HIGH-RESOLUTION PHOTOEMISSION STUDY OF $Cd_2Re_2O_7$*

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High-resolution bulk-sensitive photoemission has been measured for pyrochlore oxide $Cd_2Re_2O_7$. Temperature variations of the spectral shapes between 20 and 250 K are obviously observed for the Re $4f$ inner core and the valence band spectra. The Re 5d states are dominant for the DOS near the Fermi level.

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1. Introduction

Recently, $Cd_2Re_2O_7$ has been found to be a superconductor with $T_c \sim 1$ K [1,2]. This is the first superconductor found among the large family of pyrochlore oxides with the formula of $A_2B_2O_7$ (A = rare earth or late transition metals, B = transition metals). In this structure, A and B cations are 4- and 6-coordinated by oxygen anions. The A-O_4 tetrahedra are connected as forming a pyrochlore lattice with straight A-O-A bonds, while the B-O_6 octahedra form a pyrochlore lattice with the bent B-O-B bonds with the angle of 110∼140°. Assuming the electronic configurations in $Cd_2Re_2O_7$ as formally Cd^{2+} $4d^{10}$ and Re^{5+} $4f^{14}5d^2$, the electronic and magnetic properties are primarily dominated by the Re $5d$ electrons. $Cd_2Re_2O_7$ shows an anomaly at 200 K in the electric resistivity, magnetic susceptibility, specific heat and Hall coefficient [1–3]. An X-ray diffraction measurement reveals the existence of a second-order structural phase transition at this temperature with changing its symmetry from an ideal cubic $Fd3m$ to a lower symmetric cubic $F43m$ with lowering temperature [4]. The resistivity is almost

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temperature independent near the room temperature and drops abruptly below 200 K. The magnetic susceptibility decreases also below 200 K while it shows weak temperature dependence at higher temperature with a broad maximum near 290 K. Although the origin of this transition is not clear, it induces a large change in electronic properties. Furthermore, another transition is shown not only in electric resistivity with a hysteresis at around 120 K, but also in specific heat and thermoelectric power in the form of kink, whereas magnetic susceptibility shows no change [5]. The magnetoresistance goes once to zero with increasing temperature toward 120 K from low temperatures, but it is revived between 120 and 200 K. This transition near 120 K is also pointed out to be due to a possible electronic structural change at the Fermi level.

In order to directly study the electronic states, a high-resolution bulk-sensitive photoemission measurement is carried out for $Cd_2Re_2O_7$.

2. Experimental

The synchrotron radiation experiments were performed at beam line BL25SU in SPring-8 with using a Scienta SES-200 analyzer. The excitation photon energies were selected as 600∼1100 eV for the bulk-sensitive measurements. The overall energy resolution was set to about 80 meV for the valence band region and 200 meV for the core level photoemission. The measurements were done at the sample temperatures of 20 and 250 K below and above the transition temperature of 200 K. Clean sample surfaces were obtained by cleaving the single-crystal samples *in situ* under an ultra-high vacuum of better than 5×10^{-10} Torr.

3. Results and discussions

Fig. 1 shows the valence band spectrum at 20 K measured at the photon energy of 600 eV. A finite DOS with a sharp peak exists at the Fermi level. The deep valley structure in $1 \sim 3$ eV is clearly seen in agreement with the band calculation [6]. Considering the cross-sections at the photon energy of 600 eV, the Re $5d$ states are dominant in the peak structure. According to a band calculation, the gap structure between 1 and 3 eV is derived from the hybridizing between the Re $5d$ and O $2p$ orbits. The valence band is separated by this gap as the bonding-state near 4 eV and the anti-bonding state near the Fermi level. Meanwhile the peaks at 11 and 22 eV correspond to the Cd $4d$ and O $2s$ states.

Fig. 2 shows the difference of photoemission spectra near the Fermi level below and above 200 K. The spectral intensities of both 20 and 250 K spectra are tentatively normalized by the intensity of the localized O $2s$ inner core state. The normalization in the region above the binding energy of $E_B = 1$ eV provides the equivalent result. As shown in the inset, the DOS at the Fermi level is larger at 20 K than at 250 K. It is consistent with the

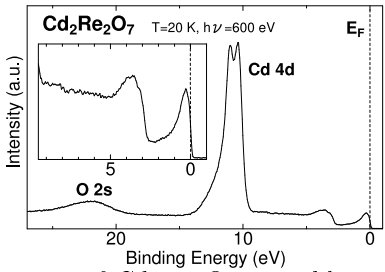

Fig. 1. Valence band spectrum of $Cd_2Re_2O_7$ pyrochlore at 20 K measured at the photon energy of 600 eV.

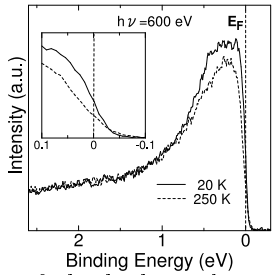

Fig. 2. Temperature variation of the high-resolution photoemission spectra near E_F. These spectra are normalized by the intensity of the O 2*s* core state.

behavior of the electric resistivity [1,2]. Furthermore, the spectral shape of the peak is obviously different between 20 and 250 K. The spectrum at 20 K has a broad and rather flat top. This change may be ascribed to the removal of the degeneracy of the Re 5*d* orbital constituting the peak below 200 K as the result of the lowering of the inversion symmetry of the B-O_6 octahedra.

As a typical inner core state, we show the temperature dependence of the Re 4*f* spectra in Fig. 3(a). The peaks at 42 and 45 eV correspond to $j = 7/2$ and $5/2$ states split by the spin-orbital interaction. A shoulder structure is also seen on the higher binding energy side of the $j = 5/2$ component. This shoulder is understood as a bulk component because its intensity shows very poor $h\nu$ dependence. With decreasing the temperature, the spectral weight transfers from the shoulder to the peak. It is recognized that the intensity of the $j = 7/2$ component increases also at 20 K whereas the intensity in the valley region decreases. According to a deconvolution, another shoulder associated with the $j = 7/2$ is hidden in the valley region. The origin of these shoulder structures is not fully known yet, but this temperature change in the spectral weight may correspond to the spectral change near the Fermi level dominated by the Re 5*d* Partial Density of State (PDOS). One possible scenario is to interpret these shoulders as Charge-Transfer (C-T) satellites. The reduction of C-T satellite at 20 K means a reduction of hybridization between the Re 5*d* and conduction band states. Then the Re 5*d* component in the state near the Fermi level will increase and provide higher intensity at 20 K. X-ray BIS study will help to check this scenario in near future.

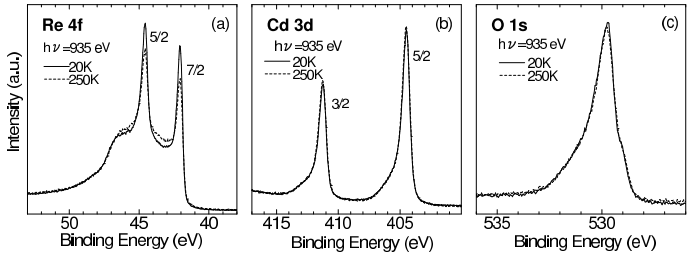

Fig. 3. Photoemission spectra of Re $4f$ (a), Cd $3d$ (b) and O $1s$ (c) inner cores at 20 and 250 K at the photon energy of 935 eV.

On the contrary, both Cd $3d$ and O $1s$ spectra in Fig. 3(b) and 3(c) show very small change between 20 and 250 K. Beside sharp main peaks small shoulders are recognized at higher binding energies. From the photon energy dependence, we ascribe these shoulders to surface components. In the O $1s$ spectrum, the shoulder at lower binding energy is not attributed to a surface component but may be derived from the existence of two different crystallographic sites in the oxygen.

4. Conclusion

The temperature dependence of the bulk-sensitive photoemission spectra are investigated in $Cd_2Re_2O_7$ by using soft X-ray synchrotron radiation. The valence band spectrum agrees qualitatively well with the recent band calculation. The temperature dependence of the Re $4f$ inner core spectra exhibits the dominance of the Re $5d$ states at the Fermi level. The characteristic change in the peak structure near the Fermi level suggests the change of band structure dominated by the Re $5d$ states across 200 K.

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