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Author(s):

G.-H. Gweon, R. Claessen, J. W. Allen, W. P. Ellis,
Y. Zhang, Z.-X. Shen, and A. Matsuzawa

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ANGLE RESOLVED PHOTOEMISSION ON $K_{0.3}MoO_3$, $TiTe_2$ AND $Ti_{1+x}S_2$

G.-H. Gweon¹, R. Claessen², J.W. Allen¹, W.P. Ellis³, Y.Zhang¹,
Z.-X. Shen⁴ and A. Matsuura⁴

¹Department of Physics, University of Michigan, Ann Arbor, MI 48109

²Universität des Saarlandes, Fachrichtung 10.2 - Experimentalphysik, D-6600
Saarbrücken, Germany

³Los Alamos National Laboratory, Los Alamos, New Mexico 87545

⁴Dept. of Applied Physics, Stanford University, Stanford, CA 94305

INTRODUCTION

We have performed high resolution angle resolved photoemission spectroscopy (HRARPES) on samples of $K_{0.3}MoO_3$, $TiTe_2$ and $Ti_{1+x}S_2$, materials which are a quasi-one dimensional metal, a quasi-two dimensional metal, and a quasi two-dimensional metal ($x > 0$) or semi-conductor ($x=0$), respectively. We are interested in looking at these samples using HRARPES as part of our general program to assess the use of photoemission to determine whether a particular system behaves like a Fermi liquid or not. Previously $TiTe_2$ has been studied¹, and its angle resolved spectra were shown to be well described by Fermi liquid theory, and not by other lineshapes, e.g., those for a marginal Fermi liquid. For this model system, we hoped to improve the data set with better resolution. For one dimensional metallic systems, angle integrated photoemission studies to date, e.g.², reveal that, contrary to higher dimensional cases where a sharp Fermi cutoff is seen at the Fermi level, there is very little weight at the Fermi level. It seems that there is yet no agreement why this is so. We think that detailed information we get from HRARPES will help us answer this question. The system $Ti_{1+x}S_2$ gives the possibility to control the filling of the Ti 3d conduction band by adjusting x . Interest in this system lies in measuring the spectra and the line shape of samples with different stoichiometry and correlating the spectroscopic data with the corresponding transport data.

EXPERIMENT

The angle resolved photoemission spectra were taken at Beamline 5 at the Stanford Synchrotron

Radiation Laboratory (SSRL). The samples were cleaved *in situ*. The pressure in the spectrometer was kept better than $\sim 5.0 \times 10^{-10}$ Torr. For $TiTe_2$ and $Ti_{1+x}S_2$ the temperature was maintained as low as possible (20 ~ 30 K). $K_{0.3}MoO_3$ was kept at ~ 200 K, which is well above its charge density wave (CDW) transition temperature (180 K). Spectra were taken from surfaces of freshly evaporated gold to obtain the Fermi level reference energy and instrumental resolution. The latter was determined to be 35 ~ 40 meV.

RESULTS

The angle resolved spectra of $K_{0.3}MoO_3$ taken along the crystallographic b direction, for which the material conducts, are shown in Fig.1. The overall features show two dispersive peaks in accordance with the band calculation³. These features were not resolved in a similar experiment reported in the literature⁴. The figure clearly shows the symmetry of the position of the first dispersive peak (whose maxima are marked with circles) around the Γ point. The second dispersive peak (whose maxima are marked with diamonds) shows a similar symmetry, although it is hard to determine where the second peak lies when $|k| \leq 0.14 \text{ \AA}^{-1}$ due to the background at energies $\sim -1 \text{ eV}$ to -2 eV . We conclude from the movement and relative intensities of the peaks in the data that the Fermi level crossing for the first dispersive peak occurs at $0.28 \text{ \AA}^{-1}$. According to the band calculation² the two Mo 4d conduction bands have Fermi level crossings at $k = 0.27$ and $0.34 \text{ \AA}^{-1}$. The observed crossing of the first peak agrees very well with the value from the band calculation. We think that because the second dispersive peak crosses the Fermi

Fig.1 Angle resolved spectra of $K_{0.3}MoO_3$ along the crystallographic b direction, which is the conducting direction of the material. The spectra are normalized to the photon flux. There are two dispersive features. Peaks marked with circles are thought to correspond to the higher lying Mo 4d conduction band, and those with diamonds to the lower lying Mo 4d conduction band in the band calculation³.

level too close to the Brillouin zone boundary (X) we cannot observe it very well in the data. It has been reported recently² that the high resolution angle integrated spectrum for $K_{0.3}MoO_3$ does not show a Fermi step above the CDW transition temperature. Our data shows that in angle resolved spectra too, even at k's where the Fermi level crossing occurs, one cannot observe a Fermi step characteristic of a metallic phase. Also if we compare the dispersions observed in the data (circles and diamonds in Fig.1) and those obtained in the band calculation³, we find that the binding energies of the former lie 2.5 to 5 times deeper than those of the latter. We are currently inclined to think that electron-electron correlations in one dimensional metallic system might play an important role here, as also discussed in Ref. 2. Analysis in this direction is being tried. Particularly,

the absence of the Fermi cutoff and the discrepancy of the observed dispersions are qualitatively consistent with the Luttinger liquid model⁵ of one dimensional electrons which predicts that the elementary excitations of the system are all bosons and that the peaks observed in photoemission are (near the Fermi surface) at positions different from those in the noninteracting band dispersion by a constant factor. Also, as argued in the literature², strong thermodynamic fluctuation in one dimension or a polaron effect in the photoemission final state may be relevant in explaining such data.

Fig.2 Angle resolved spectra of $TiTe_2$ with fixed $k_{||}$ values and varying photon energies. Spectra are normalized to the same maximum height. $k_{||} = 0.96 \text{ \AA}^{-1}$ scans are along ML lines in the k space. $k_{||} = 0.96 \text{ \AA}^{-1}$ is the value at which the Ti 3d band is at its minimum and $k_{||} = 0.535 \text{ \AA}^{-1}$ is the value at which it crosses the Fermi level in the previous study¹ where lineshapes along ΓM were studied.

For TiTe_2 , energy resolution better than in our previous measurements¹ (35 meV) was not obtained due to certain technical problems. But, with similar resolution, we have measured the dispersion of the Ti 3d band perpendicular to the surface. The dispersion along the surface normal contributes to the broadening of the peaks through the lifetime effect of the outgoing electron. So it is essential for the interpretation of the experimental lineshapes as spectral functions of the photohole that the dispersion along the surface normal should be small. Figure 2 shows the dispersions in the surface normal direction with $k_{\parallel}$ (the k component along the surface) values kept constant. The two values of $k_{\parallel}$ are chosen as the values at which the Ti 3d band is at its minimum ($0.96 \text{ \AA}^{-1} = \text{M point}$) and the value at which it crosses the Fermi level ($0.535 \text{ \AA}^{-1}$) in the previous study¹ where 21.2 eV photons were used. The first case clearly shows symmetric behavior of the peaks near the Fermi level. Whether or not this band actually crosses the Fermi level is difficult to tell since we do not have a reliable way of normalizing the intensities here. No noticeable dispersion is observed for the second case. Similar to the first case, it is difficult to tell whether there is a band crossing or not. Figure 3 shows a plot comparing the energies of the peak maxima along the ML direction (for two different values of inner potential) with the energies from an LDA band calculation performed by V. Eyert at the Max Planck Institute, Stuttgart. We can now estimate an upper limit of $0.1 \text{ eV/\AA}^{-1}$ for the dispersion perpendicular to the surface with the $k_{\parallel}$ values for which our fits¹ have been performed. (Actually this limit is basically

Fig.3 The peak maxima obtained from Fig.2 along ML compared with LDA band calculation. Solid circles are for an assumed inner potential of 14.5 eV and open circles for 13.5 eV.

determined by the uncertainties in the energy position determination; the actual dispersion may be even smaller.) This leads to an estimate of the final state lifetime contribution to the overall d-peak width of at most 10-15 meV.

The measured spectra for $\text{Ti}_{1+x}\text{S}_2$ clearly showed that indeed the filling of the d band is adjusted by the value of x, with a total absence of the d peak in the close-to-stoichiometric samples ($x=0$). Interestingly, we also observed the appearance of a peak in the semiconductor band gap for the nearly ideal stoichiometric crystals. Since it appeared to display some k dispersion, we may actually have observed the formation of an impurity band in the gap. We intend to pursue this study further in the next beam time period in cooperation with the group of Prof. Bucher (Universität Konstanz) who grow the crystals and make the transport measurements. We also hope to measure lineshape dependencies on the d band filling with enhanced experimental resolution.

CONCLUSIONS

Measurements on $\text{K}_{0.3}\text{MoO}_3$ showed two dispersive Mo 4d peaks in accordance with the band calculation. The Fermi surface crossing of the first dispersive peak occurs at a k value very close to that predicted in a band calculation. In our angle resolved spectra, a Fermi step is not observed for any of the angles, including that where the crossing occurs. The observed binding energies have values 2.5 to 5 times the band calculation values. It appears possible that a correlated one dimensional electron model may explain the observed spectra. Also, there are other effects that may result in similar spectral features. We plan to establish a theoretical collaboration to address these issues. It will also be helpful if we can find a one dimensional metallic system which has a single dispersive peak in the conducting direction. For TiTe_2 , the dispersion of the Ti 3d band perpendicular to the surface has been measured. From this, we estimate the contribution of the outgoing electron lifetime effect to the spectral linewidth to be 10-15 meV at most. For $\text{Ti}_{1+x}\text{S}_2$, it may be that we have observed a dispersing impurity band in the gap of the stoichiometric sample. This will be pursued further together with the study of the lineshape changes as a function of the d band filling x.

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