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Phase transitions in K-doped MoO₂

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 $K_{0.05}MoO_2$ has been studied by x-ray and neutron diffractometry, electrical resistivity, magnetization, heat capacity, and thermal expansion measurements. The compound displays two phase transitions, a first-order phase transition near room temperature and a second-order transition near 54 K. Below the transition at 54 K, a weak magnetic anomaly is observed and the electrical resistivity is well described by a power-law temperature dependence with exponent near 0.5. The phase transitions in the K-doped MoO₂ compound have been discussed for the first time using neutron diffraction, high resolution thermal expansion, and heat capacity measurements as a function of temperature. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4879096]

I. INTRODUCTION

Molybdenum dioxide and other transition metal dioxides are well known to be oxides with high electrical conductivity which can be comparable to some conducting metals.^{1,2} This oxide crystallizes in a low symmetry phase, monoclinic with space group $P2_1/c$,³ so-called rutile-like structure which differs very little from the TiO₂ rutile structure (tetragonal with space group $P4_2/mnm$). Rutile and rutile-like structures can be viewed as a metal ion surrounded by six oxygen atoms forming a regular octahedron in the rutile structure and a distorted octahedron in rutile-like form.

The geometry of the octahedra plays an important role on the electronic properties of these oxides. While TiO₂ and NbO₂ have rutile structures and are semiconductors,^{4,5} MoO₂ and WO₂ possess rutile-like structures and display metal-like behaviors.¹ Some of these oxides have structural phase transitions. For example, ReO₂ has a rutile-related structure (monoclinic, $P2_1/c$) but shows an irreversible structural transition around 733 K to an orthorhombic phase in which both phases display metallic conductivity.⁶ On the other hand, some of these oxides show metal-insulator transitions which are related to structural phase transitions from tetragonal to rutile-like structures. VO₂ and NbO₂ are some good examples for such transitions.^{7,8} The transition in VO₂ was first theoretically described by Goodenough⁹ who proposed that the dramatic change in the electrical conductivity around 340 K is a consequence of a periodic distortion of the lattice which separates occupied from empty states in the Vanadium 3d band. This is viewed as consistent with the Peierls transition, although some controversy remains.¹⁰⁻¹² Regarding the physical properties of MoO₂, some results suggest that this oxide displays a phase transition near 865 K,¹³ however to our knowledge there is no data in the literature showing either structural or electronic changes associated with this transition.

Metal dioxides can have their electronic properties easily tuned by substitutional doping;^{14,15} however, only little work regarding the influence of the interstitial doping on the electrical and magnetic properties have been published.^{16–18} Nevertheless, there are many transition metal oxides, for instance, the Magnéli phases¹⁹ which can have electrical properties dramatically changed by adding different amount of alkaline metals such as the well-known transition metal oxide bronzes. Usually those compounds show low-dimensional conductivity,²⁰ superconductivity,²¹ and/or charge density wave (CDW) transitions.^{22,23}

Recently, we have devoted great attention to the interstitial K doping in the MoO_2 . The doping can induce superconductivity and an anomalous electrical metallic conductivity which is still under investigation.^{17,24} Furthermore, two phase transitions have been observed in the compound, one at approximately 54 K and another near room temperature. This work deals with high resolution thermal expansion, neutron diffraction, electrical resistivity, and heat capacity measurements in order to discuss the origin of both phase transitions observed in K-doped MoO_2 .

II. EXPERIMENTAL PROCEDURE

 $K_{0.05}MoO_2$ polycrystalline samples were prepared by solid-state reaction mixing Mo, MoO₃, and K₂MoO₄ of high purity. The powders were weighed in appropriate amounts, homogenized, and pressed into pellets. The pellets were sealed in quartz tubes under vacuum (approximately 1×10^{-2} millibar) and placed in a furnace at 400 °C for 24 h and subsequently at 700 °C for 72 h. X-ray powder diffraction measurements were performed at room temperature using CuK α radiation and Ni filter. Neutron powder diffraction data were collected using the BT-1 32 detector neutron powder diffractometer at the NCNR, NBSR.²⁵ A Cu(311) monochromator with a 90° take-off angle, $\lambda = 1.5403(2)$ Å, and in-pile collimation of 60 min of arc were used. Data were collected over the range of 3°–168° 2-Theta with a step

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size of 0.05° (see Ref. 25) at 5, 50, 100, 200, and 300 K. X-ray and Neutron diffraction data were analysed and refined with PowderCell,²⁶ Vesta Crystallography,²⁷ and GSAS.^{28,29} Thermal expansion was measured from 5 to 350 K using a high resolution dilatometer cell constructed of fused-quartz³⁰ which has resolution of 0.1 Å. The relative resolution of this technique is about 3 orders of magnitudes better than diffraction techniques.³¹ In order to ensure that the whole sample would fully transform after any transition, the sample was cooled at a slow rate (approximately 1 K/min) to 5 K. Thermal expansion measurements were taken while warming the sample from 5 K to 350 K at a rate of 0.2 K/min. Electrical resistivity, magnetization, and heat capacity measurements were carried out in a Physical Properties Measurement System.

III. RESULTS

Figure 1 displays the experimental X-ray powder diffraction measurement performed at room temperature for $K_{0.05}MoO_2$ and the final Rietveld refinement using GSAS.²⁸

The refinement was very stable and converged fast yielding the goodness-of-fit $\chi^2 = 1.47$ and weighted-profile reliability factor $R_{wp} = 12.24\%$ which are reasonable values for a good x-ray diffraction refinement.²⁹ The difference between the experimental data and the refinement can be noticed by the blue line in Figure 1. The refinement shows that the sample is single phase and belongs to the monoclinic structure with space group P2₁/*c* which is similar to pure MoO₂. The lattice parameters determined by Rietveld refinement were a = 5.6082(3) Å, b = 4.8589(9) Å, c = 5.6264(5) Å, and $\beta = 120.929(6)^{\circ}$. In such refinement, the potassium atoms occupy the 2d interstitial Wyckoff position and the structure undergoes small deviations from the lattice parameters of the pattern for MoO₂.^{3,32}

In Figure 2(a), the temperature dependence of the electrical resistivity, $\rho(T)$, for K_{0.05}MoO₂ is shown for warming and cooling measurements. The most important features observed in the $\rho(T)$ curves are the peaks near room temperature and the anomalous reduction of the electrical resistivity



FIG. 1. X-ray powder diffraction pattern for $K_{0.05}MoO_2$ (asterisk), final Rietveld refinement (red line), and the correspondent difference (blue line). No additional peaks related to impurities were detected. Inset displays a magnification of the peaks between 36° and 38°.



FIG. 2. (a) Temperature dependence of the electrical resistivity for $K_{0.05}MoO_2$. This measurement was carried out first on cooling and immediately afterwards on warming. In (b) the anomalous electrical behavior at low temperatures is displayed. Inset shows the temperature dependence of the magnetization in the ZFC and FC procedures measured at 500 Oe. Two phase transitions have been indicated by the arrows at 54 and 306 K.

below 54 K. Previous results have shown similar anomalous behavior at low temperatures and a phase transition near room temperature.^{17,24} However, this is the first time in which a large increase in the electrical resistance near room temperature in $K_x MoO_{2-\delta}$ has been reported. The hysteresis between cooling and warming branches in the resistivity curves near room temperature has been related to a first-order phase transition. On the other hand, at low temperatures an anomalous electrical behavior can be observed in Fig. 2(b) which has been well described by a power law with an exponent near 0.5.³³ Furthermore, a weak magnetic anomaly, previously reported to be related to the anomalous behavior,^{17,24} has been confirmed as one can see in the inset of Fig. 2(b) for the measurements performed in the zero field cooling (ZFC) and field cooling (FC) procedures with a magnetic field of 500 Oe.

In order to study both phase transitions, we have measured high resolution thermal expansion and heat capacity as a function of temperature. Figure 3 displays linear thermal expansion measurement taken warming the sample from 5 to 350 K with a ratio of 0.2 K/min. Two important features corresponding to the temperature ranges in which the peak near room temperature and anomalous behavior appear in $\rho(T)$ have been observed.

In general, over the entire temperature range the sample shrinks with decreasing temperature, with exception for the phase transition near room temperature. At 306 K, it is



FIG. 3. Linear thermal expansion as a function of temperature for $K_{0.05}MoO_2$. Upper inset shows a magnification of the peak near 306 K (left) and the thermal expansion coefficient (right) suggesting a first-order phase transition. Lower inset shows a magnification of the region near the phase transition at 54 K.

possible to observe a peak in the thermal expansion (upper left inset). The thermal expansion coefficient, α , calculated from the derivative $1/L_{300} d(\Delta L)/dT$, shows a clear transition (upper right inset) which is associated with a first-order phase transition near room temperature in K_{0.05}MoO₂.

Neutron diffraction measurements performed in MoO₂ and K_{0.05}MoO₂ below room temperature show no evidence of structural change from the space group $P2_1/c$. However, as pointed out by Romanov and Skrobot,³⁴ one parameter which characterizes transition metal (M) dioxides is the distortion, S, of the MO_6 octahedra. It measures how much the M-O bonds in the octahedra are different from the average bond. If no distortion is present, the ideal structure should show S = zero. In general, tetragonal structures have small distortions which are typically less than 1%, however monoclinic structures have distortions which can reach up to 8% (this is the case for the VO_2).³⁴ The analyses of the Neutron diffraction data for MoO2 and K0.05MoO2 show clear distortions of the MoO₆ octahedra in both materials. The distortion for pure MoO₂ at 300 K was 2.63% and change to 2.74% at 200 K, after cooling at 2.2 K/min, which represents approximately 3% difference in this temperature range (the value at 300 K is comparable to those reported by Romanov and Skrobot³⁴). For $K_{0.05}MoO_2$, S = 2.90% and 2.40% at 300 and 200 K, respectively, which represent near 18% difference in the temperature range where the peaks in the electrical resistivity measurements occur. This suggests that the distortion can play an important role in the physical properties of the K-doped MoO_2 samples. It is important to mention that the distortion of the edge-sharing MoO₆ octahedra in the crystalline structure could indicate a CDW transition which could explain the peaks in the electrical resistivity near room temperature. Similar electrical behaviors have been reported recently for the other CDW compounds (see for instance NbSe₃,³⁵ TiSe₂,³⁶ and SmNiC₂.³⁷) Furthermore, this discussion could be closely related to the embedded Pierls instability in MoO₂ reported by Eyert et al.³⁸ X-ray powder diffraction measurements show some small differences above and below the phase transition near room temperature.³⁹ These data are still under analysis and will be reported in the future.

Regarding the behavior at low temperatures, another change in thermal expansion has been observed. In such case, the departure from linear behavior for T < 54 K coincides with the appearance of the anomalous electrical behavior and the weak magnetic anomaly shown in Figure 2. This is a clear indication of a phase transition associated with the anomalous electrical behavior. A second point is that a weak magnetic phase transition inside a CDW phase is not usual. It is probable that the phase transition near 54 K destabilizes the CDW state coming from high temperature.

Finally, let us turn our attention to the heat capacity measurements. The temperature dependence of the specific heat (C_P) for K_{0.05}MoO₂ is shown in Fig. 4. No clear feature has been observed at 54 K, which suggests that a very small entropy change is associated with this phase transition. In fact, this is reasonable due to the transition to be related to a weak magnetic anomaly. Regarding the phase transition near room temperature, it can be unambiguously observed as an anomalous sharp increase in C_P near 300 K. This seems to agree with a first-order phase transition. An example for this type of sharp transition can be found in Fig. 1 in the paper reported by Normanton and co-authors,⁴⁰ although in such case a structural phase transition with change in space group was observed.

Low temperature C_P/T versus T^2 from 2 to 6 K is plotted in the upper inset of Figure 4(b). The data can be fitted as $C_P(T) = \gamma T + \beta T^3$ which provides $\gamma = 1.5(2)$ mJ/mol K² and $\beta = 0.93(1)$ mJ/mol K.⁴ Debye temperature (θ) can be estimated from β value using the relation⁴¹ (θ)³ = (243*zR*)/ β , where *R* is molar gas constant and z = 4 is the number of atoms per formula unit. Thus, the Debye temperature is approximately 412 K for K_{0.05}MoO₂. The density of states at the Fermi level $D(E_F)$ can be estimated from Sommerfeld constant using the relation⁴¹ $\gamma = (\pi)^2 (k_B)^2 D(E_F)/3$, where k_B is the Boltzmann's constant. Under these circumstances, we obtain $D(E_F) = 0.35$ states/eV per formula unit. For the best of our knowledge, no information about Debye temperature and Sommerfeld constant was reported for MoO₂. For comparison, Debye temperature reported to VO₂ and NbO₂ are



FIG. 4. Specific heat as a function of temperature for the $K_{0.05}MoO_2$. Lower inset shows a magnification near the phase transition at 306 K. Upper inset shows C_P/T versus T^2 in which the red line represents the best linear fit used to estimate the Sommerfeld constant and Debye temperature of the $K_{0.05}MoO_2$.

750 K and 596 K, respectively.^{42,43} Furthermore, we have done heat capacity measurements in samples of the K_xMoO_{2- δ} system. We found Debye temperature values ranging from 322 K to 412 K for 0.05 < *x* < 0.3, 320 K for MoO_{1.90}, and 525 K for pure MoO₂.

IV. CONCLUSIONS

K-doped MoO₂ shows two phase transitions directly observed in thermal expansion and heat capacity measurements. A transition to weak magnetic state with anomalous electrical behavior below 54 K has been observed by both thermal expansion and electrical resistivity measurements. A first-order phase transition near room temperature is related to the peaks in the electrical resistivity measurements. Neutron diffraction measurements performed at 200 and 300 K show no structural change from the monoclinic structure with space group $P2_1/c$. On the other hand, a strong distortion of the MoO₆ octahedra has been observed from 300 to 200 K in the $K_{0.05}MoO_2$ compound in comparison to pure MoO₂. The peak in the electrical resistivity and the observation of a significantly chance in the distortion of the MoO₆ octahedra suggest a possible occurrence of a CDW transition in the $K_{0.05}MoO_2$ which is similar to other CDW compounds.

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