



Photoelectron spectroscopy study of PuCoGa₅ thin films

R. Eloirdi^{a,*}, L. Havela^b, T. Gouder^a, A. Shick^c, J. Rebizant^a, F. Huber^a, R. Caciuffo^a

^aEuropean Commission, Joint Research Centre, Institute for Transuranium Elements, P.O. Box 2340, D-76175 Karlsruhe, Germany

^bDepartment of Condensed Matter Physics, Charles University, Ke Karlovu 5, CZ-12116, Prague 2, Czech Republic

^cInstitute of Physics, Academy of Sciences of the Czech Republic, Prague 8, Czech Republic

A B S T R A C T

Thin layers of PuCoGa_x ($x = 4$ to 18) have been prepared by dc sputtering from a PuCoGa₅ single crystal target, and investigated *in situ* by X-ray and ultraviolet photoelectron spectroscopy. We could achieve broad composition variability (monitored by the Pu-4f, Co-2p and Ga-2p core-level spectra). The results are compared to the valence band spectra reported previously for PuCoGa₅. Our experiments reveal that some Ga excess (PuCoGa_{~7}) was likely for those original data. We demonstrate that there is a tendency to the segregation of Ga at the surface, which has an important effect on the valence band spectra.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The discovery of the first known Pu-based superconductor, PuCoGa₅ ($T_c = 18.5$ K) [1], initiated further studies of physical properties [2,3] aimed to clarify the nature of the superconductivity and the role played by the 5f states. The mechanism of superconductivity is still a matter of dispute, as evidenced by studies reporting on one side an almost magnetic state with an unconventional pairing mechanism [4] while others are assuming the prominence of electron–phonon coupling [5].

Photoemission spectroscopy (PES) is a powerful tool to study the nature of the 5f states. The main difficulty is to obtain a clean surface. One can cleave a single crystal, or clean the surface e.g. by ion sputtering or by laser ablation, however this may also modify the surface composition. An alternative solution is to prepare *in situ* thin layers, e.g. by sputter deposition, while monitoring the composition by PES. Joyce et al. [6] presented the first PES data on PuCoGa₅ obtained after cleaning by laser ablation at $T = 77$ K. The valence band spectra were interpreted here as due to Pu-5f electrons in two configurations, one well removed from Fermi level (E_F) and one directly at E_F . The mixed-level model calculation, in relatively good agreement with the PES data, found a total energy minimized for an atomic 5f⁴ configuration and roughly one 5f electron in delocalised Bloch states. In the present work, we describe the synthesis and PES (UPS and XPS) study of thin films obtained by the sputter deposition from PuCoGa₅ target. It was found that depending on conditions, large variations of Ga stoichiometry could be achieved, leading to PuCoGa_x ($x = 4$ to 18). A tendency

to Ga segregation at the surface was revealed especially when temperatures were elevated at the substrate.

2. Experimental

Thin layers of PuCoGa_x ($4 \leq x \leq 18$) were prepared *in situ* by dc sputtering using a small single crystal of PuCoGa₅ prepared by flux method [7] as a target. The plasma in the diode source was maintained by injection of electrons at 50–100 eV. The sputter gas, ultrahigh-purity Ar (99.9999%), was used. The deposition rate was approximately one monolayer per second and a typical deposition time of 300 s. The background pressure of the plasma chamber was 4×10^{-7} Pa. The material was deposited on Si (1 1 1) single crystal cleaned by Ar ion bombardment at a temperature of $T = 523$ K. The deposition currents were typically 1–2 mA. Photoelectron spectra were recorded using a Leybold LHS-10 hemispherical analyser. X-ray photoelectron spectra (XPS) were taken using Mg K α (1253.6 eV) radiation with an approximate resolution of 1 eV. Ultraviolet photoelectron spectroscopy (UPS) used HeI and HeII ($h\nu = 21.22$ and 40.81 eV, respectively) excitation produced by a high-intensity UV source (SPECS). The total resolution in UPS was greater than 0.05 eV. The background pressure in the analysis chamber was greater than 10^{-8} Pa. The film composition was determined from the ratio of the Pu-4f, Co-2p, and Ga-2p core-level spectra.

3. Results

3.1. Valence band study

Fig. 1 shows the HeII valence band spectra of PuCoGa_x thin films for two compositions, PuCoGa₁₆ and PuCoGa₅. The layers deposited

* Corresponding author. Tel.: +49 7247 951803; fax: +49 7247 951599.
E-mail address: rachel.eloirdi@ec.europa.eu (R. Eloirdi).

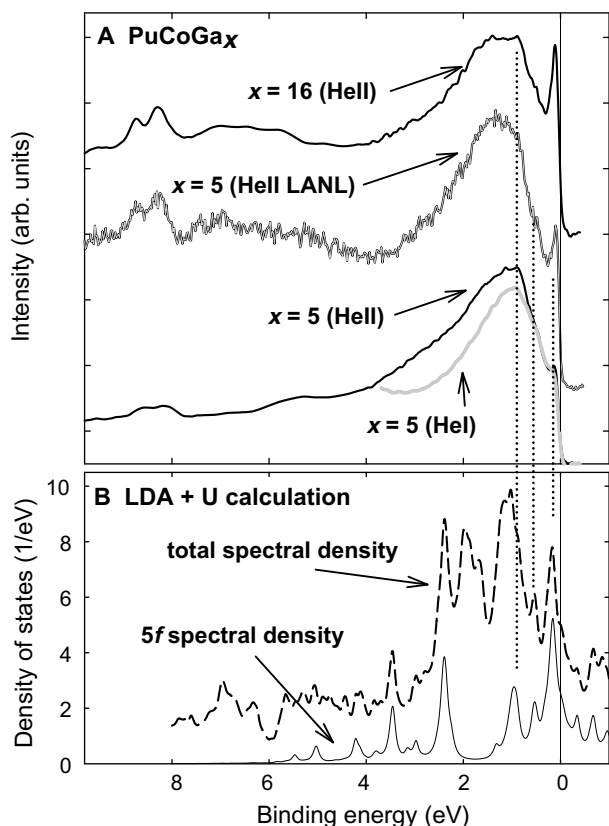


Fig. 1. (A) HeII valence band spectra of PuCoGa_{16} and PuCoGa_5 thin films. The HeI spectrum of PuCoGa_5 and the spectrum obtained on bulk PuCoGa_5 at LANL are also shown for comparison. The features in the range 5–9 eV BE belong to the emission from the Ga-3d states. (B) Spectral density of PuCoGa_5 based on LDA + U + Hubbard I calculation.

at the beginning of the experimental cycle yielded a substantial excess of Ga, due to Ga segregation at the surface of the target. As a consequence, the stoichiometry of the deposited material is shifted up to PuCoGa_{16} in the early stages of the sputtering. HeII valence band spectra show a dramatic impact of the Ga concentration variations especially on the region close to the Fermi energy.

For PuCoGa_{16} , an intense peak appears right below E_F , whereas it is largely suppressed for PuCoGa_5 . Two other weaker spectral lines, known from Pu metal [8] and numerous other Pu systems, are visible at 0.50 eV and 0.90 eV, although they are partially masked by the sloping background of the massive Co-3d emission around 1 eV. These lines are of 5f origin and stem from the $5f^5$ final-state multiplet. At higher binding energy, contributions from the $5f^4$ multiplet are expected. The cross section for the 5f excitations is negligible for the HeI excitation, therefore the difference in intensity observed for the HeII and HeI spectra in the range between 2 and 4 eV has to be attributed to the 5f emission.

The spectrum of PuCoGa_5 bulk obtained by Joyce et al. [6] after a surface cleaning by laser ablation at 77 K shows a peak at E_F with intensity higher than the one we observe for a stoichiometric sample. However, it is reproduced in our film with approximate stoichiometry PuCoGa_7 . The Ga concentration can be monitored also by the Ga-3d spectra, achievable in UPS. Also these show that the original data from [6] could have slight Ga excess.

In our study, the correct stoichiometry is achieved only after prolonged sputtering of the target, during which the target stoichiometry underwent some Ga depletion. Even then a Ga overlayer is formed at the surface if depositing at elevated temperatures (523 K). In this case the Ga-3d states are shifted by 0.1 eV towards

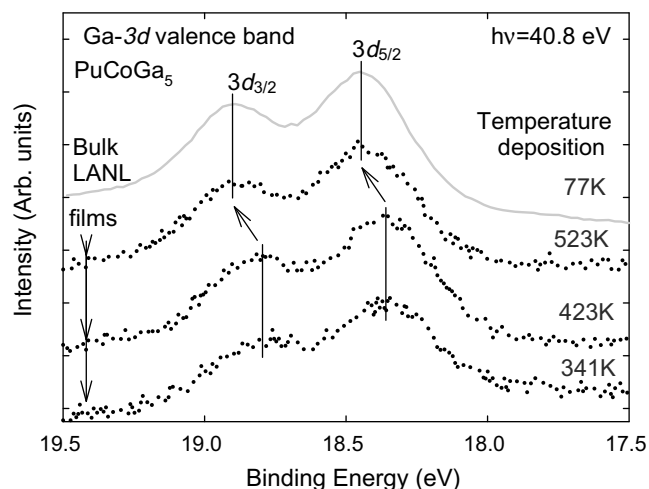


Fig. 2. UPS Ga-3d spectra of PuCoGa_5 films deposited at various temperature. Comparison with Ga-3d spectra observed for bulk PuCoGa_5 [6].

higher binding energy compared to the stoichiometric 115 phase. It is interesting to note that also the data collected in the course of the published study [6] exhibit such a shift (see Fig. 2), which can be a fingerprint of a Ga overlayer formed at the laser ablation cleaning.

Valence band PES spectra can be compared with the results of LDA + U around mean field electronic structure calculations (yielding non-magnetic ground state, occupancy of 5f states $n_{5f} = 5.39$) supplemented by Hubbard I method to account for excitations of the system. The spectral function obtained (Fig. 1(B)) reveals fingerprints of the $5f^5$ final-state multiplet close to the Fermi level (marked by the dotted lines). The spectral intensity related to unresolved $5f^4$ multiplet is concentrated mostly to the energy range 2–4 eV BE. The difference between the total and 5f spectral density is mostly due to the Co-3d states, appearing at 1–2 eV BE. Surprisingly, the calculated $5f^5$ multiplet is more intense than that for the PES for the stoichiometric PuCoGa_5 films, and the agreement is actually much better if the Ga-rich films are taken for comparison. The reason could either be the deficiency in calculations (the 5f occupancy may be too high) or surface effects in the experiment. The information depth for HeII (40.81 eV) radiation is only several atomic layers, and the morphology of surface layers is uncertain for the sputter deposited films.

Fig. 2 displays the Ga-3d spectra in PuCoGa_5 films deposited on substrate at various temperatures, $T = 341$ K, 423 K and 523 K. These are compared to the data obtained at LANL [6].

The increase of the deposition temperature enables the induction of Ga segregation at the surface of the films. The Ga segregation is especially noticeable when the substrate is heated to $T = 523$ K. This latter has strong similarities with those observed in PuCoGa_5 analysed at LANL. We suggest that a Ga monolayer was formed on the crystal examined in [6] during the laser ablation used for surface cleaning, modifying the 5f states.

3.2. Core-level spectroscopy

Fig. 3 shows the Pu-4f core-level spectrum of the stoichiometric PuCoGa_5 film compared with α -Pu [8] and PuSb [9]. The two characteristic spin-orbit split peaks ($4f_{7/2}$ and $4f_{5/2}$) obtained for PuCoGa_5 appear at binding energies 425.2 eV and 437.8 eV, respectively, which are considerably higher than in α -Pu (422.2 eV) or PuN (423.6) for $4f_{7/2}$ [10]. A closer inspection reveals that each of the peaks can consist of two spectral features separated by 2–3 eV. The so-called well-screened peak, i.e. the one at lower

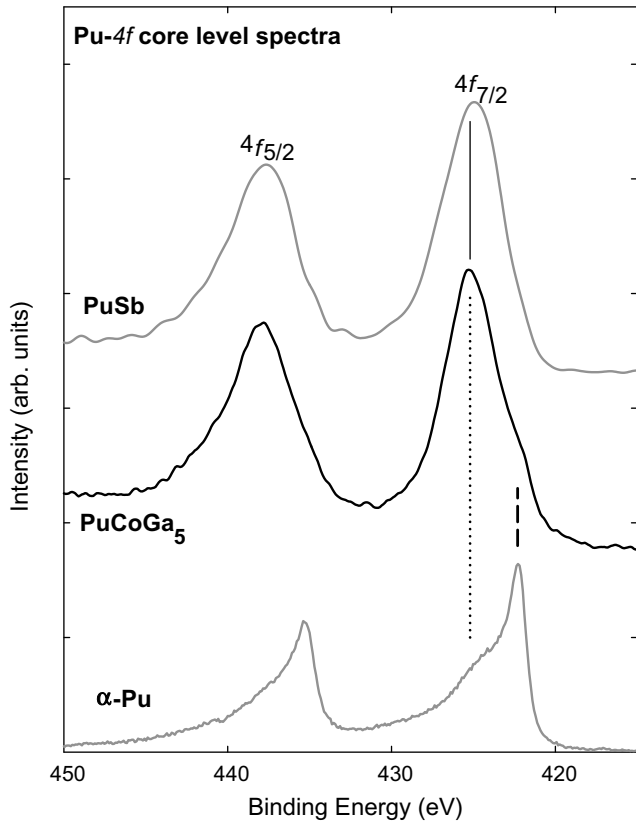


Fig. 3. Pu-4f core-level spectra of PuCoGa₅ thin film. Comparison with Pu-4f observed for α -Pu and PuSb thin films.

BE, dominates for α -Pu. This should be in conjunction with the most itinerant character of the 5f states, being capable to screen the 4f hole. This feature is absent in PuSb [10], in which the localized 5f states are unable to screen; screening has to rely on the 6d/7s states.

It yields a higher final-state energy and therefore the 4f peak appears at higher binding energy. The dominant features for PuCoGa₅ correspond to the poorly screened 4f peaks of PuSb (being somewhat narrower than in PuSb), but a weak shoulder on the low BE side, visible for 4f_{7/2}, indicates additional intensity at BE

comparable with the well-screened peak of α -Pu. The difference from the localized 5f state of PuSb can be attributed to a certain delocalisation and/or to a difference of the 5f occupancy. Within the energy resolution of XPS, the shape and position of the 4f spectra does not depend of stoichiometry variations, in particular to the Ga excess. The reason can be seen also in the much higher information depth of XPS comparing to HeII UPS spectra.

4. Conclusion

Valence band spectra of sputter deposited PuCoGa₅ can reproduce those known from previous studies, albeit with a small Ga excess. The correct stoichiometry reduces the peak at the Fermi level comparing to the published data. Higher Ga concentration emphasizes the Fermi level peak as well as other two spectral features at 0.5 eV and 0.9 eV, known to originate from the 5f⁵ final-state multiplet. The 4f core-level spectra are located at energies close to the 4f lines in PuSb, exhibiting only a weak shoulder at the well-screened positions.

Acknowledgements

Authors wish to thank T. Durakiewicz for providing detailed data from the LANL work for comparison. This work was supported by the ACTINET consortium under Project No. JP 6-18.

References

- [1] J.L. Sarrao, L.A. Morales, J.D. Thompson, B.L. Scott, G.R. Stewart, F. Wastin, J. Rebizant, P. Boulet, E. Colineau, G.H. Lander, *Nature (London)* 420 (2002) 297.
- [2] A. Hiess, A. Stunault, E. Colineau, J. Rebizant, F. Wastin, R. Caciuffo, G.H. Lander, *Phys. Rev. Lett.* 7 (2008) 76403.
- [3] E.D. Bauer, J.D. Thompson, J.L. Sarrao, L.A. Morales, F. Wastin, J. Rebizant, J.C. Griveau, P. Javorsky, P. Boulet, E. Colineau, G.H. Lander, G.R. Stewart, *Phys. Rev. Lett.* 93 (2004) 156404.
- [4] N.J. Curro, T. Caldwell, E.D. Bauer, L.A. Morales, M.J. Graf, Y. Bang, A.V. Balatsky, J.D. Thompson, J.L. Sarrao, *Nature* 434 (2005) 622.
- [5] F. Jutier, G.A. Ummarino, J.C. Griveau, F. Wastin, E. Colineau, J. Rebizant, N. Magnani, R. Caciuffo, *Phys. Rev. B* 77 (2008) 24521.
- [6] J.J. Joyce, J.M. Wills, T. Durakiewicz, M.T. Butterfield, E. Guziewicz, J.L. Sarrao, L.A. Morales, A.J. Arko, O. Eriksson, *Phys. Rev. Lett.* 91 (2003) 176401.
- [7] E.G. Moshopoulou, Z. Fisk, J.L. Sarrao, J.D. Thompson, *J. Solid State Chem.* 158 (2001) 25.
- [8] L. Havela, T. Gouder, F. Wastin, J. Rebizant, *Phys. Rev. B* 65 (2002) 235118.
- [9] T. Gouder, F. Wastin, J. Rebizant, L. Havela, *Phys. Rev. Lett.* 84 (2000) 3378.
- [10] L. Havela, F. Wastin, J. Rebizant, T. Gouder, *Phys. Rev. Lett.* 68 (2003) 85101.