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Magnetic, electrical and thermodynamic properties of $RE_8Pd_{24}In$

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A B S T R A C T

Investigations of magnetic, transport and thermodynamic properties of $RE_8Pd_{24}In$ (RE = Pr, Nd, Gd, Tb, Dy, Ho, Er and Tm) are reported through measurements of X-ray diffraction, electrical resistivity ($\rho(T)$), magnetic susceptibility ($\chi(T)$), magnetization ($\sigma(\mu_0 H)$) and heat capacity ($C_p(T)$). These ternary compounds have the cubic $AuCu_3$-type structure. Compounds with RE = Gd and Tb order antiferromagnetically (AF) and exhibit magnetic transitions observed in their $\chi(T)$ and $C_p(T)$. $\rho(T)$ results for the Gd and Tb compounds indicate a minimum above the magnetic phase transition temperature T_N, and an increase in $\rho(T)$ upon further cooling as a precursor of AF order at lower temperatures. $\chi(T)$ data at high temperatures follow the Curie–Weiss relation for all compounds and give effective moment values close to those expected for the free RE^{3+}-ion. Enhanced values of the electronic contribution to the heat capacity were observed for $Gd_8Pd_{24}In$ and $Tb_8Pd_{24}In$.

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1. Introduction

CePd$_3$ which crystallizes in the AuCu$_3$-type structure is well known to be an intermediate valence material [1]. Recently a series of related ordered ternary compounds Ce$_8$Pd$_{24}$M (M = Al, Ga, In, Si, Ge, Sn, Pb, Sb and Bi) were discovered and their transport, magnetic and thermodynamic properties were studied [2–5]. The Ce$_8$Pd$_{24}$M group of compounds exhibits antiferromagnetic (AF) order at low temperature and an enhanced electronic coefficient γ, suggesting heavy fermion character. Subsequently to these studies, Mitra et al. [6] studied Tb$_8$Pd$_{24}$M (M = Ga and Ge) while Singh and Dhar [7] investigated the $RE_8Pd_{24}Al$ compounds (RE = La, Gd, Tb, Dy, Ho, Er, Tm, Yb, Y). Antiferromagnetism was observed at low temperatures in some of the $RE_8Pd_{24}Al$ compounds (RE = Gd, Tb, Dy, Ho) and for Tb$_8$Pd$_{24}$M (M = Ga and Ge). Metamagnetic transitions are seen in both the M = Ga and Ge compounds of Tb$_8$Pd$_{24}$M [6] and for the Tb, Dy and Ho compounds of $RE_8Pd_{24}Al$ [7].

The crystal structures of both the Ce$_8$Pd$_{24}$M [2,3,5] and the $RE_8Pd_{24}Al$ [7] compounds are closely related to the Cu$_3$Au-type cubic structure of CePd$_3$. It is comprised of a cube with eight unit cells of CePd$_3$, with an a axis double that of CePd$_3$ and with the M

atom situated in the centre of only certain of the Pd octahedrals. This occurs because the larger M atom occupies a body-centred position in such CePd$_3$ unit cells and pushes the Pd atoms out from the faces of the cube resulting that the adjacent cells cannot accommodate an M atom.

In this paper, we report on X-ray diffraction (XRD) results, the electrical resistivity ($\rho(T)$), the magnetic susceptibility ($\chi(T)$), magnetization ($\sigma(\mu_0 H)$), and heat capacity ($C_p(T)$) of the $RE_8Pd_{24}In$ compounds.

2. Experimental details

Polycrystalline samples of $RE_8Pd_{24}In$ (RE = La, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm) and of RE_8Pd_{24} (RE = La, Gd, Tb, Dy, Ho, Tm) were prepared in the form of ingots by arc-melting the constituent elements on a water-cooled copper plate in an arc-furnace. Metals of the following purities in wt% were used: RE, 99.99, Pd, 99.97 and In, 99.999. Melting was performed in a titanium gettered ultra-high purity Ar atmosphere and ingots were turned over and remelted several times to ensure good homogeneity of the samples. Losses in mass after final melting were always smaller than 1%. Samples were characterized by X-ray powder diffraction using a Philips PW18301 powder diffractometer with Cu Kα radiation. No evidence of parasitic phases or unreacted elements was found in the X-ray spectra. Individual peak positions were determined using the WINPLOTR program for powder diffraction, Beta version/ LLB—February 1999. The results were used to calculate lattice

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parameters through least-squares (LSQ) fits of 5 well resolved diffraction lines of the cubic crystal using the Unit Cell program [8]. Furthermore we refine our XRD data on the basis of the CAILS-Pawley (cell and intensity least-squares) refinement method using the $Pm\bar{3}m$ space group. Powder XRD patterns of selected compounds and the variation of lattice parameters with the atomic number of the RE element in the compound are given in Section 3.1.

For $\rho(T)$ measurements, bar-shaped specimens of typical dimensions $1 \times 1 \times 6$ mm^3 were cut from the sample ingots using a diamond saw. A four probe DC method was used in this study in the temperature range 4.2–300 K. Gold contact wires were spot-welded onto the specimens. Current reversal was used to correct for possible thermal voltage in the circuitry. Temperatures were measured using a Au-0.07 at.% Fe versus chromel thermocouple with an absolute accuracy of $T \pm 0.5$ K. Magnetic measurements were performed on a single piece ($\approx$10 mg mass) of each poly-crystalline compound in the temperature range 1.9–300 K and in applied fields up to 5 T using a Quantum Design MPMS-5 SQUID magnetometer. C_p measurements were performed on the Gd$_8$Pd$_{24}$In and Tb$_8$Pd$_{24}$In compounds in the temperature range 1.9–30 K, with a relaxation technique using the Physical Property Measurement System supplied by Quantum Design.

3. Results and discussion

3.1. XRD results

Powder XRD spectra of selected compounds of RE$_8$Pd$_{24}$In and Gd$_8$Pd$_{24}$ are given in Fig. 1. It has been observed that all of the RE$_8$Pd$_{24}$In and RE$_8$Pd$_{24}$ compounds synthesized in our study crystallize in the cubic AuCu$_3$-type structure with space group $Pm\bar{3}m$. The results of the CAILS-Pawley refinement shown in Fig. 1 yield room temperature lattice parameters that are in good agreement with the values obtained from the Unit Cell program. The diffractograms illustrate the single phase character of our samples and the absence of impurity phases. Comparison of the results for Gd$_8$Pd$_{24}$ and Gd$_8$Pd$_{24}$In shows a small increase in lattice parameter a from 8.189(1) nm to 8.204(1) nm upon the introduction of In to the structure. Similar small increases were also observed in all of the other cases where comparisons were made (RE = La, Tb, Dy, Ho, Tm). Values of a for the RE$_8$Pd$_{24}$In compounds are depicted in Fig. 2 and are observed to decrease with increasing RE atomic number in accordance with the lanthanide contraction. It is noted that our powder XRD measurements could not resolve if a super-structure exists in our RE$_8$Pd$_{24}$In samples, similar to that reported for Ce$_8$Pd$_{24}$M [4,5] from weak additional diffraction peaks in single-crystal XRD studies and also from weak additional peaks in powder XRD for RE$_8$Pd$_{24}$Al samples [7].

3.2. Electrical resistivity

Results of $\rho(T)$ measured between 4 and 300 K for the RE$_8$Pd$_{24}$In compounds are depicted in Fig. 3. The overall behaviour of the $\rho(T)$ curves of all the compounds is metallic like. $\rho(T)$ data for the Gd and Tb compounds show resistivity minima at 31 K and 15 K respectively and an increase in $\rho(T)$ upon further cooling as a precursor of the AF order that occurs at a much lower temperature of 3.9 K and 3.1 K respectively for these compounds (see Section 3.3). Such a behaviour has also been observed in RE$_8$Pd$_{24}$Al with RE = Gd, Tb, Dy and Ho and were attributed to the critical scattering above T_N [7]. Other RE compounds that show distinct magnetic precursor effects in $\rho(T)$ well above T_N include Gd$_2$PdSi$_3$ [9] and GdPt$_2$Ge$_2$ [10]. Large negative magnetoresistance
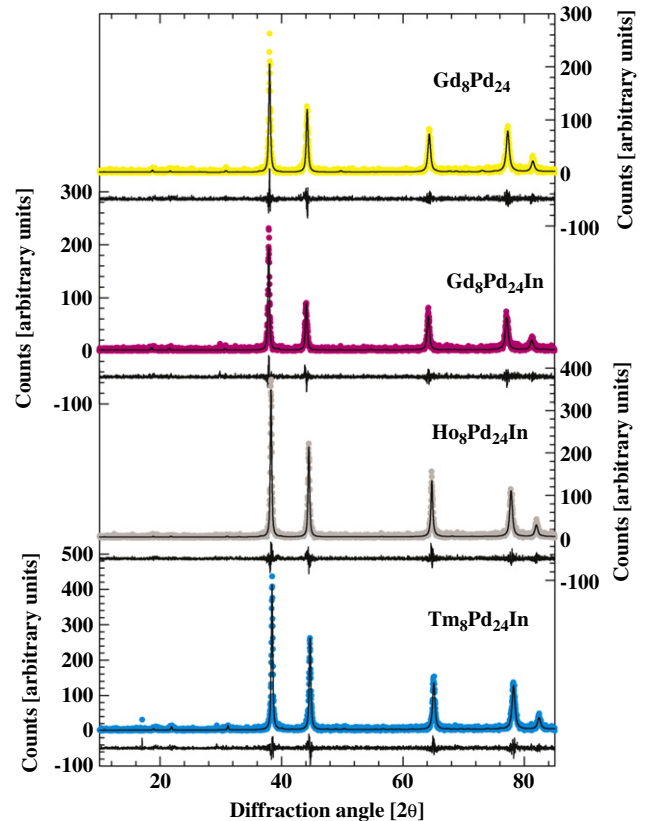

Fig. 1. (Color online) Powder X-ray diffraction pattern of selected RE$_8$Pd$_{24}$In and Gd$_8$Pd$_{24}$. The experimental data are shown by the colored symbols, while the black lines through the data represent the results of the CAILS-Pawley refinement. Difference curves are displayed below each of the diffractograms.
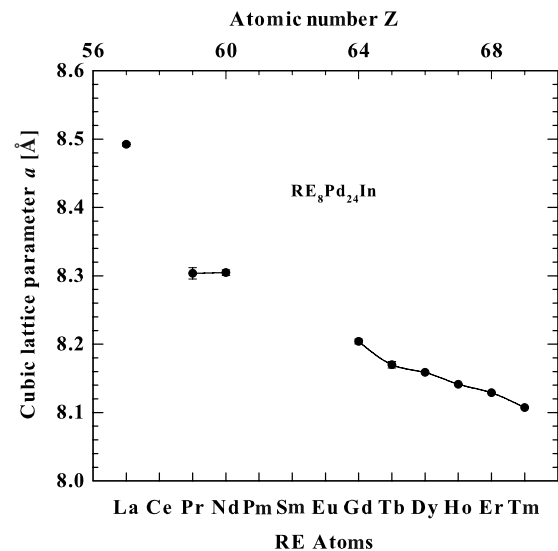

Fig. 2. The cubic lattice parameter a as a function of the RE atomic number for the RE$_8$Pd$_{24}$In compounds.

values are observed both below and above T_N for these compounds, as well as for other RE compounds (e.g. Tb$_2$PdSi$_3$, Dy$_2$PdSi$_3$ [11], GdNi$_2$Si$_2$ [12]) various possible explanations for these precursor and negative magnetoresistance effects were advanced amongst others the possibility of spin fluctuations in 3d, 4d or 5d bands due to polarization by the RE ion [12] or the concept of electron localization mediated by disordered exchange interaction [11].