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Properties of Gd_3T compounds (T = Rh, Ir, Pd)

E. Talik, A. Ślebarski

Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland

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Abstract

Gd_3Rh, Gd_3Ir and Gd_3Pd were obtained by the Czochralski method from a levitated melt. Powder diffraction patterns were studied. The crystal structure was determined as Fe_3C-type. The magnetic susceptibility was measured in a wide temperature range (4.2–800 K). For Gd_3Rh an antiferromagnetic transition was observed at 112 K, whereas for Gd_3Ir a ferromagnetic transition was obtained at 155 K. For Gd_3Pd a ferromagnetic transition was observed at 325 K. The enhancement of the effective magnetic moment calculated per gadolinium ion, in relation to the theoretical value, was $0.55\mu_B$ for Gd_3Rh, $0.18\mu_B$ for Gd_3Ir and $-0.28\mu_B$ for Gd_3Pd. This effect may be related to spin fluctuations due to hybridization of the almost empty 5d states of gadolinium with the almost full 4d (or 5d) states of the transition metal.

Keywords: Magnetic properties; Crystal structure; Transition metals

1. Introduction

The R_3T compounds (R: rare earth; T: transition metal 3d, 4d or 5d with almost full d band) belong to the R–T compounds with the highest R content. They crystallize in the Fe_3C-type of crystal structure. In this structure, the transition metal atoms are situated in trigonal prisms, the corners of which are occupied by rare earth atoms. Due to the large interatomic distances (over 0.4 nm) direct interaction between the transition metals is not expected. For R_3(Co, Ni) compounds spin fluctuation effects were observed in the magnetic susceptibility, in the electrical resistivity [1–4] and in the temperature dependence of the lattice parameters [5,6]. For R_3T compounds with non-magnetic rare earths or yttrium, a pronounced temperature dependence of the magnetic susceptibility, well fitted by the Curie–Weiss law after subtracting a temperature independent term χ_0, was observed. The electrical resistivity reaches a relatively high value and shows the negative curvature with tendency to saturate [3,4,6]. Moreover, lattice parameter instabilities were observed in these compounds [5,6]. Some R_3T compounds with non-magnetic rare earths also exhibit superconducting properties [3,7,8]. For R_3T compounds with magnetic rare earths similar features of the physical properties were observed. Moreover, an additional magnetic transition related to the ordering of the rare earth exists [1,2,4,9]. The electrical resistivity of Gd_3T (T = Co [1,2], Ni [4], Rh, Ir [9]) shows a pronounced negative curvature. The magnetic phase transitions are respectively at 100 K (Gd_3Ni), 129 K (Gd_3Co), 112 K (Gd_3Rh), 325 K (Gd_3Pd) and 155 K (Gd_3Ir). Finally, a saturation effect of the resistivity is observed at room temperature. In the low-temperature region, the drop in resistivity (except of Gd_3Ir) may be related to the ordering tendency of the T sublattice. It was found for e.g. Gd_3Co [2] at 3.7 K. XPS valence band measurements for Gd_3Ni [10], Gd_3Rh and Gd_3Ir [9] led to the conclusion of a hybridization effect between the almost full T-d band and the almost empty Gd-5d. This effect may be responsible for a small depletion of the T-d band and be the origin of spin fluctuations. The aim of this work is to examine the magnetic properties of the described compounds.

2. Experimental

Gd_3Rh, Gd_3Ir, Gd_3Pd were obtained by induction melting of the starting materials of purity: Gd, 99.9%; Rh, 99.998%; Ir and Pd, Specpure Johnson Matthey Ltd, which were placed on a water-cooled, eight-segment conical coil, in an atmosphere of pure argon. To ensure good homogeneity the samples were remelted several times. A small fragment of each sample was pulverized to obtained a diffraction pattern, using a Siemens D-

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Table 1
Powder parameters of Gd_3Pd,Fe_3C-type of crystal structure (lattice parameters used for calculation are: $a=7.710$, $b=9.188$, $c=6.635$)

$h\ k\ l$	2Θ	$2\Theta_{calc}$	d_{exp}	d_{calc}
0 1 2	28.660	28.582	3.112	3.120
1 0 2	29.236	29.281	3.052	3.047
2 2 0	30.239	30.239	2.953	2.953
1 1 2	30.882	30.888	2.893	2.892
1 3 1	34.248	34.250	2.616	2.616
1 2 2	35.319	35.313	2.539	2.539
3 1 0	36.200	36.266	2.479	2.475
2 3 1	39.900	39.941	2.434	2.250
3 2 0	40.200	40.171	2.241	2.243
0 0 3	40.546	40.762	2.223	2.212
1 0 3	42.50	42.484	2.125	2.126
3 2 1		42.510		2.125
4 1 0	48.263	48.200	1.884	1.886
2 1 3	48.45	48.431	1.877	1.87
3 3 2	54.124	54.124	1.693	1.693
3 0 3	54.71	54.706	1.676	1.676
4 0 2	55.148	55.055	1.664	1.666

5000 diffractometer. The crystal structure was determined as the orthorhombic Fe_3C-type. The structure of Gd_3Rh was described in Ref. [11]. As far as we know, the crystal structures of Gd_3Ir and Gd_3Pd have not yet been identified. However, an Fe_3C-type structure was reported for both Y_3Ir and Y_3Pd [12]. For Gd_3Pd the lattice parameters were obtained as $a=7.710$, $b=9.188$, $c=6.635$ (Table 1). For Gd_3Ir the structure was identified as a monoclinic with lattice parameters $a=7.207$, $b=9.227$, $c=6.214$ and $\beta=81.53$.

The magnetic susceptibility was measured using the Faraday method in the temperature range 4.2–800 K in fields of 200–250 Oe in a helium atmosphere.

The electrical resistivity of Gd_3Pd was measured by a conventional method in the temperature range 4.2–330 K.

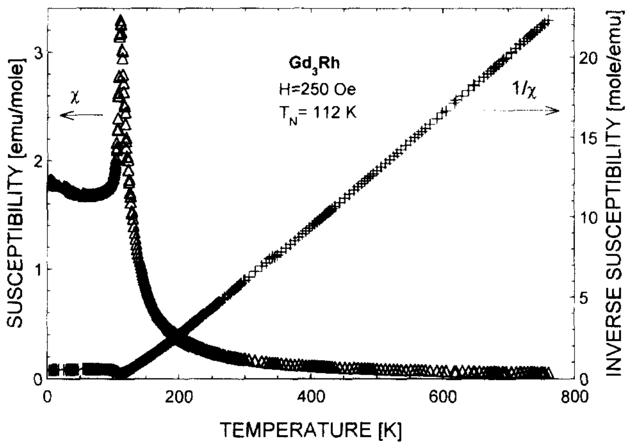

Fig. 1. Temperature dependence of the Gd_3Rh magnetic susceptibility.

Table 2
Magnetic properties of Gd_3T compounds

Compound	T_N or T_c (K)	μ_{eff}/f.u. (μ_B)	Θ	$\Delta\mu$ (μ_B)
Gd_3Ni [2]	$T_N=100$	15.63	87 K	1.09
Gd_3Rh	$T_N=112$	14.7	146 K	0.55
Gd_3Ir	$T_c=155$	14.07	169 K	0.18
Gd_3Pd	$T_c=325$	13.27	340 K	−0.28

$\Delta\mu=(\mu_{eff}/\text{f.u.})/3^{1/2}-\mu_{Gd}$.

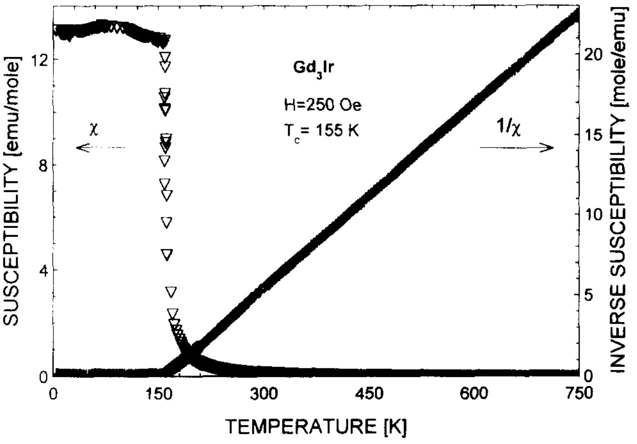

Fig. 2. Temperature dependence of the Gd_3Ir magnetic susceptibility.

3. Results and discussion

The temperature dependence of the magnetic susceptibility of Gd_3Rh (Fig. 1) shows a very sharp antiferromagnetic transition at $T_N=112$ K. Curie–Weiss behaviour occurs above 500 K with $\Theta=146$ K and μ_{eff}/f.u.$=14.7\mu_B$ (Table 2). Taking the theoretical value of $\mu_{Gd^{3+}}=7.94\mu_B$, the excess of the magnetic moment calculated per gadolinium ion $\Delta\mu=(\mu_{eff}/\text{f.u.})/3^{1/2}-\mu_{Gd^{3+}}$ equals $0.55\mu_B$.

For Gd_3Ir the temperature dependence of the magnetic susceptibility is shown in Fig. 2. A ferromagnetic transition is observed at $T_C=155$ K and Curie–Weiss behaviour is observed for temperatures above 450 K with $\Theta=169$ K and μ_{eff}/f.u.$=14.07\mu_B$, which leads to an excess of the effective magnetic moment $\Delta\mu=0.18\mu_B$ (Table 2).

The thermal variation of the magnetic susceptibility of Gd_3Pd exhibits a ferromagnetic transition at $T_C=325$ K (Fig. 3). Curie–Weiss behaviour is obeyed above 500 K with $\Theta=340$ K and μ_{eff}/f.u.$=13.27\mu_B$. Here the effective magnetic moment decreases and $\Delta\mu=-0.28\mu_B$ (Table 2).

The electrical resistivity measurements for Gd_3Pd (Fig. 4) exhibit a strong negative curvature up to the ordering temperature, the value of which is in agreement

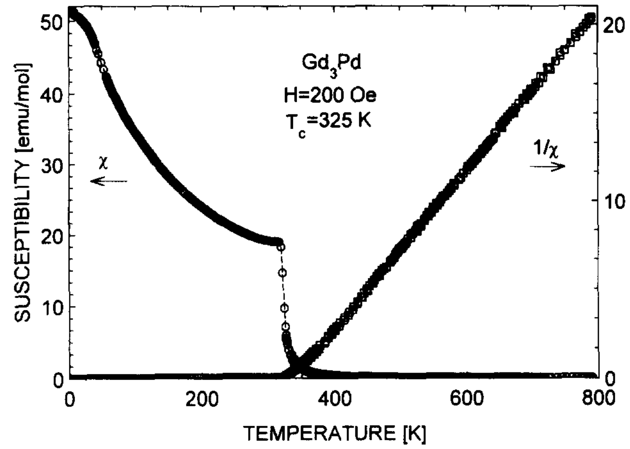

Fig. 3. Temperature dependence of the Gd_3Pd magnetic susceptibility.

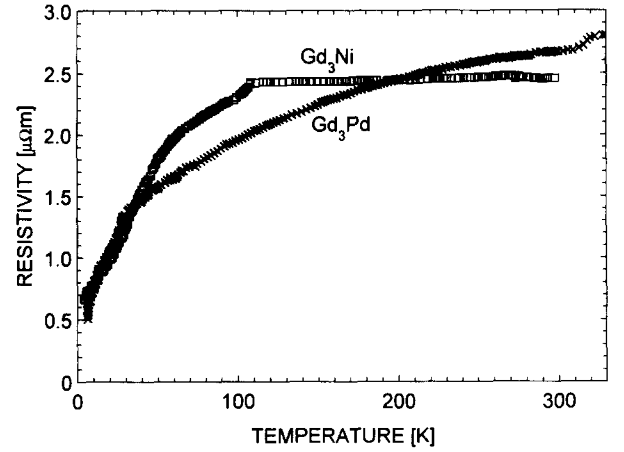

Fig. 4. Temperature dependence of the electrical resistivity of Gd_3Pd and Gd_3Ni [4].

with that from the magnetic susceptibility measurements. This behaviour is similar to that of the other Gd_3T compounds (especially Gd_3Ni [4]). At low temperatures a decrease of the electrical resistivity is observed. Generally, the electrical resistivity for Gd_3T has two non-phonon contributions, due to the localized 4f moment (the magnetic transition) and the itinerant T-d moment (the pronounced negative curvature) [9]. The saturation effect of the resistivity may be a combination of both these contributions.

Gadolinium compounds are interesting because of the S state of Gd^{3+}. This inhibits crystal field effects. From the magnetic susceptibility measurements a noticeably larger effective magnetic moment (larger than the free ion value $7.94\mu_B$) was obtained for all Gd_3T compounds (except Gd_3Pd). The enhancement is the largest for T-3d (about $1\mu_B$), medium for T-4d ($0.5\mu_B$) and rather low for T-5d ($0.2\mu_B$). According to the variation of the transition metal bandwidths [13] the widest bands are for T-5d metals and the narrowest bands for T-3d. This may influence the strength of the hybridization between the 5d states of Gd and the T-d states. From the XPS valence band measurements for Gd_3Ni very narrow Ni-3d states ($\Gamma_{FWHM}=1.2$ eV, binding energy BE = 1.7 eV) were found [4]. For Gd_3Rh a considerable narrowing of the Rh-4d states in relation to pure Rh was observed ($\Gamma_{FWHM}=2$ eV, BE = 2.1 eV). Also for Gd_3Ir a narrowing of the Ir-5d states in comparison with pure Ir was found ($\Gamma_{FWHM}=4.7$ eV, BE = 2.5 eV) [9].

For all these compounds the observed filling and narrowing of the T-d states is mainly due to a transfer of s electrons, similarly to the case of Y_9Co_7 [14]. The Gd-5d states remain almost intact, giving a small broad peak near EF. The states of the bottom of the 5d band may hybridize with the states of the top of the T-d band [9]. Due to this effect the Fermi level lies in the region of positive curvature so that spin fluctuations may be produced (e.g. in the electrical resistivity, or in magnetic properties).

According to Buschow [11], in R–T compounds the R–R interactions (RKKY-type) are the weakest. They may reach higher values if realized via 5d electrons. The ordering temperatures in compounds with no moment on the T atoms are well below 100 K. In R_3T compounds any T–T interaction is not expected due to the large interatomic distances. So the R–T interactions should play an important role. With decreasing enhancement of the effective magnetic moment one can observe a change of the magnetic ordering from the antiferromagnetic to ferromagnetic (Table 2). A particularly high value of the Curie temperature, even higher than for pure gadolinium, is observed for Gd_3Pd (with a negative value for the excess of the effective magnetic moment). A similar value of T_C was obtained for Gd_5Pd_2 [11] with unknown crystal structure but with lower than cubic symmetry of Dy_5Pd_2, as was found for R_5Pd_2 [15]. It is possible that because of the similar stoichiometry for both Gd_3Pd and Gd_5Pd_2 the Fe_3C-type of crystal structure was obtained for both cases. For both compounds a similar value of the (negative) excess effective magnetic moment was reported [11]. Such a decrease of the magnetic moment was observed for heavy rare earth impurities in Pd with increasing of rare earth content, and was explained by Hund's rule [16,17], i.e. by the negative polarization of the electron cloud of Pd surrounding the heavy rare earth ions. Note that, in contrast, a positive Pd cloud polarization observed for the light rare earths, e.g. in Pd:Pr. At this stage it is difficult to explain the increase of the magnetic susceptibility of Gd_3Pd after the ferromagnetic transition with decreasing temperature. Further examination is required.

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