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Electronic structure of $Ce_2Rh_3Al_9$

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We have investigated the XPS spectra of $Ce_2Rh_3Al_9$ and calculated the DOS by using the full potential linear augmented plane wave (FP-LAPW) and tight binding linear muffin tin orbitals (TB-LMTO-ASA) methods. The overall agreement between the calculated and measured XPS valence band spectra is good. The analysis of the 3d XPS (X-ray Photoemission) spectra, using Gunnarson–Schonhammer theory, suggests a mixed valence behaviour of Ce. FP-LAPW calculations show a half-metallic behaviour of $Ce_2Rh_3Al_9$, whereas LMTO calculations result in a semiconducting and nonmagnetic ground state. This result is, however, in contradiction to the experimental observation of resistivity $\rho(T)$, which does not show an activated behaviour. We attribute the possible appearance of a semiconducting/half-metallic gap for $Ce_2Rh_3Al_9$ to atomic disorder.

Key words: strongly correlated electron system; Kondo insulators

1. Introduction

$Ce_2Rh_3Al_9$ is known to be a nonmagnetic heavy fermion (HF) compound [1, 2] which also shows features of mixed valence (MV) Ce-compounds in its magnetic data [3] and non-Fermi liquid behaviour. This rather unconventional behaviour of $Ce_2Rh_3Al_9$, which exhibits characteristics of both intermediate valent and HF compounds, did not, however, allow a coherent description. The temperature dependences of susceptibility and specific heat do not result from the crystalline field and/or Kondo effect, and suggest rather an intermediate valent Ce-state showing additional low energy interactions [4]. The aim of this work is to investigate the electronic structure of $Ce_2Rh_3Al_9$. Our calculations reveal the gap (or pseudogap) in the bands, located at the Fermi energy ε_F. Occurrence of this gap could explain the anomalous behaviour observed in susceptibility and resistivity below 35 K.

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2. Experimental details

Polycrystalline ingots were arc-melted using Ce (99.9%), Rh (99.9%), and Al (99.99%) in a high purity argon atmosphere on a water-cooled copper hearth with Zr getter, and annealed for six days at 1100 K. The $Ce_2Rh_3Al_9$ sample was examined by X-ray diffraction (Siemens D-5000) and it was found to consist of a single phase with lattice parameters $a = 13.146$A, $b = 7.688$A and $c = 9.559$A, and suggested the $Y_2Co_3Ga_9$ structure type and a space group *Cmcm* [3]. XPS spectra were obtained with a Physical Electronics PHI-5700 XPS spectrometer using monochromatised $Al_{K\alpha}$. From the survey spectra we found that there was neither carbon nor oxygen contamination. The electronic structure was calculated using the tight binding linear muffin tin orbitals (TB-LMTO-ASA) and full potential linear augmented plane wave (FP-LAPW) methods. In the LMTO method [5, 6] (exchange correlation), the potential was used in the form proposed by von Bart and Hedin [7] with generalized gradient corrections of the Langreth–Mehl–Hu [8] type. The sphere radii were chosen in such a way that the cell volume was equal to the volume of a formula unit, hence the spheres overlapped.

The electronic structure was computed for experimental lattice parameters. For the FP-LAPW method, we used the Wien2K package [9] with the general gradient approximation [10] for electron correlations. Both types of calculations were performed with spin-polarization and relativistic effects taken into account. In order to obtain VB XPS (valence band X-ray photoemission) spectra from DOS (density of states) calculations, we multiplied the partial DOS by the cross sections [11] and convoluted it with 0.4 eV gaussians.

3. Results and discussion

Figure 1 shows the Ce 3d XPS spectra which exhibit different final states depending on the occupation of the f shell: f^0, f^1, and f^2 [12, 13]. The f^0 components are clear evidence of the MV of Ce, the f^2 components are located at the low binding energy side, and the f^1 lines are attributed within the Gunnarson–Schonhammer (GS) theoretical model to the hybridisation between the f states and conduction band. The ground state f occupation number n_f (~0.8) was obtained from the relative intensity ratio, $I(f^0)/(I(f^0) + I(f^1) + I(f^2))$ (details in [12]). The intermediate valence of Ce, $v = 3.2$ ($n_f = 0.8$), seems to be too large due to several reasons, e.g. background subtraction and plasmons with energy $h\omega_p = 12.5$ eV, which are visible in the 4d XPS spectra (see Fig. 2). The f^0 peak is usually located ca. 11 eV above the f^1 line, whereas the f^0 peak in Fig. 1 is very broad and shifted towards higher binding energies by about 3 eV. The correct Doniach–Sunjic analysis of the Ce 3d XPS spectra should also include the plasmon energy peak covered by the f^0 line. The separation of the plasmon intensities and f^0 line is, however, difficult. The hybridisation energy Δ (ca. 30 meV), was also estimated from these spectra on the basis of the GS method.

There is other evidence for the fluctuating valence of Ce ions in $Ce_2Rh_3Al_9$, as shown in Fig. 2. The Ce 4d XPS spectra exhibits two peaks above 120 eV, which are usually assigned to the f^0 final states [12].

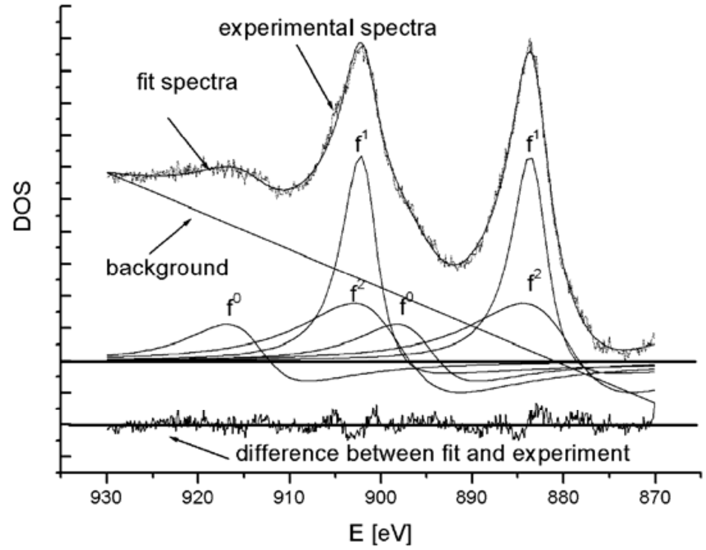

Fig. 1. Deconvolution of 3d Ce-XPS spectra for $Ce_2Rh_3Al_9$

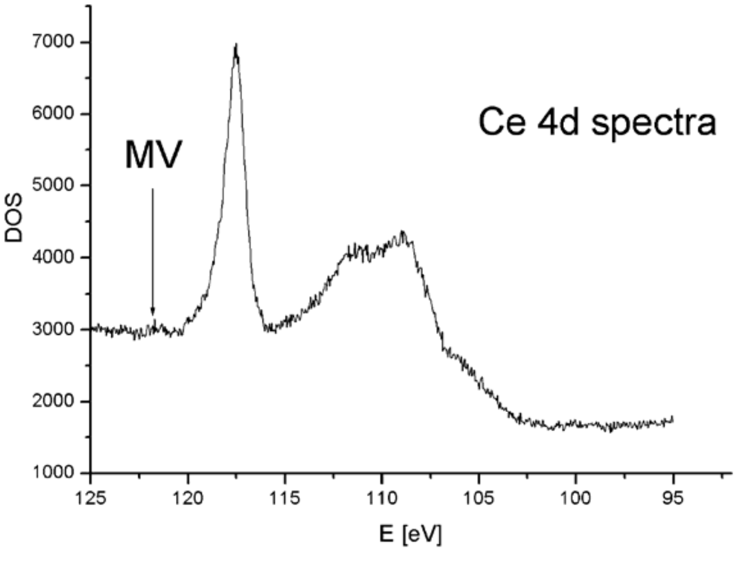

Fig. 2. Ce XPS 4d and Al 2s (sharp peak) spectra for $Ce_2Rh_3Al_9$

The overlapping peaks in Ce-3d spectra were separated using the Doniach–Sunjic approach [14,15] and the Tougaard background [16]. In Figures 3 and 4, the results of total DOS calculations are presented. LMTO results in a non-magnetic ground state with the gap of ca. 3 meV at the Fermi level, whereas LAPW gives a pseudogap in one spin direction with the DOS of about 1 state/(eV f.u.) at ε_f and 30 state/(eV f.u) in the opposite spin direction. In Figure 5, we present numerically calculated XPS valence band (VB) spectra and the measured ones. The agreement between the calculated and experimentally obtained bands is reasonably good, excluding the low-binding energies between 0 and 3 eV.

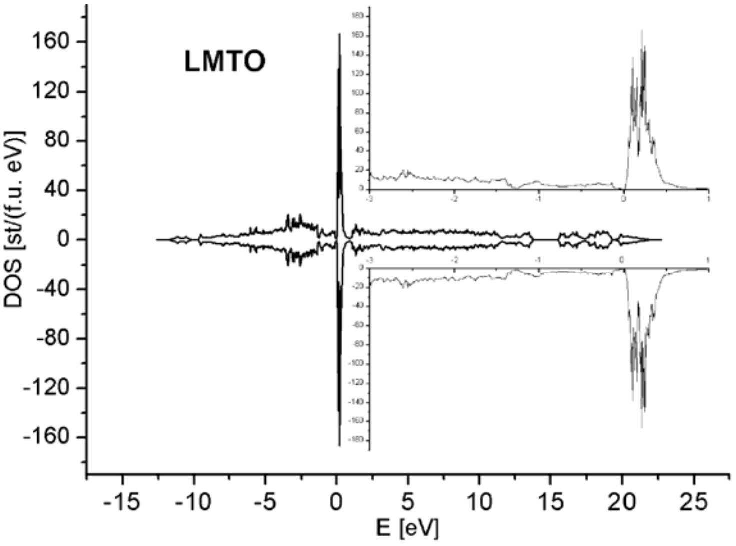

Fig. 3. LMTO calculation results for $Ce_2Rh_3Al_9$

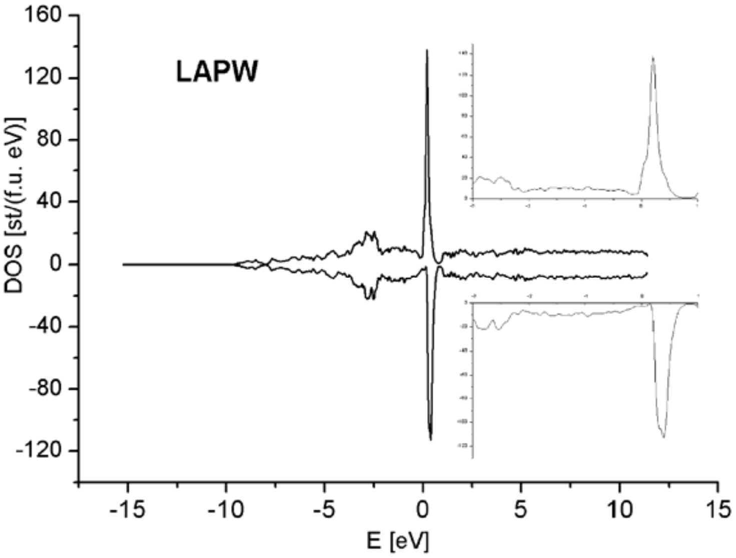

Fig. 4. LAPW calculation results for $Ce_2Rh_3Al_9$

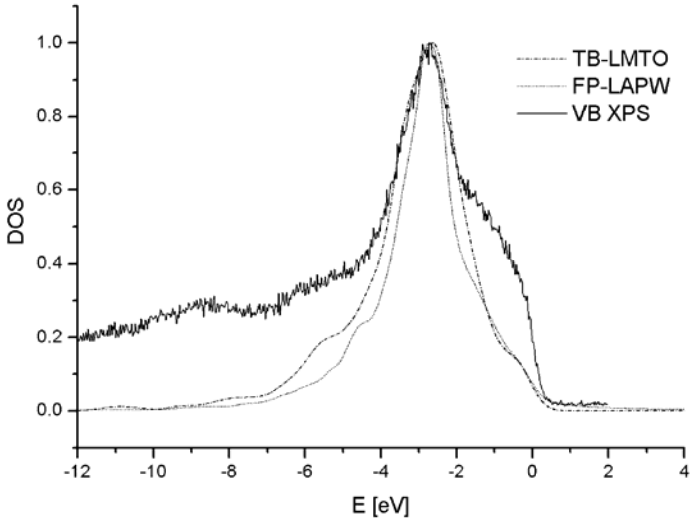

Fig. 5. VB spectra for $Ce_2Rh_3Al_9$

Moreover, the LMTO DOSs are in better agreement with the experimental data between 5 and 10 eV than the LAPW ones. We attribute the low-energy divergence between the calculated and experimentally observed VB spectra to charge transfer and/or the energy shift of Ce 4f and Rh 4d bands due to interatomic hybridisation which is not taken into account by either methods.

The gap ΔE of ca. 3 meV resulting from LMTO calculations corresponds to $T \approx 35$ K. Note that the resistivity $\rho(T)$ data do not exhibit any evidence of activated behaviour (of the $\rho = \rho_0 \exp(\Delta E/(k_B T)$ type), the resistivity $\rho(T)$ curve, however, shows a clear hump at 35 K. One should note that DFT-type calculations assume the ground state at $T = 0$ K, while the DOSs are obtained for the lattice parameters measured at the room temperature. To obtain the unit cell volume, which depends on T, we also calculated the LMTO-DOS taking into account lattice thermal expansion, namely calculations were carried out for hypothetical lattice parameters that were 3.5% smaller and larger than those measured at room temperature. In effect, the gap is still present and its width is 65 meV or 40 meV, respectively. One could therefore expect that an activation behaviour could be observed under high pressure or can result from atomic substitution. Atomic disorder could be the reason why the gap is not observed in $\rho(T)$ data. Disorder usually removes the hybridisation gap, e.g. in the Kondo insulators. LMTO calculations give an occupation number of $n_f \approx 0.9$. This value is roughly comparable with that obtained from the Ce 3d XPS spectra analysis, and indicates the MV character of the $Ce_2Rh_3Al_9$ compound.

4. Conclusion

In this paper, we have discussed gap formation at the Fermi level in the electronic bands of $Ce_2Rh_3Al_9$. The LMTO calculations predict a gap of ca. 3 meV and the nonmagnetic ground state. We also discuss the influence of lattice thermal expansion on the ground state properties, i.e. thermally decreasing the lattice parameters stabilizes the gap at ε_F. We suggest that under pressure the resistivity should exhibit an activated behaviour, like in semiconductors, and a similar behaviour could be obtained by alloying. LAPW calculations predict the magnetic ground state with the magnetic moment of $0.27\mu_B$ on Ce atoms, and the pseudogap in one spin direction band. The LAPW pseudogap corresponds well to the resistivity results, however it is in contradiction to the magnetic results. Both methods give a Sommerfeld coefficient γ (for LAPW we obtained the value of about 2.35 mJ/(mol·K) much smaller than the one experimentally obtained from the specific heat measurements [1].

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