Photoemission and band-calculation studies of the charge-density wave in CuV$_2$S$_4$

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We have studied the electronic structure and its changes across the charge-density-wave (CDW) transition in spinel-type CuV$_2$S$_4$ by photoemission spectroscopy and first-principles band-structure calculations. The photoemission spectra show pseudogap-like behavior and the gap size is estimated to be $\sim$90 meV. The large energy scale of the pseudogap compared to the transition temperature and its anomalous temperature dependence implies that the involved interaction is in the strong-coupling regime. The calculated electronic susceptibility $\chi(q)$ shows a small peak at $q = \frac{1}{2}[110]$, which is consistent with the observed wave vector $q = \frac{1}{4}[110]$ characterizing the CDW. This result suggests that Fermi surface nesting is at least partly responsible for the CDW formation.

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I. INTRODUCTION

Recently, a number of studies have been devoted to quasi-one-dimensional materials. From a theoretical point of view, one dimensionality leads to a lot of anomalous properties which differ qualitatively from higher-dimensional materials. In particular, it is well known that the metallic state is unstable with respect to the lattice distortion which forms an insulating ground state. Such an instability, called Peierls instability, in one-dimensional materials is often accompanied by the formation of a charge-density wave (CDW) with the same wave vector.

In three-dimensional systems, on the contrary, only a few materials have been reported to show CDW’s. Among them, a spinel-type compound CuV$_2$S$_4$ is known to undergo a phase transition accompanied by a CDW at 90 K. It shows the presence of an incommensurate superlattice with wave vector $q = (\frac{1}{4} - \delta)[110]$ at 90 K, which gradually locks in to a commensurate one $\frac{1}{4}[110]$ at 75 K. At 50 K, the wave vector abruptly changes from $\frac{1}{4}[110]$ to $(\frac{1}{4} - \delta)[110]$. At room temperature, CuV$_2$S$_4$ has a normal spinel structure, in which the Cu ion is tetrahedrally coordinated and the V ion is octahedrally coordinated by sulphur atoms. The symmetry at lower temperature is controversial; an electron diffraction study has shown orthorhombic symmetry, whereas x-ray diffraction has shown cubic or tetragonal symmetry. The magnetic susceptibility is independent of temperature above 90 K and shows sudden decrease at 90 K. The linewidth of the $^{51}$V NMR spectrum abruptly increases below 90 K, indicating the existence of the CDW. Electrical resistivity shows an anomalous upturn below 90 K. X-ray photoemission and x-ray emission spectroscopy studies by Lu et al. have shown that the Cu ion is in the monovalent state. Hence, the Cu 3$d$ electrons hardly contribute to the thermodynamic and transport properties and the V 3$d$ electrons mainly participate in them. They have also reported first-principles band-structure calculations and estimated the electron-phonon coupling parameter $\lambda$ to be rather large, $\sim$2.0. Because of its three-dimensional crystal structure, it is unlikely that CuV$_2$S$_4$ shows a perfect nesting, but an imperfect nesting effect like the spin-density wave (SDW) in chromium metal remains possible.

Photoemission spectroscopy has been utilized for the study of many CDW systems in the last decade because of its advantage of directly probing the CDW gap. In this paper, we present a photoemission study of CuV$_2$S$_4$, emphasizing the detailed temperature dependence of the spectra. Spectra of CuTi$_2$S$_4$, which is a paramagnetic metal down to 0.5 K, are also presented for comparison. We have also performed first-principles band-structure calculations in order to obtain insight into the possibility of CDW formation due to Fermi surface nesting.

II. EXPERIMENT

Single crystals of CuV$_2$S$_4$ and CuTi$_2$S$_4$ were synthesized in a quartz ampoule by TeCl$_4$ vapor transport at growth temperatures from 830 to 720 °C in a two-zone furnace. The x-ray diffraction pattern confirmed that the pure-spinel phase was obtained.

Ultra violet photoemission (UPS) measurements were made using the He I line ($h\nu = 21.2$ eV). The measurements were performed at various temperatures between 30 K and 340 K in order to study spectral changes above and below the transition temperature. In order to calibrate binding energies and estimate the instrumental resolution, gold was evaporated on the sample surface after each series of measurements. The resolution was estimated to be 34 meV. The samples were repeatedly scraped in situ with a diamond file. The base pressure of the spectrometer was $\sim 5 \times 10^{-10}$ Torr.

III. RESULTS AND DISCUSSION

A. Photoemission spectroscopy

Figure 1(a) shows valence-band spectra of CuV$_2$S$_4$ and CuTi$_2$S$_4$. While the overall features of the spectra are similar...
to each other, there are significant differences between the spectra near the Fermi level ($E_F$). The spectra near $E_F$ mainly consist of emission from V 3$d$/Ti 3$d$ electrons and the difference reflects the number of $d$ electrons, i.e., V 3$d^{1/2}$ versus Ti 3$d^{0/5}$.

Figure 1(b) shows a comparison between the measured spectra and theoretical photoemission spectra in the vicinity of $E_F$. To obtain the theoretical photoemission spectra, the V 3$d$ partial density of states (DOS) calculated in the present work has been convoluted with a Gaussian of 34 meV full width at half maximum (FWHM). For CuTi$_2$S$_4$, we rigidly shifted the Fermi level so that the occupied number of states per transition-metal atom becomes one fewer than that in CuV$_2$S$_4$. Agreement between the experimental and theoretical spectra is fairly good for both CuV$_2$S$_4$ and CuTi$_2$S$_4$. In the oxides of early transition metals [for example, VO$_2$ (Ref. 13)], electron correlation within the 3$d$ band is generally strong enough to result in a strong discrepancy between the band-structure calculation and the photoemission spectra. On the other hand, the discrepancy is much smaller in the sulﬁdes of early transition metals. In accordance with those studies, our result suggests that electron correlation has a relatively small effect on the electronic structure of CuV$_2$S$_4$.

The upper panels of Fig. 2 show photoemission spectra of CuV$_2$S$_4$ and CuTi$_2$S$_4$ near $E_F$ taken at 27 and 300 K. The DOS is clearly dependent on temperature and spectral weight transfer between $E_F$ and $E_F$ for each material. Lower panels: photoemission spectra with the Fermi-Dirac distribution divided out. See text for detail.
the observed discrepancy between the experiment and BCS theory is so large that the unusual temperature dependence may not be explained only by the surface effects. In order to see whether the partial nesting scenario is applicable or not, ARPES measurements of CuV$_2$S$_4$ are strongly desired. In spite of the difficulty arising from the three dimensionality, it is important to settle the anisotropy of the gap opening behavior in CuV$_2$S$_4$.

B. Band-structure calculation

In order to see whether the partial nesting scenario is valid or not, we have performed first-principles band-structure calculations on CuV$_2$S$_4$ and examined the possibility of CDW formation from the viewpoint of one-electron band theory. We have calculated the bare electronic susceptibility defined as follows:

$$\chi(q) = \sum_{\mu \nu} \chi_{\mu \nu}(q) = -\frac{1}{2} \sum_{\mu \nu} \sum_{k} \left[ f(\varepsilon_{k+q}^{\mu}) - f(\varepsilon_{k}^{\mu}) \right] n_{\nu}(\varepsilon_{k+q}^{\nu}) - n_{\nu}(\varepsilon_{k}^{\nu})$$

where $f(\varepsilon)$ is the Fermi-Dirac distribution function, $\mu$ and $\nu$ are band indices, and $\varepsilon_{k+q}^{\mu}$ and $\varepsilon_{k}^{\mu}$ are band energies at points separated by the wave vector $q$. It is generally believed that peaks in $\chi(q)$ are important in CDW formation and in fact they can explain Kohn-type anomalies in phonon spectra of Sc.$^{19}$ The present band-structure calculation for CuV$_2$S$_4$ has been carried out in the local-density approximation (LDA) using a full-potential, scalar-relativistic implementation$^{20}$ of the linear augmented-plane-wave (LAPW) method.$^{21}$ The cutoff has been set at values such that the calculation include $\sim 60$ LAPW's/atom (10-Ry plane-wave cutoff) and spherical harmonics terms up to $l=6$. The crystalline charge density and potential have been expanded with about 8900 plane waves (48-Ry cutoff) in the interstitial region and lattice harmonics with $l_{\text{max}}=6$ within the muffin-tin spheres ($R_{\text{Cu}} = 2.10$ a.u., $R_{\text{V}}=2.44$ a.u., $R_{\text{S}}=2.09$ a.u.). Brillouin-zone (BZ) integration has utilized a ten-point $k$ samples in the 1/48 irreducible wedge. Exchange and correlation effects in the LDA potential have been included via the Wigner interpolation formula.$^{22}$ The atomic Cu(3$d^{10}$4$s^1$), V(3$d^2$4$s^1$), and S(3$s^2$3$p^4$) states were treated as valence electrons in this study whereas the more tightly bound levels were included via the frozen-core approximation. The calculation of the electronic susceptibility was made for $T=0$ by application of the tetrahedron method after Rath and Freeman.$^{19}$ BZ integration has been done based on the energy eigenvalues at 916 $k$ points in the irreducible wedge directly calculated using the LAPW method.

Figure 4 shows the intraband component of the calculated susceptibility $\chi_{\mu \mu}$ for the 45th and 46th bands. Although there are five bands which cross the Fermi level, we have considered the above two bands because they occupy more than 90% weight of the density of states at $E_F$. We also calculated the interband contribution $\chi_{\mu \nu}(\mu \neq \nu)$, but it has no well-defined structures and is therefore not shown in Fig. 4. The calculation was made along the high-symmetry lines.
We have observed that the photoemission spectra of CuV$_2$S$_4$ change over a wide temperature range from 90 K to 340 K. The spectra show pseudogap-like behavior and the gap size is estimated to be $\sim 90$ meV. This pseudogap-like behavior suggests partial nesting of the Fermi surface. With increasing temperature, the pseudogap does not close but is filled by spectral weight transferred from high binding energies. Both the pseudogap and the spectral weight near $E_F$ do not show a clear change at the transition temperature of 90 K and below it. These observations do not follow the BCS behavior. The large energy scale of the pseudogap compared to the transition temperature suggests that the interaction involved is in the strong-coupling regime. We have performed first-principles band-structure calculations and have calculated the bare electronic susceptibility $\chi(q)$. We have found a peak in the electronic susceptibility at $q = \frac{11}{20}[110]$, which is consistent with the observed value of $q = \frac{1}{4}[110]$ by x-ray diffraction. This result suggests that partial nesting of the Fermi surface is indeed a possible mechanism for CDW formation.

IV. CONCLUSION

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11. M. Grioni and J. Voit, in *Electron Spectroscopies Applied to Low-