but opposite signs, i.e. $Q_{2A} = -Q_{2B}$ and $Q_{3A} = -Q_{3B}$. We write $Q_2$ and $Q_3$ in polar coordinates as $Q_2 = Q \sin \theta$ and $Q_3 = Q \cos \theta$. We then have $Q_A = -Q_B = Q_s$ or $Q_3 = 1/2(Q_A+Q_B)$.

Thus in terms of $Q_s$ Eq. (1) then becomes,

$$H = \frac{1}{2} C_T Q_s^2 - g_0 Q_s \sum_i (\sin \theta \sigma_{x_i} + \cos \theta \sigma_{z_i}) + \frac{1}{2} C_B Q_0^2 - \gamma_1 Q_0 Q_s^2 - \gamma_0 Q_0^3$$

(2)

Note that for the staggered case $C_T$ is not identical to the bulk elastic constant and $g_0$ is different from the ferroorbital case, however for simplicity we do not introduce new notations. The Hamiltonian in Eq. (2) is invariant under rotations in the doubly degenerate $e_{1g}$ subspace, the appropriate ground state orbitals $d_{3z^2-r^2}$ and $d_{3y^2-r^2}$ on A- and B- sublattices corresponding to $\theta = 30^\circ$ at low temperatures are selected by higher order JT interactions which we do not include explicitly, for the volume contraction effect this is indeed not necessary since the term proportional to $\gamma_1$ is independent of the mixing angle $\theta$. The Hamiltonian is then diagonalised and the free energy of the system is given by

$$F = -N k_B T \log Z(Q_s) + N E_0$$

$$Z(Q_s) = 2 \cosh (g_0 Q_s/k_B T)$$

(3)
\[
E_0 = \frac{1}{2} C_T Q_s^2 + \frac{1}{2} C_B Q_s^2 - \gamma_1 Q_s^2 - \gamma_0 Q_s^3
\]

In the following we will consider the JT-distortion \(Q_s\) as the primary order parameter of the transition and the volume strain, \(Q_0\), as the secondary order parameter. Minimising the free energy with respect to \(Q_0\) we arrive at the relation

\[
Q_0 = \lambda Q_s^2 \quad \text{for} \quad \frac{\gamma_0 \gamma_1}{C_B^2} Q_s^2 \ll 1 \quad (4)
\]

where we defined \(\lambda = \gamma_1/C_B\). As shown below the condition in Eq. (4) is well fulfilled. Substituting Eq. (4) into the expression of the free energy and minimising it with respect to \(Q_s\) we get the mean-field equation for the staggered order parameter:

\[
C_T Q_s - 2\lambda C_B Q_s^3 - 6\gamma_0 \lambda^3 Q_s^5 = g_0 \tanh \left( g_0 Q_s/k_B T \right) \quad (5)
\]

For the simple case \(\lambda = 0\) (no coupling of JT distortion and volume strain) we have a second order transition with

\[
k_B T_{JT} = \frac{g_0^2}{C_T} \quad F(0) = -\frac{1}{2} k_B T_{JT}
\]

\[
Q_s(0) = \frac{g_0}{C_T} \quad Q_0(0) = \lambda Q_s(0)^2 = \frac{g_0^2 \gamma_1}{C_B C_T} \quad (6)
\]

For the general case \(\lambda > 0\) the solution for the transition temperature \(T_{JT}\) and the primary \(Q_s(T)\) and secondary (Eq. (4)) \(Q_0(T)\) for \(T < T_{JT}\) has to be obtained numerically. The evolution of the free energy and the associated minimum described by the solution of Eq. (5) is shown in Fig. 1. For the parameters chosen the first order nature of the transition due to the \(\gamma_1 (\lambda)\) coupling term is clearly obvious.

### III. Numerical Results and Discussion

We now solve Eq. (6) for the JT distortion numerically to obtain the temperature dependent order parameters. The energies per volume are given in the unit of GPa for convenience and the unit cell volume is taken from [8] to be \(V = 245.64 \text{Å}^3\). Assuming that \(C_B\) and \(C_T\) are known from measurements (this is only approximately true for \(C_T\)) we have three fit parameters, the JT coupling \(g_0\) and the anharmonic constants \(\gamma_0\) and \(\gamma_1\), or equivalently \(\lambda = \gamma_1/C_B\). We fit these parameters consecutively. First the JT-coupling strength \(g_0 = 1.898 \text{ GPa}\) is determined from the experimentally observed JT transition temperature \(T_{JT} = 750 \text{ K}\) [8] using the approximate relation (Eq. (6)) \(g_0^2/C_T = k_B T_{JT}\) valid for the second order transition. Then the anharmonic coupling parameters \(\lambda\) (dimensionless) and \(\gamma_0\) were determined to be 13.0 and -400.0 GPa respectively by fitting the theoretical curves of \(Q_s(T)\) and \(Q_0(T)\), including the jumps at \(T_{JT}\), self-consistently to the experimentally observed temperature dependence of of JT-distortion and the unit cell volume.

Thereby we have also included the temperature dependence of the bulk modulus \(C_B(T)\). It may be extracted from experimental results [15] obtained for Sr-doped LaMnO\(_3\) by properly rescaling \(T_{JT}\) and fitting to the data in the temperature range between JT- and magnetic transitions. The resulting \(C_B(T)\) is shown in the inset of Fig. 3. In Fig. 2 we show the temperature dependence of the staggered JT-distortion \(Q_s\) (normalised to its value at zero temperature) from our calculation along with the corresponding experimental points. The temperature dependence of the volume strain \(Q_0\) (also normalised by the value at zero temperature) calculated...
first to second order is indeed observed for Ba-doped $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ where the volume jump vanishes already for $x = 0.025$. In Fig. 4(b) we show the temperature dependence of the entropy changing discontinuously (continuously) with temperature at the transition for first (second) order transition.

In this work we have given an explanation to the experimentally observed first order JT-transition in LaMnO$_3$. The first order transition is due to a strong coupling of primary JT-distortion and secondary volume strain order parameters. This result differs from those of previous models [10] which did not include the coupling to the volume strain but rather consider higher order terms in the JT energy. There the temperature dependence of JT-distortions is of second order type in the pure antiferro orbital order. Therefore the earlier models cannot be directly applied to the present case of LaMnO$_3$ where one has a first order transition despite having a pure staggered order parameter. From our calculation we see that the term which couples volume strain and JT-distortion in the model Hamiltonian is also responsible for the sharp collapse of the bulk volume. In the absence of such coupling [10][12], the JT-distortions are volume conserving.

We have not considered the spin degrees of freedom in our model calculation as has been discussed in [16] and [17] where it is argued that spin and orbital ordering can interfere with each other through the orbital dependent superexchange interaction. Since the magnetic transition temperature ($T_N \approx 145$ K) in LaMnO$_3$ is much lower than the orbital ordering temperature at $T_{JT} \approx 750$ K, we neglected the effect of spin correlations on the orbital order.

IV. CONCLUSION

The pronounced volume collapse in LaMnO$_3$ at the JT-transition temperature has been studied within a JT pseudospin model. Such models have been used previously to describe structural phase transitions with a JT distortion as order parameter in spinel-type crystals [10] [12]. To explain the additional volume contraction as secondary order parameter at the orbital order-disorder transition we have supplemented the model with an anharmonic interaction between bulk volume strain and the JT-distortion. We have studied the evolution from second to first order phase transition as function of the coupling strength and give a realistic parameter set valid for LaMnO$_3$ from comparison of the observed $T_{JT}$ and the associated jump in the JT distortion and the volume collapse. We also have shown that under suitable change of coupling parameters the transition changes from first to second order which may simulate the observed behaviour under small Ba-doping of the crystals.
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