**Electronic Structure of Condensed Matter** 

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## V 3d-2p soft x-ray emission spectrum of CuV<sub>2</sub>S<sub>4</sub>

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## **Introduction**

 $CuV_2S_4$  exhibits the phase transitions at 92 and 56 K [1]. It is considered that the transitions are related to the charge density wave (CDW) formation with the wave vectors along [110]. V atoms in  $CuV_2S_4$  align along [110]. The Cu 2p photoemission spectrum for  $CuV_2S_4$  reveals that Cu is monovalent below RT. Thus the V 3d electrons are closely related to the CDW transition.

We have performed the V 3d-2p soft x-ray emission spectroscopy (XES) measurements in the V 2p photoabsorption region to investigate the change in the V 3d state of  $CuV_2S_4$  through the CDW transition.

## **Results and Discussion**

Polycrystalline  $\text{CuV}_2\text{S}_4$  sample was used. The magnetic susceptibility of the sample showed the two phase transitions. XES measurements were made in the depolarized configuration [2] to investigate the V 3d state near the Fermi level  $\text{E}_{\text{F}}$ . The overall resolution was 1.0 eV.

Figs. 1(a) and 1(b) show the XES spectra measured with the excitation photon energies corresponding to (a) V  $2p_{_{3\prime2}}$  absorption peak and (b) V  $2p_{_{1\prime2}}\!,$  respectively. The spectra at 300 K (dotted curves) and at 75 K (solid) were normalized by the integrated intensity. Two peaks around 509 and 512 eV in Fig. 1(a) are also seen in Fig. 1(b). These peaks have the normal-emission like character, i.e., almost irrelevant to the electron excited from V 2p by absorption. Similarly two peaks related to the transitions to  $2p_{1/2}$  around 516 and 519 eV in Fig. 1(b) reflect the V 3d partial density of states (DOS) in the valence band and they are reminiscent of those at 509 and 512 eV, respectively. Weak features are seen just around the excitation energies in both figures. These energies almost coincide the transitions from  $E_{\rm E}$  to V  $2p_{3/2}$  and  $2p_{1/2}$ . Indeed Okada et al, have observed V 3d-derived state just below  $E_{F}$  by photoemission spectroscopy [1].

It is observed in both Figs. 1(a) and 1(b) that the spectral intensity in the emitted photon energy region from just around the excitation energy to about 2.5-eV lower energy is increased at 75 K in comparison with that at 300 K. We have observed further increase in the spectral intensity in the same energy region at 55 K (not shown). This indicates that more low-energy excitations are excited in the resonant photon emission process or that the V 3d DOS is increased at lower temperatures. According to the previous studies [1,3], it is expected that the DOS near  $E_r$  is decreased with decreasing temperature.

It is considered that the observed temperature dependence results from the enhanced localized nature of V 3d electrons after the CDW formation. It was hard to compare the non resonant XES spectra with excitation photon energies higher than the V 2p absorption peaks in order to investigate temperature dependence of the V 3d DOS of  $CuV_2S_4$  near  $E_F$ . The pressure of the measurement chamber was in the high 10<sup>8</sup> Torr region. The O K emission signal around 525 eV due to water molecules adsorbed from the residual gas was increased at low temperatures.

## **References**

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Fig. 1. V 3d-2p x-ray emission spectra for  $CuV_2S_4$  taken with the excitation photon energies of (a) 515.6 eV and (b) 522.6 eV at 300 K (dotted curves) and 75 K (solid).