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MAGNETIC AND ELECTRONIC PROPERTIES OF $GdNi_{5-x}Al_x$ INTERMETALLIC COMPOUNDS

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X-ray photoelectron spectroscopy and magnetic susceptibility of $GdNi_5$, $GdNi_4Al$, $GdNi_2Al_3$ and $GdNiAl_4$ are reported. The magnetic state of Ni $3d$-electrons strongly depends on the crystallographic structure of the compounds, showing spin fluctuations in $GdNi_5$ and $GdNi_4Al$, a similar behavior with that of metallic Ni in $GdNi_2Al_3$ and a filled $3d$-band in $GdNiAl_4$.

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1. Introduction

Four intermetallic compounds with different crystallographic structures were reported in the $GdNi_{5-x}Al_x$ series [1]. $GdNi_5$ and $GdNi_4Al$ are isostructural and crystallize in the hexagonal $CaCu_5$ structure type while the crystallographic structure of $GdNi_2Al_3$ is more complicated, namely a modulated $CaCu_5$ structure type. The compound $GdNiAl_4$ crystallizes in the orthorhombic $YNiAl_4$ structure type. The magnetic properties of $GdNi_5$ were studied earlier in the temperature range 4.2–290 K [2]. This compound is a ferromagnet with $T_c = 32$ K and a magnetic moment $\mu = 6.2\ \mu_B$/f.u. Ni is not magnetic but a negative $3d$-band polarization of 0.16 μ_B/Ni is induced by the interactions with the Gd spins. An effective magnetic moment of 7.7 μ_B/f.u. was determined from the Curie constant in the paramagnetic state and $GdNi_5$ was considered to be an exchange-enhanced Pauli paramagnet [2].

The aim of this paper is to investigate the influence of partially replacing of Ni by Al on the magnetic state of the Ni $3d$-electrons in $GdNi_{5-x}Al_x$ by using magnetic measurements and X-ray photoelectron spectroscopy (XPS) technique.

2. Experimental details

The investigated compounds $GdNi_5$, $GdNi_4Al$, $GdNi_2Al_3$, and $GdNiAl_4$ were prepared by argon arc melting. X-ray powder diffraction measurements showed

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that all compounds are single phases with the expected structure types. The lattice parameters agree with those reported in [1]. The magnetic susceptibilities were measured between 90 K and 900 K with a Weiss–Forrer magnetic balance with a sensitivity of 10^{-8} emu/g. The magnetization of $GdNi_2Al_3$ was measured at 4.2 K in high magnetic fields between 6 T and 9 T with a vibrating magnetometer. The XPS spectra were recorded using a PHI 5600ci ESCA spectrometer with monochromatized Al K_α radiation ($h\nu = 1486.6$ eV) at room temperature.

3. Results and discussions

The temperature dependence of the reciprocal susceptibilities for $GdNi_5$ and $GdNi_4Al$ are shown in Fig. 1. The $1/\chi(T)$ curves for both compounds show two linear portions with a change in the slope at about 700 K for $GdNi_5$ and 450 K for $GdNi_4Al$. The effective magnetic moments determined from the Curie constants for the two temperature ranges are as follows: $\mu_{\text{eff}} = 7.6\ \mu_B$/f.u. and 8.85 μ_B/f.u. for $GdNi_5$ and $\mu_{\text{eff}} = 7.88\ \mu_B$/f.u. and 8.72 μ_B/f.u. for $GdNi_4Al$. The first values of the effective magnetic moments show that the Ni atoms do not carry localized magnetic moments because of charge transfer of Gd $5d$ electrons to the Ni $3d$ band, as in all RNi_5 compounds. The deficit magnetic moment in $GdNi_5$ is related mainly to the negative polarization of the Ni $3d$ band which persists also in the paramagnetic state. This is not the case for the $GdNi_4Al$ compound. On the other hand, from the Curie constants of $GdNi_5$ for $T > 700$ K and of $GdNi_4Al$ for $T > 450$ K a value of about 1.76 μ_B/Ni is deduced which is very close to that of the free Ni^+ ion. We may explain such a behavior in a similar way as for the $YNi_{5-x}Al_x$ system [3, 4]. In the paramagnetic state, the average amplitude of the local spin fluctuations $\langle S_L^2 \rangle = 3k_B T \sum_q \chi_q$ (where χ_q is the wave number dependent susceptibility) increases with temperature until it reaches an upper limit determined by the charge neutrality condition [5]. The temperature dependence of χ is the result of the increase in the local moments with increasing temperature. The amplitude $\langle S_L^2 \rangle$ of thermally longitudinal spin fluctuations saturates at a certain temperature T^* (700 K for $GdNi_5$ and 450 K for $GdNi_4Al$), above which the susceptibility is governed by local moment-type fluctuations and therefore a Curie–Weiss behavior is observed.

The temperature dependence of the reciprocal susceptibility for $GdNi_2Al_3$ is presented in the inset of Fig. 1. The susceptibility obeys a Curie–Weiss law modified by a temperature-independent part χ_0 with a paramagnetic Curie temperature $\theta = 37$ K and $\chi_0 = 14 \times 10^{-4}$ emu/mol. The effective magnetic moment per Ni atom determined from the Curie constant is $\mu_{\text{Ni}} = 1.74\ \mu_B$, taking for the effective magnetic moment per Gd atom the value for the free Gd^{3+} ion. The effective Ni moment in $GdNi_2Al_3$ is close to that of Ni^+ ion, considering only the spin contribution, and to the value found in Ni metal (1.64 μ_B). This means that the magnetic state of Ni atoms in $GdNi_2Al_3$ is almost the same as in pure Ni. This conclusion is also supported by the values of the magnetization measured at 4.2 K in the high magnetic fields up to 9 T. The saturation magnetization was obtained by extrapolating $1/B$ to zero and has the value $M_s = 5.9\ \mu_B$/f.u. This value is smaller than the theoretical moment of 7.0 μ_B for free Gd^{3+} and suggests that the Ni atoms have a non-zero magnetic moment and the Ni sublattice moments couple

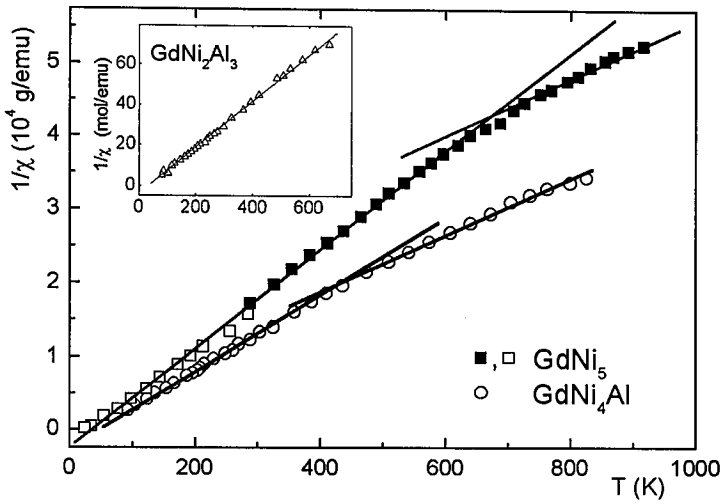

Fig. 1. Magnetic susceptibilities measured for the $GdNi_{5-x}Al_x$ system. Open squares are data taken from Ref. [2].

antiparallel to the Gd moments. For this ferrimagnetic arrangement the magnetic moment per Ni atom in the ordered state is deduced to be 0.55 μ_B, which is very close to that found in Ni metal (0.6 μ_B).

The valence bands of $GdNi_5$, $GdNi_4Al$, presented in Fig. 2, arise mainly from the Ni 3*d* electrons which are close to the onset of ferromagnetism. The 3*d* states are hybridized with 5*d* states. The occupied part of the valence bands are over 4 eV wide. The well-defined structure about 6 eV is a satellite structure related to the Ni *d* states [7]. One can see also a marked feature near the maximum of the valence bands of $GdNi_5$ and $GdNi_4Al$. This may be explained as a partial quenching of the spin fluctuations by the strong magnetic moments of Gd atoms. Furthermore, the substitution of Ni by Al leads to an increase in the localization of the Ni 3*d* electrons, reflected by an energy shift of the valence band maximum to higher binding energies. This is also supported by the different values of the saturation temperature of the spin fluctuations T^* obtained for $GdNi_5$ and $GdNi_4Al$.

One can observe marked differences both in the shape and in the position of the valence bands in $GdNiAl_4$ and Ni. The density of states at the Fermi level in $GdNiAl_4$ is drastically reduced in comparison with pure Ni and the maximum of the valence band is shifted to higher binding energy, namely from 0.59 eV in Ni to 2.3 eV in $GdNiAl_4$. The states at the Fermi level have 3*d* and *s*–*p* character in Ni and $GdNiAl_4$, respectively. In *d*-band metals and alloys the 3*d* states are shifted gradually to higher binding energy with the increase in the *d*-state occupancy and consequently a decrease in the density of states at E_F occurs [6]. These results reveal the complete filling of Ni 3*d*-band by charge transfer of Gd 5*d* electrons and the *s*–*p* character of the states at the Fermi level in $GdNiAl_4$. This conclusion is also confirmed by comparing the Ni 2*p* core level spectra for pure Ni and $GdNiAl_4$ (inset of Fig. 2). In the Ni 2*p* core level spectrum of pure Ni, satellites also are

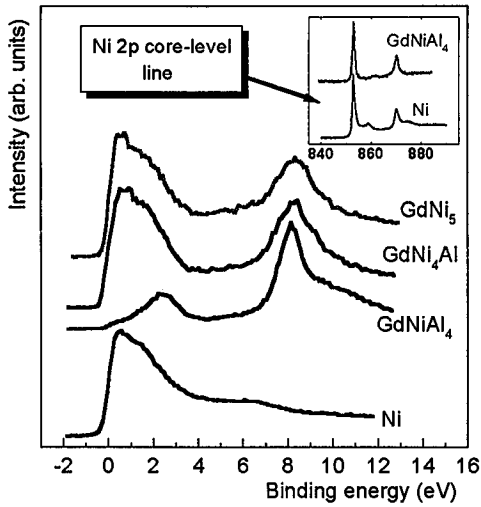

Fig. 2. XPS spectra recorded for the $GdNi_{5-x}Al_x$ system.

present as an evidence for the d character in unoccupied states. The absence of these satellites in the Ni $2p$ level spectrum of $GdNiAl_4$ shows that the $3d$-band in this compound is filled.

Summarizing the results, one may conclude that the Ni $3d$-band in $GdNi_{5-x}Al_x$ compounds is sensitive to the local environment, showing a large variety of magnetic behaviors by partially replacing of Ni by Al atoms.

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