



Structural and magnetic studies of the $\text{REPt}_{5-x}\text{M}_x$ ($\text{RE} \equiv \text{La}, \text{Nd}$; $\text{M} \equiv \text{Al}, \text{Ga}, \text{In}$) systems

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Received 22 April 1994

Abstract

Crystallographic and magnetic studies of the $\text{LaPt}_{5-x}\text{M}_x$ and $\text{NdPt}_{5-x}\text{M}_x$ ($\text{M} \equiv \text{Al}, \text{Ga}, \text{In}$) systems have been carried out. It was found that platinum in LaPt_5 and NdPt_5 can be replaced by aluminium or gallium preferentially in the intermediate layer of the prototype structures up to LaPt_2Al_3 , LaPt_2Ga_3 , NdPt_3Al_2 and NdPt_3Ga_2 respectively. However, substitution of indium for platinum was possible only in the system $\text{NdPt}_{5-x}\text{In}_x$ and at the composition NdPt_4In , but with a change to the cubic crystal structure of the MgSnCu_4 type. Magnetic measurements indicate that the Curie–Weiss behaviour of NdPt_5 is retained in all single-phase ternary samples. Generally the negative paramagnetic Curie temperatures decrease and the effective magnetic moments increase as the content of the substituent increases. In the lanthanum-containing systems the diamagnetism of LaPt_5 changes to a weak paramagnetism when platinum is replaced by aluminium or gallium.

Keywords: Magnetic studies; Aluminium; Gallium; Indium

1. Introduction

It is well known that many rare earth intermetallics of the composition $\text{RE}T_5$ (RE , rare earth; T , transition metal) crystallize with the hexagonal CaCu_5 type of structure. Replacement of the T component in these compounds by various other metals or metalloids often strongly affects the crystallographic and physical (especially magnetic) properties of the basic compound. For example, a series of crystal structures related to the hexagonal CaCu_5 type were reported to consist of an ordered replacement of cobalt atoms by boron in the basal mixed layer ($\text{RE} + \text{Co}$) of the prototype alloy RECo_5 [1]. Several other CaCu_5 -related structures of the composition RET_3M_2 ($\text{M} \equiv \text{Al}, \text{Ga}$) can be obtained by ordered replacement of transition metal atoms (T) by aluminium or gallium in the intermediate layer containing small atoms only [2–6].

Statistical replacement of T atoms in the intermediate layer by aluminium, gallium or tin is possible in many systems (see e.g. Refs. [7–11]), while replacement of one T atom by indium or some noble metals ($\text{Au}, \text{Ag}, \text{Pd}$) often changes the structure into a cubic one of the MgSnCu_4 type [7,9,12]. There are also data on more or less random occupation of both available

non-rare earth sites in the CaCu_5 type of structure by transition metal and aluminium (gallium) atoms [13].

Besides the extraordinary magnetic properties of SmCo_5 -based compounds, one can also mention the strongly substitution-affected antiferromagnetic properties of CePt_5 [9,11]. The change from an antiferromagnetic to a heavy fermion behaviour when platinum in CePt_5 is replaced by indium [12] and the cross-over from a divalent behaviour of Yb in YbCu_5 to a stable $3+$ behaviour when two copper atoms are replaced by aluminium [14] are also interesting findings.

Magnetic measurements on REPt_5 ($\text{RE} \equiv \text{La}, \text{Nd}$) compounds have been carried out and it was found that LaPt_5 is diamagnetic while NdPt_5 orders antiferromagnetically with a Néel temperature $T_N = 1.8$ K [15,16]. There are also some published data on the structural and magnetic properties of LaPt_4In and NdPt_4In [17].

The study presented in this paper was carried out with the aim of obtaining further information on the properties of rare-earth-containing intermetallics when the electronic density of states is drastically affected by substitution.

2. Experimental procedures

The alloys were prepared from metals of high commercial purity (Johnson–Matthey, UK, min. 99.99 wt.%) in a water-cooled copper boat under ultrahigh vacuum using high frequency induction melting. To ensure homogeneity, samples were turned upside down and remelted and then homogenized at 1070 K for 7 days.

The phase purity and the lattice parameters have been determined from X-ray powder diffraction patterns obtained with a computerized Siemens D-5000 diffractometer; nickel-filtered Cu K α radiation was employed. The line positions were corrected with respect to silicon used as an internal standard. The intensities were calculated with the LAZY PULVERIX program [18]. Magnetic measurements were performed on a vibrating sample magnetometer (VSM) over a temperature range of 77–300 K and at a field strength up to 10 kOe. Pure nickel was used as a calibrant.

3. Results and discussion

3.1. Structure

The X-ray powder diffraction data of the alloys LaPt_{5-x}Al_x, LaPt_{5-x}Ga_x and their neodymium analogues indicate that single-phase samples exist up to the compositions LaPt₃Al₂, LaPt₃Ga₂, NdPt₃Al₂ and NdPt₃Ga₂ respectively. All the single-phase compounds crystallize with the hexagonal CaCu₅ type of structure (space group *P6/mmm*), i.e. the same structure in which the prototypes LaPt₅ and NdPt₅ crystallize [19].

In this type of structure there exist two crystallographically inequivalent platinum sites: 2(*c*) in the basal plane layer of mixed atoms (RE + Pt) and 3(*g*) in the intermediate layer known also as a Kagome net. A

detailed diffraction intensity data analysis was carried out and it was determined that aluminium (gallium) atoms statistically replace platinum atoms in the Kagome net only. No ordering similar to that encountered in several related compounds (ThCo₃Ga₂ [3,4], NdCo₃Ga₂ [5], CePt₃Al₂ [6]) and some other rare earth–transition metal–gallium analogues [17] was observed regardless of the heat treatment.

In the systems REPt_{5-x}In_x (RE \equiv La, Nd) the only single-phase ternary sample was NdPt₄In, but with a cubic structure of the MgSnCu₄ type [20]. This structure should be regarded as being derived from the cubic NdPt₂ Laves structure by ordered replacement of half of the Nd atoms by indium rather than by replacement of Pt atoms in a hypothetical cubic NdPt₅ structure of the AuBe₅ type. The narrow homogeneity range along the Nd_{1-x}In_xPt₂ composition supports this assumption. The results described above differ slightly from those given in Ref. [17], where the existence of an MgSnCu₄ type of structure was reported for the lanthanum-containing system too.

The relevant lattice parameters are presented in Table 1. The expansion of the *c* axis is larger than that of the *a* axis (indication of preferential substitution!), but both axes expand monotonically with an increasing content of the substituent.

It should be noted that substitution in the systems with the hexagonal structure takes place only until two-thirds of the platinum atoms in the Kagome net are replaced by aluminium (gallium) rather than proceeding until the whole layer is replaced as observed in the related CePt_{5-x}Al_x system [6].

3.2. Magnetic properties

The magnetic measurements indicate that all ternary lanthanum-containing alloys exhibit a weak tempera-

Table 1
Unit cell parameters and magnetic data for the REPt_{5-x}M_x (RE \equiv La, Nd; M \equiv Al, Ga, In) systems

Composition	Structure type	<i>a</i> (Å)	<i>c</i> (Å)	θ_p (K)	C_M (e.m.u. K mol ⁻¹)	μ_{eff} (μ_B)
LaPt ₅	CaCu ₅	5.385	4.376	$\chi = -0.042 \times 10^{-3}$	e.m.u. mol ⁻¹	
LaPt ₄ Al	CaCu ₅	5.394	4.441	$\chi = 0.021 \times 10^{-3}$	e.m.u. mol ⁻¹	
LaPt ₃ Al ₂	CaCu ₅	5.403	4.507	$\chi = 0.049 \times 10^{-3}$	e.m.u. mol ⁻¹	
LaPt ₄ Ga	CaCu ₅	5.388	4.430	$\chi = 0.020 \times 10^{-3}$	e.m.u. mol ⁻¹	
LaPt ₃ Ga ₂	CaCu ₅	5.400	4.498	$\chi = 0.042 \times 10^{-3}$	e.m.u. mol ⁻¹	
NdPt ₅	CaCu ₅	5.346	4.392	-6.0	1.287	3.21
NdPt ₄ Al	CaCu ₅	5.361	4.436	-4.9	1.425	3.38
NdPt ₃ Al ₂	CaCu ₅	5.383	4.494	-1.0	1.516	3.48
NdPt ₄ Ga	CaCu ₅	5.359	4.435	-4.8	1.360	3.30
NdPt ₃ Ga ₂	CaCu ₅	5.379	4.480	-3.1	1.464	3.42
NdPt ₄ In	MgSnCu ₄	7.601		-1.9	1.523	3.49
Nd _{1.2} Pt ₄ In _{0.8}	MgSnCu ₄	7.604		-1.9	1.535	3.50

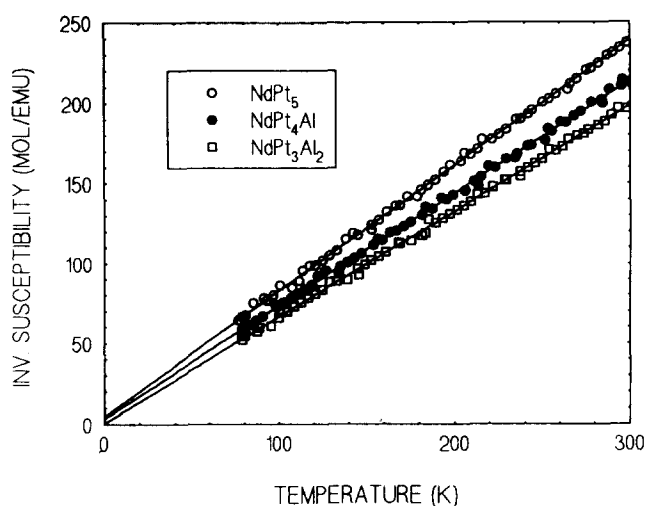


Fig. 1. Inverse magnetic susceptibility vs. temperature for the $\text{NdPt}_{5-x}\text{Al}_x$ system at 10 kOe.

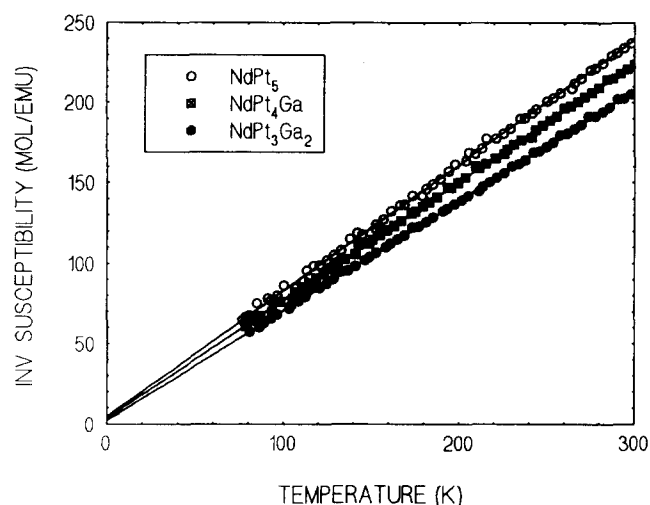


Fig. 2. Inverse magnetic susceptibility vs. temperature for the $\text{NdPt}_{5-x}\text{Ga}_x$ system at 10 kOe.

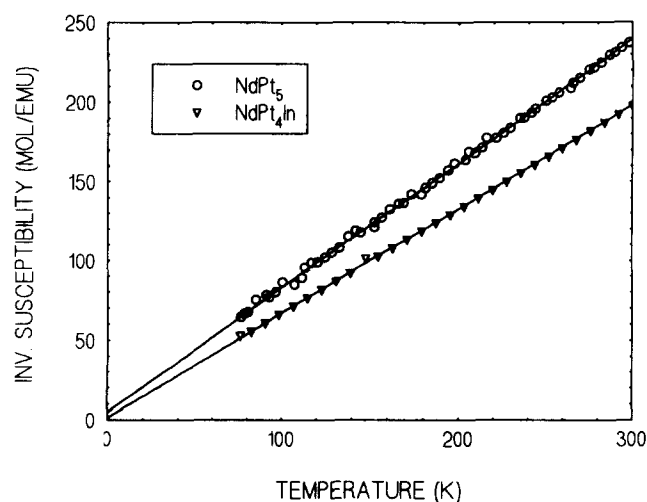


Fig. 3. Inverse magnetic susceptibility vs. temperature for the $\text{NdPt}_{5-x}\text{In}_x$ system at 10 kOe.

ture-independent susceptibility. In contrast, the neodymium-containing alloys exhibit a temperature-dependent susceptibility following the Curie–Weiss law $\chi = C/(T - \theta_p)$, where χ is the susceptibility, C is the Curie constant and θ_p is the paramagnetic Curie temperature. The inverse magnetic susceptibilities for all single-phase alloys at 10 kOe are shown in Figs. 1–3 (experimental data are presented as points and the best fits are denoted by solid lines). The effective paramagnetic moments were calculated from the Curie constants. All the results are summarized in Table 1.

The magnetic features of the investigated systems can be summarized as follows. Binary LaPt_5 exhibits a temperature-independent negative susceptibility indicating this compound to be diamagnetic. Replacement of platinum atoms by aluminium or gallium changes the susceptibility to weak positive values.

The Nd-based alloys are paramagnetic (linear magnetization vs. field) and the Curie–Weiss behaviour of the susceptibility indicates localized magnetic moments. The effective magnetic moments of the single-phase ternary region are close to the free- Nd^{3+} -ion value and the negative Curie temperature indicates antiferromagnetic interactions. The susceptibility and effective magnetic moments increase slightly while the paramagnetic Curie temperature decreases with increasing content of aluminium (gallium). The above effects are more pronounced for the alloys containing aluminium. When indium plays the role of the substituent, the resulting changes in magnetic moments and paramagnetic Curie temperature are more pronounced (compared with aluminium and gallium), but the susceptibility values are better fitted if a temperature-independent term of 0.5×10^{-5} is subtracted from the total susceptibility. The results for NdPt_4In and the pure binary compounds are in agreement with literature data [15–17].

The magnetic behaviour of the intermetallic compounds described in this paper can be discussed in terms of substituent atoms acting as electron donors to the system. As a result, in the ternary region the diamagnetism of binary LaPt_5 is masked with a stronger paramagnetic susceptibility (lanthanum-based compounds) or the Nd magnetic moments observed for binary NdPt_5 are somewhat increased in the ternary region of the neodymium-based compounds.

4. Conclusions

As a conclusion of the structural and magnetic study of the systems $\text{LaPt}_{5-x}\text{M}_x$ and $\text{NdPt}_{5-x}\text{M}_x$ ($\text{M} \equiv \text{Al}, \text{Ga}, \text{In}$) we can say that substitution of platinum by aluminium or gallium takes place up to the compositions LaPt_3Al_2 , LaPt_3Ga_2 , NdPt_3Al_2 and NdPt_3Ga_2 respectively. Aluminium or gallium atoms statistically replace platinum

atoms preferentially in the intermediate Kagome net. Substitution of platinum atoms by indium atoms was possible only in the Nd-containing system at the composition NdPt₄In, with a narrow homogeneity range along the Nd_{1-x}In_xPt₂ tie-line. The crystal structure of this compound is a cubic one of the MgSnCu₄ type. The negative susceptibility of LaPt₅ is temperature independent, with changes to positive values in the ternary region. The susceptibility for all Nd-containing alloys follows a Curie–Weiss law with effective magnetic moments close to that for the Nd³⁺ ion.

Acknowledgment

Thanks are expressed to Dr. Nick Bernhoeft, Department of Physics, University of Durham, Durham, UK, who made the above experiments possible.

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