

Valence-band structure of the skutterudite compounds CoAs_3 , CoSb_3 , and RhSb_3 studied by x-ray photoelectron spectroscopy

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The valence-band structure of CoAs_3 , CoSb_3 , and RhSb_3 with a skutterudite-type crystal structure has been investigated by x-ray photoelectron spectroscopy. The photoemission spectra are compared with recent density-of-states calculations. Our photoemission spectra results and theoretical results are in good agreement for the energy positions in the metal d states and the pnictogen p states, but relatively large differences are found for the positions in the pnictogen s states. Based on our photoemission spectra, the electronic bonding states and the chemical trends are explained qualitatively in terms of a simple tight-binding model. The double localized and itinerant nature of the metal d states is also discussed in relation to the properties of the skutterudites. The metal d -derived density of states feature is clearly observed at about 1.2-, 1.4-, and 2.4-eV binding energies for CoSb_3 , CoAs_3 , and RhSb_3 , respectively. From the point of view of the crystal-field effects, it can be considered that this d -character band originates predominantly from the d orbitals with T_{2g} symmetry, while d orbitals with E_g symmetry hybridize strongly with the p orbitals forming the conduction band. Since the t_{2g} states are considered to be almost completely filled, corresponding to the zero spin $S=0$ state ($^1A_1, t_{2g}^6$), most of skutterudites exhibit diamagnetic properties. On the other hand, the slight chemical shifts of the core levels as compared with the pure elements indicate a small charge transfer from metal to pnictogen atoms in the skutterudites, leading to hybridization between metal d states and pnictogen p states. p - d hybridization causes not only a substantial screening of atomic Coulomb interactions at metal sites, but also a strong covalent bonding in these materials. Concerning a particular point of the band structure in skutterudites, our photoemission spectra near the valence-band edge show clear experimental evidence of a small density of states around the Fermi level due to a single band crossing the pseudogap.

I. INTRODUCTION

Some compounds with a skutterudite-type crystal structure (the body-centered-cubic structure; space group $Im\bar{3}$) and with the general formula MX_3 , where $M = \text{Co, Rh, Ir}$ and $X = \text{P, As, Sb}$, have been identified as candidates for advanced thermoelectric materials.¹⁻³ Most of the compounds in this family have good semiconducting properties, especially extremely high hole mobility (ranging from 2000 to 8000 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature),⁴⁻⁸ and diamagnetic properties.^{4,5,9-11} Among the skutterudite compounds, CoSb_3 recently received special attention because of the relatively high thermoelectric figure of merit for use in thermoelectric applications at high temperatures.^{6,12-14} It is indispensable to know the band structure (electronic bonding) for understanding the interesting properties of these materials, which depend strongly on the crystal structure. As shown in Fig. 1, a skutterudite-type crystal structure is characterized by the formation of four-membered pnictogen rings (X_4) that are located in the centers of cubes formed by metal atoms.^{15,16} For every four metal cubes, there is one empty cube, without an X_4 ring. The X_4 rings are arranged in mutually orthogonal linear arrays that run parallel to each crystallographic direction. Each pnictogen is located in a distorted tetrahedral environment formed by two pnictogens and two transition metals. Furthermore, the skutterudite structure can be described as consisting of distorted MX_6 octahedra (local

D_{3d} symmetry) sharing each corner with only one neighboring octahedron.

Dudkin¹⁵ proposed an electronic bonding model to qualitatively explain the semiconducting and diamagnetic properties of these compounds. The authors of Ref. 17 performed band-structure calculations on a prototype skutterudite by an extended Hückel tight-binding (EHTB) method. They pointed out that presence of X_4 rings in the skutterudite structure is of great importance in determining the nature of the electronic bands around the Fermi level, and therefore the transport properties. Singh and Pickett¹⁸ reported self-consistent band-structure calculations for IrSb_3 , CoAs_3 , and CoSb_3 , using an extended general potential linearized augmented-plane-wave (LAPW) method. Their calculations show that a single band crosses a pseudogap around the Fermi level, touches the conduction band minimum at the Γ point in CoAs_3 and IrSb_3 , and almost touches it in CoSb_3 . Thus IrSb_3 and CoAs_3 are predicted to be zero-gap semiconductors; CoSb_3 has a very narrow direct gap of 50 meV. For skutterudite antimonides, the single band crosses over to a linear behavior extremely close to the band edge. These results are in substantial agreement with those obtained by recent band calculations using different methods and approximations.¹⁹⁻²³ Furthermore, they pointed out that this unique electronic structure yields interesting transport effects, for example, doping dependencies of the hole mobility and Seebeck coefficient different from ordinary semiconductors with parabolic bands. The detailed analyses of the trans-

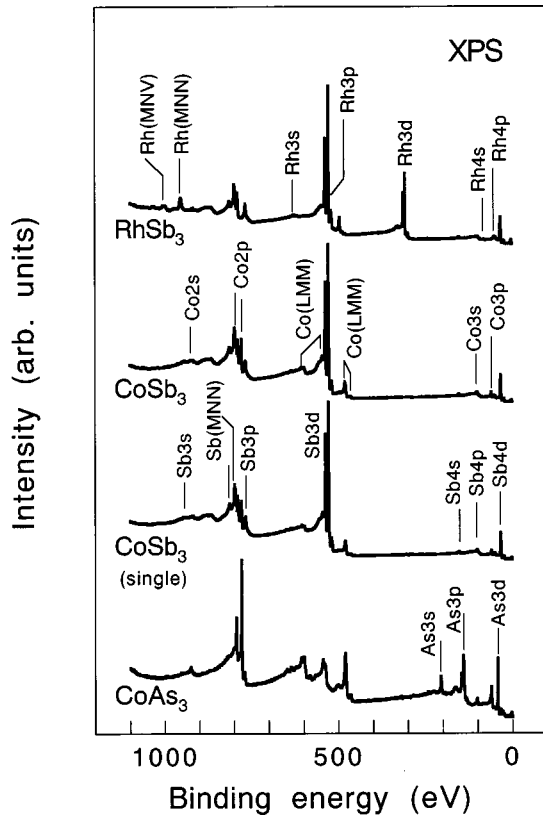


FIG. 2. Wide-scan photoemission spectra for CoAs_3 , CoSb_3 , and RhSb_3 polycrystals, and a CoSb_3 single crystal.

III. RESULTS AND DISCUSSION

Figure 2 shows wide-scan x-ray photoemission spectra for CoAs_3 , CoSb_3 , and RhSb_3 polycrystals, and CoSb_3 single crystal. The photoemission spectrum for a CoSb_3 polycrystal is almost identical with that for a CoSb_3 single crystal, indicating that the crystallographic quality of the polycrystal is as high as that of the single crystal. To obtain information concerning the bonding states of these compounds, we took into account the energy positions of selected core levels. Figure 3 shows the photoemission spectra of $\text{Co } 2p_{3/2}$ and $2p_{1/2}$ core levels for pure Co, CoAs_3 and CoSb_3 polycrystals, and a CoSb_3 single crystal. Figure 4 shows the photoemission spectra of $\text{Sb } 3d_{5/2}$ and $3d_{3/2}$ core levels for pure Sb, CoSb_3 , and RhSb_3 polycrystals, and a CoSb_3 single crystal. The binding energy values of the core levels for Co and Sb metals are almost equal to the reported values ($\text{Co } 2p_{3/2} = 777.9 \text{ eV}$, $\text{Co } 2p_{1/2} = 792.95 \text{ eV}$, $\text{Sb } 3d_{5/2} = 528.05 \text{ eV}$, and $\text{Sb } 3d_{3/2} = 537.40 \text{ eV}$).²⁸ In comparison to the standards of Co and Sb metals, the photoemission lines in the $\text{Co } 2p$ and $\text{Sb } 3d$ core-level spectra for CoSb_3 shifted to somewhat lower binding energies (about -0.2 eV). However, the binding energies of the core levels in CoAs_3 and RhSb_3 were slightly higher (about $0.1\text{--}0.2 \text{ eV}$) than the standard values in the constituent metals.²⁸ The chemical shifts of the core levels can be qualitatively explained in terms of the differences in the electronegativity between constituent atoms (e.g., the electronegativity in Pauling's model: $\text{Co}=\text{Sb}<\text{As}<\text{Rh}$). Thus the small core-level shifts suggest a small charge transfer between transition metal and pnictogen atoms in these skutterudite compounds. In addition, the dif-

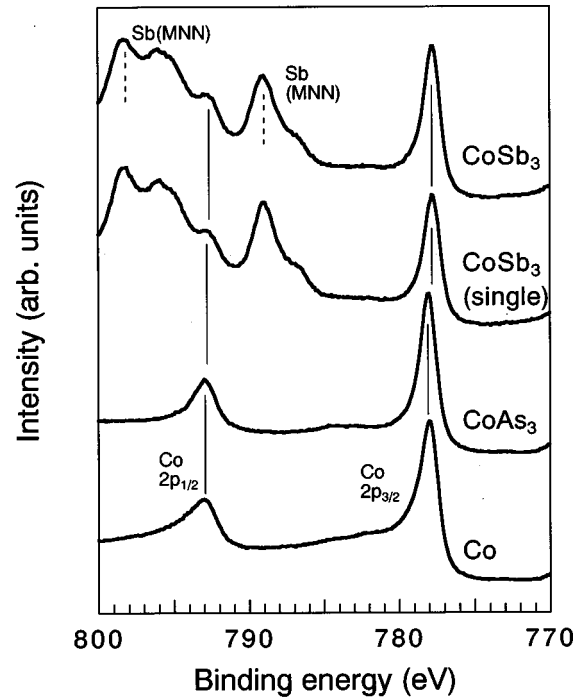


FIG. 3. $\text{Co } 2p_{3/2}$ and $2p_{1/2}$ core-level spectra for Co, CoAs_3 , and CoSb_3 polycrystals, and a CoSb_3 single crystal.

ferences in the spin-orbit splitting of the core levels between CoAs_3 and CoSb_3 and between CoSb_3 and RhSb_3 were found very small (less than 0.05 eV). From a systematic investigation of the photoemission spectra in III-V and II-VI compounds, Ley *et al.*²⁹ reported that the change in the spin-orbit splitting of core levels is caused by the coupling of the spin-orbit interaction with the crystal-field interaction. Thus our data suggest that the effect of crystal fields on the spin-orbit

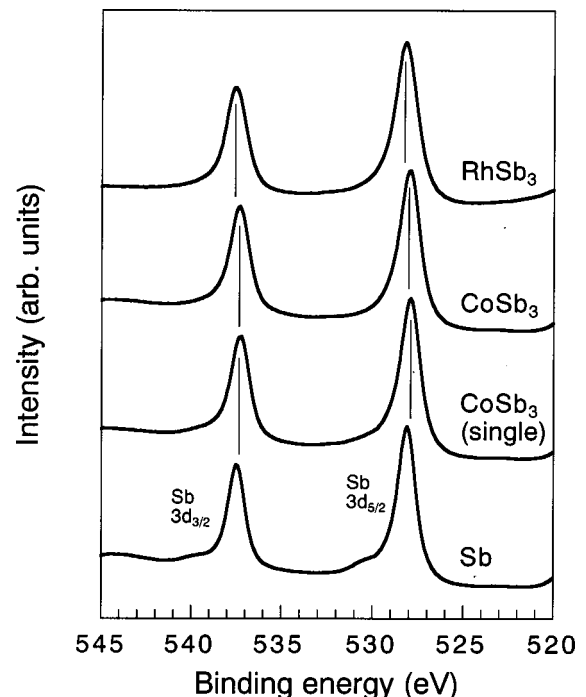


FIG. 4. $\text{Sb } 3d_{5/2}$ and $3d_{3/2}$ core-level spectra for Sb, CoSb_3 , and RhSb_3 polycrystals, and a CoSb_3 single crystal.

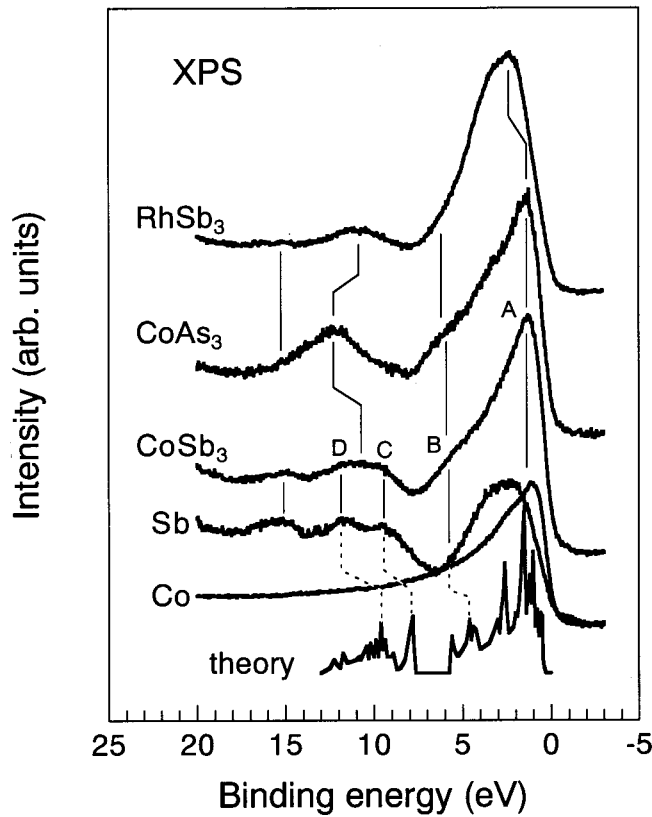


FIG. 5. X-ray photoemission spectra of the valence band for CoAs_3 , CoSb_3 , and RhSb_3 polycrystals, and the density of states calculation for CoSb_3 (Ref. 21). The photoemission spectra for Co and Sb metals are also shown as references.

splitting is small in skutterudite compounds. When the transition metals Co and Rh in the octahedral crystalline fields formed by pnictogens have a high ionic charge number (i.e., trivalent states Co^{3+} and Rh^{3+} , ionic formula $M^{3+}X_3^{-1}$), one can expect large chemical shifts of the photoemission lines in the core-level spectra and a strong crystal-field effect. For example, large chemical shift about 3 eV to higher binding energy is observed for Co $2p_{3/2}$ core level of a typical complex $[\text{Co}(\text{NH}_3)_6]^{3+}$,²⁸ in which Co is well known to be trivalent zero spin state (Co^{3+} , $S=0:t_{2g}^6$) due to large crystalline field splitting. Therefore, it is suggested that the small chemical shifts and the suppression of the crystal-field effect in skutterudite compounds can be explained in terms of the screening effect. This screening effect is probably due to the hybridization of transition-metal d orbitals with pnictogen p orbitals (covalent bonding between pnictogens and transition metals) and/or strong pnictogen-pnictogen covalent bonding in the X_4 rings. EHTB calculations show that π -type bonding of the X_4 rings and the coupling of the X_4 rings through the interaction between p orbitals of pnictogens and s and p orbitals of transition metals play an important role in electronic bonding of skutterudite compounds.^{17,19,20}

Figure 5 shows the x-ray photoemission spectra of the valence band for CoAs_3 , CoSb_3 , and RhSb_3 polycrystals, and the valence-band density of states calculation for CoSb_3 made by Sofo and Mahan.²¹ As is the case for the core-level spectra, the valence-band photoemission spectra for CoSb_3 polycrystals with different grain sizes were the same as that

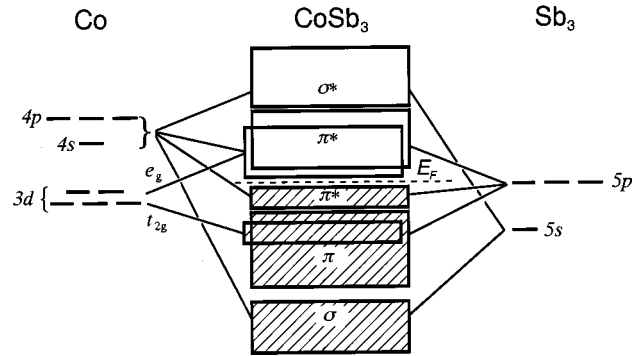


FIG. 6. A tight-binding energy-level scheme for CoSb_3 , in which only important bonding states are shown and nonbonding states are neglected, on the basis of extended Hückel tight-binding calculations (Refs. 17, 19, and 20).

for the single crystal. Thus we neglect the effects of grain size on the photoemission spectra of the valence band. The observed valence-band structures can be roughly divided into two separate binding-energy regions: the first one ranging from approximately 15 to 8 eV, the other from 8 eV to the top of the valence band. As indicated by A, B, C, and D in Fig. 5, the important features in the valence-band spectra agree qualitatively with those in the density of states calculation for CoSb_3 . Since these results also agree in the main features qualitatively well with those obtained from EHTB calculations,^{17,19,20} we discuss the bonding states in these materials on the basis of a simple tight-binding energy scheme, as shown in Fig. 6. According to the EHTB calculations,^{17,19,20} the lower-energy region in the valence band is due basically to the σ -bonding orbitals of the pnictogen X_4 rings with a large contribution of the pnictogen s orbital. The higher-energy region is formed mainly by both nonbonding and bonding π -type molecular orbitals of the X_4 rings. The conduction band is due mainly to antibonding molecular orbitals of the X_4 rings, of both π -type (lower-energy band) and σ -type (higher-energy band) molecular orbitals. d orbitals with the T_{2g} symmetry of the transition metal form a relatively narrow band below the top of the valence band. On the other hand, the metal d orbitals with E_g symmetry hybridize strongly with the p orbitals forming the lower part of the conduction band. One of the interesting features in the band structure is that a single band (the top of the valence band) at the Γ point in the pseudogap region is formed by the π -type antibonding orbital of the X_4 rings. Note that these π -type antibonding orbitals cannot combine with the d orbitals of the metal atom, but they can combine with p orbitals because of the local symmetry.

The photoemission structures C and D, characteristics of the s -derived bands, were clearly observed at about 9.4 and 11.8 eV for CoSb_3 and rather broad structures centered at 10.8 eV for RhSb_3 . The s -derived structures observed for CoSb_3 agree well with those for pure Sb, but are different from those for the band calculation in the energy positions, perhaps because of the problem of approximations in the band calculations. These s -derived structures shift to higher binding energy when the pnictogen sites change from Sb to As. This energy shift of the s -derived bands can be explained qualitatively in terms of the tight-binding model, as expected from chemical trends.

Strong photoemission peaks were clearly observed at about 1.2- and 1.4-eV binding energies for CoSb₃ and CoAs₃, respectively, in good agreement with the peak position observed for metal Co. For RhSb₃ the main peak appeared at about 2.4-eV binding energy. The agreement in the valence-band structure between photoemission spectra and the density of states calculation is quite good in the binding energy range of 0–6 eV. In addition, the projection of the density of states for the metal atoms clearly shows that the strong peak of the *d*-derived states appears in a binding-energy range of about 1–3 eV.^{18–20} Therefore, the main peak is attributed to the large contributions of the transition-metal *d* orbitals with T_{2g} symmetry to the density of states. On the basis of the tight-binding picture, the change in the energy position of the main peak from around 1.3 eV for CoSb₃ and CoAs₃, to 2.4 eV for RhSb₃, can be explained by the differences in the ionization potential between the transition-metal atoms. The shoulders (denoted by *B*) of the main peaks are probably attributed to the *p* states of the X_4 rings, and their positions are almost independent of the pnictogen, in contrast to the pnictogen dependence of the *s*-derived bands.

These is also a special interest in the nature of the transition-metal *d* states (localized and itinerant character) in skutterudite compounds, which is a crucial problem for a better understanding of the diamagnetic and transport properties of these materials. The crystal-field effect plays a more important role in semiconductors than in metals, and the strength of the electron coupling within a d^N subshell strongly depends on the site symmetry. From this point of view, we discuss *d* states of the transition metals in the skutterudite compounds. The octahedral crystalline field formed by pnictogens in the skutterudite structure causes the splitting of the metal *d* states into the triplet t_{2g} states (lower energy) and the doublet e_g states (higher energy). From symmetry considerations, t_{2g} states are only slightly broadened by hybridization, but e_g states hybridize strongly with the pnictogen *p* states. Akai and Matsuura^{22,23} performed a band calculation of CoSb₃ by the full-potential LAPW method, and discussed the Co 3*d* states in detail.³⁰ Calculations of 3*d*-derived components show that the energy gap between 3*d*-derived bands with t_{2g} -like character (below the Fermi level) and bands with the e_g -like character (above the Fermi level) is approximately 1 eV for CoSb₃ (corresponding to the pseudogap value).³⁰ This result agrees qualitatively with that obtained from the tight-binding model. In a zeroth-order approximation, it may be inferred that the energy gap between *d*-derived bands is caused by the crystal-field effect. In the tight-binding model, since t_{2g} states are located inside the valence band, these states are considered to be almost completely filled, and therefore correspond to the zero spin $S = 0$ state ($^1A_1, t_{2g}^6$), resulting in the diamagnetic properties of skutterudite compounds. According to ligand field theory, the energy (Tanabe-Sugano) diagram for the electron configuration d^6 shows that the ground state changes from a high-spin state ($^5T_2, t_{2g}^4e_g^2$) to a low-spin state ($^1A_1, t_{2g}^6$) when the crystalline field splitting $10Dq$ increases more than about 2.6 eV.³¹ Thus the energy gap between the t_{2g} - and e_g -like character bands is considerably smaller than the crystalline field splitting $10Dq$ in the localized picture. This problem is one of interesting topics in the skutterudite com-

pounds. To obtain detailed information, we need to further investigate the *d* states of transition metals in skutterudite compounds by x-ray absorption spectroscopy, resonant photoemission spectroscopy, etc. Furthermore, we need to analyze the energy levels by taking into account the effects of the hybridization of *d* orbitals, e.g., the configuration interaction (CI). The nature of 3*d* states of transition metals was extensively investigated in the semimagnetic semiconductors such as $Cd_{1-x}Mn_xTe$, and the CI theory can give a unified description of the double localized and itinerant nature of the 3*d* states in the materials.^{32,33} On the other hand, the hybridization of metal *d* states with pnictogen *p* states (the itinerant nature of the *d* states) in the skutterudite compounds is caused by the low charge transfer Δ due to small differences in the electronegativity between the metal and pnictogen atoms. This *p-d* hybridization effect results in not only a substantial screening of the atomic Coulomb interactions U at the metal sites, but also in strong covalent bonding in these materials. As discussed before, the core-level spectra (the small chemical shifts of core levels) strongly support these arguments. Slack³⁴ pointed out that the covalent nature of the bonds is of importance in selecting promising candidates for thermoelectric materials from a consideration of the average electronegativity differences, which is defined by the chemical compositions and the crystal structures of materials. According to his model, electronegativity differences in skutterudite compounds are smaller than those in an ordinary binary semiconductor GaAs with high carrier mobility. In fact, our lightly doped samples have an extremely high hole mobility ranging from 2000 to 6000 $cm^2 V^{-1} s^{-1}$ at room temperature, as shown in Table I. This is closely related to the strong covalent nature of the bonding.

The authors of Ref. 35 proposed a theory for describing band gaps and electronic structures of transition-metal compounds in terms of the *d-d* Coulomb and exchange interactions U and the charge transfer Δ . According to their theory, skutterudite compounds belong to charge-transfer-type semiconductors ($U > \Delta$), in which the band gap E_{gap} is proportional to Δ ; holes are light (anion valence band) and electrons are heavy (*d* bands); the energy scheme is shown in Fig. 7. Thus it is considered that the narrow band gap or zero gap in skutterudite compounds is closely related to the small charge-transfer energy (the small electronegativity difference). In addition, the trends in the effective mass predicted from this theory agree qualitatively with experiments.^{4–6,8,14,24–26} Since the electron configuration and the electronegativity are factors determining the parameters U and Δ , which are closely related to the electronic properties, the consideration of these parameters is important for the optimization of skutterudite compounds as good thermoelectric materials.

One of the important features in the electronic structure, as pointed by Singh and Pickett,¹⁸ is that a single band which exhibits a linear dispersion along different high-symmetry directions of the Brillouin zone exists in the pseudogap region. Several authors^{4,6} already reported on experimental evidence that transport properties of *p*-type CoSb₃ are modified by this linear dispersion of the single band from those expected for ordinary semiconductor behavior. Thus we investigated the contribution of a single band to valence-band structures for skutterudite compounds. Figure 8 shows a close-up of the photoemission spectra around the top of the valence band for CoAs₃, CoSb₃, and RhSb₃ polycrystals, and

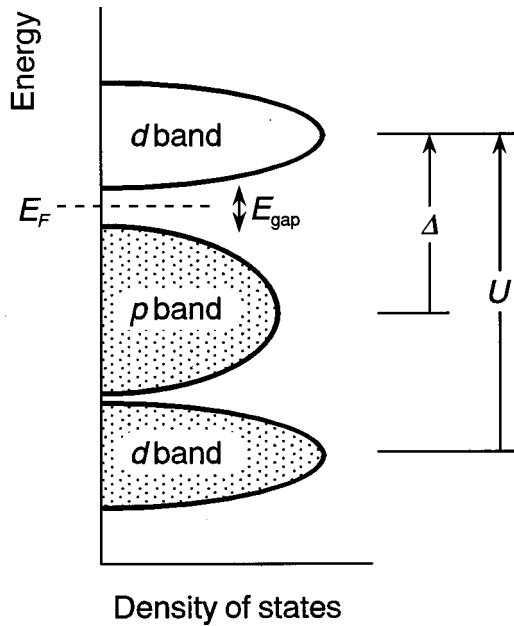


FIG. 7. An energy diagram for charge-transfer-type band structure according to the theory (Ref. 35), in which the d - d Coulomb and exchange interactions U are larger than the charge transfer Δ . For skutterudite compounds, the p band corresponds to the single band formed by π -type antibonding p orbitals of the pnictogen rings, and the lower and higher d bands correspond to the t_{2g} and e_g states of metal d orbitals, respectively.

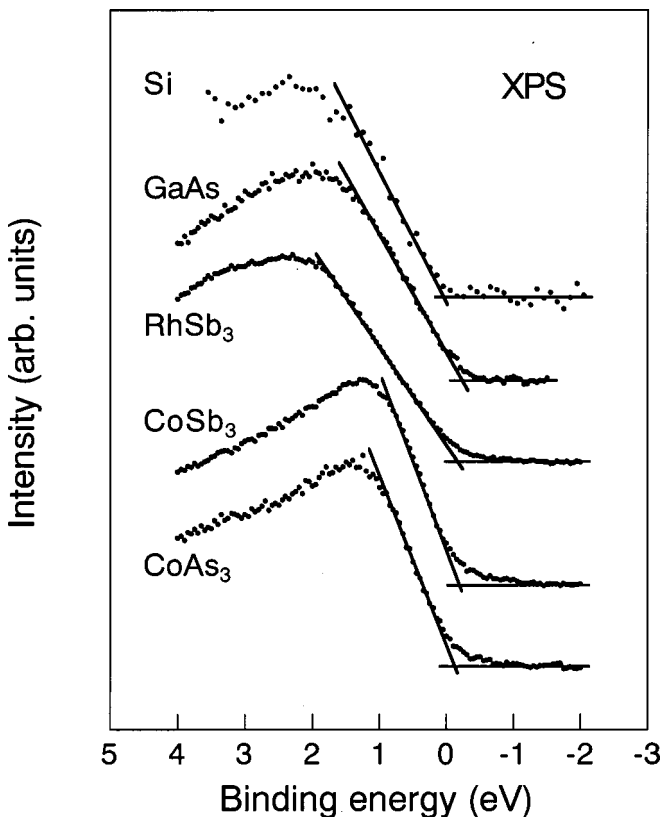


FIG. 8. Close-up of valence-band photoemission spectra near the band edge for CoAs_3 , CoSb_3 , and RhSb_3 polycrystals, and those for typical semiconductors Si and GaAs with parabolic bands.

those for typical semiconductors Si and GaAs with parabolic bands. In comparison with the sharp edges of the valence-band spectra for Si and GaAs, long tails (broadening of the edges) are clearly seen for skutterudite compounds. Band calculations show that the density of states in the pseudogap region is relatively small due to the small contribution of the single band.^{18,20,21} Therefore, the observed feature in the photoemission spectra show experimental evidence of the low density of states in the pseudogap region of the band structure for these materials.

IV. CONCLUSION

We have experimentally determined the valence-band electronic structures of CoAs_3 , CoSb_3 , and RhSb_3 by x-ray photoelectron spectroscopy. The observed band structures agree substantially with recent band-structure calculations, except for the relatively large differences in the energy position of the s states of pnictogen rings. Based on photoemission spectra, electronic bonding states and chemical trends are explained qualitatively well in terms of a simple tight-binding model. We have also discussed the relation of the double localized and itinerant nature of transition-metal d states to the properties of skutterudite compounds. The large contribution of the metal d orbitals to the density of states was clearly observed at about 1.2-, 1.4-, and 2.4-eV binding energies for CoSb_3 , CoAs_3 , and RhSb_3 , respectively. From the point of view of crystal-field theory, this metal d contribution can be considered to originate predominantly from the triplet t_{2g} states split by the octahedral crystalline field formed by pnictogens in the skutterudite structure, while doublet e_g states hybridize strongly with pnictogen p states forming the conduction band. Since t_{2g} states are considered to be almost completely filled, and correspond to the zero spin $S = 0$ state (1A_1 , t_{2g}^6), most skutterudite compounds exhibit diamagnetic properties. On the other hand, small chemical shifts of the photoemission lines of core levels strongly suggest that the hybridization of the metal d states with pnictogen p states is caused by the low charge transfer due to small differences in the electronegativity between the metal and pnictogen atoms. This p - d hybridization effect plays a dominant role in not only a substantial screening of atomic Coulomb interactions at metal sites but also in the strong covalent bonding in these materials. As pointed by Singh and Pickett from band calculations,¹⁸ one of the important features of the electronic structure is a single band with a linear dispersion in the pseudogap region. By comparing with data for typical semiconductors Si and GaAs with the parabolic bands, our photoemission spectra show clear experimental evidence that the contribution of the single band to the density of states is small in the pseudogap region for these materials. Finally, inverse-photoemission studies of skutterudite compounds will directly determine the conduction-band structure, and the resonant photoemission spectroscopy is needed to obtain detailed information about the metal d contribution to the electronic structure.

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