The case for the bulk nature of the spectroscopic Luttinger liquid signatures observed in angle resolved photoemission of Li$_{0.9}$Mo$_6$O$_{17}$

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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 fit 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.

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The low energy physics of a 1-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\cite{9,10}, 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-1 dimensional metal having highly anisotropic electronic properties.\textsuperscript{9,10} We have studied this material extensively by angle resolved photoemission spectroscopy (ARPES)\textsuperscript{2,3,4,5,6,7,8}. The momentum dependent spectra reveal a band structure that is in good general agreement with that of tight-binding band calculations\textsuperscript{11}, and detailed comparison to LL spectral theory\textsuperscript{12} shows that the ARPES lineshape has 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 low power law suppression of the near $E_F$ DOS. The power law DOS has also been observed in scanning tunnelling spectroscopy\textsuperscript{13}. Most recently we have found\textsuperscript{14} 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 new spectroscopic element presented here is to show that ARPES data obtained at high photon energy ($h\nu \geq 500$ eV) yield the same value of $\alpha$ as obtained for the ARPES performed to date, done with much lower photon energy ($h\nu \leq 30$ 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 A, such that even the chains nearest the surface are shielded from the external environment by two layers of MoO$_6$ octahedra and MoO$_4$ tetrahedral, and locally have the bulk environment. Thus, even though the value of the low energy electron mean free path (EMFP) is $a$ priori very uncertain because it depends on the details of low energy excitations of a material, and could be as small as $<5$A, 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.\textsuperscript{15} Published data\textsuperscript{15} 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\textsuperscript{16} in synchrotron radiation and electron detection technologies have made it possible\textsuperscript{17,18} to obtain spectra that can be meaningfully compared to low $h\nu$ spectra. As a result, examples are now known where spectra us-
FIG. 1: (Color online) (a), (b): Energy vs. momentum spectra along Γ(k = 0) - Y direction at $h\nu = 500$ eV and 30 eV, with resolutions $\Delta E \approx 180$ meV and 18 meV, respectively. The color represents the spectral intensity, with white for the highest and black for the lowest. The image in (b) is symmetrized from data taken between $k = 0 - 0.4 \, \text{Å}^{-1}$. (c), (d): Stack view of panel (a) and (b), with the thick lines highlighted for $k = k_F$, within momentum resolution. The dashed lines in (c) and (d) highlight the band dispersions. Band D is suppressed by matrix element in this geometry and is indicated by parenthesis.

High $h\nu$ ARPES measurements were made at the twin-helical undulator beam line BL25SU of SPring-8, using circularly polarized photons with energy 500 eV. The beamline is equipped with a SCIENTA SES200 electron kinetic energy 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 $2 \times 10^{-10}$ Torr to expose clean surfaces of the $ab$-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 hours of measurement. We carefully chose the experiment parameters so that all the data presented in this paper were taken within 3 hours 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.

Fig. 1(a) and (b) show a comparison of the energy vs. momentum ($k$) spectra measured at $h\nu = 500$ eV and $h\nu = 30$ eV, respectively. Both spectra are measured along the Γ-Y direction and at $T = 50$ K. Li$_{0.9}$Mo$_6$O$_{17}$ has 4 Mo 4$d$ bands near $E_F$, labeled as A-D in the stack plots of Fig. 1(c) and 1(d). The 4th 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 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. 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-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-C bands not well resolved. The band minimum of C is actually at $\sim 0.55$ eV, as becomes clear in Fig. 1(b), where the A and B bands are weaker near Γ 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. Fig. 2(a) shows the full spectrum corresponding to the $h\nu = 500$ 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. Fig. 2(b) shows the near $E_F$ spectrum for $h\nu = 500$ 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 $h\nu = 30$ eV data.
values of $\alpha$ from the trum (not shown) yields a curve differing only slightly of sample dependence observed previously this analysis, direct broadening of the binding energy, as shown in Fig. 2(c). As expected from very little variation of $\alpha$ trum gives in Fig. 2(b). The same analysis of the $h\nu$ fitting uncertainty, estimated to be $\sim \pm 0.05$. Both alpha values extracted are also in very good agreement with the scanning tunneling result which gives $\alpha = 0.62 \pm 0.17$ at 5 K, considering that the T dependent study shows very little variation of $\alpha$ for temperatures below 50K. 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 $h\nu = 500$ 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 lineshapes observed for Li$_{0.9}$Mo$_6$O$_{17}$ are a bulk property.

Acknowledgments

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