Photoemission study of the skutterudite compounds
Co(Sb$_{1-x}$Te$_x$)$_3$ and RhSb$_3$

H. Ishii, K. Okazaki, and A. Fujimori

Department of Physics and Department of Complexity Science and Engineering, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

Y. Nagamoto and T. Koyanagi

Department of Symbiotic Environmental Systems Engineering, Graduate School of Science and Engineering, Yamaguchi University, Ube 755-8611, Japan

J. O. Sofo

Centro Atómico Bariloche and Instituto Balseiro, Comisión Nacional de Energía Atómica, (8400) Bariloche, RN, Argentina

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We have studied the electronic structure of the skutterudite compounds Co(Sb$_{1-x}$Te$_x$)$_3$ ($x = 0, 0.02, 0.04$) by photoemission spectroscopy. Valence-band spectra revealed that Sb 5$p$ states are dominant near the Fermi level and are hybridized with Co 3$d$ states just below it. The spectra of $p$-type CoSb$_3$ are well reproduced by the band-structure calculation, which suggests that the effect of electron correlations is not strong in CoSb$_3$. When Te is substituted for Sb and $n$-type carriers are doped into CoSb$_3$, the spectra are shifted to higher binding energies as predicted by the rigid-band model. From this shift and the free-electron model for the conduction and valence bands, we have estimated the band gap of CoSb$_3$ to be 0.03-0.04 eV, which is consistent with the result of transport measurements. Photoemission spectra of RhSb$_3$ have also been measured and revealed similarities to and differences from those of CoSb$_3$.

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I. INTRODUCTION

The family of compounds called skutterudites, with the general chemical formula $TX_3$ ($T$ = Co, Rh, Ir; X = pnictogen P, As, Sb), has recently received much attention due to their potential for thermoelectric applications. The ability of thermoelectric materials is defined as the thermoelectric figure of merit,

$$Z = \frac{S^2 \sigma}{\kappa_c + \kappa_l} \propto \frac{m^*^{3/2} \mu}{\kappa_l},$$

(1)

where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $\kappa_c$ is the electronic thermal conductivity, $\kappa_l$ is the lattice thermal conductivity, $m^*$ is the effective mass, and $\mu$ is the carrier mobility. Among the skutterudite compounds, CoSb$_3$ has attracted particular attention because it has a high carrier mobility (for $p$-type) and a heavy effective mass (for $n$-type). Band-structure calculations have been performed by several groups. Singh and Pickett suggested that its linear band dispersion near the Fermi level ($E_F$) causes the unusual transport properties. On the other hand, Sofo and Mahan reported that its band structure is typical of a narrow gap semiconductor. Moreover, Jung et al. proposed the chemical picture that the top of the valence band at the $\Gamma$ point in the Brillouin zone corresponds to the antibonding combinations of the $\pi_4$ orbitals of the Sb ring along a crystallographic axis. It is also reported that the effective mass of the conduction band in the band-structure calculations is nearly by a factor of ten smaller than that estimated from the transport experiments, which may indicate the existence of some effects not described by the conventional band picture. X-ray photoemission (XPS) experiments on CoAs$_3$, CoSb$_3$, and RhSb$_3$ were performed, but the energy resolution was not sufficient to investigate the electronic structures near $E_F$. Therefore, it is important to perform a photoemission study of CoSb$_3$ with higher energy resolution.

In this paper, we report on the results of a photoemission study of Co(Sb$_{1-x}$Te$_x$)$_3$ ($x = 0, 0.02, 0.04$) including ultraviolet photoemission spectroscopy (UPS). First, we show the valence-band spectra of CoSb$_3$ ($x = 0$), which were taken with much higher resolution than in the previous reports, and revealed that Sb 5$p$ orbitals are indeed dominant near $E_F$ in CoSb$_3$. Second, we compare the valence-band spectra of CoSb$_3$ with a theoretical spectrum derived from the band-structure calculation. The photoemission spectra are well reproduced by the theoretical spectrum, which suggests that the effect of electron correlations is not strong in CoSb$_3$. Third, we show a rigid-band like spectral shift in Co(Sb$_{1-x}$Te$_x$)$_3$ ($x = 0, 0.02, 0.04$) as a function of $x$. From the spectral shift we have estimated a band gap of CoSb$_3$ to be 0.03-0.04 eV. We also compare the spectra of CoSb$_3$ with those of RhSb$_3$ and discuss the differences between them. Finally, the temperature dependence of the spectra near $E_F$ have been studied and have revealed unusual behaviors in both compounds.
II. EXPERIMENT

Samples of Co(Sb$_{1-x}$Te$_x$)$_3$ ($x = 0, 0.02, 0.04$) were prepared by the following method. Co (99.998% pure), Sb (99.9999% pure) and Te (99.9999% pure) powders were used as starting materials. They were mixed in stoichiometric ratio Co(Sb$_{1-x}$Te$_x$)$_3$ ($x = 0, 0.02, 0.04$) in a plastic vial before being loaded in a steel die, where they were compressed into a dense cylindrical pellet. The pellet was loaded on a graphite boat in an Ar atmosphere, which was heated for two days at 823 K. The product was then crushed and ground in an alumina mortar. Following the powder reaction, several samples of Co(Sb$_{1-x}$Te$_x$)$_3$ were sintered by the spark plasma sintering method. The spark plasma sintering was performed under a pressure of 30 MPa at 853 K for 10 min. CoSb$_3$ was single-crystalline and showed p-type transport, while Co(Sb$_{0.98}$Te$_{0.02})_3$ and Co(Sb$_{0.96}$Te$_{0.04})_3$ were polycrystalline and showed n-type transport.

We performed the photoemission experiments using a hemispherical electron energy analyzer. The light sources were the He I ($h\nu = 21.2$ eV) and He II ($h\nu = 40.8$ eV) resonance lines for UPS, and the Mg Kα ($h\nu = 1253.6$ eV) line for XPS. Energy calibration and estimation of the instrumental resolution were done for Au film evaporated on the samples after each series of measurements. The energy resolution was about 25 meV, 100 meV, and 0.7 eV for He I UPS, He II UPS and XPS, respectively. Measurements were done at 30 K, 100 K and 300 K for He I, and only at 300 K for He II and XPS. The base pressure in the spectrometer was $\sim 1 \times 10^{-10}$ Torr for UPS and $\sim 5 \times 10^{-10}$ Torr for XPS. The surfaces of the samples were repeatedly scraped in situ with a diamond file. When they were scraped at low temperatures ($T < 100$ K), however, the structures caused by the adsorption of impurity were observed in the photoemission spectra. Therefore, we measured only 30 K spectra after scraping at 100 K and lowering the temperature down to 30 K.

III. RESULTS AND DISCUSSION

Figure 1(a) and (b) show the valence-band photoemission spectra of CoSb$_3$ in the entire valence-band region (a) and in the vicinity of $E_F$ (b).

![Figure 1](image-url)

**FIG. 1.** Valence-band photoemission spectra of CoSb$_3$ in the entire valence-band region (a) and in the vicinity of $E_F$ (b).
the He I photoemission spectrum and the theoretical spectrum derived from the band-structure calculation by Sofo and Mahan. To derive the theoretical photoemission spectrum we have taken into account the contribution of the Co 3d, Sb 5s and Sb 5p partial density of states (DOS). They have been weighted by the corresponding photoionization cross-sections at that photon energy. This weighted DOS has been broadened by convoluting with a Gaussian and a Lorentzian which represent the instrumental resolution and the lifetime broadening, respectively. We assume that the lifetime width increases linearly with energy $E$ measured from $E_F$, i.e., $\text{FWHM} = \alpha|E - E_F|$. The coefficient $\alpha$, which represents the lifetime of the photo-hole and increases with increasing binding energy, is empirically determined to be $\sim 0.1$. Finally, we have added the background of Henrich type to the broadened DOS, as shown by a dashed line in Fig. 2(a). The spectra have been normalized to the area between $E_F$ and 6 eV.

In the wide energy range [Fig. 2(a)], the photoemission spectrum is in good agreement with the theoretical spectrum. The main structures, A, B, and C, which were defined in Fig. 1, are well reproduced in the theoretical simulation. These results suggest that electron correlations are not important in CoSb$_3$. However, there exists a small discrepancy in the fine structures in A between the photoemission spectrum and the theoretical spectrum. The intensity ratio $b/a$ is different between experiment and calculation. The intensity of $b$ is as high as that of $a$ in the photoemission spectrum, while it is apparently higher than that of $a$ in the theoretical spectrum. As mentioned above, $a$ and $b$ can be assigned to relatively pure Co 3d and Co 3d states hybridizing with Sb 5p states, respectively. The local-density approximation used for the band-structure calculation tends to overestimate the hybridization between the Co 3d and Sb 5p electrons, and hence the hybridization strength may have been overestimated.

**TABLE I. Values for the Fermi energy $\epsilon_F$, the effective mass $m^*$, and the carrier concentration $n$.** The values of $m^*$ are taken from Ref. 4 and $m_e$ is the free-electron mass.

| Type       | $\epsilon_F$ [eV] | $m^*$ [$m_e$] | $n$ [$\text{cm}^{-3}$] |
|------------|-------------------|--------------|------------------------|
| CoSb$_3$   | p                 | 0.03         | 0.15                   | 1.4 $\times$ 10$^{18}$ |
| Co(Sb$_{0.96}$Te$_{0.04}$)$_3$ | n                 | 0.06         | 3.5 $\times$ 10$^{20}$ |

FIG. 2. Photoemission spectra of CoSb$_3$ compared with the band-structure calculation in the entire valence-band region (a) and in the vicinity of $E_F$ (b). The dashed curve shows the background (see text). The spectra have been normalized to the area between $E_F$ and 6 eV.

FIG. 3. Photoemission spectra of Co(Sb$_{1-x}$Te$_x$)$_3$ ($x = 0$, 0.02, 0.04) near $E_F$. The inset shows wide-range spectra. The spectra have been normalized to the height of the Co 3d peak.

Figure 3 shows the valence-band spectra.
of Co(Sb$_{1-x}$Te$_x$)$_3$ in the vicinity of $E_F$. The spectra have been normalized to the height of the peak at $\sim$ 1.2 eV. The spectra of the $x = 0.02$ and $x = 0.04$ samples are more blurred than the $x = 0$ sample, probably because the substitution of Te for Sb caused potential disorder in the crystal. Energy shifts of them were determined by comparing the positions of the low binding energy side of the Co 3$d$ peak, as indicated by a solid line in the figure. The spectra of Co(Sb$_{1-x}$Te$_x$)$_3$ are shifted to higher binding energy with increasing $x$. This is what would be expected from the rigid-band model since Te has one more valence electron than Sb and hence each substituted Te atom donates one electron to the conduction band. We obtained the spectral shifts of 0.05-0.06, 0.06-0.07, and 0.12-0.13 eV for $x = 0 \rightarrow 0.02$, $x = 0.02 \rightarrow 0.04$, and $x = 0 \rightarrow 0.04$, respectively. From these shifts we estimated the band gap of CoSb$_3$ as follows. The $x = 0$ and $x = 0.04$ samples are $p$-type and $n$-type degenerate semiconductors, respectively, and their chemical potentials are located below the valence-band maximum for the $p$-type material and above the conduction-band minimum for the $n$-type material, as illustrated in Fig. 4. In the regions between $\mu$ and the band edge, one can regard the energy band to be parabolic. Then the separation between $\mu$ and the band edge corresponds to the Fermi energy $\epsilon_F$ of the carriers and is given by:

$$\epsilon_F = \frac{\hbar^2 k_F^2}{2m^*},$$  

(2)

where $k_F$ and $m^*$ are the Fermi wave vector and the effective mass of the carriers, respectively. $k_F$ is given by:

$$k_F = \left(3\pi^2 n\right)^{1/3},$$  

(3)

and obtains the value of 0.03-0.04 eV for $E_g$. This value is consistent with the value of $E_g \sim 0.05$ eV deduced from the transport experiment within the experimental uncertainties.

Figure 5 shows the valence-band photoemission spectra of RhSb$_3$. In analogy to CoSb$_3$, we refer to the main structures as $A^*$ (from 0 to 4 eV), $B^*$ (from 4 to 6 eV) and $D^*$ (from 7 to 12 eV) as indicated in the figure, corresponding to $A$, $B$ and $D$ in the CoSb$_3$ spectra. Structure $C^*$, which should correspond to $C$, is not observed, probably because it is hidden by $A^*$ and $B^*$, which are located at higher binding energies and are broader than those in CoSb$_3$. Moreover, fine structures $a^*$, $b^*$ and $c^*$ within $A^*$ are also defined as indicated in the figure. As in the case of CoSb$_3$, structure $A^*$ is assigned to Rh 4$d$. $A^*$ is broader than $A$, which indicates that the Rh 4$d$ band is wider than the Co 3$d$ band. Moreover, the intensity ratio $b^*/a^*$ is different from $b/a$ of CoSb$_3$. For CoSb$_3$, $b$ is as strong as $a$ in the He I spectrum and is much weaker than $a$ in the He II spectrum. On the other hand, for RhSb$_3$, 

FIG. 4. Schematic illustration of the spectral DOS for $p$-type and $n$-type semiconductors, which is observed by photoemission spectroscopy.

FIG. 5. Photoemission spectra of RhSb$_3$ compared with those of CoSb$_3$. 
$b^*$ is stronger than $a^*$ both in the He I and He II spectra, although the intensity ratio $b^*/a^*$ is slightly smaller in the He II spectrum. One can explain these differences as follows. From the results of the CoSb$_{3}$ spectra, we can regard $a^*$ as pure $d$ character and $b^*$ as hybridized $d$ character. Since Rh 4$d$ electrons are more itinerant than Co 3$d$ electrons, $b^*/a^*$ for RhSb$_{3}$ is larger than CoSb$_{3}$. The hump just below $E_F$, $c^*$, is also identified in RhSb$_{3}$ and can be assigned to Sb 5$p$ states. Structures $B^*$ and $D^*$ are assigned to Sb 5$p$ character and to Sb 5$s$ character, respectively, in the same way as $B$ and $D$. Comparing the RhSb$_{3}$ spectra with the CoSb$_{3}$ spectra, $B^*$ is located at a higher binding energy than $B$ in the same way as $A^*$ ($A$), which is of $d$ character. On the other hand, structures $D^*$ is located at the same binding energies as $D$, $C^*$ is probably hidden by $B^*$ and, if this is the case, it is located at the same energy as $C$. These results suggest that $B^*$ ($B$) hybridizes with $d$ states and that $C^*$ ($C$) does not.

Finally, Fig. 6 shows the temperature-dependent spectra of CoSb$_{3}$ and RhSb$_{3}$ in the region near $E_F$. The spectra have been normalized to the area between -0.1 and 2 eV for CoSb$_{3}$ and between -0.1 and 4 eV for RhSb$_{3}$. One can see that the intensities of the spectra around $E_F$ decrease with decreasing temperature. To isolate the temperature dependence of the spectral DOS from the temperature dependence of the Fermi-Dirac (FD) distribution function, we have divided the spectra by the FD distribution function (convoluted with a Gaussian corresponding to the instrumental resolution) as indicated in Fig. 7. In the figure, we find in each spectrum the formation of a dip in the DOS at $E_F$, which becomes deeper with decreasing temperature. The magnitudes of these dips (pseudogaps) are $\sim 0.05$ and $\sim 0.1$ eV for CoSb$_{3}$ and RhSb$_{3}$, respectively. These results may indicate spectral weight transfer over large energies of order eV. This anomalous temperature dependence near $E_F$ cannot be explained by the simple band picture. Here we may suggest two candidates which can cause the above phenomena. First, we may consider electron-electron interaction between the Sb 5$p$ electrons forming the antibonding combinations of the $\pi_4$ orbitals of the Sb ring, which was reported by Jung et al. This possibility is, however, rather unlikely because of the itinerant nature of the Sb 5$p$ electrons. Second, electron-phonon interactions may be considered. It has been reported that the most prominent lines in Raman spectra of CoSb$_{3}$ and RhSb$_{3}$ are due to the Sb$_{4}$-ring breathing modes and their energy is $\sim 0.02$ eV which may modulate the electronic states around the valence-band maximum with decreasing temperature from 300 K. Indeed, Sofo and Mahan reported that small changes in the positions of the Sb atoms affect strongly the electronic structures near $E_F$. Further studies are necessary to elucidate the origin of the unusual observations.

![Graph 1](image1.png)

FIG. 6. Temperature-dependent photoemission spectra of CoSb$_{3}$ and RhSb$_{3}$ in the region near $E_F$. The spectra have been normalized to the area between -0.2 and 2 eV for CoSb$_{3}$, and between -0.2 and 4 eV for RhSb$_{3}$.

![Graph 2](image2.png)

FIG. 7. Temperature-dependent spectral DOS, which have been obtained by dividing the spectra in Fig. 6 by the Fermi Dirac distribution function.
IV. CONCLUSION

We have performed the photoemission study of Co(Sb$_{1-x}$Te$_x$)$_3$ ($x = 0, 0.02, 0.04$) and RhSb$_3$. The top of the valence band of CoSb$_3$ is of Sb 5$p$ character hybridized with Co 3$d$ state just below it. The photoemission spectra of CoSb$_3$ were well reproduced by the band-structure calculation, which suggests that electron correlation does not play an important role in the electronic structure of CoSb$_3$. When Te is substituted for Sb and electrons are doped into CoSb$_3$, the photoemission spectra are rigidly shifted to higher binding energies. From this spectral shift, we have estimated the band gap of CoSb$_3$ to be 0.03-0.04 eV, which is consistent with the transport experiments. The spectra of RhSb$_3$ are similar to CoSb$_3$ to some extent, whereas some differences are caused by the wider band width of Rh 4$d$. Unusual temperature-dependence has been observed for the spectra of CoSb$_3$ and RhSb$_3$ in the region near $E_F$, which we tentatively attribute to the effect of Sb$_4$-ring breathing phonons.

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