Anisotropic electrical resistivity of quasi-one-dimensional $Li_{0.9}Mo_6O_{17}$ determined by the Montgomery method

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Anisotropic electrical resistivity of quasi-one-dimensional $Li_{0.9}Mo_6O_{17}$ was measured using the Montgomery method. The average resistivity ratio at 300 K was found to be $\rho_b:\rho_c:\rho_a \sim 1:2.5(0.4):6(2)$.

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For more than two decades, scientists have studied the physical properties of purple bronze $Li_{0.9}Mo_6O_{17}$ (Ref. 1) which is believed to be the best example of a Luttinger liquid metal.[2,3] This compound has a monoclinic structure with the highest conductivity along the b axis due to the existence of one-dimensional (1D) Mo(1)-O(11)-Mo(4) zigzag chains in this direction.[4] An important issue is the crossover from metallic to insulating-like behavior near 28 K.[5] Recently, this question was addressed by high resolution thermal expansion (HRTE) experiments[3] performed on high quality single crystals. The HRTE experiments suggested a crossover in dimensionality near 28 K due to a purely electronic charge density wave,[6] which sets the stage for superconductivity at ~1.9 K.

Surprisingly, after more than twenty years, some basic physical properties of this compound remain unclear, probably due to the difficulty in growing single crystals of good size. For instance, the electrical resistivity as a function of temperature, $\rho(T)$, along the c axis[8] has never been published. The first $\rho(T)$ data for the b and a axes[7] (*the a axis is out-of-plane*) were reported by Greenblatt *et al.*[1] The results showed the highest conductivity along b and anisotropic resistivity ratio at 300 K of $\rho_b:\rho_c:\rho_a \sim 1:10:250$.[1,8] However, the measured crystals were small platelets, and it is generally accepted that the Montgomery method is necessary to correctly determine the resistivities along each direction; this method was *not* applied in the work of Greenblatt *et al.*[1] Optical measurements[5] seem to provide further support for the highly anisotropic resistivity.

In this Brief Report, measurements of the anisotropic electrical resistivity in all crystallographic directions of $Li_{0.9}Mo_6O_{17}$ are revealed using the well-known Montgomery method.[9] The results confirm the quasi-one-dimensionality of the compound, but reveal a smaller anisotropic resistivity ratio than previously reported.[1,5]

$Li_{0.9}Mo_6O_{17}$ single crystals were prepared and characterized as reported previously.[3] Single crystals with purple and bronze colors exhibiting crossover from metallic to insulatinglike behavior and superconductivity at ~1.9 K were selected for this work. Low-resistance gold contacts were used for measuring electrical resistance by Montgomery[9] and standard four-probe methods. In both cases, single crystals were polished in order to obtain rectangular shapes for better determination of the geometric factors. For the Montgomery method, two crystals of sizes $0.410\times0.387\times0.405$ and $0.184\times0.455\times0.673$ mm^3 (a, b, and c axes, respectively) were used for the measurements. To simplify the calculation of the three resistivity components using the Montgomery method,[9] the crystalline structure was considered as orthorhombic;[4] since $\beta=90.61°$, this is a reasonable approximation. We report the average of two measurements in each direction and the corresponding uncertainties. In addition, the conventional four-probe method was used to check the absolute values of the electrical resistivity along b and c. To accomplish this, two crystals were oriented using Laue x-ray diffraction and carefully polished into parallelepiped shape with long axes along b and c. The polished single crystals were 1.506 and 1.509 mm in length, 0.201 and 0.131 mm in thickness, and 0.208 and 0.445 mm in width for the measurements along b and c, respectively. This process was impossible for the a axis due to the small thickness of the single crystals. Uncertainties in this method were estimated by comparing the size of the voltage contacts (~0.1 mm) with the distance between them (0.237 and 0.288 mm for b and c, respectively).

Figure 1 displays typical electrical resistance behavior of the single crystals along the b axis. Figure 1(a) highlights the superconducting transition, while the crossover from metallic to insulating-like behavior at T_M is shown in Fig. 1(b). These features demonstrate the good quality of the crystals.

Figure 2 shows the $R(T)$ raw data obtained for the three crystallographic directions of one crystal using a geometry suitable for later analysis with the Montgomery method.[9] The values near the curves indicate the resistance at 300 K (R_{300}) for each axis. The temperature dependencies and magnitude of R_{300} (not shown) are similar for the second crystal.

Figure 3 displays electrical resistivity as a function of temperature calculated using the Montgomery procedure.[9] The average resistivities at 300 K (ρ_{300}) based on the results of the two single crystals are $\rho_a=110$ (40) mΩ cm, $\rho_b=19$ (1) mΩ cm, and $\rho_c=47$ (5) mΩ cm. The resistivities at 300 K for b and c differ by factors of ~2 and 0.5, respectively, with the values reported by Greenblatt *et al.* ($\rho_b=9.5$ mΩ cm and $\rho_c \sim 100$ mΩ cm).[8] On the other hand, a-axis resistivity has an extreme disagreement ($\rho_a=2470$ mΩ cm) by a factor of ~20. Using the resistivities at 300 K, one can estimate the anisotropic resistivity ratio as $\rho_b:\rho_c:\rho_a \sim 1:2.5$ (0.4):6 (2) which differ significantly from the report of Greenblatt *et al.*[1]

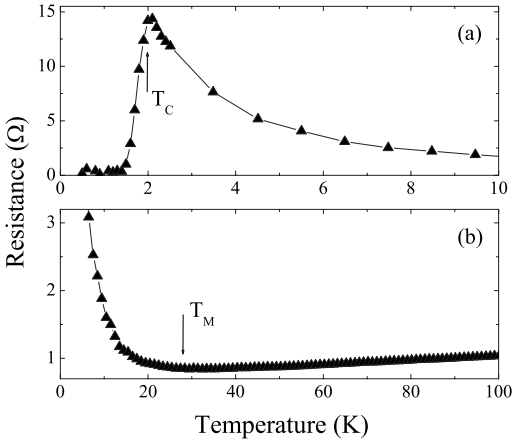

FIG. 1. Electrical resistance as a function of temperature for a typical $Li_{0.9}Mo_6O_{17}$ single crystal along the b axis. Lines are guides for the eye. (a) The superconducting transition at T_C. (b) The crossover from metallic to insulatinglike behavior at T_M.

To cross-check the values determined above, and the validity of the Montgomery method, we measured $\rho(T)$ along the b and c axes using the standard four-probe technique (on the crystals polished into parallelepipeds). These results are shown in Fig. 4. Resistivities at 300 K for b and c are $\rho_b = 12$ (5) mΩ cm and $\rho_c = 52$ (18) mΩ cm, respectively. This provides an anisotropic ratio of $\rho_b : \rho_c \sim 1:4$ (3) which agrees with the ratio obtained through the Montgomery method. Although these values possess large uncertainties, they provide confidence that the electrical resistivities determined by the Montgomery method are reliable.

The results provide insight into the anisotropic behavior of the purple bronze. Similar temperature dependencies for $R(T)$ and $\rho(T)$ for all axes suggest that the anisotropic behavior of $Li_{0.9}Mo_6O_{17}$ is in someway interconnected in the three crystallographic directions. This can be understood by looking at the crystalline structure.[4] It has zigzag chains running along b, which have projections onto the a and c directions.

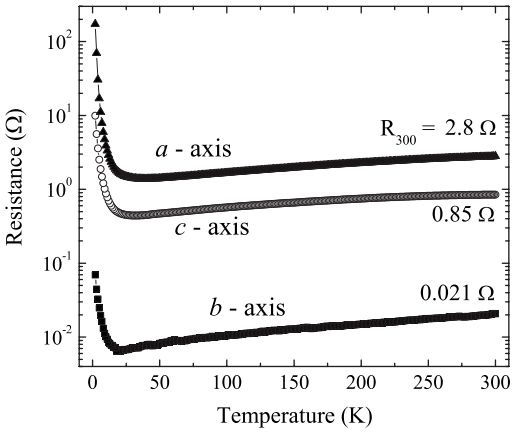

FIG. 2. Electrical resistance for the three crystallographic directions of one $Li_{0.9}Mo_6O_{17}$ single crystal measured using the Montgomery method. The R_{300} values indicate the resistance at 300 K for each axis.

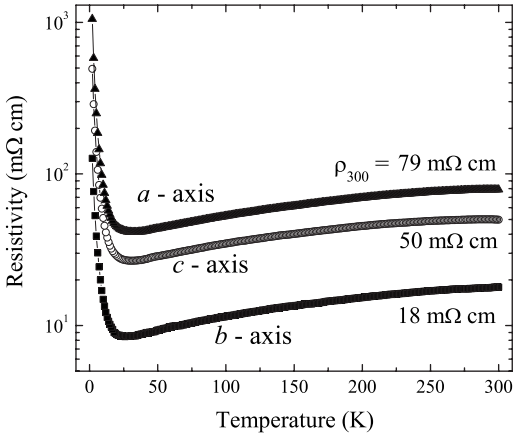

FIG. 3. Electrical resistivity as a function of temperature for the three crystallographic directions of one $Li_{0.9}Mo_6O_{17}$ single crystal. The ρ_{300} values indicate the resistivity at 300 K for each axis.

By taking into account that electrons move between the zigzag chains through interchain hopping and choose the most conducting path (an example is the Mo6-[Mo4-O11-Mo1]-Mo6 path, where the [Mo4-O11-Mo1] path is in the zigzag chain), it appears reasonable to conclude that the electrical resistivities in the a and c axes may not be ρ_b independent. This anomalous zigzag conducting behavior of $Li_{0.9}Mo_6O_{17}$ is absent in other quasi-1D systems[10–13] and high-temperature superconductors,[14–16] which show remarkably different temperature dependencies of ρ for different crystallographic directions. Furthermore, this anomalous zigzag conducting behavior may provide an explanation of why the electrical resistivity measurements reveal a much smaller anisotropy than that of the optical conductivity experiments.[5] However, resolution of this issue will require measurements and analysis beyond the scope of the present work.

In summary, the electrical resistivity for all crystallographic axes has been determined using the Montgomery method for $Li_{0.9}Mo_6O_{17}$. The results confirm the quasi-one-dimensionality but clearly show a much smaller anisotropy

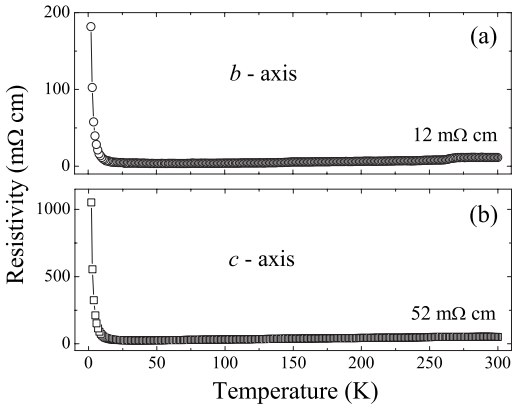

FIG. 4. Electrical resistivity as a function of temperature for two single crystals in (a) b and (b) c axes performed using standard four-probe method.

than previously reported. Similar temperature dependencies in all directions suggest that the purple bronze conducts differently than other low-dimensional systems. This is thought to be related to the projection of the zigzag chains onto the *a* and *c* directions.

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[1] M. Greenblatt, Chem. Rev. (Washington, D.C.) **88**, 31 (1988); M. Greenblatt, R. Neifeld, M. Croft, and J. V. Waszczak, Solid State Commun. **51**, 671 (1984).

[2] F. Wang, J. V. Alvarez, S.-K. Mo, J. W. Allen, G.-H. Gweon, J. He, R. Jin, D. Mandrus, and H. Höchst, Phys. Rev. Lett. **96**, 196403 (2005).

[3] C. A. M. dos Santos, B. D. White, Y.-K. Yu, J. J. Neumeier, and J. A. Souza, Phys. Rev. Lett. **98**, 266405 (2007).

[4] Z. S. Popović and S. Satpathy, Phys. Rev. B **74**, 045117 (2006), and references therein.

[5] J. Choi, J. L. Musfeldt, J. He, R. Jin, J. R. Thompson, D. Mandrus, X. N. Lin, V. A. Bondarenko, and J. W. Brill, Phys. Rev. B **69**, 085120 (2004).

[6] D. Boies, C. Bourbonnais, and A.-M. S. Tremblay, Phys. Rev. Lett. **74**, 968 (1995).

[7] Crystallographic axes are defined here as in Refs. 3 and 4.

[8] The *c*-axis resistivity was assumed to have the value of $\sim 100\ \mathrm{m}\Omega\,\mathrm{cm}$ due to the ratio reported in Ref. 1, but, to the best of our knowledge, no $\rho_c(T)$ curve was reported.

[9] H. C. Montgomery, J. Appl. Phys. **42**, 2971 (1971).

[10] C. A. Kuntscher, S. Schuppler, P. Haas, B. Gorshunov, M. Dressel, M. Grioni, F. Lichtenberg, A. Hernberger, F. Mayr, and J. Mannhart, Phys. Rev. Lett. **89**, 236403 (2002).

[11] C. A. Kuntscher, D. van der Marel, M. Dressel, F. Lichtenberg, and J. Mannhart, Phys. Rev. B **67**, 035105 (2003).

[12] R. Tarkiainen, M. Ahlskog, J. Penttilä, L. Roschier, P. Hakonen, M. Paalanen, and E. Sonin, Phys. Rev. B **64**, 195412 (2001).

[13] S. N. Artemenko, and S. V. Remizov, Phys. Rev. B **72**, 125118 (2005); S. V. Zaitsev-Zotov, M. S. H. Go, E. Slot, and H. S. J. van der Zant, Phys. Low-Dimens. Semicond. Struct. **1-2**, 79 (2002).

[14] S. W. Tozer, A. W. Kleinsasser, T. Penney, D. Kaiser, and F. Holtzberg, Phys. Rev. Lett. **59**, 1768 (1987).

[15] G. Briceño, M. F. Crommie, and A. Zettl, Phys. Rev. Lett. **66**, 2164 (1991).

[16] U. Welp, S. Fleshler, W. K. Kwok, J. Downey, Y. Fang, G. W. Crabtree, and J. Z. Liu, Phys. Rev. B **42**, 10189 (1990).