Importance of conduction electron correlation in a Kondo lattice, Ce$_2$CoSi$_3$

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Abstract

Kondo systems are usually described by the interaction of the correlation induced local moments with the highly itinerant conduction electrons. Here, we study the role of electron correlations among conduction electrons in the electronic structure of a Kondo lattice compound, Ce$_2$CoSi$_3$, using high resolution photoemission spectroscopy and ab initio band structure calculations, where Co 3d electrons contribute in the conduction band. High energy resolution employed in the measurements helped to reveal the signatures of Ce 4f states derived Kondo resonance features at the Fermi level and the dominance of Co 3d contributions at higher binding energies in the conduction band. The lineshape of the experimental Co 3d band is found to be significantly different from that obtained from the band structure calculations within the local density approximations, LDA. Consideration of electron–electron Coulomb repulsion, $U$, among Co 3d electrons within the LDA + $U$ method leads to a better representation of experimental results. The signature of an electron correlation induced satellite feature is also observed in the Co 2p core level spectrum. These results clearly demonstrate the importance of the electron correlation among conduction electrons in deriving the microscopic description of such Kondo systems.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The study of Ce-intermetallics has drawn significant attention during the past few decades due to the observation of many unusual properties such as valence fluctuations, Kondo screening, and heavy fermion superconductivity in these systems [1, 2]. Such properties arise due to the proximity of the Ce 4f level to the Fermi level, leading to strong hybridization between the Ce 4f states and the conduction electronic states [3]. Such a hybridization often leads to a logarithmic enhancement of electrical resistivity at low temperatures in contrast to a decrease expected in a metal. This is known as the Kondo effect [4]. In the case of strong Kondo coupling, the antiparallel coupling of the Ce moment with the conduction electrons forms a singlet ground state called a Kondo singlet that manifests as a sharp feature (Kondo resonance feature) in the electronic structure in the vicinity of the Fermi level, $\epsilon_F$, below a characteristic temperature, $T_K$ [5]. A lot of success has been achieved to describe these systems within the Anderson impurity models [6–16]. Here, the parameters defining the hybridization between 4f states and valence electronic states are often estimated using band structure calculations based on local density approximations (LDA).

The scenario can be different if these materials contain transition metals: the electron–electron Coulomb repulsion strength among d electrons forming the conduction band is finite. Since electron correlation induced effects in the electronic structure are underestimated in the LDA calculations, the applicability of the band structure results within LDA to derive the hybridization parameters is questionable. Moreover, electron correlation among conduction electrons is expected to influence the Kondo coupling strength and call for the need to go beyond LDA prescriptions to capture the electronic structure of these systems. However, in almost all the previous studies of such Ce-intermetallic systems [6–11], the conduction band is described within the LDA approach with an implicit assumption that such electron correlations have negligible influence on the electronic structure of these systems.
A Kondo lattice compound, Ce2CoSi3, is a good candidate to address this issue. Ce2CoSi3 crystallizes in a AlB2 derived hexagonal structure (space group P6/mmm) and is a mixed valent (Kondo lattice) compound [17–19]. The estimated Kondo temperature, \( T_K \), is found to be higher than 44 K. Substitution of Rh at Co sites leads to a plethora of interesting features due to the increasing dominance of indirect exchange interactions [19]. For example, a \( x = 0.4 \) composition in Ce2Co1-xRhxSi3 exhibits quantum critical behavior. Intermediate compositions having higher Rh concentration exhibit the signature of a spin density wave (SDW) state [19]. Rh substitution at the Co sites is expected to change the electronic structure significantly. For example, (i) larger radial extension of the Rh 4d orbitals relative to that of Co 3d orbitals leads to a reduction in electron correlation strength. (ii) The binding energy of Rh d states is usually higher than the binding energy of Co d states. (iii) Rh substitution for Co leads to a marginal increase in lattice constant which will tend to reduce the d–f hybridization strength, while the larger radial extension of 4d states will make the hybridization stronger. Clearly, a change in d electronic states corresponding to these transition metals has a profound role in determining the electronic properties in this interesting class of compounds.

In this paper, we report our results of investigation of the electronic structure of Ce2CoSi3 using high resolution photoemission spectroscopy and \textit{ab initio} band structure calculations. The high energy resolution employed in our measurements enabled us to reveal a Kondo resonance feature and the corresponding spin orbit split satellite. The comparison of the experimental spectra and the calculated ones indicates that the correlation strength among Co 3d electrons is significant (\( \sim 3 \) eV). The band structure results within the local density approximations indicate the significant influence of Co 3d electron correlation on Co 3d–Ce 4f hybridization.

### 2. Experimental details

Ce2CoSi3 was prepared by melting together stoichiometric amounts of high purity (>99.9%) Ce, Co and Si in an arc furnace. The single phase was confirmed by the absence of impurity peaks in the x-ray diffraction pattern. The specimen was further characterized by scanning electron microscopy measurements and energy dispersive x-ray analysis [19]. The photoemission measurements were performed using a Gammadata Scienta SES2002 analyzer and monochromatic laboratory photon sources. The energy resolutions were set to 0.4 eV, 5 meV and 5 meV at Al K\( \alpha \) (1486.6 eV), He I\( \alpha \) (40.8 eV) and He II (21.2 eV) photon energies, respectively. The base pressure in the vacuum chamber was 3 \( \times \) 10\(^{-11} \) Torr. The temperature variation down to 20 K was achieved by an open cycle He cryostat, LT-3M from Advanced Research Systems, USA. The sample surface was cleaned by \textit{in situ} scraping using a diamond file and the surface cleanliness was ensured by the absence of O 1s and C 1s features in the x-ray photoelectron (XP) spectra and the absence of impurity features in the binding energy range of 5–6 eV in the ultraviolet photoelectron (UP) spectra. The reproducibility of the spectra was confirmed after each trial of the cleaning process.

### 3. Calculational details

The electronic band structure of Ce2CoSi3 was calculated using a \textit{state-of-the-art} full potential linearized augmented plane wave (FLAPW) method using WIEN2k software [21] within the local density approximations, LDA. The convergence for different calculations was achieved by considering 512 \( k \) points within the first Brillouin zone. The error bar for the energy convergence was set to <0.2 meV per formula unit (f.u.). In every case, the charge convergence was achieved to be less than 10\(^{-3} \) electronic charge. The lattice constants used in these calculations are determined from the x-ray diffraction patterns considering a AlB2 derived hexagonal structure and are found to be \( a = 8.104 \) Å and \( c = 4.197 \) Å [17]. The muffin-tin radii (\( R_{MT} \)) for Ce, Co and Si were set to 2.5 au, 2.28 au and 2.02 au, respectively.

### 4. Results and discussions

The valence band in Ce2CoSi3 consists of Ce 5d, Ce 4f, Co 3d and Si 3p electronic states. Since the transition probability of the photoelectrons in the photo-excitation process strongly depends on the excitation energies, a comparison of the photoemission spectra collected at different excitation energies would help to identify experimentally the character of various features constituting the valence band. In figure 1(a), we show the valence band spectra collected at 20 K using the Al K\( \alpha \) photon energy. The He I\( \alpha \) and He II\( \alpha \) spectra are shown in figure 1(b). In order to compare the spectral functions, it is important to subtract a suitable background from the raw data. The background function in the experimental spectra arises due to the inelastic scattering of the photoelectrons and hence depends on the photoemission signal. This can be estimated by proportionating the background intensity at a particular energy to the integral area under the curve till that energy from the higher kinetic energy side. This is found to be quite successful in estimating the background function in a small energy window. We have, thus, subtracted such an integral background from Al K\( \alpha \) and He II\( \alpha \) spectra, as shown in figure 2. Since the thermalized electrons lead to a large increase in background at low kinetic energies, the background function in the He I spectrum are found to be better defined by a quadratic polynomial (\( b(\epsilon) \propto \epsilon^2, \epsilon = \text{binding energy} \)) as shown in figure 2(a). Evidently, the background contribution in the energy range 0–3 eV binding energies is quite small in every case indicating negligible influence on the conclusions. Moreover, the conclusion of electron correlation is based on the calculated spectra for the XP spectrum where the background contribution is quite small and well defined by the integral functional form.

In figure 1(b), the intensity close to the Fermi level, \( \epsilon_F \), exhibits significantly different behavior as a function of...
Figure 1. Valence band spectra collected using (a) Al Kα (XPS), and (b) He II and He I excitation energies. The solid line in (a) represents the broadened He II spectrum to take into account the energy resolution corresponding to the XP spectrum. The dashed line represents the calculated XP spectrum as described later in the text. (c) The Ce 4f spectral function obtained by subtracting the HeI spectrum from the He II spectrum. The distinct features, S and K, corresponding to the spin orbit satellite of the Abrikosov–Suhl resonance (ASR) and the main peak of ASR, respectively, could clearly be identified [23].

In addition to the resonance feature at $\epsilon_F$, each spectrum exhibits two distinct features, A and B at about 2.3 eV and 1 eV binding energies, respectively. The relative intensity of these features does not change, although the incident photon energy is changed from Al Kα to He I. This is an important observation as the photoemission cross sections corresponding to Ce 5d, Ce 4f, Co 3d and Si 3p electronic states have significantly different excitation energy dependence [22]. To verify the change in lineshape with better clarity, we have broadened the He II spectrum by convoluting a Gaussian of full width at half maximum (FWHM) = 0.4 eV to make the resolution broadening comparable to that of the XP spectrum. The broadened spectrum is shown as a solid line superimposed over the XP spectrum in figure 1(a). The lineshapes of both the spectra are almost identical. In figure 1(b), the He I and He II spectra are superimposed over each other to investigate the change in lineshape when the energy resolution broadening is the same ($\sim$5 meV). The spectra in the binding energy range beyond 1 eV are found to be almost identical.

All the above observations are interesting and can not be associated to the surface preparation via scraping for the following reasons. Using scraping, one breaks the sample grains in a non-selective manner that helps to expose a clean surface for the measurements. In addition, scraping usually enhances the surface roughness. Such a process will enhance the surface contribution in the spectra. Moreover, the linewidth of the features may also get enhanced due to scraping. This latter possibility can be ruled out as it is shown experimentally [24, 25] that cleaving and scraping have insignificant influence on the spectral lineshape at
higher binding energies, as the intrinsic linewidth of these features are already large due to various lifetime effects. As for the enhancement of surface contributions, it is already known that photoemission with He I and He II photons have significant surface sensitivity (probing depth ~8–10 Å). Thus, these spectra may contain large surface contributions due to scraping. However, the Al Kα valence band spectra possess dominant bulk contributions (probing depth ~25 Å). It is experimentally found that these spectra can often be considered as representative of the bulk electronic structure [24, 26–28] suggesting that the influence of scraping will have less influence on the Al Kα spectrum. Thus, the observations of similar lineshape in the energy range of 1–3 eV binding energies in figures 1(a) and (b) suggest that the surface sensitivity in the He I and He II spectra are compensated by scraping, which is unlikely as scraping enhances surface contributions that will make the differences more prominent. The other possibility is that the surface and bulk electronic structures are quite similar and scraping has an insignificant influence on the spectral lineshape.

In order to verify the character of the features theoretically, we have calculated the electronic band structure using the FLAPW method. The calculated partial densities of states (PDOS) are shown in figure 3. The dominant contribution in this energy range arises from the Ce 5d, Ce 4f, Co 3d and Si 3p PDOS as shown in figures 3(a), (b), (c) and (d) respectively. All the other contributions are negligible in this energy range. Evidently, Ce 5d contributions are small and almost equally distributed over the whole energy range shown. The Ce 4f band is intense and narrow as expected. In order to provide clarity, we have rescaled the Ce 4f partial density of states (PDOS) by 25 times and shown it as a thick solid line in figure 3(b). The 4f PDOS contributes essentially in the vicinity of the Fermi level (<1 eV binding energy). The intensity of the Ce 4f band is significantly weak at higher binding energies. This is consistent with the observation in figure 1(b). Co 3d states also have finite contributions in this energy range due to the hybridization between Co 3d and Ce 4f states.

Co 3d and Si 3p electronic states are strongly hybridized and appear dominantly in the binding energy range larger than 0.5 eV. The bonding states contribute in the energy range higher than 2 eV binding energy, where the Si 3p PDOS has large contributions. The antibonding features appear in the energy range 0.5–2 eV, where Co 3d contributions are dominant. This suggests that the feature B in figure 1 has dominant Co 3d character and the intensities corresponding to Si 3p photoemission contribute to feature A. The dominance of Co 3d contributions shown in this whole energy range presumably leads to an unchanged spectral lineshape with the change in photon energy, as observed in figures 1(a) and (b).

In order to compare the experimental spectrum with the calculated results, we have calculated the XP spectrum in the following way: the Ce 5d, Ce 4f, Co 3d and Si 3p PDOS per formula unit were multiplied by the corresponding photoemission cross sections at Al Kα energy. The sum of all these contributions was convoluted by the Fermi distribution function at 20 K and broadened by the Lorentzian function to account for the photo-hole lifetime broadening. The resolution broadening is introduced via further broadening of the calculated spectrum by a Gaussian function of FWHM = 0.4 eV.

The calculated spectrum is shown by the dashed line in figure 4 after normalizing by the total integrated area under the curve. The intensities near εF in the experimental spectrum appear to be captured reasonably well in the calculated spectra. In the higher binding energy region, the intensity around 1 eV is overestimated and that around 2.5 eV is underestimated (see figure 1). Since this energy range contains a dominant contribution from the Co 3d states, it naturally indicates that the Co 3d PDOS region is not well described and correlations among Co 3d electrons may be important in determining the electronic structure in this energy range. In order to verify this, we have calculated the electronic density of states considering a finite electron correlation, $U_{dd}$, among Co 3d electrons. The spectral functions corresponding to different $U_{dd}$ values are calculated from the LDA + $U$ results following the procedure described above.

The lines in figure 4 represent the spectral functions for different $U_{dd}$ values which are superimposed on the experimental XP spectrum represented by open circles. In figure 4(a) we show the calculated spectra without the Ce 4f contributions, and the ones including Ce 4f contributions are shown in figure 4(b). The feature C appearing near εF is better defined when Ce 4f contributions are considered. It is evident from the figure that the signature of the feature around 2.3 eV (feature A) becomes more and more prominent.
with the increase in $U_{dd}$. Consequently, the intensity of feature B reduces. Thus, the feature A can be attributed to the photoemission signal from electron correlation induced Co 3d bands (lower Hubbard band) in addition to the Si 3p contributions. It is to note here that although the feature A has comparable contributions from Co 3d and Si 3p states from band structure calculations, the photoemission intensity from the Co 3d states would be larger than that of Si 3p states at XPS photon energies due to the matrix element effects.

It is clear that the calculated spectral functions corresponding to $U_{dd} \sim 3$ eV are closer to the experimental spectrum compared to all other cases. For higher values of $U_{dd}$, the correlation induced feature becomes stronger and appears at higher binding energies. The finding of such a correlation among Co 3d electrons is not unrealistic as it is often found in the literature that Co 3d electrons are quite strongly correlated [30–34]. It worth noting here that the estimation of $U_{dd}$ obtained within the LDA + $U$ calculations in this study suggests the signature of significant correlation among the Co 3d electrons. An accurate estimate of $U_{dd}$ requires further study using other methods, e.g. LDA + DMFT (DMFT = dynamical mean field theory).

Having established the presence of finite electron correlation among the Co 3d electrons, we now turn to the issue of the influence of $U_{dd}$ on the Ce 4f electronic states and thereby Kondo resonance formation. We show the calculated partial density of states (PDOS) corresponding to Co 3d and compare it with Co 3d states for $U_{dd} = 0$ and 4 eV in figure 5. To visualize the energy distribution of Ce 4f PDOS at higher binding energies, we have replotted the Ce 4f PDOS in figure 5(b) with an expanded y-scale. Evidently, the energy range and nature of distribution of the density of states corresponding to Co 3d and Ce 4f states. The change in $U_{dd}$ from 0 to 4 eV leads to a transfer of Co 3d PDOS to higher binding energies and an increase in Co 3d contributions near $\epsilon_F$. A corresponding redistribution of the Ce 4f PDOS occurs. This indicates that the hybridization between Co 3d and Ce 4f is influenced by finite $U_{dd}$.

The results in figures 4 and 5 establish the importance of $U_{dd}$ in the electronic structure of this system and its influence in the vicinity of $\epsilon_F$. Although there is a finite contribution from Co 3d PDOS near $\epsilon_F$ due to Co 4d–Ce 4f hybridization, the corresponding electronic states have dominant Ce 4f character. The electron correlation among Ce 4f electrons is strong, leading to strong local moment formation. Therefore, it is of interest to verify within the limit of local density approximations whether such an effect leads to significant spectral intensity at higher binding energies. We show the Ce 4f PDOS calculated for $U_{dd} = 0$ and 4 eV in figure 6. The unoccupied part of the spectral function exhibits a large

Figure 4. The x-ray photoemission valence band spectrum (open circles) is compared with the calculated spectral functions corresponding to different $U_{dd}$-values. (a) The calculated spectral functions without Ce 4f contributions. (b) The calculated spectral functions contains Ce 4f contributions. Clearly, the results in (b) provide a better description than that in (a) revealing the signature of Ce 4f contributions in the vicinity of the Fermi level.

Figure 5. Calculated (a) Ce 4f and (c) Co 3d partial density of states (PDOS) for $U_{dd} = 0$ eV (filled area) and 4 eV (thick lines). In (b), the same Ce 4f PDOS is plotted with an expanded y-scale to visualize the higher binding energy part. The influence of $U_{dd}$ on the Ce 4f states is clearly visible due to finite hybridization between the Co 3d and Ce 4f electronic states.
Figure 6. Calculated Ce 4f partial density of states for two different electron correlation strengths, $U_{\text{ff}}$, among Ce 4f electrons. The results corresponding to the whole energy range is shown in (a) and that near Fermi level is shown in (b).

spectral redistribution. The occupied part exhibits a change in lineshape close to the Fermi level as shown with better clarity in figure 6(b). Evidently, the 4f contributions appear essentially in the vicinity of the Fermi level even if the 4f correlations are considered.

It should be noted here that the LDA + $U$ method is often found inadequate to capture the electron correlation induced effects among strongly correlated electrons such as 4f electrons [35]. In such a case, dynamical correlation due to Coulomb interaction among 4f electrons needs to be considered, as has been done in several recent studies using the LDA + DMFT method instead of the static correlation considered in the LDA + $U$ method [36]. We hope that this work will encourage future study in this direction.

The signature of electron correlations among conduction electrons can also be observed in the core level spectra [30, 32, 37]. In figure 7, we show the Co 2p spectrum collected at 20 K using Al Kα radiation. The spectrum consists of two spin orbit split features Co 2p$^{3/2}$ and Co 2p$^{1/2}$ at 778 eV and 792.9 eV binding energies, respectively (energy separation of about 14.9 eV). These binding energies are identical to those found in elemental Co metal [38, 39]. This indicates that the valence state of Co in this material is very similar to that of the elemental Co metal. In addition, every spin orbit split feature exhibits a weak but distinct shoulder at higher binding energies. This has been shown more clearly by rescaling and shifting this energy region in the same figure. Although the satellite intensity looks small, it appears to be quite intense compared to the ones observed in earlier studies in other materials [38, 39]. The energy separation between the main peak and the satellite is about 4 eV.

It is well known that the core level spectra reveal multiple features representing differently screened final states [37]. The intense feature at lower binding energy is usually called the well-screened feature and the ones at higher binding energies are called poorly screened features/satellites. Such satellites appear due to the finite electron correlations. The finite intensity of the satellite feature in the present case, independently establishes the presence of electron correlations among Co 3d electrons as concluded from valence band spectra [37]. Thus, our results establish that the electron correlation strength among Co 3d electrons is significant and needs consideration to derive the electronic structure of these systems.

The mixed valency and/or Kondo effect depends on the Kondo coupling strength, $J \sim V_{\text{cf}}^2$, where $V_{\text{cf}}$ is the hybridization strength between the conduction and the 4f electronic states, and $\epsilon_{\text{df}}$ is the binding energy of the 4f electrons. In the present case, Co 3d electrons primarily form the conduction band and are found to be correlated. Finite electron correlation introduces local character among 3d electronic states, which means that the band dispersion will be weaker than the case without electron correlation. In addition, the formation of the lower Hubbard band at higher binding energies relative to the uncorrelated band due to the electron correlation will influence the effective energy separation between the Ce 4f band and the conduction electrons. Thus, $J$ and various hopping parameters involving Co 3d electronic states are expected to reduce, leading to an effective reduction in the degree of mixed valency of Ce.

On the other hand, we find significant $U_{\text{dd}}$ induced changes in the density of states in the energy bands formed by Co 3d–Ce 4f hybridization (see figure 5). The Co 3d contribution increases in the vicinity of the Fermi level with the
increase in \( U_{dd} \) indicating more pronounced coupling. Thus, the role of \( U_{dd} \) on Kondo resonance formation appears to be complex. An estimation of the change in hybridization parameters and consequent effect on the Kondo effect can presumably be simulated using the periodic Anderson model, which is beyond the scope of our study. We hope these results will help to initiate such activity by other groups.

5. Conclusions

In summary, we have studied the electronic structure of \( \text{Ce}_2\text{CoSi}_3 \) using high resolution photoemission spectroscopy and \textit{ab initio} band structure calculations. The experimental results indicate the dominance of Co 3d contributions in the valence band. Si 3p states appear at higher binding energies (2–3 eV). The Ce 4f contributions appear essentially in the vicinity of the Fermi level. The high resolution employed in this study helped to probe the Kondo resonance feature appearing at the Fermi level.

Although the contribution of the Co 3d states at the Fermi level is weak, Co 3d states are found to be strongly hybridized with the Ce 4f states. The comparison of the experimental results with the calculated ones reveal the distinct signature of electron correlation among Co 3d electrons, which influences the Ce 4f partial density of states. These results suggest that the description of the electronic structure and various interesting electronic properties involving such Kondo systems requires consideration of the correlation among conduction electrons.

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