Electronic Structure near the Fermi Surface in the Quasi-One-Dimensional Conductor $Li_{0.9}Mo_6O_{17}$

Jinyu Xue, L.-C. Duda,* and Kevin E. Smith†
Department of Physics, Boston University, Boston, Massachusetts 02215

Alexei V. Fedorov and Peter D. Johnson
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973

Steve L. Hulbert
National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York 11973

William McCarroll and Martha Greenblatt
Department of Chemistry, Rutgers University, New Brunswick, New Jersey 08903
(Received 16 April 1999)

The electronic properties of the quasi-one-dimensional (1D) oxide conductor $Li_{0.9}Mo_6O_{17}$ have been investigated using high-momentum and energy resolution photoelectron spectroscopy at temperatures above and below the metal-semiconductor transition temperature. Considerable spectral intensity at the Fermi energy (E_F) is observed at room temperature, and a sharp feature corresponding to a band crossing E_F is clearly resolved for states along the quasi-1D axis. Below the metal-semiconductor transition at 24 K, a gap is clearly observed to open at E_F. Our data do not support the assertion that the low energy excitations of electrons in $Li_{0.9}Mo_6O_{17}$ should be described in a Luttinger liquid model.

PACS numbers: 79.60.–i, 71.20.Dg, 71.30.+h

Much controversy surrounds the interpretation of the results of angle-resolved photoemission spectroscopy (ARP) studies of the electronic structure of quasi-one-dimensional (1D) solids [1–4]. In principle, ARP should provide a wealth of valuable information about quasi-1D solids, including measurements of the structure of the Fermi surface, and of possible non-Fermi liquid behavior of electrons close to the Fermi level (E_F). In practice, many aspects of the spectroscopy make straightforward interpretation of the spectra difficult. Not least of these is its surface sensitivity, which often puts significant limitations on its application [4]. It has been reported that photoemission from states near E_F in quasi-1D conductors differs significantly from that measured from two- and three-dimensional solids, with (among other differences) an anomalously low emission intensity at E_F [1,5,6]. There are a number of possible explanations for these observations, including problems with surface defects and stoichiometry [4,7,8], charge-density wave (CDW) fluctuations leading to a pseudogap [9], or a Luttinger liquid state [10–13].

We report here the results of a temperature dependent ARP study of the electronic structure close to E_F in the quasi-1D conductor $Li_{0.9}Mo_6O_{17}$. This material is one of a class of quasi-low-dimensional conductors known as molybdenum oxide bronzes. Molybdenum bronzes are ideal for ARP studies since large high-quality crystals can be grown [14,15], and surfaces suitable for ARP measurements can be prepared by cleaving the crystals in vacuum [4]. $Li_{0.9}Mo_6O_{17}$ is metallic at room temperature, becomes semiconducting at 24 K, and finally becomes superconducting at 1.9 K [14,16]. It is unknown whether the transition at 24 K is caused by a CDW or a spin density wave (SDW). Using very high momentum and energy resolution ARP, we have clearly resolved a band dispersing across the Fermi surface, we have measured substantial emission intensity at E_F in the metallic phase, and have observed a gap opening at E_F as the sample is cooled through the metal-semiconductor transition. Our results differ from many earlier ARP studies of quasi-1D solids [6], and in particular with ARP results on the same material reported recently by Denlinger *et al.* [17]. In that work, no evidence of the opening of a gap at E_F upon cooling was observed, nor was significant emission intensity at E_F observed in the metallic phase. The differences are likely due to an order of magnitude improvement in angular resolution (and corresponding improvement in momentum resolution) for the spectrometer used in the present studies. Our data provide not only an experimental understanding of the electronic structure of $Li_{0.9}Mo_6O_{17}$, but also a significant test of ARP from quasi-1D metals.

A tight binding band structure calculation for $Li_{0.9}Mo_6O_{17}$ predicts two fully occupied and two partially occupied Mo $4d$-derived bands within 0.3 eV of E_F for states along the quasi-1D conducting direction [18]. The two partially filled bands are degenerate at E_F, and the predicted Fermi surface consists of two parallel straight lines. In an earlier lower resolution ARP study of $Li_{0.9}Mo_6O_{17}$ we measured such a Fermi surface by mapping a discontinuity in the dispersion of the d-band emission near E_F [19]. This study verified the shape of the Fermi surface, but the measured nesting vector was larger (0.7 $Å^{-1}$) than expected from the calculations, and we did not observe much of the predicted

band dispersion [18]. Subsequently, Gweon *et al.* also studied $Li_{0.9}Mo_6O_{17}$ using ARP [6]. Their experiment was performed with better energy resolution and with the sample at a lower temperature than our earlier study, but they also were unable to fully resolve the predicted band dispersion. Both studies revealed little spectral weight at E_F. The most recent ARP study of $Li_{0.9}Mo_6O_{17}$ by Denlinger *et al.*, performed with an energy resolution of 50 meV and an angular resolution of $\pm 1°$, did observe some band dispersion, but again could not observe any emission intensity at E_F [17].

Our experiments were carried out on undulator beam line U13UB at the National Synchrotron Light Source, Brookhaven National Laboratory. The ARP measurements were performed using a commercial SES 200 Scienta hemispherical analyzer, modified so that the total spectral response can be measured as a function of angle and energy, simultaneously. Operated in such a mode, the angular resolution of the analyzer is approximately $\pm 0.1°$ and the total energy resolution reached in the present measurements is approximately 33 meV for temperatures between 17 and 300 K at a photon energy of 21.4 eV. The Fermi energy and the energy resolution were determined by evaporating a gadolinium film onto the sample and measuring the Fermi distribution cutoff. For the photon energy employed here, the instrument angular resolution results in a momentum resolution of better than 0.01 $Å^{-1}$, which is crucial for resolving a rapidly dispersing band. The $Li_{0.9}Mo_6O_{17}$ single crystals were grown by a temperature gradient flux technique reported elsewhere [16]. Clean surfaces were obtained by cleaving the sample *in situ* in the measurement chamber, which had a base pressure of 2×10^{-11} Torr. In order to avoid electron damage to the surface [4], each sample was cleaved twice before taking spectra. After the first cleave, low energy electron diffraction (LEED) was used to determine the orientation of the crystal with respect to the polarization vector of the radiation and the spectrometer axis. The sample was then cleaved again in the desired orientation to expose a new surface for photoemission measurements. $Li_{0.9}Mo_6O_{17}$ has a monoclinic unit cell with the ΓY direction parallel to the 1D axis [010] and the crystal cleaves to expose a (001) surface. Cooling of the sample was achieved using a liquid He cryostat. The sample temperature was monitored using a silicon diode attached to the sample holder. At the completion of the experiment the diode was then calibrated against another directly attached to the sample in order to account for the temperature gradient between the holder and the sample.

Figure 1 presents the photoemission intensity map of the total spectral response measured at room temperature. The horizontal axis is the angle of emission, converted to the equivalent k-space values [20]. Two dispersive features are observed within 700 meV of E_F. One feature disperses symmetrically around the Brillouin zone center (Γ point) and reaches a maximum binding energy of approximately 630 meV at Γ. A second feature splits from

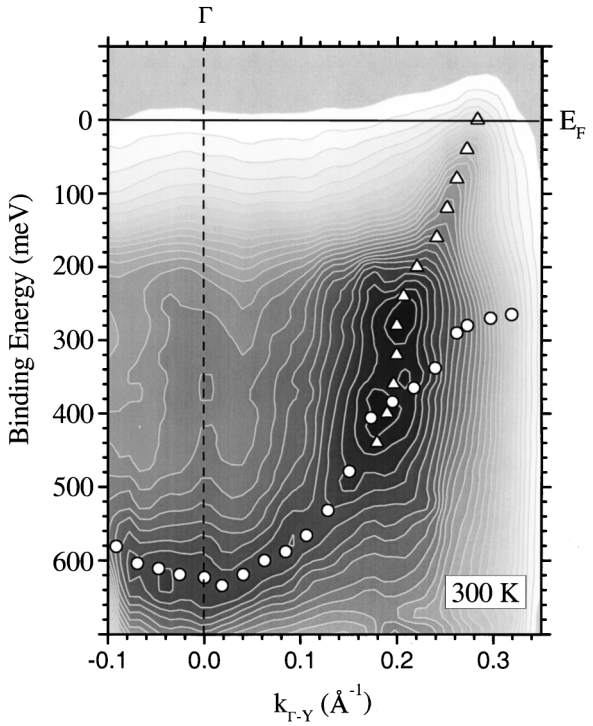

FIG. 1. Intensity map of photoemission from $Li_{0.9}Mo_6O_{17}$. $T = 300$ K, $h\nu = 21.4$ eV. Also plotted is the experimentally determined dispersion of d bands; open triangles are transitions determined from MDCs and the open circles those determined from EDCs. See text for details.

the first band, and disperses across E_F. The dispersion of the bands is indicated in Fig. 1 as filled and open symbols overlaid on the intensity map. The values of these points are extracted from both energy distribution curves (EDCs) and momentum distribution curves (MDCs). By slicing the intensity map of Fig. 1 at a constant value of the emission angle, conventional photoemission spectra are generated; i.e., plots of photoemission intensity versus energy, or EDCs. By slicing the intensity map of Fig. 1 at a constant value of the binding energy, plots of photoemission intensity versus angle (and hence momentum) are generated, and called MDCs. Dispersion determined from EDCs is usually not as accurate as that from MDCs for a rapidly dispersing band. We therefore used the MDCs to identify the location of the band crossing E_F. We attribute our observation of the dispersive states visible in Fig. 1 to our very high energy and momentum resolution, as well as a careful alignment by LEED of the orientation of the sample; even a small misalignment of the sample orientation leads to significant changes in the spectra. We have not resolved all the predicted bands, but have clearly observed the predicted band splitting near k_F [18]. Note, however, that only one emission feature is observed to cross E_F. Data taken at 27 K (not shown) also display only one emission feature crossing E_F.

Figure 2 shows the EDCs close to k_F for states along the quasi-1D direction (ΓY), extracted from the data of Fig. 1. The dispersion of a state across E_F is clearly visible. The

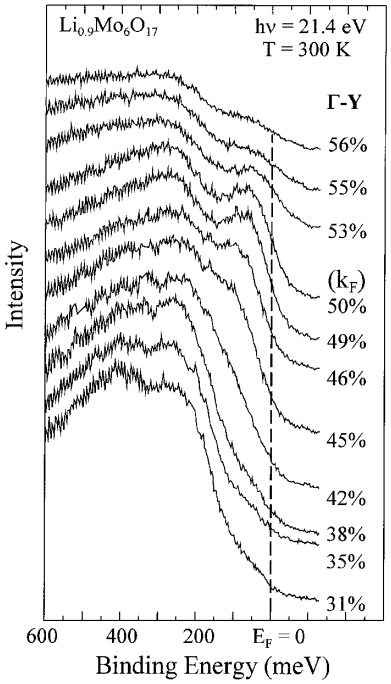

FIG. 2. EDCs extracted from the intensity map (Fig. 1) for states along the ΓY direction at room temperature. $T = 300$ K, $h\nu = 21.4$ eV.

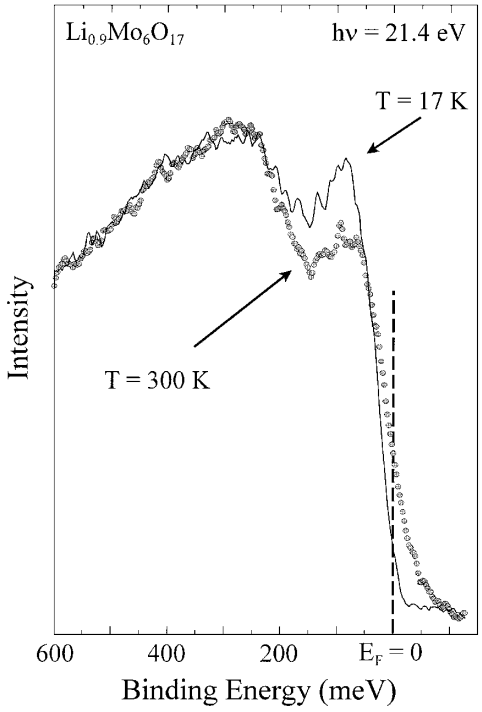

FIG. 3. EDCs extracted from the intensity map (Fig. 1) for states at k_F with the sample at 300 and 17 K. $h\nu = 21.4$ eV.

data in Figs. 1 and 2 reveal considerable photoemission intensity at E_F as the band crosses the Fermi surface. The well-defined crossing enables the determination of the nesting vector of the Fermi surface. With $k_F = 0.28$ Å^{-1}, the nesting wave vector is therefore $2k_F = 0.56$ Å^{-1}. We also determined $2k_F$ by directly measuring the distance in reciprocal space of two symmetric bands crossing the Fermi surface in the first Brillouin zone and obtained the same value. This value is slightly larger than predicted by theory ($2k_F = 0.51$ Å^{-1}) [18], but closer than that obtained in our previous lower resolution measurement [19]. It is essentially the same as that reported by Denlinger *et al.* [17]. The total measured dispersion of the *d* band below E_F is larger by a factor of 2 than predicted [18]. Such a discrepancy has also been observed in earlier measurements for $K_{0.3}MoO_3$ and $Li_{0.9}Mo_6O_{17}$ [6].

In Fig. 3 we show EDCs corresponding to $k = k_F$, taken with the sample at 300 and 17 K, above and below the metal-semiconductor transition temperature. The spectral function in our experiment exhibits significant intensity at E_F for the sample at room temperature and this intensity is nonzero even at 17 K when resistivity measurements indicate that a gap has opened [16]. The leading edge shift of the spectra between 300 and 17 K is estimated to be approximately 40 meV giving a total gap opening of $2\Delta \approx 80$ meV. Figure 4 presents the **k**-integrated emission spectrum at room temperature, for k close to k_F. This spectrum is obtained by integrating the data of Fig. 1 around k_F over an angular window of 2° (approximately 0.2 Å^{-1}). This is large enough to reflect the density of states (DOS) for the band crossing the Fermi surface since the band disperses rapidly. With an energy resolution of 33 meV in our experiment, the resolution broadening is negligible compared with the large thermal broadening at 300 K. Figure 4 also shows that the spectral intensity near

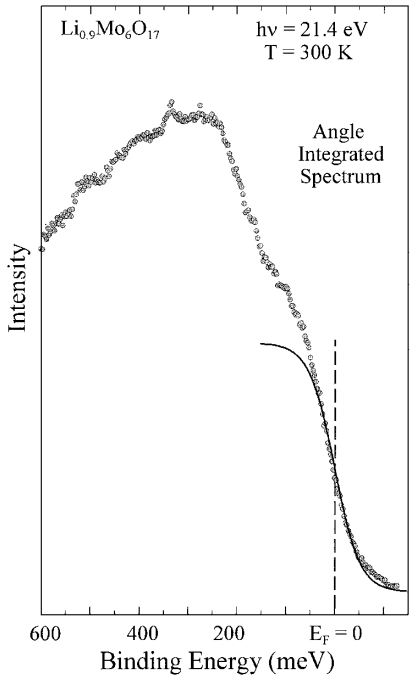

FIG. 4. Angle integrated spectrum (circles) and the Fermi function (solid line), both at 300 K. The spectrum is obtained by integrating the intensity map for states around $k = k_F$. See text for details.

E_F matches the Fermi function at 300 K. This is in contrast to the vanishing spectral weight at E_F, as measured by angle-integrated photoemission for many quasi-1D metals [4].

The observation of the Fermi cutoff can be understood as evidence for 3D metallic behavior. Despite the quasi-1D transport and optical properties of $Li_{0.9}Mo_6O_{17}$, it has a pronounced 3D crystal structure [14,16], and a large Debye temperature [14]. Furthermore, a significant interaction between the Mo_4O_{18} chains parallel to the b axis is predicted [18]. This interchain coupling was evident in our earlier observation of slight dispersion of the d band perpendicular to the 1D chain of $Li_{0.9}Mo_6O_{17}$ [19]. The interchain coupling reduces the 1D metallic character and may give rise to 3D electron dynamics, resulting in a Fermi liquid. In a pure 1D interacting electron system, the low-energy excitations are correctly described by a Luttinger liquid, and electron-electron interactions are predicted to induce a strong suppression of the photoemission intensity at E_F [2,10]. Furthermore, the **k**-integrated single-particle spectrum of a Luttinger liquid exhibits a power-law dependence of the electron binding energy near E_F, and the line shape of the spectral function (k-resolved single-particle spectrum) depends strongly on the value of the correlation exponent α [2,21–23]. If we attempt to interpret our spectra in a Luttinger framework, then given that we clearly observe a Fermi surface crossing, $Li_{0.9}Mo_6O_{17}$ must fall in the small-α class ($\alpha \leq 1$) of the Luttinger electron system [2]. However, no separate peaks are observed in our measured EDCs or MDCs that can be interpreted as being due to holons and spinons, and this puts a lower limit of 0.5 on α [2,21–23]. At best, if our data are interpreted in a Luttinger framework, then $Li_{0.9}Mo_6O_{17}$ has $0.5 \leq \alpha \leq 1$.

In conclusion, we have used high energy and momentum resolution ARP to study the electronic structure close to E_F in $Li_{0.9}Mo_6O_{17}$. We have resolved a band dispersing across E_F, and found a nesting vector close to that predicted, although the total bandwidth is at least twice as large as predicted [18]. Consistent with resistivity measurements, a gap has been observed to open up in the band structure at E_F associated with the metal-semiconductor transition. Our observations of Fermi surface crossings and a Fermi functionlike density of states are consistent with the room temperature metallic character of this material in the quasi-1D direction. Our observations are not consistent with a recent report of non-Fermi liquid phenomena in $Li_{0.9}Mo_6O_{17}$ which was based on a line shape analysis of emission spectra from states near E_F [17]. Using lower energy and momentum resolution than that available in the present study, Denlinger *et al.* were unable to observe the state forming the Fermi surface, the opening of the gap, nor significant intensity at E_F [17]. The data reported in the present paper thus call into doubt the conclusion of Denlinger *et al.* [17] that the low energy excitations of electrons in $Li_{0.9}Mo_6O_{17}$ should be described in a Luttinger liquid model.

The Boston University research was supported in part by the U.S. Department of Energy under No. DE-FG02-98ER45680. The BNL research was supported in part by the U.S. DOE under No. DE-AC02-98CH10886. Experiments were undertaken at the NSLS, which is supported by the U.S. DOE, Divisions of Materials and Chemical Sciences.

*Present address: Department of Physics, Uppsala University, P.O. Box 530, Uppsala, S-751 21, Sweden.
†Author to whom correspondence should be addressed. Electronic address: ksmith@bu.edu

[1] J. W. Allen, G. H. Gweon, R. Claessen, and K. Matho, J. Phys. Chem. Solids **56**, 1849 (1995).
[2] M. Grioni and J. Voit, "High Resolution Photoemission Studies of Low-Dimensional Systems," in Electron Spectroscopies Applied to Low Dimensional Materials, edited by H. Stanberg and H. Hughes (Kluwer Academic Publishers, Dordrecht, to be published).
[3] M. Grioni, D. Malterre, and Y. Baer, J. Low Temp. Phys. **99**, 195 (1995).
[4] K. E. Smith, Annu. Rep. Prog. Chem. C **90**, 115 (1995).
[5] B. Dardel, D. Malterre, M. Grioni, P. Weibel, Y. Baer, J. Voit, and D. Jerome, Europhys. Lett. **24**, 687 (1993).
[6] G. H. Gweon *et al.*, J. Phys. Condens. Matter **8**, 9923 (1996).
[7] K. Breuer, K. E. Smith, M. Greenblatt, and W. McCarroll, J. Vac. Sci. Technol. A **12**, 2196 (1994).
[8] K. Breuer, K. E. Smith, M. Greenblatt, W. McCarroll, and S. L. Hulbert, J. Phys. Chem. Solids **57**, 1803 (1996).
[9] H. P. Geserich and G. Scheiber, Physica (Amsterdam) **143B**, 198 (1986).
[10] H. J. Schulz, Physica (Amsterdam) **235C**, 217 (1994).
[11] J. M. Luttinger, J. Math. Phys. **4**, 1154 (1963).
[12] S. Tomonaga, Prog. Theor. Phys. **5**, 349 (1950).
[13] J. Solyom, Adv. Phys. **28**, 201 (1979).
[14] M. Greenblatt, Chem. Rev. **88**, 31 (1988).
[15] *Low Dimensional Electronic Properties of Molybdenum Bronzes and Oxides*, edited by C. Schlenker (Kluwer Academic Publishers, Dordrecht, 1989).
[16] M. Greenblatt, W. H. McCarroll, R. Niefeld, M. Croft, and J. V. Waszczak, Solid State Commun. **51**, 671 (1984).
[17] J. D. Denlinger, G.-H. Gweon, J. W. Allen, C. G. Olson, J. Marcus, C. Schlenker, and L.-S. Hsu, Phys. Rev. Lett. **82**, 2540 (1999).
[18] M.-H. Whangbo and E. Canadell, J. Am. Chem. Soc. **110**, 358 (1988).
[19] K. E. Smith, K. Breuer, M. Greenblatt, and W. McCarroll, Phys. Rev. Lett. **70**, 3772 (1993).
[20] *Angle Resolved Photoemission*, edited by S. D. Kevan (Elsevier, Amsterdam, 1991).
[21] V. Meden and K. Schonhammer, Phys. Rev. B **46**, 15 753 (1993).
[22] J. Voit, Synth. Met. **70**, 1015 (1995).
[23] J. Voit, Rep. Prog. Phys. **58**, 977 (1995).