Unconventional metallic behavior and superconductivity in the K-Mo-O system

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Transport properties and magnetization measurements of the $K_xMoO_{2-\delta}$ ($0 \leq x \leq 0.25$) compound are reported. The compound crystallizes in the oxygen deficient MoO_2 monoclinic structure with potassium atoms occupying interstitial positions. An unconventional metallic behavior with power-law temperature dependence is related to a magnetic ordering. Superconducting transition with small volume fraction is also observed near 7 K for a sample with low potassium composition.

I. INTRODUCTION

Interplay between superconductivity and magnetism has excited the scientific community due to the possibility to understand unconventional electron-pairing mechanisms.[1–5] The recent discovery of the iron-based superconductors with high critical temperature[1,6] and rich temperature-composition phase diagrams[3,7,8] has offered an unique opportunity for studying a possible magnetic-ordering-mediated high-temperature superconductivity.[1–3,9] Furthermore, the existence of superconductivity in unconventional metals such as $Li_{0.9}Mo_6O_{17}$,[10,11] Na_xCoO_2,[12] and cuprates[9,13] is still a challenge to be understood.

In all of these compounds the existence of anisotropy seems to play an important role for the appearance of superconductivity.[10,14–16] One of the most important mechanisms for the high anisotropic conductivity was predicted by the Luttinger liquid (LL) theory.[17] In this model no discontinuity is expected in the momentum distribution at the Fermi surface.[17] Furthermore, spin-charge separation and power-law temperature (T) dependence of the correlation functions are key features of the LL physics.[17] In cuprate superconductors, possible LL behavior is controversial and remains under discussion.[18] However, in the purple bronze $Li_{0.9}Mo_6O_{17}$ compound the quasi-one-dimensional (1D) conductivity has been unambiguously related to the appearance of the superconducting state.[10,14] Recently, the normal-state electrical resistance of the $Li_{0.9}Mo_6O_{17}$ compound has been properly described by a two-band LL with two power-law T terms.[10] Due to this power-law T dependence,[10] high anisotropic ratio in the electrical conductivity[15,19] and thermal expansion[14] along crystallographic axes, photoemission experiments,[20] and band-structure calculations,[21] the $Li_{0.9}Mo_6O_{17}$ compound is nowadays recognized as the best example for the LL behavior.

Despite the excellent agreement with the LL physics provided by the $Li_{0.9}Mo_6O_{17}$ compound[10,14,20,21] many other molybdenum phases have been considered for the study of low-dimensional behavior.[19,22–26] Basically, Mo compounds have Mo-Mo or Mo-O-Mo channels along one axis providing high anisotropic conductivity necessary for quasi-1D behavior.[14,15,19,26–28] One difficult task for studying Mo compounds is related to the preparation of high-quality samples

(single and polycrystals) with workable sizes. This is primarily due to the difficulty to control the stoichiometry since formation of volatile MoO_3 is common at the temperatures used during sample preparations.[29–31] Furthermore, many oxidation states of the Mo atoms could play important role for the formation of Mo compounds with particular physical properties.[31]

Based upon above mentioned questions, searching for new unconventional metals exhibiting superconductivity could be very important for clarifying possible unconventional electron pairing mechanisms. In this paper we report on the crystalline structure, transport properties, and magnetization measurements of a phase $K_xMoO_{2-\delta}$. An unconventional metallic behavior with power temperature dependence has been observed. Sample with low potassium composition has shown superconductivity near 7 K. The interplay between the unconventional metallic behavior and magnetic ordering is also discussed.

II. EXPERIMENTAL

Polycrystalline samples were prepared as pellets using high purity K_2CO_3, MoO_3, and Mo powders. The precursor K_2MoO_4 was obtained after heat treating K_2CO_3 and MoO_3 in air at 400 °C for 24 h followed by a treatment at 700 °C for 24 h. Polycrystalline samples of $K_xMoO_{2-\delta}$ ($0 \leq x \leq 0.25$) were sintered between 650 and 750 °C for 3 days in quartz tube under vacuum after compacting appropriate amounts of K_2MoO_4, MoO_3, and Mo powders. Different heat treatments resulted in different potassium (x) and oxygen content due to the volatilization of some atoms inside quartz tubes. MoO_2 samples were prepared using a similar procedure. Compositions of some samples were verified by flame atomic absorption spectrometry (FAAS) analyzes. Standard deviations of 3% and 4% were observed in the FAAS measurements for K and Mo atoms, respectively. X-ray diffractometry and simulations were performed using Cu $K\alpha$ radiation and POWDER CELL program,[32] respectively. Electrical resistance measurements as a function of temperature were carried out in a MagLab Oxford or physical properties measurement system (PPMS) system from 2 to 300 K. Magnetization measurements were performed using vibrating-sample

TABLE I. Crystallographic data for the $K_xMoO_{2-\delta}$ compound. The cell is monoclinic space group $P2_1/c$ (14) with lattice a =5.58Å, b=4.84Å, c=5.61Å, and β=121°.

Atom	Wyckoff	x	y	z
Mo	4e	0.232	0.000	0.017
O1	4e	0.110	0.210	0.240
O2	4e	0.390	0.700	0.300
K	2d	0.500	0.000	0.500

magnetometer coupled in a PPMS or superconducting quantum interference device.

III. RESULTS

Table I shows crystallographic data used in the simulations of x-ray powder-diffraction patterns for the $K_xMoO_{2-\delta}$ compound. Experimental and simulated x-ray diffractograms[32] for the $K_xMoO_{2-\delta}$ compound are shown in Fig. 1. They agree each other and are very similar to that of the MoO_2.[33]

Only slight displacements of diffraction peaks are observed in MoO_2 potassium-doped samples. This can be clearly observed for the peaks shown in Fig. 2. The displacements to lower angles imply increasing of the lattice parameters which can be attributed to the increasing of the potassium composition in the $K_xMoO_{2-\delta}$ compound.

Based upon the crystallographic data, the crystal lattices of both MoO_2 and $K_xMoO_{2-\delta}$ monoclinic structures were simulated. Crystalline structures are shown in Fig. 3.

MoO_2 forms a distorted rutile structure having Mo-Mo metallic bonds along a axis of the monoclinic structure.[34–36] Due to those Mo-Mo bonds and other structural aspects, MoO_2 is supposed to show anisotropic behavior. Structural and electronic properties of this dioxide remain under investigation.[34,37]
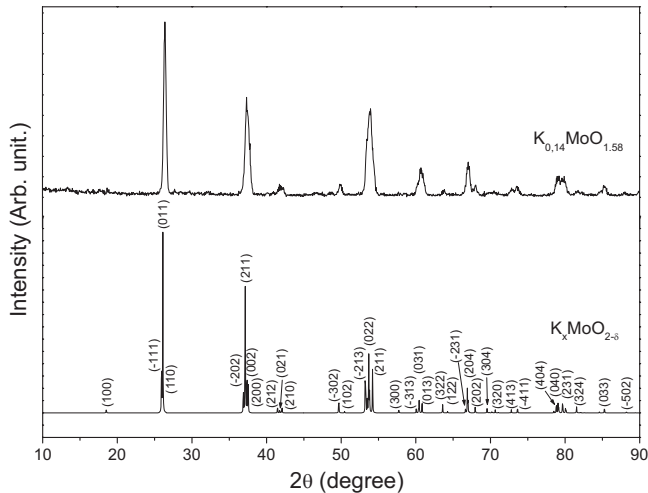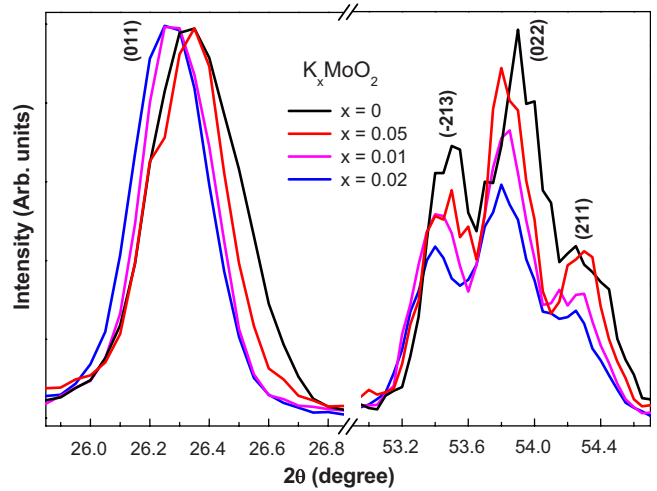

FIG. 2. (Color online) Diffraction peaks showing displacements to lower angles with increasing potassium composition in the $K_xMoO_{2-\delta}$ compound. This suggests that potassium atoms increase the lattice parameters of the MoO_2 crystal structure.

For the $K_xMoO_{2-\delta}$ compound, simulations of x-ray powder diffractograms suggest that potassium atoms occupy interstitial positions of the oxygen deficient MoO_2 as indicated on the right panel of the Fig. 3. Possible interstitial Wyckoff positions are $2a$, $2b$, $2c$, and $2d$. However, the simulations suggest that the most probable position is $2d$. Other positions are unlikely because potassium atoms would occupy interstitial positions closer to the molybdenum atoms. Furthermore, potassium atoms occupying $2d$ sites have another importance since none of them occupy positions between Mo-Mo bonds along a axis.

Based upon starting sample compositions and atomic absorption spectroscopy, the $K_xMoO_{2-\delta}$ compound has potassium composition between 0.05 and 0.25 and oxygen contents ranging from 1.5 to 2.0. $K_xMoO_{2-\delta}$ compound is a new phase in the K-Mo-O system. Close compositions reported in literature are $M_xMo_2O_4$ and $M_xMo_4O_6$ with M=K, Ba, Li, Na, In, and Sn.[38–41] However, neither of these compounds

FIG. 1. Experimental (above) and simulated (below) x-ray diffractograms for the $K_{0.14}MoO_{1.58}$ sample. Parameters used in the simulation are given in Table I.

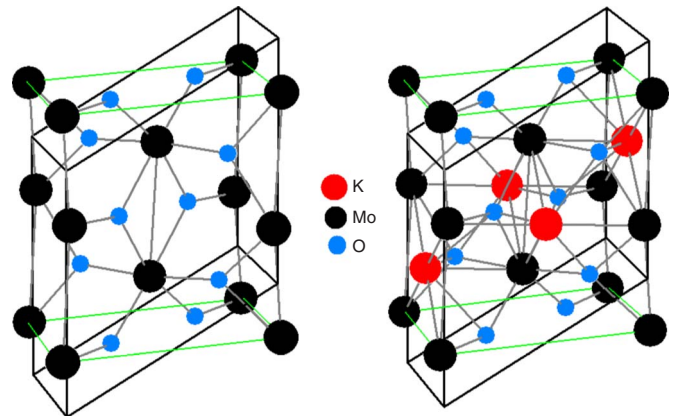FIG. 3. (Color online) Crystal structures of the MoO_2 (left) and $K_xMoO_{2-\delta}$ (right). Both crystal lattices are monoclinic. In the simulation for the $K_xMoO_{2-\delta}$ compound, potassium atoms occupy $2d$ interstitial Wyckoff positions of the oxygen deficient MoO_2.
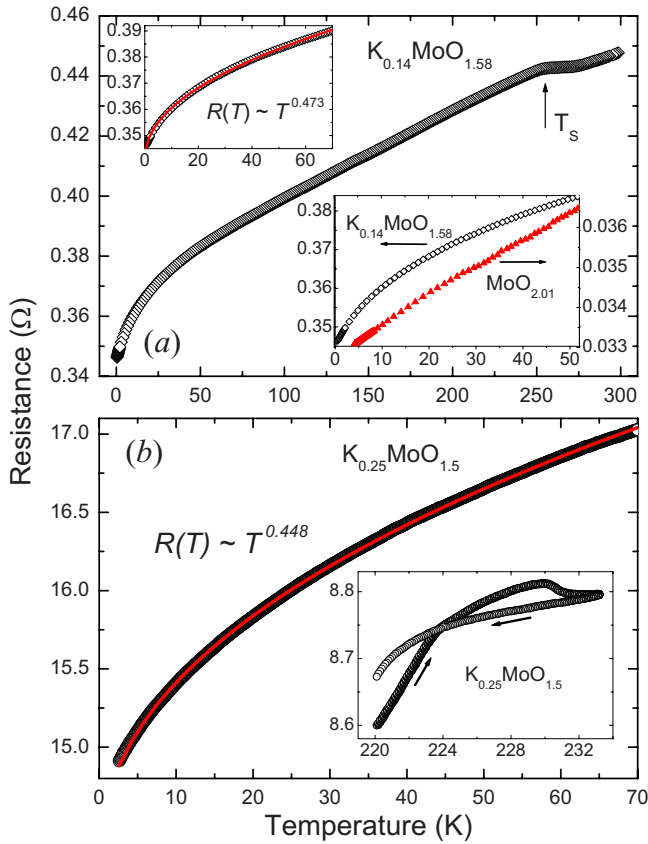
FIG. 4. (Color online) (a) Typical resistance as function of temperature for the $K_xMoO_{2-\delta}$ compound. An anomalous metallic behavior with decreasing $R(T)$ can be noticed below 70 K (see upper inset). Lower inset displays a comparison between electrical behavior of MoO_2 and a K-doped sample. In (b) is shown the anomalous behavior in $R(T)$ curve for another sample. The kink near T_S =250 K in (a) and the hysteresis in the inset of (b) are attributed to a first-order phase transition.

FIG. 5. (Color online) (a) Magnetization measurements for the $K_{0.14}MoO_{1.58}$ sample (upper curve). A magnetic ordering can be observed at $T_M \sim 70$ K. The anomalous behavior of $R(T)$ at low temperatures is unambiguously related to the magnetic ordering (lower curve). Inset shows the magnetization curves for the $K_{0.3}MoO_2$ sample. No signal of magnetic ordering is observed near the first-order phase transition. In (b) are shown three $m(H)$ curves for temperatures above and below T_M. The inset displays the magnetic hysteresis at 1.8 K.

have similar diffraction patterns nor physical properties as follow. In Fig. 4(a) is displayed the electrical resistance as a function of temperature, $R(T)$, for the $K_{0.14}MoO_{1.58}$ sample.

The compound shows a metal-like behavior. An anomalous metallic behavior can be noticed below ~70 K in which $R(T)$ reduces at low temperatures instead showing a typical saturation or linear T dependence as for conventional metallic conductors.[42] Similar behaviors have been found for several samples with different K compositions in the 0.05 $\leq x \leq 0.25$ range [see upper inset of the Fig. 4(a) and main panel of the Fig. 4(b)]. Near T_S=250 K, the $K_{0.14}MoO_{1.58}$ sample displays a phase transition. Results for several samples show that this transition is very sensitive to the potassium composition. Hysteresis near 225 K in the $R(T)$ curves for the $K_{0.25}MoO_{1.5}$ sample, shown in inset of the Fig. 4(b), suggests that the transition is a first-order phase transition. In lower inset of the Fig. 4(a) one can see the conventional linear temperature dependence for a $MoO_{2.01}$ sample[43,44] which is displayed together with the anomalous behavior of the $K_{0.14}MoO_{1.58}$. The results unambiguously demonstrate the relevance of K doping or oxygen deficiency on the appearance of the anomalous metallic behavior at low temperatures.
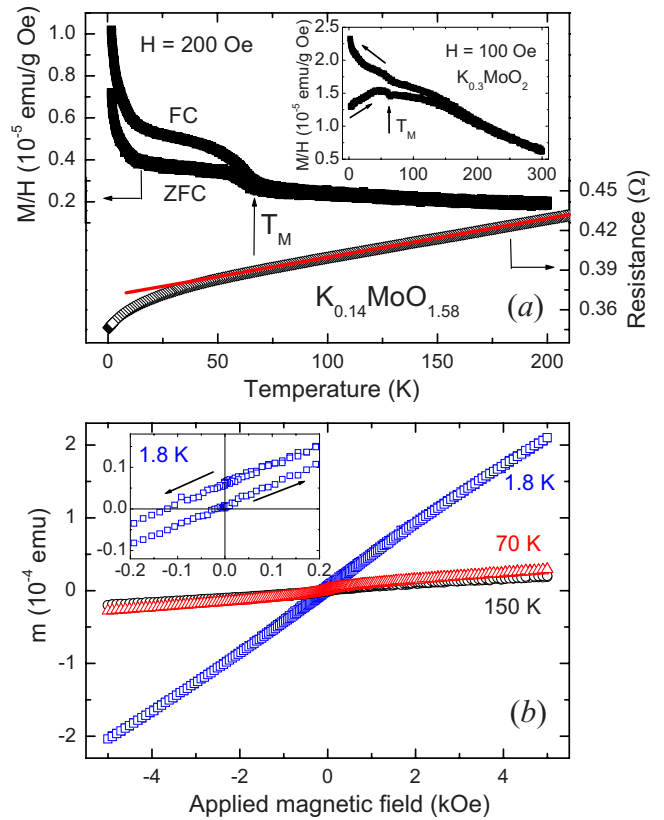
We have observed that a simple power law, $R(T) \sim T^\alpha$, with α=0.53±0.07 has fitted the results for several $K_xMoO_{2-\delta}$ samples with $0.05 \leq x \leq 0.25$. The origin of this power-law temperature dependence is under investigation but could indicate a possible quasi-1D character of the $K_xMoO_{2-\delta}$ compound despite the possible extrinsic intergranular effects on the electrical transport. This behavior is similar to the discussion reported recently for the $Li_{0.9}Mo_6O_{17}$,[10,14] however the power-law temperature dependence for compound reported here has only one power-law term with positive α exponent.[14,18] Furthermore, this unconventional behavior could be in agreement with the anisotropic behavior expected to the Mo-Mo channels along a axis of both MoO_2 and $K_xMoO_{2-\delta}$ compounds (see Fig. 3).

Magnetization measurements in zero-field-cooled (ZFC) and FC procedures, shown in Fig. 5(a), suggest that the unconventional metallic behavior is related to a magnetic ordering below $T_M \simeq 70$ K. The $M(T)$ curves in ZFC and FC for the $K_{0.3}MoO_2$ sample are displayed in the inset of the Fig. 5(a). No magnetic ordering is observed near the first-order phase transition. The increasing of the magnetic moment at lower temperatures and the hysteresis shown in Fig.
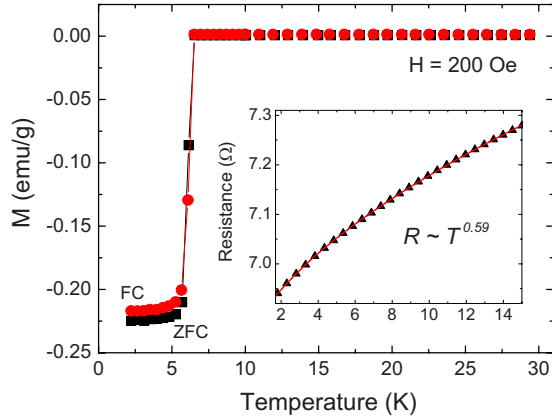
FIG. 6. (Color online) Magnetization as a function of temperature for the $K_{0.05}MoO_{1.63}$ sample. A superconducting transition can be observed near 6.5 K for 200 Oe. In inset the $R(T)$ behavior of the sample is displayed. No drop in $R(T)$ is observed near the diamagnetic superconducting transition. Due to the low superconducting fraction of the sample, the power-law temperature dependence remains responsible for the electrical behavior.

5(b) suggest an unusual weak ferromagnetic ordering below T_M. We have noticed that the general magnetic and electrical behaviors of the $K_xMoO_{2-\delta}$ samples are very similar to those reported for the Na_xCoO_2 compound with $x=0.75$ and 0.82.[12,45] The origin of the similarities is under investigation.

Finally, let us turn our discussion to the observation of superconductivity in low K-doped sample. Figure 6 displays magnetization measurements for the $K_{0.05}MoO_{1.63}$ sample with rod shape in order to reduce demagnetization effects. Figure 6(a) shows the magnetization as a function of temperature in the ZFC and FC procedures. A clear superconducting transition can be observed near 6.5 K for 200 Oe. This is the highest superconducting critical temperature reported for the K-Mo-O system up to now. Only one previous report suggests superconductivity near 4.2 K in this system.[46] No drop in the resistance as a function of temperature has been observed (see inset of Fig. 6), indicating that the sample has low superconducting volume fraction.[47] Estimation of the superconducting volume fraction based upon the magnetization measurement shown in Fig. 6 gives 4% which is much lower than that expected for the percolation limit.[47,48]

In Fig. 7(a) one can see the magnetization versus applied field measured at different temperatures below T_c. Clear Meissner and mixed states can be noticed. Based upon the points in the $M(H)$ curves indicated by arrows for different temperatures, one can find the H_{C1} and H_{C2} lines shown in Fig. 7(b) using the $H_{Ci}[1-(T/T_C)^2]$ equation with $i=1$ or 2. From the fittings it is possible to estimate the critical temperature at zero-magnetic field as 7.25 K. H_{C1} and H_{C2} at zero temperature are also estimated to be 450 Oe and 802 Oe, respectively. Those values provide $\xi(0)=641$ Å, $\lambda(0)$
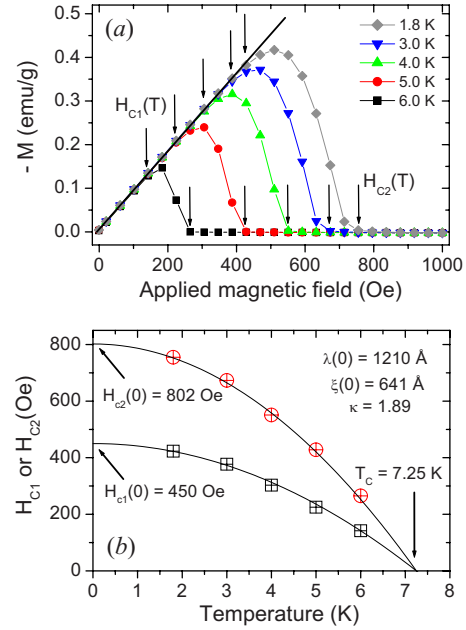

FIG. 7. (Color online) (a) Magnetization versus applied magnetic field for the $K_{0.05}MoO_{1.63}$ sample at different temperatures. Arrows indicate the $H_{C1}(T)$ and $H_{C2}(T)$. (b) T_C at zero field, and H_{C1} and H_{C2} at zero temperature were determined as the best fitting parameters using the $H_{Ci}[1-(T/T_C)^2]$ equation with $i=1$ or 2. $H_{C1}(0)$ and $H_{C2}(0)$ allow one to estimate $\xi(0)$, $\lambda(0)$, and κ as indicated.

$=1210$ Å, and $\kappa=1.89$, indicating that the $K_xMoO_{2-\delta}$ compound is a type-II superconductor.[49]

IV. CONCLUSION

A phase in the K-Mo-O system with $K_xMoO_{2-\delta}$ composition is reported. An anomalous metallic behavior with power-law temperature dependence has been found for several samples in $0.05 \leq x \leq 0.25$ range. The anomaly with an exponent $\alpha \sim 0.5$ is related to a magnetic ordering below 70 K. Small superconducting volume fraction has been observed for a sample with low K doping. Correlation between the unconventional metallic behavior and the magnetic ordering below T_M in closely related superconducting sample is under investigation.

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