

# Luttinger liquid angle-resolved photoemission line shapes from samples of $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ grown by the temperature-gradient-flux technique

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Angle-resolved photoemission spectroscopy line shapes measured for quasi-one-dimensional  $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$  samples grown by a temperature-gradient-flux technique are found to show Luttinger liquid behavior, consistent with all previous data by us and other workers obtained from samples grown by the electrolyte reduction technique. This result eliminates the sample growth method as a possible origin of considerable differences in photoemission data reported in previous studies of  $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ .

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$\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ , also known as the Li purple bronze, is a quasi-one-dimensional metal which displays metallic  $T$ -linear resistivity and temperature independent magnetic susceptibility for temperatures down to  $T_X \approx 24$  K, where a phase transition of unknown origin is signaled by a very weak anomaly in the specific heat.<sup>1</sup> As  $T$  decreases below  $T_X$ , the resistivity increases. However the dc magnetic susceptibility is unchanged below  $T_X$ ,<sup>1,2</sup> implying no single particle gap opening, and infrared optical studies<sup>3</sup> below  $T_X$  also show no gap opening down to 1 meV. Consistent with this evidence for the lack of a single particle gap, repeated x-ray diffraction studies<sup>4</sup> show no charge density wave or spin density wave.

The various transport and spectroscopy studies of this fascinating material have been made on samples prepared by two methods, an electrolyte reduction technique<sup>1</sup> and a temperature gradient flux technique.<sup>5</sup> Angle-resolved photoemission spectroscopy (ARPES) is the only measurement for which any major inconsistency in data obtained from samples prepared by the two different methods has been reported, and the inconsistency is very serious. In particular an extensive set of ARPES data from two groups<sup>6-12</sup> obtained on electrolyte reduction samples show non-Fermi-liquid ARPES line shapes consistent<sup>7,9-12</sup> with Luttinger liquid (LL) behavior and no low temperature Fermi energy ( $E_F$ ) gap, whereas ARPES data reported<sup>13-15</sup> for temperature-gradient-flux grown samples show Fermi liquid (FL) line shapes, a large low temperature  $E_F$  gap and an additional feature inconsistent with the known band structure of the material. These differences between the two ARPES data sets are summarized in Ref. 8. The LL line shapes have been verified repeatedly in subsequent studies<sup>8-12</sup> of samples prepared with the electrolyte reduction technique. Nonetheless it has been a lingering possibility that FL line shapes and a large low temperature gap could perhaps be characteristic of temperature gradient flux grown samples. This Brief Report dispels that possibility by reporting ARPES spectra for temperature gradient flux grown samples that are in full agreement with the line shapes obtained for electrolyte reduction samples.

The spectra reported here were obtained on the PGM beamline at the Wisconsin Synchrotron Radiation Center. Photons of energy 30 eV were used to excite photoelectrons whose kinetic energies and angles were analyzed with a Scienta SES 200 analyzer. Measurement on a freshly prepared Au surface was used to determine the position of  $E_F$  in the spectra and the overall energy resolution of 21 meV due to both the monochromator and the analyzer. The angle resolution was set at  $\pm 0.1^\circ$ , better than that  $\pm 0.25^\circ$  in our earlier work<sup>8</sup> and exactly the same as used in previous ARPES studies<sup>13-15</sup> of temperature gradient flux samples. The sample surface was obtained by cleaving *in situ* and the data were taken at a sample temperature of 200 K, much higher than the transition temperature 24 K.

For the endstation in place at the time of taking the data reported here, the angular dispersion direction of the SES 200 analyzer was vertical. ARPES symmetry analysis of the data obtained shows that the one dimensional  $\Gamma$ - $Y$  chain axis direction was (unintentionally) oriented at an angle of  $13^\circ$  to the vertical. Nonetheless we will refer to this geometry as the “vertical geometry” from here on in the paper. Due to this small angular offset, the dispersions in this data set are slightly different from those that we obtained previously along the  $\Gamma$ - $Y$  axis, as documented carefully in discussing Fig. 2 below. We have repeated the measurement in exactly the same geometry as that of our previous experiments,<sup>7-12</sup> i.e., one in which both the one-dimensional chain axis and the angular dispersion direction of the analyzer are horizontal and well aligned, and found dispersions essentially identical to those of the previous<sup>7-12</sup> data. We will refer to this geometry as the “horizontal geometry” below. Despite the small angular offset, we present here the data taken in the vertical geometry because (1) these data happen to show the  $E_F$ -crossing line shapes most clearly among all of our data sets, by virtue of having fortuitously the maximum intensity of the band crossing  $E_F$  relative to the intensities of the bands that do not cross  $E_F$ , and (2) the differences in dispersions have been verified to arise from the small offset and are in any case so slight as to be insignificant for the central thrust of this paper. Both of these points are elaborated below. An-

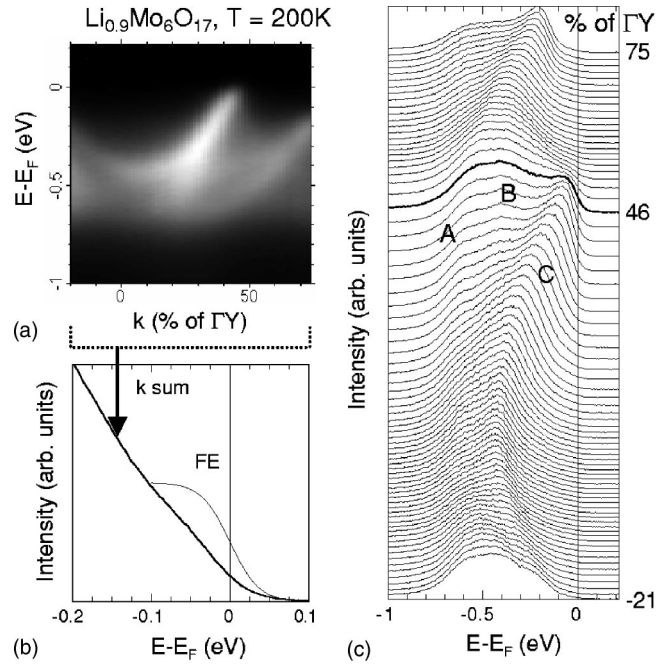


FIG. 1. ARPES data obtained for samples of  $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$  prepared by the temperature gradient flux growth. (a)  $k$ -energy map where  $k$  is the momentum projected onto the  $\Gamma$ - $Y$  axis. (b) The  $k$ -sum of the data in (a). A Fermi edge (FE) spectrum for the employed energy resolution (21 meV FWHM) and the measurement temperature (200 K) is shown to demonstrate the non-FE nature of the  $k$ -sum. (c) An energy distribution curve (EDC) stack representation of the data shown in (a). The spectrum corresponding to  $k_F$  is drawn with a thick line. The momentum increment is 1.3% of  $\Gamma$ - $Y$ .

other advantage of the vertical geometry setup was that it allowed acquisition of intensity maps like the one presented above (Fig. 1) for many parallel one dimensional paths crossing the FS. Thereby we could verify that the LL behavior holds for such paths anywhere in the Brillouin zone, regardless of the exact location of the momentum space cut across the Fermi surface, so that Fermi liquid behavior does not occur for some very specific cut, as reported previously<sup>13,14</sup> for temperature gradient flux samples.

Figure 1 shows ARPES spectra taken in the vertical geometry on a sample grown by the temperature gradient method. Panels (a) and (c) summarize the overall electronic structure with  $k$  labels denoting the  $k$  values projected onto the  $\Gamma$ - $Y$  axis. We label the bands  $A, B, C$  in the order of decreasing binding energy at  $\Gamma$ . As we will discuss in connection with Fig. 2 below, the overall band structure revealed by the data is consistent with the data in the literature<sup>6-12</sup> obtained on samples grown by the electrolyte reduction method, as well as with band theory.<sup>16</sup> Furthermore, the LL line shapes observed previously<sup>7-12</sup> are not just confirmed, but actually better observed due to the enhanced strength of band  $C$  relative to that of bands  $A, B$  in the present data. For example, we can now clearly observe that the spectral weight of band  $C$  shows a back-bending behavior after the peak has crossed the Fermi level (darker curve), one of the key signatures of the LL line shape. In panel (b) we show the  $k$ -sum of the ARPES data. As found previously, the resulting line

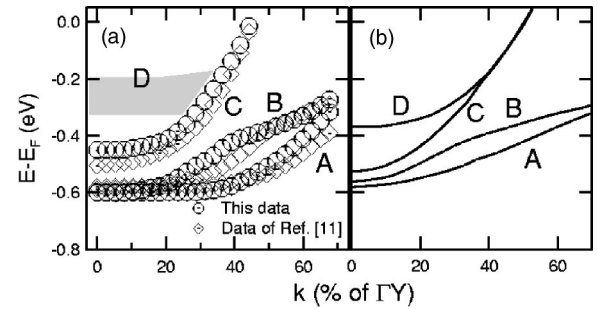


FIG. 2. Agreement of the overall band structures obtained on the two samples grown with different methods. (a) Momentum-energy dispersion relations as extracted by taking the peak positions of energy distribution curves [e.g., in Fig. 1(c)]. The data plotted in circles correspond to the data of the current sample (Fig. 1) grown by the temperature gradient flux method and the data plotted in diamonds correspond to the data reported in Ref. 10 for sample grown by the electrolyte reduction method. See text for discussion of small differences visible, arising from slightly different  $k$ -paths. The approximate position of the band  $D$  for both samples is indicated as a gray region. (b) Extended Hückel tight binding band structure calculation (Ref. 16) for comparison. Note that the energy scale of the calculation was multiplied by a factor of 2.2 in order to roughly match the dispersion of the experiment.

shape is far from the Fermi edge line shape expected of a FL and instead is described much better by a LL with  $\alpha > 0.5$ , where  $\alpha$  is the so-called anomalous dimension of the LL.

Panel (a) of Fig. 2 summarizes the overall band structure determined from the present data (open circles) and compares it with that from our previous result (diamonds) taken on a sample grown by the electrolyte reduction technique. The small differences arising from the slightly different  $k$ -paths can be seen. For example, in the new data band  $B$  becomes almost nondispersive when peak  $C$  crosses  $E_F$  while this occurs for larger  $k$  values for the data perfectly along  $\Gamma$ - $Y$ . As shown in panel (b) band theory predicts bands  $A, B$ , and  $C$  essentially as observed, and also a fourth band  $D$ . Bands  $A$  and  $B$  do not cross  $E_F$  and  $C$  and  $D$  become degenerate and cross  $E_F$  together. All four bands have been observed<sup>7-9</sup> for various  $k$ -paths, although band  $D$  is typically very weak, just a slight shoulder on the leading edge of peak  $C$ , and is clearly seen only for a particular  $k$ -path<sup>7,10</sup> where it appears as a main peak. In the vertical geometry data, band  $D$  is nearly undetectable [see Fig. 1(c)] but was observed very weakly in the horizontal geometry data, consistent with previous results. For completeness, we mark the approximate position of band  $D$  thus found for the present sample as a gray region. This position is similar to that found for previous samples along the same, i.e., the  $\Gamma$ - $Y$ , direction as well as along the special  $k$ -path<sup>7,10</sup> where  $D$  is strong.

Figure 3 compares the  $E_F$  crossing line shapes measured on the samples grown by the two different methods, with panel (a) showing the new data in the vertical geometry for the temperature gradient flux sample, and panel (b) showing data from Ref. 10 taken at the same photon energy for the electrolyte reduction sample. In each panel, the data are presented with the spectra for the various  $k$ -values overplotted to better show the approach and  $E_F$  crossing of peak  $C$ . As

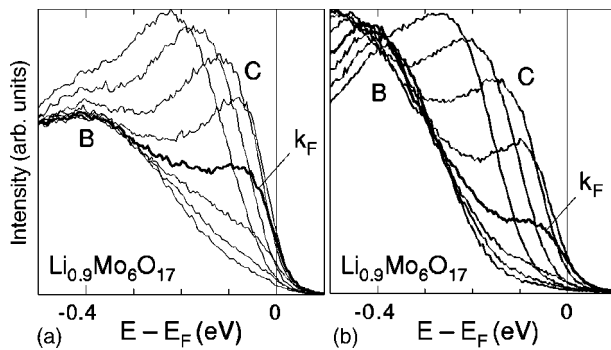


FIG. 3. Identical nature of LL ARPES line shapes obtained for samples of  $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$  prepared by (a) the temperature gradient flux growth and (b) electrolyte reduction methods. The data in (b) are from Ref. 10. In both panels, the momentum increment is 2.6% of  $\Gamma$ -Y.

explained in the previous paragraph, a small difference of the band *B* dispersion arises from the slightly different *k*-paths. The general features of the two sets of spectra are nearly identical, except that, as mentioned already, in (a) the strength of band *C* relative to that of the non- $E_F$  crossing band *B* is greater than in (b). Therefore the intrinsic line shape features of band *C*, which we have shown<sup>7,9-12</sup> to be well described by the LL line shape theory, are now even more clearly visible. These include the spinon edge and the holon peak, which disperse with different velocities, the diminution of intensity as  $E_F$  is approached, and the back dispersing edge after the peak has crossed  $E_F$ . One is now forced to conclude that the large disagreement of the overall band dispersions and  $E_F$  crossing line shapes found previously<sup>8</sup> for the ARPES data reported by Xue *et al.*<sup>13,15</sup>

and those reported by ourselves and others<sup>6-12</sup> do not stem from the sample growth method.

Before concluding, we note that samples prepared by us (J.H., R.J., and D.M.) in the same way as for those used in the ARPES reported here, have also been used for new measurements of the temperature dependencies of the resistivity, specific heat, magnetic susceptibility and optical properties.<sup>17</sup> These results have reconfirmed that no gap opening is associated with the low *T* resistivity rise and have been interpreted as showing the probable importance of localization effects for the properties below  $T_X$ . Although the lower energy limit of the new optical study is 10 meV, larger than the minimum energy of 1 meV of a previous optical study,<sup>3</sup> it is nonetheless smaller than the energy resolutions used in any ARPES studies on the material to date ( $\geq 15$  meV). Further, the new optical study found that the spectral weight *increases* below  $T_X$  in the low energy sector ( $< 100$  meV) for which previous ARPES studies<sup>13-15</sup> on temperature gradient flux samples found a large gap opening ( $2\Delta \approx 80$  meV).

To summarize, we have shown that the ARPES spectra of  $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$  samples prepared by temperature gradient flux growth display LL behavior the same as seen for samples prepared by the electrolyte reduction method, thus augmenting further the strong case for LL ARPES line shapes already established by our past ARPES work on this material.

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