Case for bulk nature of spectroscopic Luttinger liquid signatures observed in angle-resolved photoemission spectra of Li_{0.9}Mo_{6}O_{17}


1Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan 48109, USA
2Pohang Accelerator Laboratory, Pohang 790-784, Korea
3Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996, USA
4Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
5Department of Material Physics, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan

(Received 3 May 2006; revised manuscript received 1 August 2006; published 20 September 2006)

Angle-resolved photoemission spectroscopy (ARPES) has been performed on quasi-one-dimensional Li_{0.9}Mo_{6}O_{17} using photon energy $h\nu=500$ eV. Measured band dispersions are in agreement with those from both low-photon-energy measurements and band structure calculations. The momentum-integrated ARPES spectrum is well fitted by the finite-temperature Luttinger liquid (LL) spectral function, with an anomalous exponent 0.6 that is the same within experimental uncertainty as the value found with $h\nu=30$ eV. These identical findings at both low and high $h\nu$ are entirely consistent with reasoning based on the crystal structure that the quasi-one-dimensional chains lie two layers below the cleavage plane so that the observed spectroscopic LL behavior of Li_{0.9}Mo_{6}O_{17} is a bulk property.

DOI: 10.1103/PhysRevB.74.113107 PACS number(s): 71.10.Pm, 71.10.Hf, 79.60.–i

The low-energy physics of a one-dimensional (1D) interacting electron system is described by the Luttinger liquid (LL) picture, in which there are no single-particle excitations, but only collective modes of the charge and spin density, holons and spinons, respectively. In approaching the Fermi energy ($E_F$), the energy dependence of the momentum-summed single-particle density of states (DOS) displays a power-law decay with an anomalous exponent, i.e., $|E|^\alpha$. This Brief Report adds an important element to the spectroscopic evidence presented in previous work that Li_{0.9}Mo_{6}O_{17} provides a paradigm solid material for the study of LL physics.

Li_{0.9}Mo_{6}O_{17} is a quasi-one-dimensional metal having highly anisotropic electronic properties. We have studied this material extensively by angle-resolved photoemission spectroscopy (ARPES). The momentum-dependent spectra reveal a band structure that is in good general agreement with that of tight-binding band calculations, and detailed comparison to LL spectral theory shows that the ARPES line shape has the expected holon and spinon features moving with different velocities. As is then expected, and of direct interest for this paper, the momentum-integrated spectrum shows a clear power-law suppression of the near-$E_F$ DOS. The power-law DOS has also been observed in scanning tunneling spectroscopy. Most recently we have found that $\alpha$ shows a strong temperature-($T$)-dependent renormalization such that the values found in tunneling and ARPES are quantitatively consistent, and that this renormalization is the result of marginal interactions among charge neutral modes present explicitly because of the two-band nature of Li_{0.9}Mo_{6}O_{17}.

The additional spectroscopic element presented here is to show that ARPES data obtained at high photon energy ($h\nu \approx 500$ eV) yield the same value of $\alpha$ as obtained for the ARPES performed to date, done with much lower photon energy ($h\nu \approx 30$ eV). This finding bears on the case that the LL properties found in low-$h\nu$ ARPES and tunneling spectroscopy are characteristic of the bulk solid. The case is already strong, because, from the crystal structure, the likely cleavage plane is separated from the quasi-1D conducting chains by 4–8 Å, such that even the chains nearest the surface are shielded from the external environment by two layers of MoO_{6} octahedra and MoO_{4} tetrahedra, and locally have the bulk environment. Thus, even though the value of the low-energy electron mean free path (EMFP) is $a$, very uncertain because it depends on the details of low-energy excitations of the material, and could be as small as $<5$ Å, it is highly plausible that the chain electronic structure measured in tunneling and low-$h\nu$ ARPES is a bulk property. Indeed, no aspect of these data has suggested otherwise. Nonetheless the importance of the issue motivated further testing, here by using increased $h\nu$ to increase the likelihood of a large EMFP through higher-kinetic-energy photoelectrons.

The EMFP of electrons with large kinetic energy (>150 eV) is much less affected by the details of low-energy excitations and characteristically increases monotonically with the kinetic energy. Published data typically show EMFP's to be larger at 500 eV than at 30 eV by factors of 2 and even more. Although energy and momentum resolutions available in high-$h\nu$ ARPES are still not as good as those available at low $h\nu$, recent improvements in synchrotron radiation and electron detection technologies have made it possible to obtain spectra that can be significantly compared to low-$h\nu$ spectra. As a result, examples are now known where spectra using high $h\nu$ as in this report have revealed new features not found at low $h\nu$. Some of these examples are low-dimensional materials. Although it is not possible to be quantitative as to the increase in EMFP for Li_{0.9}Mo_{6}O_{17} from 30 to 500 eV, it is certain that differing...
Single-crystal Li_{0.9}Mo_{6}O_{17} samples grown using the helical undulator beamline BL25SU of SPring-8,\textsuperscript{16} using circularly polarized photons with energy 500 eV. The beamline was oriented by Laue diffraction so that the 1D conducting direction (b axis) was aligned to the analyzer slit direction. The samples were cleaved in situ in a vacuum better than 2×10^{-10} Torr to expose clean surfaces of the \textit{ab} plane. The Fermi level and overall energy resolution (\(\Delta E \approx 180\) meV) were determined from a Fermi edge spectrum taken on freshly evaporated Au. The momentum resolution was about 0.05 Å\(^{-1}\). The temperature was controlled by an embedded resistive heater and a closed-cycle He cryostat. Photon-induced sample damage, which appears as an extra peak around 2 eV binding energy, was observed after 5–6 h of measurement. We carefully chose the experiment parameters so that all the data presented in this paper were taken within 3 h of the time that a freshly cleaved surface was newly exposed to the light. For example, our use of a 50 meV energy step size was deemed to be a good balance between reducing the time to take data and yet having adequate point density for the data analysis presented below. Measurements with linearly polarized photons at \(h\nu = 30\) eV were performed at the Synchrotron Radiation Center of the University of Wisconsin, with similar angle resolution and thus somewhat better momentum resolution, but with \(\Delta E \approx 18\) meV, and with other experimental details the same as in Ref. 8.

Figures 1(a) and 1(b) show a comparison of the energy vs momentum (k) spectra measured at \(h\nu = 500\) and 30 eV, respectively. Both spectra are measured along the \(\Gamma-Y\) direction and at \(T = 50\) K. Li_{0.9}Mo_{6}O_{17} has four Mo 4d bands near \(E_{F}\), labeled as A–D in the stack plots of Figs. 1(c) and 1(d). The fourth band (D), which has the lowest binding energy and disperses to merge with band C before crossing \(E_{F}\), is known to have a greatly suppressed intensity along this k path and hence is not seen. This band is observable\textsuperscript{8} along another path in k space that was not readily accessible for the experimental setup used here. The spectra obtained using the two different photon energies are generally very similar to each other and to the results of band structure calculations.\textsuperscript{11} Differences between the two sets of data arise from the differing resolutions and also from differing photoelectron matrix elements, including perhaps the effect of the differing photon polarizations, that highlight the A and B bands differently. For example, in Fig. 1(a) the high intensity centered at binding energy \(\sim 0.7\) eV and \(k = 0\) is from the A and C bands, which are not well resolved. The band minimum of C is

ARPES results for the two \(h\nu\) values would signal a serious problem with the case for bulk LL spectroscopic signatures based on the reasoning from the crystal structure set forth above. However, as described below, no such difference is found.

High-\(h\nu\) ARPES measurements were made at the twin-helical undulator beamline BL25SU of SPring-8,\textsuperscript{16} using circularly polarized photons with energy 500 eV. The beamline is equipped with a SCIENTA SES200 electron analyzer. Single-crystal Li_{0.9}Mo_{6}O_{17} samples grown using the temperature gradient flux method were oriented by Laue diffraction so that the 1D conducting direction (b axis) was aligned to the analyzer slit direction. The samples were cleaved in situ in a vacuum better than 2×10^{-10} Torr to expose clean surfaces of the \textit{ab} plane. The Fermi level and overall energy resolution (\(\Delta E \approx 180\) meV) were determined from a Fermi edge spectrum taken on freshly evaporated Au. The momentum resolution was about 0.05 Å\(^{-1}\). The temperature was controlled by an embedded resistive heater and a closed-cycle He cryostat. Photon-induced sample damage, which appears as an extra peak around 2 eV binding energy, was observed after 5–6 h of measurement. We carefully chose the experiment parameters so that all the data presented in this paper were taken within 3 h of the time that a freshly cleaved surface was newly exposed to the light. For example, our use of a 50 meV energy step size was deemed to be a good balance between reducing the time to take data and yet having adequate point density for the data analysis presented below. Measurements with linearly polarized photons at \(h\nu = 30\) eV were performed at the Synchrotron Radiation Center of the University of Wisconsin, with similar angle resolution and thus somewhat better momentum resolution, but with \(\Delta E \approx 18\) meV, and with other experimental details the same as in Ref. 8.

Figures 1(a) and 1(b) show a comparison of the energy vs momentum (k) spectra measured at \(h\nu = 500\) and 30 eV, respectively. Both spectra are measured along the \(\Gamma-Y\) direction and at \(T = 50\) K. Li_{0.9}Mo_{6}O_{17} has four Mo 4d bands near \(E_{F}\), labeled as A–D in the stack plots of Figs. 1(c) and 1(d). The fourth band (D), which has the lowest binding energy and disperses to merge with band C before crossing \(E_{F}\), is known to have a greatly suppressed intensity along this k path and hence is not seen. This band is observable\textsuperscript{8} along another path in k space that was not readily accessible for the experimental setup used here. The spectra obtained using the two different photon energies are generally very similar to each other and to the results of band structure calculations.\textsuperscript{11} Differences between the two sets of data arise from the differing resolutions and also from differing photoelectron matrix elements, including perhaps the effect of the differing photon polarizations, that highlight the A and B bands differently. For example, in Fig. 1(a) the high intensity centered at binding energy \(\sim 0.7\) eV and \(k = 0\) is from the A and C bands, which are not well resolved. The band minimum of C is
FIG. 2. (Color online) (a) Momentum-integrated spectra of Fig. 1(a). (b),(c) Fit of momentum-integrated spectra with finite-\( T \) LL theory. The solid lines in (b) and (c) are the best fit and the dashed lines are calculations with \( \alpha \) slightly off the optimal value, as indicated by the arrows.

actually at ~0.55 eV, as becomes clear in Fig. 1(b), where the \( A \) and \( B \) bands are weaker near \( T \) and the energy resolution is much better. The Fermi vector extracted from the 500 eV spectra is \( 2k_F=0.52 \text{ Å}^{-1} \) compared to \( 2k_F=0.55 \text{ Å}^{-1} \) obtained at 30 eV photon energy, adequate agreement within the momentum resolution.

The spectra in Fig. 1 were \( k \) integrated to obtain the spectra shown in Fig. 2. Figure 2(a) shows the full spectrum corresponding to the \( h\nu=500 \text{ eV} \) data of Fig. 1(a). Compared to the gold Fermi edge measured for the same experimental conditions and also shown in the figure, it is clear that there is a suppression of near-\( E_F \) spectral weight. Figure 2(b) shows the near-\( E_F \) spectrum for \( h\nu=500 \text{ eV} \) on an expanded energy scale, with the data plotted as circles, and for comparison, Fig. 2(c) shows the near-\( E_F \) spectrum corresponding to the \( h\nu=30 \text{ eV} \) data of Fig. 1(b). The former shows a noticeable broadening relative to the latter due to the relatively poorer energy resolution for \( h\nu=500 \text{ eV} \).

To quantitatively characterize the \( k \)-integrated line shapes taken at the two photon energies, we compare them with the theoretical LL DOS for finite \( T \) from Ref. 12. It is very important to account for the differing experimental energy resolutions, by convolving the calculated line shape for \( T=50 \text{ K} \) with a Gaussian of width set to the appropriate resolution \( \Delta E \). For \( h\nu=500 \text{ eV} \) we find that the theory line shape fits the spectrum very well up to binding energy 0.14 eV with \( \alpha=0.6 \) as shown in Fig. 2(b). The same analysis of the \( h\nu=30 \text{ eV} \) spectrum gives \( \alpha=0.65 \) with a fitting range up to 0.12 eV binding energy, as shown in Fig. 2(c). As expected from this analysis, direct broadening of the \( h\nu=30 \text{ eV} \) spectrum (not shown) yields a curve differing only slightly from the \( h\nu=500 \text{ eV} \) spectrum. The slightly different values of \( \alpha \) are within expectations either from the degree of sample dependence observed previously, or from the fitting uncertainty, estimated to be ~±0.05. Both \( \alpha \) values extracted are also in very good agreement with the scanning tunneling result, which gives \( \alpha=0.62±0.17 \text{ at } 5 \text{ K} \), considering that the \( T \)-dependent study shows very little variation of \( \alpha \) for temperatures below 50 K. Thus we conclude that the momentum-integrated spectra at both photon energies reflect the same underlying LL spectrum.

In summary, we have presented the results of bulk-sensitive ARPES spectroscopy on Li_{0.9}Mo_{6}O_{17} performed with \( h\nu=500 \text{ eV} \). The measured band structure and an analysis of the momentum-integrated spectrum are in good agreement with the results of ARPES experiments using low photon energies. This finding is fully consistent with our reasoning based on the crystal structure, that the chains lie well below the cleavage plane and hence are well shielded from the effects of the surface, such that the LL ARPES line shapes observed for Li_{0.9}Mo_{6}O_{17} are a bulk property.

This work was supported at UM by the U.S. NSF (Grant No. DMR-03-02825), at UT by the U.S. NSF (Grant No. DMR 00-72998), by the Office of Basic Energy Sciences, U.S. DOE (Grant No. DE-AC05-0022725) at ORNL, managed by UT-Battelle, LLC, by the Center for Strongly Correlated Materials Research, Korea, by a Grant-in-Aid for COE Research (Grant No. 10CE2004) and a Grant-in-Aid for Creative Scientific Research (Grant No. 15GS0213) of MEXT, Japan, and by the 21st Century COE Program (G18) of the Japan Society for the Promotion of Science.