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Journal of Solid State Chemistry 171 (2003) 291–294

JOURNAL OF
SOLID STATE
CHEMISTRY

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Structural and electronic investigation of TbPdAl by means of EXAFS and XANES measurements

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Received 29 April 2002; received in revised form 15 August 2002; accepted 26 August 2002

Abstract

The ternary intermetallic compound TbPdAl crystallizes in the hexagonal ZrNiAl-type and the orthorhombic TiNiSi-type structures. The former compound undergoes two successive antiferromagnetic transitions with the Nëel temperatures of $T_{N1} = 43\,K$ and $T_{N2} = 22\,K$. It is also characteristic that this compound exhibits an isostructural phase transition at around $T = 100\,K$. In this work, to investigate the origin of this transition, we have carried out extended X-ray absorption fine structures (EXAFS) and X-ray absorption near edge structure (XANES) measurements at the Tb L_3- and Pd K-edge. It was found that Fourier transforms for k^3-weighted Tb L_3-edge EXAFS spectra changed below and above the transition temperature, which is consistent with the existence of the structural transition. In addition, slight temperature dependence was observed in the Pd K-edge XANES spectra, whereas the spectra at the Tb L_3-edge showed no obvious change. This result suggests that the transition is caused mainly by the change of the electronic structure of Pd.

1. Introduction

Recently, the heavy rare-earth *R*PdAl compounds were found to crystallize in both structures, hexagonal ZrNiAl type as metastable high-temperature modification (HTM) and orthorhombic TiNiSi type as stable low temperature modification (LTM). Heavy rare-earth *R*PdAl compounds are good candidates to investigate differences of magnetic and electronic properties between HTM and LTM.

In particular, TbPdAl has very interesting magnetic properties and structural phase transition, as described below. TbPdAl undergoes two successive antiferromagnetic transitions with the Nëel temperatures of $T_{N1} = 43\,K$ and $T_{N2} = 22\,K$. This compounds has a complex magnetic structure below T_{N2} and shows a metamagnetic phase transition [1].

It is also characteristic that this compound exhibits an isostructural phase transition at around $T = 100\,K$ [2,3].

In this work, we investigate the origin of this isostructural phase transition and magnetic transition by means of extended X-ray absorption fine structures (EXAFS) and X-ray absorption near edge structure (XANES) measurements.

2. Experimental

Polycrystalline TbPdAl samples were prepared by arc melting stoichiometric amounts of the pure elements (Tb, 3N; Pd, 4N; Al, 5N) in argon atmosphere. The samples were melted several times by tuning over each time until a homogeneous button was formed. For annealing, the TbPdAl samples were wrapped in Ta and Zr foil and enclosed in a quartz tube under high vacuum. The metastable high-temperature modification HTM was prepared by annealing as-cast material at 1050 K for 120 h and rapidly quenching to room temperature. The powder X-ray diffraction patterns could be indexed completely with the hexagonal ZrNiAl-type crystal structure.

The EXAFS spectra of the Tb L_3- and Pd K-edge for intermetallic rare-earth aluminide TbPdAl were obtained at the R&D (III) beam-line 38B1 of SPring-8, Japan. The beam line was composed of a double-crystal monochormator equipped with an Si 1 1 1 crystal and

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doi:10.1016/S0022-4596(02)00179-2

an Si mirror for eliminating the higher harmonics. The EXAFS spectra were recorded under a transmission mode using two ionization chambers as a detector. For the EXAFS measurements, the powdered samples were uniformly spread on Scotch tape. All of the EXAFS data were obtained at one scan.

The data were analyzed using the REX2000 (Rigaku Co.) program. The background was removed by extrapolating the pre-edge region onto the EXAFS region in the form of Victoreen's polynominals. Three cubic splines were used to constrict the smooth part of the absorption coefficients. The radial distribution function (RDF) was calculated from the EXAFS spectra in $k^3\chi(k)$ as a modulus of the Fourier transform at the wave number interval 3.5–13.5 Å^{-1}.

The Hanning window between 2.4 and 4.5 Å isolated the significant Fourier transform peaks, which were then back-transformed into k-dependent data. The best-fit distance (R), coordination numbers (N), Debye–Waller (σ) factors and edge shift ($E0$) were obtained from multishell fits to the Fourier-filtered data using empirical phase and amplitude function.

3. Results and discussion

3.1. EXAFS spectrum at the terbium L_3-edge

Fig. 1 shows the EXAFS $k^3\chi(k)$ function of the Tb L_3-edge in TbPdAl at several different temperatures. The solid lines show the antiferromagnetic phase. The broken lines show the HTM II phase after the isostructural phase transition. The dotted lines show the HTM I phase. The magnitude of EXAFS oscillation decreased as the temperature increased. In the region in which the wave numbers are higher than 8 Å^{-1}, the spectral shape could be changed at around $T = 30$ and 100 K, which correspond to the magnetic and the isostrucutral phase transition, respectively.

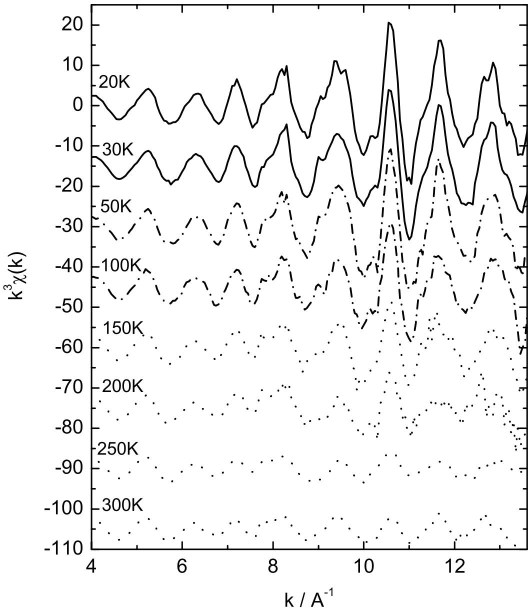

Fig. 1. k^3-Weighted Tb L_3-edge EXAFS spectra of TbPdAl temperature dependence.

Fig. 2 shows the typical fit of the isolated and back-transformed peaks between 2.4 and 4.5 Å. The dots correspond to the experimental data and the solid line corresponds to fit of the backed transformed co-ordinations with a three-shell model (Tb–Pd, Tb–Al and Tb–Tb co-ordinations). As the result of fitting, R, N, σ and $E0$ were determined at each temperature, respectively. R and σ of these value are shown in Table 1. Fig. 3 shows the Fourier transformation of the $k^3\chi(k)$ function of the Tb L_3-edge in TbPdAl at several different temperatures. The solid lines correspond to the antiferromagnetic phase, the broken lines to the HTM II phase, and the dotted lines to the HTM I phase. Fourier transformations were performed on the Tb L_3-edge EXAFS spectrum in about the 3.0−13.5 Å^{-1} region. All of the radial distoribution function (RDF) in Fig. 3 show three peaks. As the result of fitting, the first peak at 2.4 Å corresponds to Tb–Pd bonds, the second peak at 2.9 Å to Tb–Al bonds and the third peak at 3.4 Å to Tb–Tb bonds. These values were consistent with the data of neutron diffraction [2]. The Tb–Al bonds were located at the same position at all temperatures. On the other hand, the Tb–Tb and Tb–Pd bond lengths of the paramagnetic phase became longer than that of the antiferromagnetic phase, and the temperature dependence in the XANES spectra at the Tb L_3-edge could not be observed. These results mean that the change in the Tb–Tb and Tb–Pd bond lengths is strongly correlated to the magnetic phase transition. Especially, the Tb–Tb bond length in TbPdAl played an

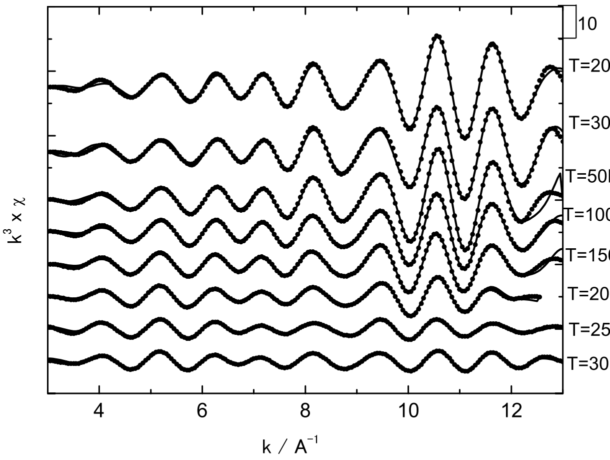

Fig. 2. k^3-Weighted Tb L_3-edge EXAFS data (dotes) and fitting curves (solid lines) from 20 to 300 K.

Table 1
Structural information from EXAFS analysis

T (K)	$R_{\mathrm{Tb-Pd}}$	$\sigma_{\mathrm{Tb-Pd}}$	$R_{\mathrm{Tb-Al}}$	$\sigma_{\mathrm{Tb-Al}}$	$R_{\mathrm{Tb-Tb}}$	$\sigma_{\mathrm{Tb-Tb}}$
20	2.93	0.052	3.28	0.061	3.71	0.057
50	2.94	0.049	3.25	0.080	3.73	0.047
100	2.93	0.063	3.26	0.069	3.74	0.064
150	2.92	0.069	3.25	0.079	3.74	0.062
300	2.91	0.097	3.27	0.108	3.67	0.078

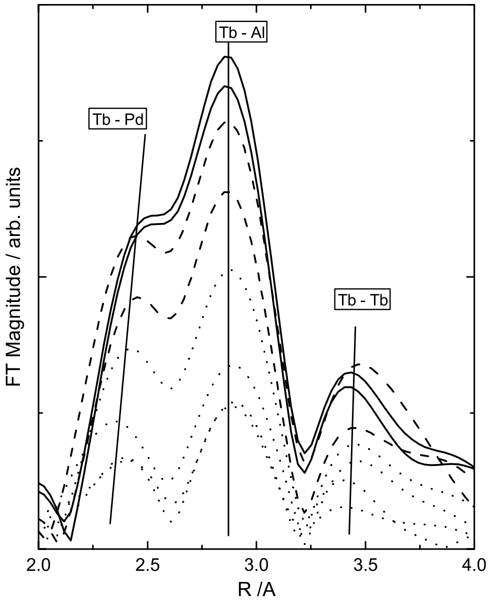

Fig. 3. Fourier transformation of k^3-weighted Tb L_3-edge EXAFS spectra of TbPdAl temperature dependence.

important role for the magnetic interaction of TbPdAl, as in the case of the other intermetallic rare-earth (R) aluminides RPdAl. However, the state of the 5d electrons which belong to the conduction electrons at the Tb site was unrelated with this magnetic phase transition.

3.2. XANES spectrum at the terbium L_3-edge and the palladium K-edge

Figs. 4 and 5 show the derivative curve of XANES at the Tb L_3-edge and at the Pd K-edge at several temperatures. The solid lines correspond to the antiferromagnetic phase, the broken lines to the HTM II phase and the dotted lines to the HTM I phase. In Figs. 4 and 5, the derivative curves were obtained after XANES spectra were differentiated and then were smoothed at once. At the Tb L_3-edge, these spectra had a positive peak around 7514 eV and a negative peak around 7520 eV. The change in the spectral shape and energy differences between the two peaks, mentioned above, could have occurred between the HTM I and the HTM II phases. At the Pd K-edge, there were two positive peaks around 24350 and 24360 eV. The shape of all the derivative XANES spectra at the Pd K-edge was similar to each other. However, the energy difference between the two peaks increased at an isostructural phase transition temperature. This energy shift comes under the influence of noise effect in the XANES spectra. As the XANES spectra could be considered as the unoccupied density of states in the first approximation, this change was strongly correlated to the partial electronic density of states at

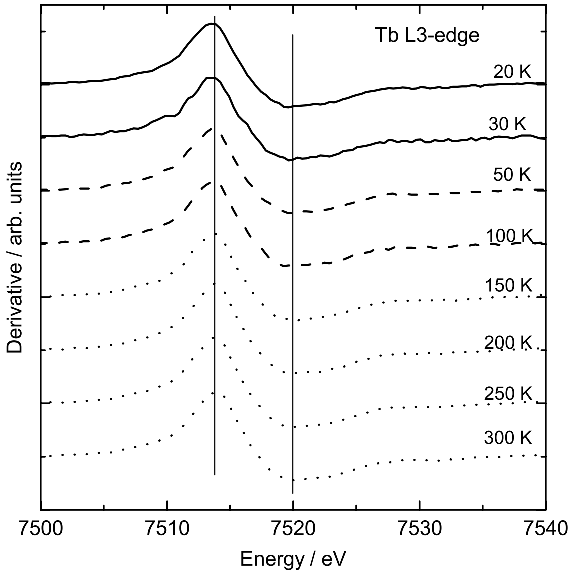

Fig. 4. Derivative curves of XANES spectra at the Tb L_3-edge in the region from 20 to 300 K.

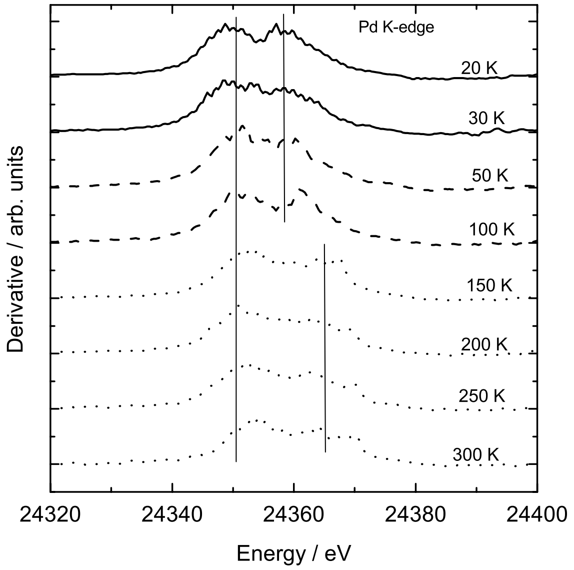

Fig. 5. Derivative curves of XANES spectra at the Pd K-edge in the region from 20 to 300 K.

the Pd site. In brief, this isostructural phase transition is mostly caused by the change in the electronic structure of Pd.

4. Conclusion

The ternary intermetallic compound TbPdAl exhibits an isostructural phase transition at around $T = 100\,\mathrm{K}$. We have carried out EXAFS and XANES measurements at the Tb L_3- and Pd K-edges to investigate the origin of this transition. The spectra were recorded at the R&D (III) beam-line 38B1 of SPring-8, Japan.

It was found that the Fourier transforms for the k^3-weighted Tb L_3-edge EXAFS spectra changed below and above the transition temperature, which is consistent with the existence of the structural transition. In addition, a slight temperature dependence was observed in the Pd K-edge XANES spectra, whereas the spectra at the Tb L_3-edge showed no obvious change. This result suggests that the transition is mainly caused by the change in the electronic structure of Pd.

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