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Structural, electronic, and magnetic entropy contributions of the orbital order–disorder transition in LaMnO_3

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Measurements of X-ray diffraction, electrical resistivity, and magnetization are reported across the Jahn–Teller phase transition in LaMnO_3 . Using a thermodynamic equation, we obtained the pressure derivative of the critical temperature (T_{JT}), $dT_{JT}/dP = -28.3 \text{ K GPa}^{-1}$. This approach also reveals that $5.7(3) \text{ J (mol K)}^{-1}$ comes from the volume change and $0.8(2) \text{ J (mol K)}^{-1}$ from the magnetic exchange interaction change across the phase transition. Around T_{JT} , a robust increase in the electrical conductivity takes place and the electronic entropy change, which is assumed to be negligible for the majority of electronic systems, was found to be $1.8(3) \text{ J (mol K)}^{-1}$.

Keywords: phase transition; magnetic entropy; orbital transition; order–disorder transition; electronic entropy; structural entropy

The general physical properties of the transition-metal oxides showing interacting electrons are explained not only by the electronic charge and spin, but also in many cases by the orbital degree of freedom as well [1]. Indeed, the partially filled $3d$ shell of the transition-metal ion leaves room for the observation of interesting coupled physical properties [1,2]. Research progress on different orbital ordering phases and their correlation with charge and spin phases reveals the close interplay between charge, lattice, spin, and orbital degrees of freedom in several systems [1,3,4]. For instance, the onset of orbital order at high temperature is suggested to be a necessary requirement for the onset of charge or spin order at low temperature in manganites [3,4]. More recently, theoretical works have achieved further understanding on the origin of Jahn–Teller distortion [5–7]. Within this context, detailed characterization of all degrees of freedom and a better understanding of the orbital phase transitions assume significant importance.

LaMnO_3 is the parent compound of colossal magnetoresistance manganites [4]. LaMnO_3 orders with an A-type antiferromagnetic structure at $T_N = 139 \text{ K}$ where the Mn magnetic moments in the $a - b$ plane are ferromagnetically ordered, but successive planes are coupled antiferromagnetically [8,9]. This magnetic structure is brought about by an

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orbital order–disorder phase transition (Jahn–Teller transition) at $T_{JT}=710$ K which is still not understood properly. In this order–disorder transition, the e_g orbitals ($4d$ -electrons in Mn^{3+} ions) are long-range ordered below (orbital ordered (OO)) T_{JT} and become disordered above (orbital disordered (OD)) T_{JT} [10,11]. Physical properties above and below the orbital order–disorder transition have largely been studied [13–16]. This transition is accompanied by an abrupt change in the lattice parameters, electrical resistivity, magnetization, thermoelectric power, and Weiss constant revealing strong correlated physical properties [12–15]. Sanchez et al. [16] have analyzed this orbital transition on the bases of the microscopic three-state Potts model. However, a better understanding of the nature of this phase transition on a thermodynamic basis involving each degree of freedom is still missing. In this work, the pressure derivative of T_{JT} and the lattice, spin, and electronic entropy contributions are evaluated.

According to thermodynamics, a first-order phase transition leads to a discontinuity in the first derivative of the Gibbs free energy. Changes in entropy $\partial S/\partial T$ and volume $\partial V/\partial T$ determine the strain sensitivity of the interaction energy defining an ordering temperature. At the phase transition point, two phases (here the high-temperature OD and the low-temperature OO phases) have equal free energies but different entropies. Thus, a latent heat is needed to convert the low-temperature phase into the high-temperature phase by increasing the entropy of the system from S_{OO} to S_{OD} . Simultaneously, the two phases are separated by an energy barrier in a way they can coexist within a certain temperature interval. The latent heat and coexistence of the two phases, which can be measured experimentally, are characteristic features of discontinuous phase transitions.

It is well known that the Mn^{3+} Jahn–Teller distorted ions couple the magnetic and lattice degrees of freedom. Indeed, the magnetic, structural and electrical transport properties are intertwined in these systems. Therefore, in order to introduce spin degrees of freedom and fully study the OO/OD phase boundary, we use the magnetic extension of the Clausius–Clapeyron equation. The differential Gibbs free energy in both phases is $dG = -SdT + VdP - MdH$. Since along the phase boundary line $dG_{OO} = dG_{OD}$, one can write [17]:

$$\Delta S = (V_{OD} - V_{OO}) \frac{dP}{dT_{JT}} - (M_{OD} - M_{OO}) \frac{dH}{dT_{JT}}, \quad (1)$$

where $\Delta S = (S_{OD} - S_{OO})$. That is,

$$\Delta S = \frac{(V_{OD} - V_{OO})}{dT_{JT}/dP} - \frac{(M_{OD} - M_{OO})}{dT_{JT}/dH}, \quad (2)$$

This thermodynamic formalism leads to the pressure derivative of the critical temperature,

$$\frac{dT_{JT}}{dP} = \frac{\Delta V}{\Delta S + \frac{\Delta M}{dT_{JT}/dH}}. \quad (3)$$

The term dT_{JT}/dH is the phase boundary separating the ordered and disordered phases in magnetic fields. Since the volume of the disordered phase is smaller than that of the ordered phase and heat is absorbed in a transition from order to disorder, dT_{JT}/dP is negative. To study the nature of the orbital order–disorder JT phase transition, we have measured the thermodynamic quantities related to the Equation (3).

A polycrystalline sample of nominal composition $LaMnO_3$ was prepared using standard solid-state reaction. The average manganese valence was measured using

iodometric titration. Under the assumption that La, Ca, and O have the valences of +3, +2, and -2 , respectively, we found the oxygen content of LaMnO_3 to be 3.04 ± 0.01 . Four-probe electrical resistivity was measured in flowing Ar gas using a home-made apparatus with a platinum thermometer mounted close to the sample; silver epoxy was used to make contacts to the specimens [18]. Magnetization measurements from room temperature to 900 K were performed using a standard vibrating sample magnetometer (VSM) from Quantum Design. X-ray diffraction experiments were carried out in a Bruker-AXS Powder X-ray diffractometer model D8 Advance with Ni-filtered $\text{CuK}\alpha$ radiation, operating in the Bragg–Brentano configuration. This X-ray diffractometer is equipped with an Anton Paar (Model HTK-16) high-temperature sample chamber with a platinum Pt resistive heating attachment and a PSD X-ray detector. A thin platinum strip with a Pt–10%RhPt thermocouple underneath, used for temperature measurement, was used as the sample holder, which was coated with ~ 100 mg of the powdered sample. The crystal structure was refined by the Rietveld method using the $Pbnm$ space group [10].

Figure 1 displays the cell parameters and volume as a function of temperature for LaMnO_3 . As the temperature increases, a robust volume contraction of about 0.45% takes place at $T_{JT} = 710$ K. The volume change obtained through the phase transition is $\Delta V = -0.0045 \cdot v$ (where $v = 3.57 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ is the molar volume). Figure 2 shows the crystal strain $s = (a - b)/2(a + b)$ due to orthorhombic distortion as a function of temperature. These results are in very good agreement with previously works [10,12,15], even though our sample has a little bit oxygen excess. The Jahn–Teller distortion contributes strongly to the s factor in addition to the inherent tilting of the octahedra. One can see that it decreases monotonically to zero becoming a pseudocubic-like structure on passing from orbital order to disorder. As the Jahn–Teller effect is not operative (no-lattice distortion effect) [19] in a pseudocubic space group, the orbital ordering is destroyed. As we shall see in electrical resistivity measurements, it will lead to a much weaker charge-lattice coupling delocalizing the charge carriers.

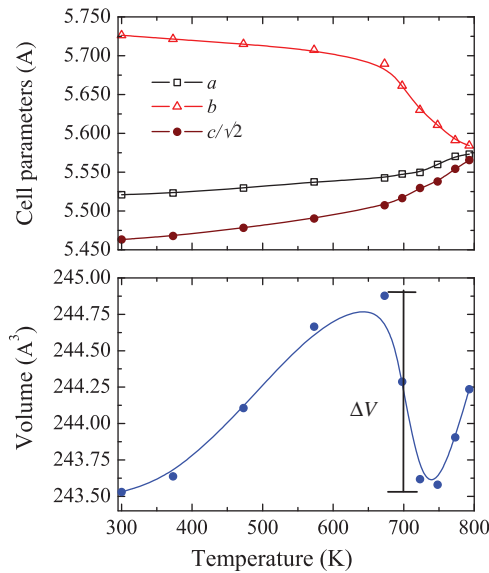


Figure 1. Temperature dependence of lattice parameters and unit cell volume.

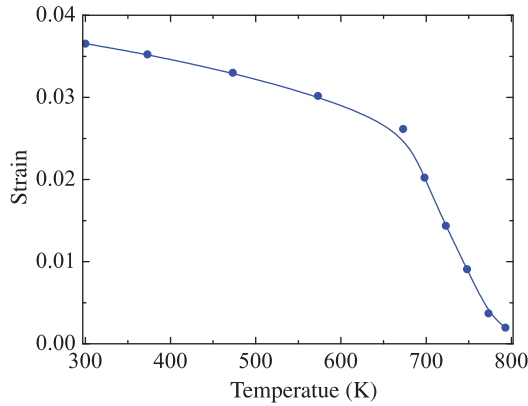


Figure 2. Orthorhombic strain as a function of temperature.

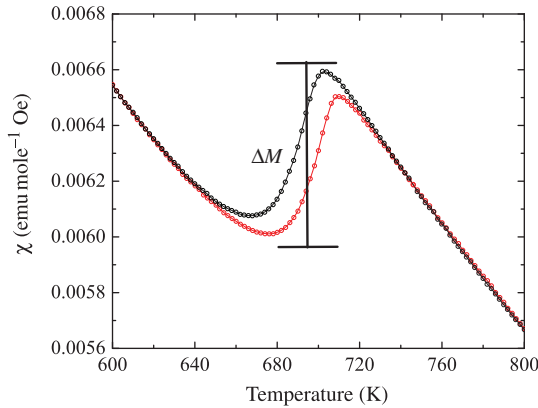


Figure 3. Magnetic susceptibility as a function of temperature. A paramagnetic state is observed above $T_N = 139$ K. If the inverse of the susceptibility is plotted as a function of temperature, one can find the Weiss constants (x -intercept) associated with both phases (not shown). It changes from 63 (ordered) to 168 K (disordered).

Magnetic susceptibility (χ) data as a function of temperature for LaMnO_3 are shown in Figure 3. Around T_{JT} , a distinct change in χ versus T accompanied by a robust thermal hysteresis indicates the first-order nature of the transition. The Weiss constant changes from 63 K (below T_{JT}) to 168 K (above T_{JT}) which indicates that the molecular field strength has also changed. This result is in agreement with previous work [13,14,20]. The molecular field (B_{mf}) measures the effect of ordering of the system due to the microscopic magnetic exchange interaction between manganese ions. One can assume that $B_{mf} = \lambda M$, where λ is an empirical constant that parameterizes the strength of molecular field as a function of magnetization. Therefore, a change in B_{mf} brings about a change in M (ΔM) related here to different orbital states. From Figure 3, we obtain $\Delta M = 0.66 \times 10^{-3} \text{ emu (mol Oe)}^{-1}$. Magnetization measured under different magnetic fields of 1 kOe and 7 kOe (not shown) yields a slope of $dT_{JT}/dH = 0.0017 \text{ K Oe}^{-1}$. Therefore, the magnetic counterpart of Equation (3) is found to be $\Delta M_{T_c}/(dT_{JT}/dH) = 0.8(2) \text{ J (mol K)}^{-1}$. This magnetic entropy

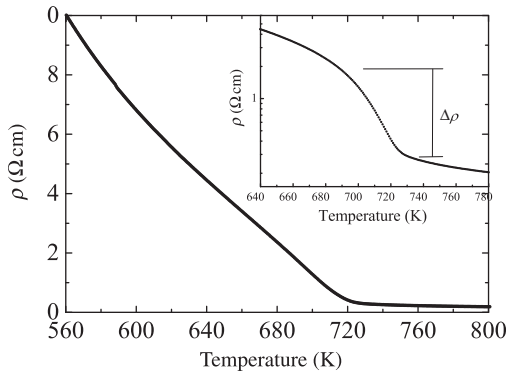


Figure 4. Electrical resistivity as a function of temperature for LaMnO_3 . The inset shows an expanded view around T_{JT} on a log scale. A variation of $\Delta\rho=82\%$ is observed.

change is driven by a cooperative orbital effect resulting in a different magnetic configuration. This magnetic jump ΔM as a function of temperature measured in a fixed magnetic field can also be related with magnetic entropy by the Maxwell relation $(\partial M/\partial T)_H = (\partial S/\partial H)_T$. Interestingly, we have measured heat capacity and estimated the magnetic entropy due to the antiferromagnetic transition at $T_N = 139$ K (not shown) [21]. The obtained value is much smaller than the expected theoretical value indicating that the entropy is not totally removed at T_N , even taking into account the value obtained here at elevated temperatures.

The total entropy change obtained through heat capacity across the phase transition is $\Delta S = 4.9 \text{ J (mol K)}^{-1}$ [22]. Using Equation (3) and the values obtained above, we obtain $dT_{JT}/dP = -28.3 \text{ K GPa}^{-1}$. A higher value of 36.2 K GPa^{-1} was obtained, but without taking into account the magnetic counterpart [12]. As a consequence, the entropy change caused by the volume contraction can be calculated as $\Delta V/(dT_{JT}/dP) = (-0.01606 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1})/(-0.002828 \times 10^{-5} \text{ m}^3 \text{ K J}^{-1}) = 5.7(3) \text{ J (mol K)}^{-1}$.

Simultaneously to the change in the magnetic susceptibility and the cell parameters at T_{JT} , there is also a distinct change in the electrical resistivity behavior as shown in Figure 4. The observed reproducibility in subsequent thermal runs assures that this result is not related to changes in oxygen content which would change the average oxidation state of Mn. Optical conductivity measurements have revealed that the gap in the electronic structure of LaMnO_3 closes above T_{JT} [23]. Band structure calculations reveal this gap only below T_{JT} [24]. Interestingly, Fuhr et al. [25] predicted a transition from an insulator to a metal in LaMnO_3 induced by pressure. Figure 4 shows that the resistivity decreases down to $200 \mu\Omega \text{ cm}$ as T_{JT} is approached and becomes nearly constant which is a characteristic of a fixed mean free path for itinerant electrons. This value is close to the Mott–Ioffe–Regel limit for a bad metal (considering $k_F l = 1$; where k_F and l are Fermi wavenumber and mean free path, respectively) [26]. In order to explain the bad metal behavior, Zhou and Goodenough [14] have proposed a vibronic conductivity mechanism. In this case the mobility $\mu = e\tau/m^*$ is reduced by a heavy effective mass due to the enhanced coupling with phonons.

Taking into account that the density of states is finite and temperature is independent above T_{JT} , one can use the Sommerfeld model to estimate the electronic entropy variation [27]. The resulting entropy associated with electronic excitations considering the lowest order in temperature is given by $S_{\text{el}} = (1/3)\pi^2 k_B^2 T n(\epsilon_F)$, where k_B is the Boltzmann

constant and $n(\epsilon_F)$ is the density of states at the Fermi level. Using the value of density of states $n(\epsilon_F) = 0.21 \times 10^{24} \text{ eV}^{-1} \text{ mol}^{-1}$ and $0.66 \times 10^{24} \text{ eV}^{-1} \text{ mol}^{-1}$ for LaMnO_3 and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$, respectively, obtained through heat capacity measurements [28], one can obtain a value of $S_{\text{el}} = 0.58$ or $1.8 \text{ J (mol K)}^{-1}$. The value of the density of states of the $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ should be closer to the system studied here (above T_{JT}). This assertion is based on fact that the $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ has a metallic ground state and higher crystal symmetry similar to the OD phase above T_{JT} [28]. As the gap opens below T_{JT} , $n(\epsilon_F) = 0$ in the OO phase.

Usually the electronic entropy contribution is small because only electrons with energies close to the Fermi level can be raised to higher energy states contributing to the specific heat. However, as S_{el} is proportional to the temperature, which here is very high 710 K, it becomes pronounced. Of course, the ground state involving electronic vibrons, where the electronic conductivity is also assisted by phonons, is more complex than the scenario above. However, so far, an envisaged analytical expression for the entropy involving this coupling is not available and it is beyond the scope of this work. We hope the discussion presented here will attract attention to this open problem.

In summary, we have studied the nature of an orbital order–disorder phase transition in LaMnO_3 using the Clausius–Clapeyron equation. The pressure derivative of the critical temperature was found to be, $dT_{JT}/dP = -28.3 \text{ K GPa}^{-1}$. This analysis reveals that the entropy change at the orbital order–disorder transition comes from the volume change, which is $5.7(3) \text{ J (mol K)}^{-1}$, and magnetic exchange interaction change, $0.8(2) \text{ J (mol K)}^{-1}$. Taking into account a bad metal system above T_{JT} , the electronic entropy change was found to be $1.8(3) \text{ J (mol K)}^{-1}$.

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