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X-ray photoemission study of CeTIn_5 ($T = \text{Co, Rh, Ir}$)

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Abstract

We investigated CeTIn_5 ($T = \text{Co, Rh, Ir}$) using temperature- and angle-dependent x-ray photoemission spectroscopy. The Ce 3d core level has a very similar shape for all three materials and is indicative of weak f-hybridization. The spectra were analyzed using a simplified version of the Anderson impurity model, which yields a Ce 4f occupancy that is larger than 0.9. The temperature dependence shows a continuous, irreversible and exclusive broadening of the Ce 3d peaks, due to oxidation of Ce at the surface.

Keywords: x-ray photoemission spectroscopy, heavy fermion superconductors, Anderson impurity model, strongly correlated electrons

(Some figures may appear in colour only in the online journal)

1. Introduction

Heavy fermion materials are characterized by a subtle interplay of the f-electron system and the conduction electrons. Below the coherence temperature T^* the f-electrons hybridize with the non-f conduction electrons and form flat bands of heavy mass. At high temperatures the hybridization vanishes and the f-electrons act as incoherent scatterers and are expelled from the Fermi surface.

The single impurity Anderson model has been very successful in describing the core level spectroscopy of heavy fermion materials [1, 2]. The key material parameters, which govern a wide range of macroscopic properties, are the f-occupation number n_f and the hybridization between f-levels and conduction states Δ . These parameters can be extracted e.g. from x-ray photoemission spectroscopy (XPS).

Here we investigate the electronic structure of the material class CeTIn_5 ($T = \text{Co, Rh, Ir}$) by XPS. The CeTIn_5 materials have attracted much attention because of the close neighborhood of magnetism and superconductivity in their phase diagram, the presence of quantum critical points for the magnetic field and pressure, and because of the relatively high superconducting transition at $T_c = 2.3$ K for CeCoIn_5 , which is the

record so far for Ce-based heavy fermion superconductivity [3–8]. Co, Ir and Rh are isovalent but differ in size. Therefore, different chemical pressures are exerted on the tetragonal HoCoGa_5 -type crystal structure.

A weak tendency of this material class towards hybridization and to have n_f close to 1, has been inferred from previous spectroscopic investigations: x-ray absorption spectroscopy (XAS) measurements show a small f^0 signal at the Ce $M_{4,5}$ edge [9, 10] and at the L_3 edge [11, 12], and the f^1 related spectral weight at E_F was found to be low in resonant photoemission experiments at the Ce 4d–4f [13, 14] and Ce 3d–4f transition [9]. Here we consider the Ce 3d line by XPS of cleaved single crystals and apply a simplified version of the Gunnarsson–Schönhammer theory to describe the spectra and obtain the relevant parameters [15]. XPS Ce 3d spectra of polycrystals have been reported by Gamza *et al* [16].

Photoemission measurements of Ce compounds are often plagued by surface effects. The surface may have a different hybridization than the bulk [17–19], and, additionally, may degrade very easily since Ce is a very reactive chemical element. In this respect it is important to disentangle surface and bulk effects. A probe such as the Al $K\alpha$ XPS used here, seems

Figure 1. Ce 3d core level photoemission spectra measured with an Al K_{α} source at normal emission $\theta = 0^{\circ}$ (dotted curves). The samples were cleaved at 30 K and immediately analyzed. Best fit model calculations are displayed with red solid lines. Spin orbit doublets with two (blue), one (black) or no (green) f-electrons in the final state are disentangled for the model curve.

appropriate for this objective, due to its increased bulk sensitivity compared to low energy photoemission.

2. Experimental details

XPS measurements were performed using a Scienta SES 200 electron analyzer and a monochromatized Al K_{α} source with $h\nu = 1486.6$ eV and an energy resolution of about 0.4 eV. The Au $4f_{7/2}$ signal (84 eV) of a sputtered gold foil was used to calibrate the binding energy. Single crystals of the investigated Ce intermetallic compounds were grown in an In flux [4]. Clean surfaces were prepared by *in situ* cleavage. The base pressure in the experimental chamber was 1×10^{-10} mbar.

3. Results and discussion

Figure 1 shows the Ce 3d core level spectra for all three compounds cleaved at $T = 30$ K. The spectra are very similar and have a typical complex lineshape. They are split due to spin orbit coupling into the $d_{5/2}$ and $d_{3/2}$ peaks and each of the spin orbit components consists further of three, partly overlapping final states. The most intense doublet belongs to a state of mainly $3d^9 4f^1$ character, whereas the states with mainly

Table 1. Parameters extracted from fitting the spectra in figure 1 with equation (1). All values are given in eV except for n_f .

Sample	ϵ_f	Δ	U	U_{fc}	n_f
CeCoIn ₅	-1.26	0.51	8.4	11.8	0.90
CeRhIn ₅	-1.03	0.47	7.8	11.5	0.88
CeIrIn ₅	-1.23	0.52	7.9	11.9	0.90

$3d^9 4f^2$ and $3d^9 4f^0$ are situated at a lower or higher binding energy, respectively, and are much less intense. These many body effects in the core level spectra of rare earths compounds have been studied for several decades and are well known [1]. An approximate link to the ground state properties is provided by the low intensity of the $3d_{3/2}-f^0$ peak at $E = 918$ eV, which indicates that n_f does not deviate much from unity. In fact, the spectra resemble typical γ -like Ce materials [20].

For a more quantitative treatment, we used a simplified version of the Gunnarsson-Schönhammer approach proposed by Imer and Wuilloud [15] to fit the data. In this model Imer and Wuilloud took advantage of the large degeneracy of the f-level and considered only an infinite narrow valence band. Multiplet effects and plasmonic losses are neglected. This amounts to the diagonalization of the Hamiltonian:

$$H = \begin{pmatrix} 0 & \Delta & 0 \\ \Delta & \epsilon_f - U_{fc} & \sqrt{2}\Delta \\ 0 & \sqrt{2}\Delta & 2(\epsilon_f - U_{fc}) + U \end{pmatrix} \quad (1)$$

where U is the Coulomb repulsion between f-levels, U_{fc} is the core hole Coulomb interaction, ϵ_f is the energy of the f-level and Δ the effective hybridization energy between 4f states and the conduction band.

The results from this model are shown as red lines in figure 1. A Shirley background has been added and Gaussian (1.5 eV) and Lorentzian (2.3 eV) broadening were applied to simulate resolution, multiplet splitting and the finite lifetime. The match with the experimental data is satisfactory. Small deviations occur at the high energy side of the $d_{3/2}-f^1$ related peak due to missing multiplet splitting. As a result of this, the intensity of the model for this peak is always larger than the measured spectra. The parameters extracted from the fit are summarized in table 1. The obtained spin orbit splitting of 18.5 eV is the same for all three compounds and coincide with previous reports [16]. The values for U and U_{fc} are in the range of other Ce-based materials [21] as well as the values obtained for ϵ_f [18, 20].

The n_f values are as expected close to 1. In fact, $n_f = 0.9$ should still be considered as a lower boundary because a plasmon satellite is situated below the $3d_{3/2}-f^0$ peak and limits the precision of the analysis. figure 2 presents an electron energy-loss spectroscopy (EELS) spectrum [22] of an approximately 150 nm thick CeRhIn₅ film, cut with an ultramicrotome. A clear peak is observed around $E = 13$ eV, which can be assigned to an interband plasmon. This excitation of the electron density appears as satellite peaks in the photoemission spectra, as shown for the In 3d line. Nevertheless the values of the hybridization parameter Δ are significantly lower than previous results for strongly

Figure 2. Comparison of electron energy-loss spectroscopy (EELS) measurement of CeRhIn₅ with In 3d and Ce 3d photoemission spectra. The position of the interband loss at $E = 13$ eV seen in EELS coincides with the plasmon satellite of the In 3d and Ce 3d lines.

hybridized Ce compounds obtained by the same approach [17] and show clearly that CeTIn₅ are weakly hybridized systems at $T = 30$ K with an occupation number close to one. This is in qualitative agreement with our ARPES results [14, 23, 24]. n_f values close to 1 have been found using more bulk-sensitive XAS at the Ce L_3 edge ($n_f > 0.9$ for CeRhIn₅ and CeIrIn₅ [11], $n_f \approx 0.9$ for CeCoIn₅ [12]). XAS at the Ce $M_{4,5}$ edge showed there was minimal f^0 admixture for all three compounds, and it was somewhat stronger for CeIrIn₅ and CeCoIn₅ compared to CeRhIn₅ [10]. Resonant photoemission was used to show that there is a larger f^1 component at the Fermi energy, signaling increased hybridization, for CeIrIn₅ with respect to CeRhIn₅ [13].

In the standard Kondo model, the f -hybridization should slowly disappear at high temperatures. We studied, therefore, the temperature dependence of the Ce 3d line through a gradual warming of the cryostat up to room temperature. At certain temperatures additional XPS measurements were performed on the sample that was originally cleaved at 30 K to evaluate the temperature dependence. Unfortunately, the intrinsic effects, if they are present, are overlaid by surface effects, as demonstrated in figure 3 for CeIrIn₅. These spectra have been measured at room temperature. They are significantly broadened compared to the 30 K spectra. Cooling the samples down to low temperatures does not recover the narrow line shape. At higher emission angles, i.e. for higher surface sensitivity, the broadening increases. The top spectrum is for a sample that has been exposed to oxygen ($p_{O_2} = 1 \times 10^{-7}$ mbar for 10 min). It strongly resembles Ce₂O₃ [25–27], i.e. the surface is fully oxidized by this procedure and no further changes with higher oxygen exposure were observed. The room temperature data in the middle of figure 3 can be simulated almost perfectly by a superposition of this Ce₂O₃ type spectrum (gray shaded

Figure 3. Ce 3d core level spectra of CeIrIn₅ taken at 300 K for different emission angles θ with respect to the surface normal. The spectra are superimposed (red curves) on a Shirley background (dashed line), the 30 K signal (black line) and the spectra of an oxidized crystal (upper spectra and gray shaded area in the lower part), typical for trivalent cerium oxide Ce₂O₃ [25–27].

area in figure 3) and the narrow low temperature spectrum (red line in figure 3). No other contamination was discernible in the XPS overview spectra besides a small amount of oxygen, which was absent in the 30 K spectra. This indicates that the surface Ce becomes oxidized when the temperature is increased. The change of the chemical state primarily concerns Ce. figure 4 presents temperature-dependent spectra for Ir and In. Whereas the temperature-dependent changes are hardly discernible at all, the fully oxidized surface shows a moderate high energy component.

In order to evaluate quantitatively the extent of oxidation of the surface, we applied the fitting procedure from figure 3 for the full temperature scan. In this way the relative intensity of the surface component can be extracted by the integrated intensity ratio of the Ce₂O₃ type and the whole spectra. figure 5(a) demonstrates that this component increases monotonically when the temperature is increased from $T = 30$ K and shows signs of saturation at higher temperatures. Angle-dependent measurements yield higher values, as expected for a surface component, and show in particular, that the oxidation has started at the lowest temperatures achieved here. The relative intensity can be translated into the thickness of the oxidized surface layer under the assumption that there is a sharp interface and the electron

Figure 4. Temperature dependence of the In 3d and Ir 4f lines of CeIrIn_5 . Unlike Ce 3d, the spectral shape and width are nearly unaffected and only moderate changes for the fully oxidized sample can be seen.

escape length λ is known. The latter has been calculated from the TPP-2M model to be $\lambda = 14 \text{ \AA}$ [28]. The intensity I of photoexcited electrons at a distance x from the sample surface is damped exponentially by $I(x) \propto \exp(-x/\lambda \cos \theta)$, where θ is the angle between the outgoing electrons and the surface normal. Using these assumptions, the surface layer thickness has been calculated from the relative intensity of the surface component.

Figure 5(b) shows that the oxidized component starts from about a fourth of a monolayer at low temperatures and levels off around one monolayer at high temperatures, i.e. full surface coverage. The most natural explanation for the formation of the oxide layer is that desorption occurs as the system is warmed up. This process is difficult to avoid and a base pressure of 1×10^{-10} mbar is not enough to prevent it. However, the temperature increase itself may promote surface oxidation as well. The oxidation will take place most easily when the cleavage plane has the CeIn_3 layer at the top surface. The formation of a Ce_2O_3 -like phase was also reported as a result of prolonged x-ray irradiation [25]. However, in the present case the oxidation process is clearly

Figure 5. (a) Relative intensity of the oxidized signal as a function of temperature extracted by the fitting procedure described in figure 3. (b) Thickness of the oxidized surface component calculated from the data points in (a) in units of monolayers as a function of temperature.

linked to the temperature development and a slight increase in pressure rather than the irradiation time. This fact is confirmed by the Ce 3d spectra of a sample cleaved at room temperature (not shown), which was already broadened in comparison to the 30 K spectra and resembles the spectra of the warmed-up sample. Previous XPS measurements on polycrystals at room temperature also showed the spectral signatures of oxidation [16].

4. Concluding remarks

In conclusion, we investigated the CeTIn_5 family using core level photoemission. From the Ce 3d line at low temperature ($T = 30 \text{ K}$) we obtained a lower bound of the f-occupation number $n_f \geq 0.9$ for all three compounds, which characterizes them as weakly hybridized, consistent with previous measurements. The differences in n_f found by other techniques were masked by plasmonic loss excitations in the Ce 3d core level photoemission experiments. The surface tends to oxidize rapidly, independent of the transition metal, in particular when the sample is warmed up. Quantitative analysis shows that the first layer is fully oxidized at room temperature. This effect must be taken into account when making temperature-dependent and surface-sensitive measurements.

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References

- [1] Fuggle J C, Hillebrecht F U, Zolnieriek Z, Lässer R, Freiburg Ch, Gunnarsson O and Schönhammer K 1983 Electronic structure of Ce and its intermetallic compounds *Phys. Rev. B* **27** 7330–41
- [2] Gunnarsson O and Schönhammer K 1983 Electron spectroscopies for Ce compounds in the impurity model *Phys. Rev. B* **28** 4315–41
- [3] Hegger H, Petrovic C, Moshopoulou E G, Hundley M F, Sarrao J L, Fisk Z and Thompson J D 2000 Pressure-induced superconductivity in quasi-2D CeRhIn₅ *Phys. Rev. Lett.* **84** 4986–9
- [4] Petrovic C, Pagliuso P G, Hundley M F, Movshovich R, Sarrao J L, Thompson J D, Fisk Z and Monthoux P 2001 Heavy-fermion superconductivity in CeCoIn₅ at 2.3 K *J. Phys.: Condens. Matter* **13** L337
- [5] Petrovic C, Movshovich R, Jaime M, Pagliuso P G, Hundley M F, Sarrao J L, Fisk Z and Thompson J D 2001 A new heavy-fermion superconductor CeIrIn₅: a relative of the cuprates? *Eur. Phys. Lett.* **53** 354
- [6] Sidorov V A, Nicklas M, Pagliuso P G, Sarrao J L, Bang Y, Balatsky A V and Thompson J D 2002 Superconductivity and quantum criticality in CeCoIn₅ *Phys. Rev. Lett.* **89** 157004
- [7] Bianchi A, Movshovich R, Vekhter I, Pagliuso P G and Sarrao J L 2003 Avoided antiferromagnetic order and quantum critical point in CeCoIn₅ *Phys. Rev. Lett.* **91** 257001
- [8] Paglione J, Tanatar M A, Hawthorn D G, Boaknin E, Hill R W, Ronning F, Sutherland M, Taillefer L, Petrovic C and Canfield P C 2003 Field-induced quantum critical point in CeCoIn₅ *Phys. Rev. Lett.* **91** 246405
- [9] Fujimori S *et al* 2003 Nearly localized nature of f electrons in CeTIn₅ (T = Rh, Ir) *Phys. Rev. B* **67** 144507
- [10] Willers T *et al* 2010 Crystal-field and Kondo-scale investigations of CeMIn₅ g (M = Co, Ir, and Rh): a combined x-ray absorption and inelastic neutron scattering study *Phys. Rev. B* **81** 195114
- [11] Daniel M, Han S-W, Booth C H, Cornelius A L, Pagliuso P G, Sarrao J L and Thompson J D 2005 X-ray absorption studies of the local structure and f-level occupancy in CeIr_{1-x}Rh_xIn₅ *Phys. Rev. B* **71** 054417
- [12] Booth C H, Durakiewicz T, Capan C, Hurt D, Bianchi A D, Joyce J J and Fisk Z 2011 Electronic structure and f-orbital occupancy in Yb-substituted CeCoIn₅ *Phys. Rev. B* **83** 235117
- [13] Fujimori S *et al* 2006 Direct observation of a quasiparticle band in CeIrIn₅: an angle-resolved photoemission spectroscopy study *Phys. Rev. B* **73** 224517
- [14] Koitzsch A *et al* 2008 Hybridization effects in CeCoIn₅ observed by angle-resolved photoemission *Phys. Rev. B* **77** 155128
- [15] Imer J-M and Wuilloud E 1987 A simple model calculation for XPS, BIS and EELS 4f-excitations in Ce and La compounds *Z. Phys. B: Condens. Matter* **66** 153–60
- [16] Gamza M, Ślebarski A and Deniszczyk J 2008 Electronic structure of Ce_nM_mIn_{2m+3n}, where n = 1, 2; m = 0, 1; M = Co, Rh or Ir: experiment and calculations *J. Phys.: Condens. Matter* **20** 115202
- [17] Laubschat C, Weschke E, Holtz C, Domke M, Strebel O and Kaindl G 1990 Surface-electronic structure of α-like Ce compounds *Phys. Rev. Lett.* **65** 1639–42
- [18] Kim H-D, Tjernberg O, Chiaia G, Kumigashira H, Takahashi T, Duò L, Sakai O, Kasaya M and Lindau I 1997 Surface and bulk 4f-photoemission spectra of CeIn₃ and CeSn₃ *Phys. Rev. B* **56** 1620–4
- [19] Braicovich L, Brookes N B, Dallera C, Salvietti M and Olcese G L 1997 High-energy Ce-3d photoemission: bulk properties of CeM₂ (M = Fe, Co, Ni) and Ce₇Ni₃ *Phys. Rev. B* **56** 15047–55
- [20] Liu L Z, Allen J W, Gunnarsson O, Christensen N E and Andersen O K 1992 α-γ transition in Ce: a detailed analysis of electron spectroscopy *Phys. Rev. B* **45** 8934–41
- [21] Schneider W-D, Delley B, Wuilloud E, Imer J-M and Baer Y 1985 Electron-spectroscopic manifestations of the 4f states in light rare-earth solids *Phys. Rev. B* **32** 6819–31
- [22] Fink J 1989 Recent developments in energy-loss spectroscopy *Adv. Electron. Electron Phys.* **75** 121–232
- [23] Koitzsch A *et al* 2009 Electronic structure of CeCoIn₅ from angle-resolved photoemission spectroscopy *Phys. Rev. B* **79** 075104
- [24] Koitzsch A, Kim T K, Treske U, Knupfer M, Büchner B, Richter M, Opahle I, Follath R, Bauer E D and Sarrao J L 2013 Band-dependent emergence of heavy quasiparticles in CeCoIn₅ *Phys. Rev. B* **88** 035124
- [25] Paparazzo E 1990 XPS studies of damage induced by x-ray irradiation on CeO₂ surfaces *Surf. Sci.* **234** L253–L8
- [26] Xiao W, Guo Q and Wang E G 2003 Transformation of CeO₂(111) to Ce₂O₃(0001) films *Chem. Phys. Lett.* **368** 527–31
- [27] Bêche E, Charvin P, Perarnau D, Abanades S and Flamant G 2008 Ce 3d XPS investigation of cerium oxides and mixed cerium oxide (Ce_xTi_yO_z) *Surf. Interface Anal.* **40** 264–26
- [28] Tanuma S, Powell C J and Penn D R 2003 Calculation of electron inelastic mean free paths (IMFPs) VII. Reliability of the TPP-2M IMFP predictive equation *Surf. Interface Anal.* **35** 268–75