Valence Band of Ce$_2$Co$_{0.8}$Si$_3$ and Ce$_2$RhSi$_3$ Studied by Resonant Photoemission Spectroscopy and FPLO Calculations

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This work presents studies of the valence band of two Kondo lattice systems: Ce$_2$Co$_{0.8}$Si$_3$ and Ce$_2$RhSi$_3$, which are paramagnetic with the Kondo temperature $T_K \approx 50$ K and Ce$_2$RhSi$_3$, which is antiferromagnetic below $T_N = 4.5$ K and exhibits $T_K \approx 9$ K. The photoemission spectra, which are obtained with photon energy tuned to Ce 4d-4f resonance, reveal a Kondo peak at the Fermi energy ($E_F$), its spin-orbit splitting partner at 0.24 eV and a broad maximum related to Ce 4f$^0$ final state. The spectra indicate that Kondo peak has a higher intensity for Ce$_2$Co$_{0.8}$Si$_3$. The off-resonance photoemission data reveal that a maximum in the 3d electron density of states is shifted towards $E_F$ for Ce$_2$Co$_{0.8}$Si$_3$ as compared to Ce$_2$RhSi$_3$. Full-potential local-orbital calculations were realized with local spin density approach + $U$ approach for 213 stoichiometry. They show that a higher density of states near $E_F$ is observed for Ce$_2$Co$_{0.8}$Si$_3$. The calculations also reveal the existing tendencies for antiferromagnetic and ferromagnetic ground states in a case of Ce$_2$RhSi$_3$ and Ce$_2$Co$_{0.8}$Si$_3$, respectively.

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1. Introduction

Cerium intermetallics exhibit a variety of ground states depending on the role played by Ce 4f electrons [1]. These electrons may possess magnetic moments in magnetically ordered phases, participate in the formation of a Kondo singlet, form heavy fermion ground states, or even are incorporated in wider bands. The first important factor determining these phenomena is hybridization between f-electrons and conduction band electrons, based on the Kondo effect. The second important factor is the Ruderman-Kittel-Kasuya-Yoshida (RKKY) exchange interaction. Strength of these interactions can be modified by chemical doping, pressure, magnetic field, etc., which can lead to quantum phase transitions (QPTs) between different ground states, with all the fundamental and exciting problems behind [2].

The investigated compounds, Ce$_2$RhSi$_3$ and Ce$_2$Co$_{0.8}$Si$_3$, crystallize in a hexagonal structure derived from AlB$_2$ type (Fig. 1). The space group is $P6/mmm$ and the lattice parameters are $a = 8.2240(12)$ Å and $c = 4.2261(8)$ Å [3]. Cerium atoms occupy two Wyckoff positions 1a (Ce1) and 3f (Ce2). Ce$_2$Co$_{0.8}$Si$_3$ with the lattice constants $a = 8.1037(7)$ Å and $c = 4.2204(3)$ Å was reported to be isostructural to Ce$_2$RhSi$_3$ [4]. In this compound, the Wyckoff 2d position is occupied by 80% of Co and 20% of Si, although the target stoichiometry in single crystal growth was Ce$_2$Co$_{0.8}$Si$_3$ [4].

Ce$_2$RhSi$_3$ is a Kondo lattice system with antiferromagnetic order below $T_N = 4.5$ K [3], low Kondo temperature $T_K \approx 9$ K and enhanced electronic specific heat $C/T = 290$ mJ/(molCe K$^2$) at 0.4 K. In turn, Ce$_2$Co$_{0.8}$Si$_3$ is paramagnetic down to 0.4 K. It exhibits properties of a Kondo lattice with coherence temperature of about 80 K, the Kondo temperature $T_K \approx 50$ K and large electronic specific heat $C/T = 290$ mJ/(molCe K$^2$) at 0.4 K [4]. Different ground states in Ce$_2$RhSi$_3$ and Ce$_2$Co$_{0.8}$Si$_3$ motivated searching for QPT in the solid solution Ce$_2$Rh$_{1-x}$Co$_x$Si$_3$ [5]. However, as demonstrated in the recent study on a single crystal of Ce$_2$Co$_{0.4}$Rh$_{0.4}$Si$_3$ [6], inherent atomic disorder prevents the occurrence of QPT and leads at low temperatures to the formation of a Griffiths phase.

Photoemission spectroscopy (PES) can deliver a single particle spectral function, which provides a more direct insight into the Kondo effect. Previous PES studies
indicated the presence of a Kondo resonance in antiferromagnetic Ce$_2$RhSi$_3$ [7] and paramagnetic Ce$_2$CoSi$_3$ [8]. It appears that the Kondo resonance has higher intensity for Ce$_2$CoSi$_3$ when compared to Ce$_2$RhSi$_3$ system with coexisting magnetic order and Kondo interaction [9]. Recently, a moment dependence of the Kondo peak was established in Ce$_2$Co$_{0.8}$Si$_{3.2}$ by means of angle-resolved photoemission spectroscopy (ARPES) [10]. This finding was interpreted as the evidence of a strong momentum dependence of the hybridization between conduction band and 4$f$ electrons.

In the current paper our investigations are focused on the electronic valence band structure of antiferromagnetic (Ce$_2$RhSi$_3$) and paramagnetic (Ce$_2$Co$_{0.8}$Si$_{3.2}$) Kondo lattices. Resonant Ce $4d \rightarrow 4f$ photoemission spectroscopy delivers a contribution of the Ce 4$f$ states to the valence band. The results are compared to theoretical calculations performed by means of full-potential local-orbital (FPLO) code.

2. Experimental

Single crystals of Ce$_2$RhSi$_3$ and Ce$_2$Co$_{0.8}$Si$_{3.2}$ were grown by the Czochralski pulling method in a tetra-arc furnace. Their synthesis and detailed characterization was described elsewhere [3, 4]. Studies of resonant photoemission spectroscopy (RESPES) were conducted at MAX-lab, Lund University, using 14 beamline of the MAX III storage ring [11]. The crystals were measured at 100 K with incident photon energies between 80 eV and 140 eV. Photoelectrons were recorded by SPECS Phoibos 100 electron analyzer with the total energy resolution of 80 meV. Band structure calculations were performed by the scalar relativistic version of the FPLO code [12] with the Perdew-Wang exchange-correlation potential [13]. Local spin-density approximation (LSDA) $+U$ was used with the around-mean-field scheme [14].

3. Results and discussion

Ce$_2$RhSi$_3$ and Ce$_2$Co$_{0.8}$Si$_{3.2}$ were investigated by means of RESPES at the Ce $4d \rightarrow 4f$ absorption edge, which occurs at the incident photon energy of approximately 120 eV. The spectra recorded with the photon energy $h\nu = 120$ eV (Fig. 2) are characterized with the enhanced intensity from Ce 4$f$ electrons when compared to the data obtained with the off-resonance photon energy, e.g. $h\nu = 114$ eV. The data were partially angle integrated. One can distinguish the Kondo peak observed near the Fermi energy ($f_{7/2}$ final state), the peak related to $f_{7/2}$ final state at 0.24 eV and a broad peak with contribution from $f^0$. The Kondo peak intensity is clearly higher for Ce$_2$Co$_{0.8}$Si$_{3.2}$, in line with stronger hybridization in this compound. This agrees with the previous PES studies [9]. The off-resonance spectra are dominated by 3$d$ electrons from Co and Rh. It is observed in the off-resonance spectra that for Ce$_2$Co$_{0.8}$Si$_{3.2}$ the maximum in density of states (DOS) is closer to $E_F$ than in the case of Ce$_2$RhSi$_3$. The present results of resonant photoemission are in qualitative agreement with the recent ARPES studies carried out for Ce$_2$Co$_{0.8}$Si$_{3.2}$ [10]. Previously, the $f_{5/2}$ and $f_{7/2}$ peaks were found to be non dispersive. A broad peak around binding energy of 2 eV was attributed to electrons from the Ce $f^0$ final states and the Co 3$d$ states [10].

Theoretical calculations were performed for both Ce$_2$RhSi$_3$ and Ce$_2$CoSi$_3$ (here assuming ideal 213 stoichiometry) by means of FPLO with LSDA+$U$ approximation. They were realized with $U_{1f} = 0$ and $U_{4f} = 6$ eV and for the ground states with parallel (ferromagnetic) and antiparallel (antiferromagnetic) orientation of the Ce magnetic moments. For Ce$_2$RhSi$_3$, the ground state energy was found lower for antiferromagnetic arrangement, whereas ferromagnetic orientation was found favored for Ce$_2$CoSi$_3$.  

![Fig. 2. Resonant photoemission spectra obtained for (a) Ce$_2$Co$_{0.8}$Si$_{3.2}$ and (b) Ce$_2$RhSi$_3$ with photon energies: $h\nu = 120$ eV (on Ce $4d \rightarrow 4f$ resonance) and $h\nu = 114$ eV (off Ce $4d \rightarrow 4f$ resonance) at the temperature $T = 100$ K.](image-url)
Fig. 3. Total and partial (corresponding to particular orbitals) densities of states (DOS) calculated by means of FPLO method for Ce$_2$CoSi$_3$ and Ce$_2$RhSi$_3$. LSDA+$U$ approximation was applied with the parameter $U = 0$ and $U = 6$ eV.
The gain in energy due to the preferred magnetic order yielded for CeRhSi$_3$ the theoretical Néel temperature $T_N$-theor = 11.8 K. The theoretical value of the Curie temperature in Ce$_2$CoSi$_3$ was $T_C$-theor = 12.3 K. $T_N$-theor is quite higher than the real $T_N$ value. On the other hand, ferromagnetic order is not realized in Ce$_2$Co$_{0.8}$Si$_{3.2}$. These results indicate certain tendencies for magnetic ordering existing in the considered materials. However, in the real systems the Kondo interaction competing with RKKY magnetic exchange results in partial or full suppression of the magnetic order. The saturation magnetic moment on Ce obtained from the calculations with $U_{4f} = 6$ eV amounted to 1.0 $\mu_B$ for both compounds. It is in reasonable agreement with the experimental value from neutron diffraction, which equals 1.3 $\mu_B$ per Ce atom [15]. Magnetic moments received from the calculations with $U_{4f} = 0$ are between 0.02 and 0.36 $\mu_B$ per Ce depending on the crystallographic site and the compound.

Figure 3 displays the total density of states (DOS) and partial DOS associated with particular orbitals obtained from FPLO calculations with LSDA+$U$. The results for Ce$_2$CoSi$_3$ with $U_{4f} = 0$ and $U_{4f} = 6$ eV are shown for the antiferromagnetic ground state. The same is for Ce$_2$RhSi$_3$ with $U_{4f} = 6$ eV. However, in the case of Ce$_2$RhSi$_3$ and $U_{4f} = 0$ the calculations always converged to the ferromagnetic ground state. In fact, for $U_{4f} = 0$, difference in the total energy between the parallel and antiparallel orientation of the Ce magnetic moments is very small and a choice of magnetic ordering may be random.

Partial DOS (Fig. 3) related to the Ce 4f orbitals is dominated by a peak at 0.3-0.4 eV above the Fermi energy for $U_{4f} = 0$. The increase of $U_{4f}$ to 6 eV splits and redistributes the 4f spectral weight. The calculated results indicate that the Co 3d and Rh 3d states have an important contribution to the valence band near $E_F$. In turn, the Si 3p states are located at relatively high binding energy. It is noteworthy that the 3d electrons of Co are closer to $E_F$ and yield higher DOS near $E_F$ as compared to the Rh 3d states. This finding is in agreement with the resonant PES results (Fig. 2).

4. Conclusions

Ce$_2$Co$_{0.8}$Si$_{3.2}$ and Ce$_2$RhSi$_3$ were studied by means of resonant photoemission spectroscopy at the Ce 4d $\rightarrow$ 4f absorption edge. The on-resonance spectra revealed enhanced contribution from the Ce 4f states. Ce$_2$Co$_{0.8}$Si$_{3.2}$ exhibits a more distinct Kondo peak in the on-resonance studies. For the Co-bearing system, a maximum of valence band intensity is shifted towards $E_F$, which is seen in both off-resonance measurements and FPLO calculations. These results imply that Ce$_2$Co$_{0.8}$Si$_{3.2}$ has higher DOS in a vicinity of the Fermi level and exhibits stronger f-ligand hybridization. The transition from antiferromagnetic Kondo lattice Ce$_2$RhSi$_3$ to paramagnetic Kondo lattice Ce$_2$Co$_{0.8}$Si$_{3.2}$ is thus accompanied by the increase in carrier density in the valence band near $E_F$.

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