Materials Science-Poland, Vol. 26, No. 3, 2008

Electronic structure of CePdAl Experiment and calculations*

W. GŁOGOWSKI, J. GORAUS, A. ŚLEBARSKI**

Institute of Physics, University of Silesia, 40-007 Katowice, Poland

CePdAl exhibits an antiferromagnetic phase below $T_N = 2.7$ K; its physical properties are typical of heavy fermion compounds (specific heat coefficient $\gamma \equiv C/T = 270$ mJ/(mol·K^2)). The triangular coordination symmetry of the magnetic Ce ions gives rise to geometrical frustration and leads to an incommensurate antiferromagnetic structure below T_N, showing a coexistence of ordered and frustrated Ce moments. The purpose of this work was to discuss electronic structure of CePdAl and its influence on the geometrical frustration in the Kagomé-like lattice and the Kondo effect in CePdAl. We present the results of the X-ray diffraction analysis and the XPS Ce 3d core and valence band spectra. We also present the spin-polarized band structure calculations for CePdAl, using the LAPW method.

Key words: *strongly correlated electron systems; electronic structure*

1. Introduction

Our investigations of CePdAl have been carried out as part of the investigations of the $\mathrm{CeRh}_{1-x}\mathrm{Pd}_x\mathrm{Al}$ compounds. It is of interest to examine in detail the effect of the increasing number of conduction electrons in solid solutions of $\mathrm{CeRh}_{1-x}\mathrm{Pd}_x\mathrm{Al}$ on changes in the metallic ground state properties across the series.

CePdAl is a heavy fermion (HF) antiferromagnet with $T_N = 2.7$ K [1] with ZrNiAl type crystal structure [2, 3] where Ce atoms form a Kagomé-like lattice in the *c* plane. According to the neutron diffraction studies [4], the magnetic structure of CePdAl is incommensurate and Ce atoms located on the crystallographic 3f site exhibit a coexistence of ordered moments (2/3) and disordered moments (1/3). Reasons are effects of geometrical frustration [4] and/or the interplay of Kondo screening and exchange interaction [5]. These disordered moments are paramagnetic down to 30 mK, as was con-

---

[*] Presented at the Conference of the Scientific Network "New Materials for Magnetoelectronics – MAG-EL-MAT 2007", Będlewo near Poznań, 7–10 May, 2007.

[**] Corresponding author, e-mail: slebar@us.edu.pl

firmed by recent NMR measurements [6]. Considerations of the group theoretical symmetry analysis also confirmed that for frustrated Ce atoms (1/3 in 3f atomic sites) any magnetic moment parallel to the magnetically easy *c* axis is forbidden by symmetry [4].

It is also worth noting that antiferromagnetic order in CePdAl disappears above 1.1 Gpa [7] which suggests a quantum phase transition. CePdAl is well described by the phase diagram proposed by Doniach [8] in the T_NP plane, with a maximum of T_N at about 0.75 GPa [9]. This behaviour suggests large value of $\rho(\mathcal{E}_F)J_{fc}$, where J_{fc} is the strength of exchange interaction between f electron and conduction electrons and ρ is the density of states (DOS) at the Fermi level, and in result location of this compound near the maximum in the Doniach diagram.

In this work, we present results of calculations of electronic structure which suggest a weak magnetic ground state of CePdAl and strong interatomic hybridization between Ce f states and Pd d states in the *c* plane. From the Ce 3d XPS spectra we estimated the value of the onsite hybridization energy V_{fc} between the f electrons and the conduction states. A simple analysis gives $\rho(\mathcal{E}_F)J_{fc} \approx 0.3$ eV which is quite large and well supports the T_N vs. P experimental data.

2. Experimental

CePdAl has been prepared by arc melting and then annealed at 800 °C for 3 weeks. The crystal structure of the sample was found to be hexagonal of the ZrNiAl -type (space group $P\bar{6}2m$). The X-ray photoelectron spectroscopy spectra (XPS) were obtained with monochromatized Al K_α radiation using a PHI 5700 ESCA spectrometer. From the survey spectra we found that there was neither carbon nor oxygen contamination. The electronic structure was computed for experimental lattice parameters using FP-LAPW (Wien2k) code, with GGA96 type gradient corrections [10]. The calculations were performed with spin-polarization and relativistic effects taken into account.

3. Results and discussion

In Figure 1, we present numerical calculations of the electronic density of states (total LAPW DOS) of CePdAl. Also shown in the figure, for comparison, are the XPS valence band (VB) spectra subtracted by a background, calculated by means of a Tougaard algorithm [11]. The characteristic features in the XPS VB spectrum are in good agreement with the calculated total DOS. The total DOS decomposes into three clearly separated parts. A band located in the binding energy range of 0–2 eV consists mainly of the Ce f states (see Fig. 2). A part of the VB which extends from ca. 2 eV and 4.5 eV is composed mainly of Pd d states, while the Al s states become dominant of the total DOS between 5 eV and ca. 8 eV. In band structure calculations the 4f electrons are treated as band electrons. The calculated electronic specific heat coefficient $\gamma = 1/3\pi^2\rho(\mathcal{E}_F)k_B^2 \approx 22$ mJ/(mol·K)^2 is about 1/3 of the γ_0 obtained from the linear dependence of C/T on T^2 at $T = 0$.

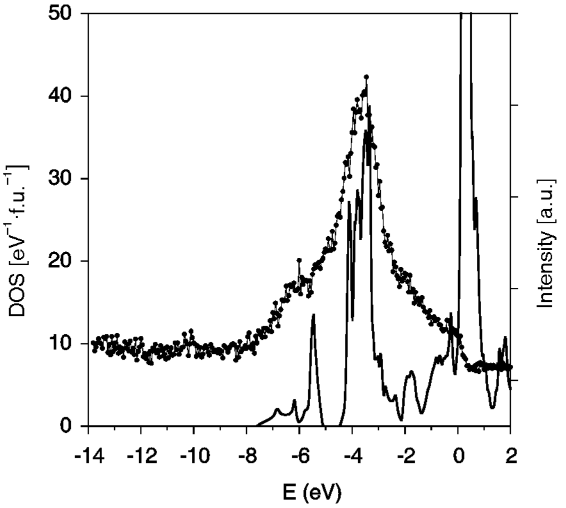

Fig. 1. LAPW total DOS calculated for CePdAl, and measured XPS valence bands corrected by the backgrounds (points)

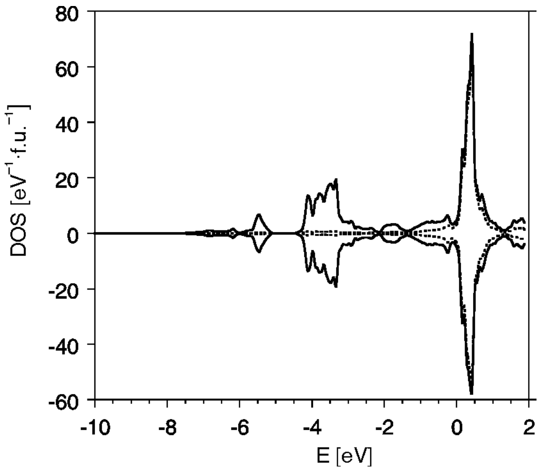

Fig. 2. The total DOS for both spin directions for the magnetic ground state (solid line). The Ce states in eV^{-1} per Ce atom are shown too (dotted line)

It is generally accepted that at low temperatures a narrow band of heavy electrons gives rise to the large electronic specific heat coefficient γ, and originates from the renormalized hybridization of the conduction band (c) states with the atomic f states. The strength of the fc exchange interaction can be turned by either the composition or pressure, and results in a competition between the intrasite Kondo and intersite Ruderman–Kittel–Kasuya–Yosida (RKKY) interactions. The first such model of the HF was proposed by Doniach [8], who examined the one-dimensional Kondo lattice and obtained the magnetic ground state with a simple phase diagram, which displays the magnetic ordering temperature T_{RKKY} in function of $\rho(\mathcal{E}_F)J_{fc}$, where $J_{sf} \sim V_{fc}^2/(\mathcal{E}_{\mathrm{F}} - E_f)$, with E_f being the location of the f level in the band. This simple diagram describes often well the magnetic → nonmagnetic ground state transformation observed for many Ce compounds. CePdSb is the first Ce compound where the pressure dependence of T_{RKKY} is well explained by this diagram [12]. Recently [13], we have obtained the hybridization energy $V_{fc} \approx 82$ meV from the Ce 3d XPS spectra based on the Gunnarsson–Schönhammer theoretical method [14]. According to the Anderson model, $J_{sf} \approx 0.03$ eV, if E_f is about 0.24 eV (see Fig. 2). We can obtain $\rho(\mathcal{E}_F)J_{fc} \approx 0.3$ which locates CePdAl on the left side near the maximum in the T_N–$\rho(\mathcal{E}_F)J_{fc}$ diagram, in agreement to Ref. [9].

The diagram, however, due to its simplicity does not explain the character of the low temperature magnetic ground state. Also, it does not account for the f electron itineracy observed in many compounds. Doradziński and Spałek (DS) [15] discussed the magnetic phases in the periodic Anderson model and determined the conditions under which there appears a stable Fermi liquid state with a small antiferromagnetic moment of f electrons, largely compensated by the conduction electrons. In DS model, the stability of paramagnetic vs. magnetic ground state in the Kondo lattice limit is strongly dependent on the on-site hybridization magnitude V_{fc}, the bare f level position, the number conduction electrons and finally, on the intrasite f–f interaction U. Basing on our XPS data and calculations, the DS phase diagram on the V_{fc}–n_e plane (n_e is the total number of electrons per site) well describes CePdAl as an antiferromagnetic Kondo lattice compound.

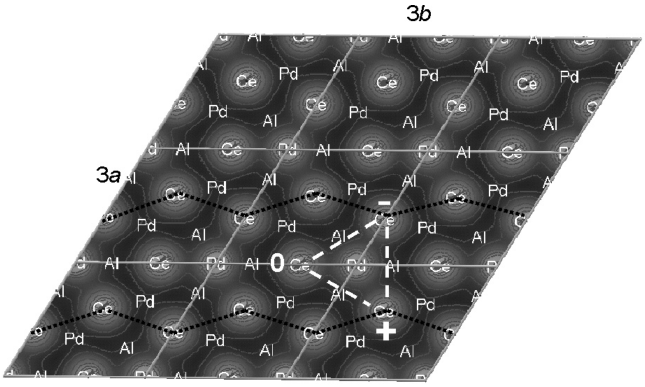

Fig. 3. The charge density distribution in the c plane. +, – and 0 represent Ce ions with antiferromagnetic orientation of the magnetic moments (+, –), and paramagnetic frustrated Ce ions (0); the figure shows 9 unit cells

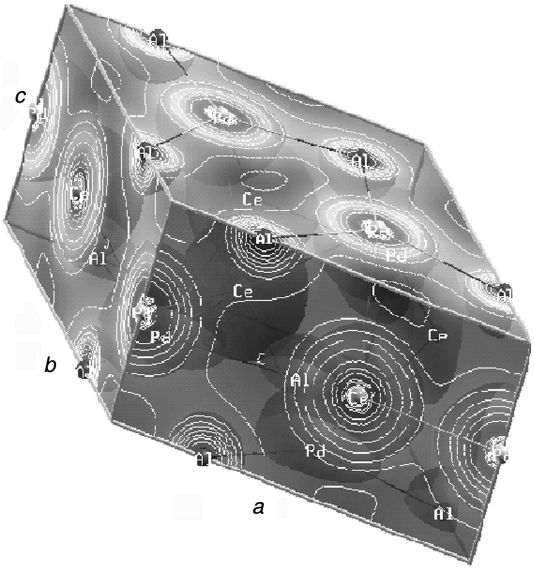

Fig. 4. The charge density distribution in the unit cell of CePdAl.
The planes *a*, *b* and *c* show the charge contours

In Figures 3 and 4 we present the charge densities distributed in the plane *c*, perpendicular to the *z* axis (Fig. 3) and in the planes *a* and *b*, respectively. In Fig. 3 the Ce magnetic moments (+, –) with antiferromagnetic orientation (see Ref. [4]) provoke the frustration of the third Ce ion (0) in Kagomé-like lattice. Pd atoms are located in center of this lattice and are strongly hybridized with Ce due to fd hybridization. The fd hybridization stabilizes the magnetic structure of CePdAl and could decide about the magnetic properties of this compound under external pressure. In CePdAl the fp hybridization is negligible.

In conclusion, we calculated the DOS of CePdAl, which was compared to the XPS VB spectra. The agreement is good. Based on the electronic structure calculations and the XPS spectra (VB XPS, Ce 4d XPS) we determined the hybridization energy V_{fc} between the Ce 4f and conduction electrons, occupation number of the f shell, $n_f = 1$, and the exchange coupling strength J_{fc}. In the Kondo lattice, the Kondo effect and the RKKY magnetic interaction are competing with each other depending on the value of $\rho(\mathcal{E}_F)J_{fc}$ (the Kondo interaction $T_K \sim \exp(-1/\rho(\mathcal{E}_F)J_{fc})$ and $T_{\mathrm{RKKY}} \sim \rho(\mathcal{E}_F)J_{fc}^2$), we found CePdAl located in the T_{RKKY}–$\rho(\mathcal{E}_F)J_{fc}$ diagram close to the maximum of T_{RKKY} at $\rho(\mathcal{E}_F)J_{fc} \approx 0.3$. Our calculations show strong interatomic hybridization effect between Ce f and Pd d states which seems to be important in formation of the ground state properties of CePdAl.

Acknowledgements

The authors thank for financial support from Projects No. 1 P03B 052 28, No. 1 P03B 094 30, and No. N202 038 31/1805 of the Ministry of Science and Higher Education.

References

[1] KITAZAWA H., MATSUSHITA A., MATSUMOTO T., SUZUKI T., Physica B, 199–200 (1994), 28.

[2] HULLIGER F., J. Alloys Comp., 196 (1993), 225.

[3] XUE B., SCHWER H., HULLIGER F., Acta Cryst. C, 50 (1994), 338.

[4] DÖNNI A., EHLERS G., MALETTA H., FISCHER P., KITAZAWA H., ZOLLIKER M., J. Phys.: Condens Matter., 8 (1996), 11213.

[5] NUNEZ-REGUEIRO M.D., LACROIX C., CANALS B., Physica C, 282–287 (1997), 1885.

[6] KAMIOKA K., OYAMADA A., HASHI K., MAEGAWA S., GOTO T., KITAZAWA H., ISIKAWA Y., Physica B, 259–261 (1999), 121.

[7] HANE S., GOTO T., ABE T., ISIKAWA Y., Physica B, 281–282 (2000), 391.

[8] DONIACH S., Physica B, 91 (1977), 231.

[9] TANG J., MATSUSHITA A., KITAZAWA H., MATSUMOTO T., Physica B, 217 (1996), 97.

[10] BLAHA P., SCHWARZ K., MADSEN G.K.H., KVASNICKA D., LUITZ J., *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculatin Crystal Properties*, Karlheinz Schwarz, Techn. Universität Wien, Austria, 2001. ISBN 3-9501031-1-2; PERDEW J.P., BURKE K., ERNZERHOF M., Phys. Rev. Lett., 77 (1996), 3865.

[11] TOUGAARD S., SIGMUND P., Phys. Rev. B, 25 (1982), 4452.

[12] CORNELIUS A.L., GANGOPADHYAY A.K., SCHILLING J., ASSMUS W., Phys. Rev. B, 55 (1997), 14109.

[13] GŁOGOWSKI W., ŚLEBARSKI A., Mater. Sci.-Poland, 24 (2006), 551.

[14] FUGGLE J.C., HILLEBRECHT F.U., ZOLNIEREK Z., LÄSSER R., FREIBURG CH., GUNNARSSON O., SCHÖNHAMMER K., Phys. Rev. B, 27 (1983), 7330.

[15] DORADZIŃSKI R., SPAŁEK J., Phys. Rev. B, 56 (1997), R14239; ibid. 58 (1998), 3239; for a brief review see: SPAŁEK J., DORADZIŃSKI R., [in:] *Magnetism and Electronic Correlations in Local-Moment Systems: Rare Earth Elements and Compounds*, M. Donath, P.A. Dowben, W. Nolting, World Scientific, New Jersey, 1998), p. 387; Acta Phys. Polon. A, 96 (1999), 677; 97 (2000), 71.

Received 10 May 2007
Revised 21 January 2008