Fermi Surface of a Quasi-One-Dimensional Oxide Conductor

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(Received 10 February 1993)

We report the first determination of the Fermi surface for a quasi-one-dimensional oxide conductor, $Li_{0.9}Mo_6O_{17}$. The Fermi surface has been measured within the cleavage plane of the crystal using high-resolution angle-resolved photoemission spectroscopy. The Fermi surface consists of two parallel straight lines, separated by a nesting vector of approximately 0.7 ± 0.05 Å^{-1}. A large density of states at E_F is observed from the measured band dispersion, despite a low photoemission spectral intensity at E_F. The measured Fermi surface allows the prediction of the magnitude of the displacement vector associated with soft phonons and a postulated Peierls transition in $Li_{0.9}Mo_6O_{17}$.

PACS numbers: 71.25.Hc, 71.25.Pi, 71.45.Lr

The physical properties of both organic and inorganic quasi-low-dimensional solids have been the subject of numerous investigations since these materials allow many fundamental theories of one- and two-dimensional systems to be directly tested. With the advent of high-resolution spectroscopic probes, such as photoemission, the detailed electronic structure of these solids can now be accurately measured [1]. Transition metal oxide bronzes are a class of inorganic quasi-low-dimensional solids that are ideal prototypical systems for spectroscopic studies due to the size and quality of available crystals [2–4]. Among the unusual properties of these oxides are quasi-low-dimensional electron transport, metal-insulator and metal-metal transitions, periodic lattice distortions, and charge-density wave transport. Interest in these oxides is further enhanced by the similarity of their properties to those of the high-temperature oxide superconductors. A fundamental characteristic of one-dimensional metals is the possibility of a Peierls transition in the metal lattice. This lattice instability is a direct consequence of the coupling between vibrational modes of the lattice and electrons at the Fermi level (E_F). Of particular importance in this coupling is the structure of the Fermi surface itself, since the degree of nesting and the density of states radically alters the magnitude of the anomaly in the generalized susceptibility that drives the lattice towards instability. Despite this fundamental role, the actual structure of the Fermi surface in these quasi-low-dimensional systems has never previously been measured.

We present here the first determination of the Fermi surface for a quasi-one-dimensional (1D) oxide conductor. The Fermi surface was measured using high-resolution angle-resolved photoemission spectroscopy, and the particular oxide studied was $Li_{0.9}Mo_6O_{17}$, which shows quasi-1D transport properties within the cleavage plane of the crystal [2–5]. We find that the measured Fermi surface *within* the cleavage plane consists of two parallel straight lines, separated by a nesting vector of 0.7 Å^{-1}. However, we have also measured slight dispersion of emission from the states forming the Fermi surface in a direction *perpendicular* to the planes, revealing that interlayer bonding in this system may be significant; this would reduce the effect of the quasi-1D properties within the planes. We predict significant phonon mode softening and/or a Peierls transition in $Li_{0.9}Mo_6O_{17}$.

High-resolution angle-resolved photoemission (ARP) is a versatile tool for the measurement of Fermi surfaces in general, and quasi-low-dimensional Fermi surfaces in particular [1]. For example, it has been used successfully to measure the two-dimensional Fermi surfaces associated with surface localized states on the surfaces of metals such as W and Mo [6]. It is also being used successfully to determine Fermi surfaces in certain high-temperature oxide superconductors. In this method, the full Fermi surface is determined by using ARP to map the dispersion of states close to E_F along all directions in the Brillouin zone. The experiments reported here were undertaken on beam line U4A at the National Synchrotron Light Source. This beam line is equipped with a 6 m toroidal grating monochrometer, and ARP spectra were obtained using a custom designed hemispherical electron analyzer [7]. Typical energy and full angular resolution used were less than 100 meV and 1°, respectively. All the experiments reported here were performed at room temperature on samples cleaved in the measurement chamber where the base pressure was 8×10^{-11} Torr. $Li_{0.9}Mo_6O_{17}$ has a monoclinic unit cell, and cleaves to expose a (001) surface. The [010] direction (short axis) of the rectangular surface unit cell is the quasi-1D direction, along which current flows most easily. The structure of $Li_{0.9}Mo_6O_{17}$ is detailed in Ref. [3]. $Li_{0.9}Mo_6O_{17}$ is metallic at room temperature, then becomes insulating at 24 K, and finally superconducting at 1.9 K [5]. The metallic nature of $Li_{0.9}Mo_6O_{17}$ can be understood as originating from the donation of Li s electrons into originally empty hybrid Mo 4d states to form the conduction band; the related compound MoO_3 is an insulator. The cleaved surface of $Li_{0.9}Mo_6O_{17}$ was found to be relatively inert in ul-

0031-9007/93/70(24)/3772(4)$06.00

trahigh vacuum; the crystals remained free of contamination, as determined by relative changes in the intensity of spectral features close to E_F, for upwards of 72 h. Samples gave sharp low-energy electron-diffraction (LEED) patterns. In order to avoid electron-induced damage to the oxide, LEED patterns were studied after the photoemission experiments were completed.

Figure 1 shows a series of ARP spectra from cleaved $Li_{0.9}Mo_6O_{17}$. The spectra in Fig. 1 are taken with 18 eV photons incident at 25° to the sample normal, along the [010] direction in the surface Brillouin zone (SBZ). The projection of the bulk monoclinic Brillouin zone onto the (001) cleavage plane gives a rectangular SBZ, with the long axis along [010], denoted the ΓY direction, and the short axis along [100], denoted the ΓX direction. The SBZ is shown as an inset to Fig. 1. The detector was rotated in the [010] direction in the SBZ, and each of the spectra in Fig. 1 represents a change in detector angle. The spectra are conventionally labeled with the value of the k vector associated with a state at E_F for the appropriate angle. The spectra show only the region within 2 eV of E_F. The spectral feature visible in Fig. 1 is due to emission from the partially occupied Mo $4d$ states. This feature clearly gains in intensity and disperses toward E_F as the detector is moved to sample states away from normal. Since three-dimensional interlayer bonding is supposed to be weak in these oxides, we begin by treating this Mo $4d$ state as a surface state. Thus as the detector is moved off normal, states with nonzero $k_\parallel$ vectors in the SBZ are measured. As the Mo $4d$ state approaches E_F, the line shape and intensity of the feature change abruptly at $k_\parallel \approx 0.35$ Å^{-1}. For $k_\parallel > 0.35$ Å^{-1}, the feature disperses very slowly away from E_F, and its intensity is considerably reduced. This behavior is repeated along directions parallel to ΓY in the zone, with the discontinuity even more pronounced when off the ΓY symmetry axis. However, no discontinuity is observed for states along ΓX. Instead, a well-defined spectral feature is observed close (< 0.5 eV) to E_F throughout the zone, which shows no anomalous behavior.

The explanation for the observed discontinuity in dispersion of the spectral feature is that part of the d band has dispersed above E_F. $Li_{0.9}Mo_6O_{17}$ has four occupied d bands with 5.8 d electrons per unit cell. Thus two of the d bands are full, and the remaining 1.8 electrons are shared by the remaining two d bands. Tight-binding calculations by Whangbo and Canadell reveal that all these bands lie within 0.3 eV on E_F [8]. (The results of these calculations are reproduced in Fig. 2.) In these calculations, the two filled bands slowly disperse from 0.3 eV below E_F at Γ to 0.1 eV at Y (at 0.57 Å^{-1}), while the two partially filled bands disperse across E_F at $k_{\Gamma Y} = 0.25$ Å^{-1}. At this value of k, the filled bands are only 0.1 eV below E_F. Consequently, given the resolution of our spectrometer, and the inevitable broadening of the spectral line shape due to hole lifetime, screening, and thermal effects the crossing of the Fermi level by these two bands manifests itself in our spectra as the discontinuity in the intensity and dispersion shown in Fig. 1. Using this discontinuity as a measure of the point at which the bands cross E_F, the full quasi-low-dimensional Fermi surface for $Li_{0.9}Mo_6O_{17}$ can be measured by taking similar scans along other directions in k space. Figure 3 presents the results of this measurement. As is evident, the Fermi surface consists of two parallel straight lines, running parallel to the ΓX direction, approximately 0.7 Å^{-1} apart. The spectra reveal that there is a well-defined Fermi surface crossing in the direction of high conductivity, and a continual high density of states along the [001] direction in the SBZ, where the conductivity is found to be the lowest. The calculated band structure (Fig. 2) reproduces the behavior of the measured bands

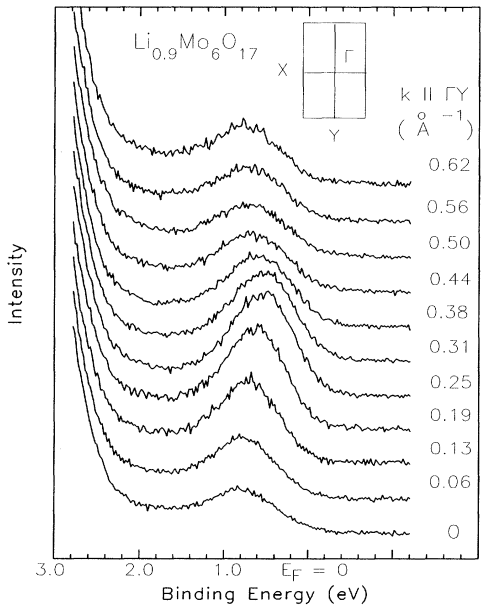

FIG. 1. ARP spectra taken from cleaved $Li_{0.9}Mo_6O_{17}(001)$. $h\nu = 18$ eV, $\theta_i = 25°$. $k_\parallel$ and $h\nu$ are along the (010) direction. The surface Brillouin zone is shown as an inset.

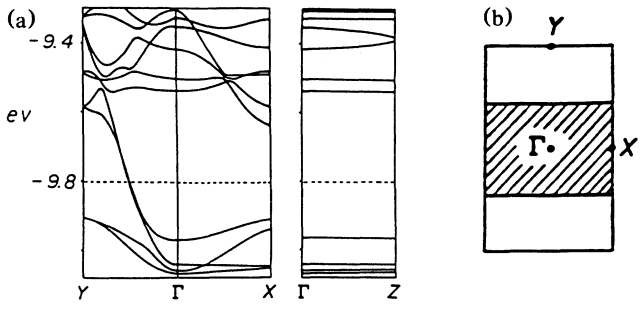

FIG. 2. Calculated d bands and Fermi surfaces for $Li_{0.9}Mo_6O_{17}$ (Ref. [8]). E_F is indicated by the dashed line. $k_F = 0.51$ Å^{-1}.

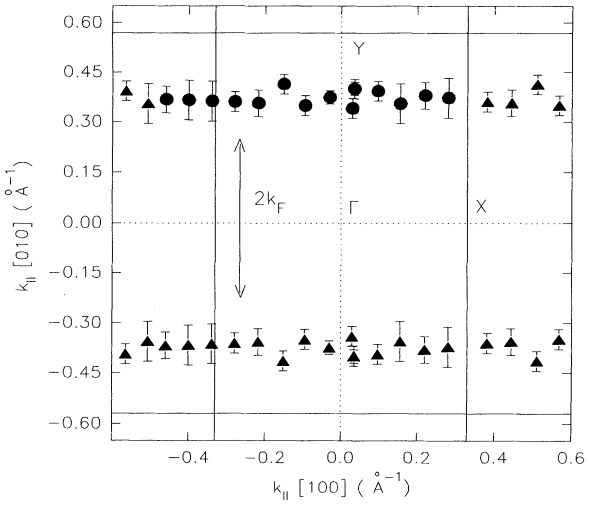

FIG. 3. Measured Fermi surface for $Li_{0.9}Mo_6O_{17}(001)$. $2k_F = 0.7 \pm 0.05$ Å^{-1}. ●, measured points; ▲, symmetry mapped points.

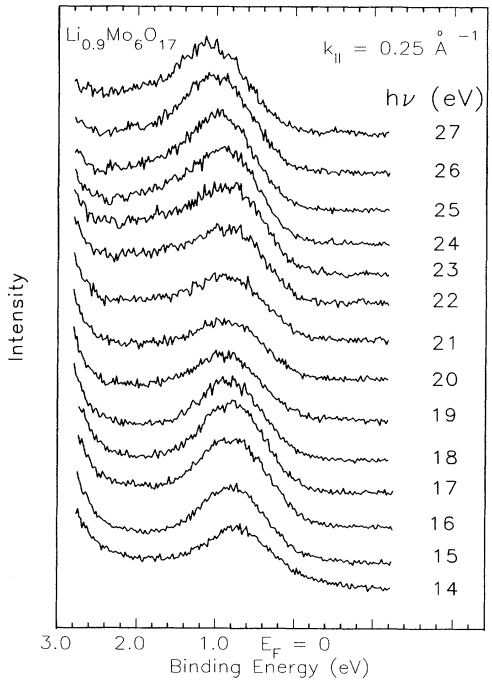

FIG. 4. ARP spectra from $Li_{0.9}Mo_6O_{17}(001)$ taken for photon energies between 14 and 27 eV. $k_\parallel = 0.25$ Å^{-1} along ΓY (010).

along ΓX and ΓY with the exception that the Fermi surface crossing is found to occur further from the zone center than predicted, which changes the nesting vector. The measured nesting vector is 0.7 Å^{-1}, while the theory predicts a nesting vector of only 0.51 Å^{-1}. Errors in determining the Fermi surface by this method lie primarily in the assignment of the wave vector associated with the crossing of any particular spectral feature above E_F. This assignment is made in a consistent fashion, and thus the Fermi surface is assured of having the correct structure but may contain a systematic error in size. We estimate the plausible error in the measured nesting vector to be ± 0.05 Å^{-1}. Note that the calculations indicate that the d bands are degenerate and flat at the Y point, while the data in Fig. 1 reveal slight dispersion of the emission feature away from E_F for $k_\parallel > 0.38$ Å^{-1}. This shift of the peak is probably related to interference with the empty d states just above E_F rather than indicative of dispersion of the band at Y.

The measurement of such a heavily nested Fermi surface leads us to predict the occurrence of a Peierls transition, with a displacment vector $q = 2k_F = 0.7$ A^{-1}. However, x-ray diffraction measurements have not yet been undertaken at the metal-insulator transition temperature of 24 K, and thus the existence of this lattice instability is unknown. This prediction comes with a caveat, however. The underlying assumption in treating this material as a quasi-1D system is that interlayer bonding is weak, and this is reflected in the calculated band structure (Fig. 2) that shows flat nondispersive bands in the ΓZ (001) direction. We believe this assumption to be somewhat erroneous. Figure 4 shows a series of ARP spectra where the detector is positioned to keep $k_{\Gamma Y}$ constant at 0.25 Å^{-1}, and the photon energy swept from 14 to 28 eV. This value of $k_{\Gamma Y}$ was chosen due to the intensity of the feature and the position of the relevant k vector for the associated state inside the Fermi surface. Any motion of the Mo 4d emission originates from dispersion of the d states *perpendicular* to the cleavage plane. The spectra in Fig. 4 clearly show dispersion of the d states as the photon energy is varied. Furthermore, measurements of the structure of the O 2p band (not shown) show very strong dispersion of the O states perpendicular to the cleavage plane. The dispersion of the Mo 4d emission feature is plotted in Fig. 5. The values of k_z are generated by assuming a free electron final state and an inner potential of 7 eV. The binding energy of the spectral feature is quasiperiodic in k space, with the two points of closest approach to E_F corresponding almost exactly to the calculated positions of the bulk Brillouin zone centers. Thus emission from the states forming the Fermi surface shows a periodicity characteristic of the interplane direction in k space. This periodicity has been verified by changing both the location in the SBZ of the state measured and the plane along which the light was incident. It should be stressed, however, that Fig. 5 plots the position of the centroid of the emission feature and not an individual d state. As shown in Fig. 2, there are four d bands contributing to this single emission feature. In the absence of dispersion, this feature should remain at a fixed binding energy. That it does not indicates that there is some dispersion, although which of the d bands are contributing is unknown. The measurements presented here show that the assumption of an absolute 1D Fer-

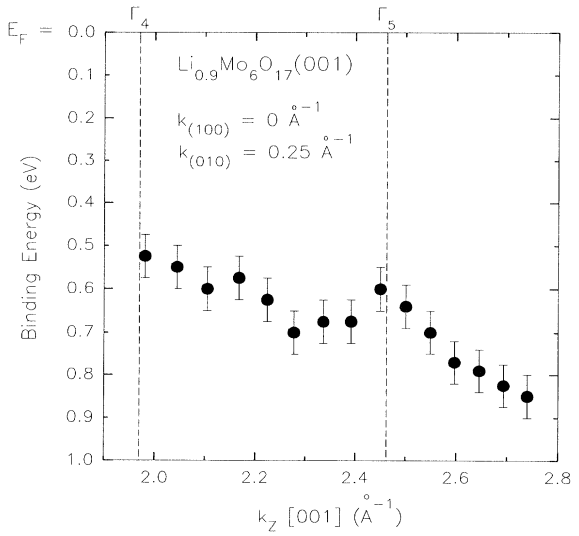

FIG. 5. Dispersion of Mo 4*d* state forming the Fermi surface in the interlayer (ΓZ) direction. See text for details.

mi surface may be incorrect. This may result in smaller nesting than in a classic 1D system and may reduce the probability of a true Peierls transition. Note that the deviation of the measured nesting vector from the theoretically predicted value is further evidence for higher order bonding.

The results of this study should be considered in the context of other recent spectroscopic investigations of electronic structure in quasi-low-dimensional systems. Dardel *et al.* reported recently angle-integrated photoemission spectra from another quasi-1D oxide conductor, $K_{0.3}MoO_3$ [9], that show a surprising lack of intensity at E_F. We observe a similar lack of emission intensity at E_F in $Li_{0.9}Mo_8O_{17}$. This lack of intensity is attributed to a difference between the photoemission spectral function and the quasiparticle density of states. However, Dardel *et al.* include as part of their argument supporting this assertion the claim that the Mo 4*d* state shows no dispersion and that the emission feature is constantly located at approximately 0.3 eV below E_F in $K_{0.3}MoO_3$ [10]. We have made recent measurements, to be presented elsewhere, that do show dispersion of the Mo 4*d* state in $K_{0.3}MoO_3$ towards E_F (although not in agreement with an earlier study [11]), and, more significantly, show a much higher intensity of the Mo 4*d* emission away from the zone center, similar to that shown in Fig. 1 for the Mo 4*d* state in $Li_{0.9}Mo_6O_{17}$. However, irrespective of any subtle differences close to E_F between the spectral function and the quasiparticle electronic structure, the data presented here provide conclusive evidence that not only can the dispersion of states close to E_F in low-dimensional systems be measured by photoemission, but a Fermi surface can also be determined. Any differences between the spectral function and the electronic structure are small enough that they do not interfere with the measurement of the Fermi surface. Furthermore, since we have measured shallow one-electron bands (the bands are never more than 0.4 eV away from E_F) that disperse through E_F, the density of states at E_F is quite large. A further study of electronic structure in a low-dimensional metal, $(TaSe_4)_2I$, does show dispersion of the quasi-1D state [12], but does not show the unambiguous evidence for a Fermi surface crossing provided by the data in Fig. 1. Of vital importance in these systems will be further high-resolution studies of electronic structure, coupled with detailed measurements of phonon structure. The vibrational structure of these systems should be accessible using He atom scattering, and measurements to test our prediction are planned.

The authors wish to gratefully acknowledge numerous helpful discussions with M. El-Batanouny. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the ACS, for partial support of this work. This work was performed at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. DOE, Divisions of Materials Sciences and Chemical Sciences.

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