Journal of Alloys and Compounds 317–318 (2001) 385–389

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Electronic structure and ESR in GdTAl ternary compounds; T=3d, 4d transition metals

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Abstract

Ternary GdT aluminides were obtained with the use of an arc furnace and the Czochralski method with levitated melt. The X-ray diffraction examination showed a variety of crystallographic structures depending on the transition metal involved. The XPS investigation of all these compounds revealed the importance of the transition metal d states in the formation of valence bands. The ESR measurements were performed at the paramagnetic state at temperatures above the ordering temperature. In all cases the relaxation rate between the localised Gd 4f magnetic moment system and the conduction electron system reflected the contribution of the d-type electrons to the density of states at the Fermi level. The different mechanisms of the opening of bottleneck existing in these compounds were observed.

Keywords: ESR; Electronic structure; Ternary GdT aluminides

1. Introduction

It is well known that d-type electrons play a very significant role in the GdTAl intermetallic, ternary compounds with the transition metal T. The crystallographic structure, magnetic and transport properties depend on the electronic structure and the d bands related to the T metals, determining the density of the states at the Fermi level. The s and p electrons seem to contribute less to forming the valence band in these compounds [1]. The d bands are filled to a different degree causing the lack of magnetic moment in Ni atoms (3d band completely filled), absence of magnetic moment in Co, despite the fact that the 3d band is not completely filled, and the presence of the magnetic moment in Fe atoms owing to the unfilled 3d band.

Ferromagnetic ordering was found for all the investigated compounds except for GdFeAl in which the Gd moments exhibited the antiferromagnetic ordering. In GdRhAl [2] and GdNiAl [1,3] a complex magnetic behaviour was reported together with a transition between two crystallographic forms followed by a rapid change of the lattice constants and of the thermal broadening of the ESR lines. In this paper we examine the effect of the position of the d band and the density of states at the Fermi level on the energy relaxation rates in ESR.

2. Experimental

The GdTAl intermetallic compounds were synthesized by the induction or arc melting of the stoichiometric amounts of high purity elements. They exhibited orthorhombic TiNiSi-type structure (GdRhAl); hexagonal ZrNiAl-type structure (GdNiAl, GdCuAl); hexagonal $MgZn_2$-type structure (GdCoAl, GdFeAl) and cubic $MgCu_2$-type structure ($GdAl_2$). The XPS measurements were performed using Physical Electronics PHI 5700 spectrometer with monochromatized Al Kα radiation under a vacuum of 10^{-10} Torr. The ESR measurements were performed within the X-band in the paramagnetic state of the compounds. The samples were prepared with the particle size smaller than the skin depth in order to record symmetrical lines proportional to the imaginary part of the complex susceptibility.

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PII: S0925-8388(00)01443-2

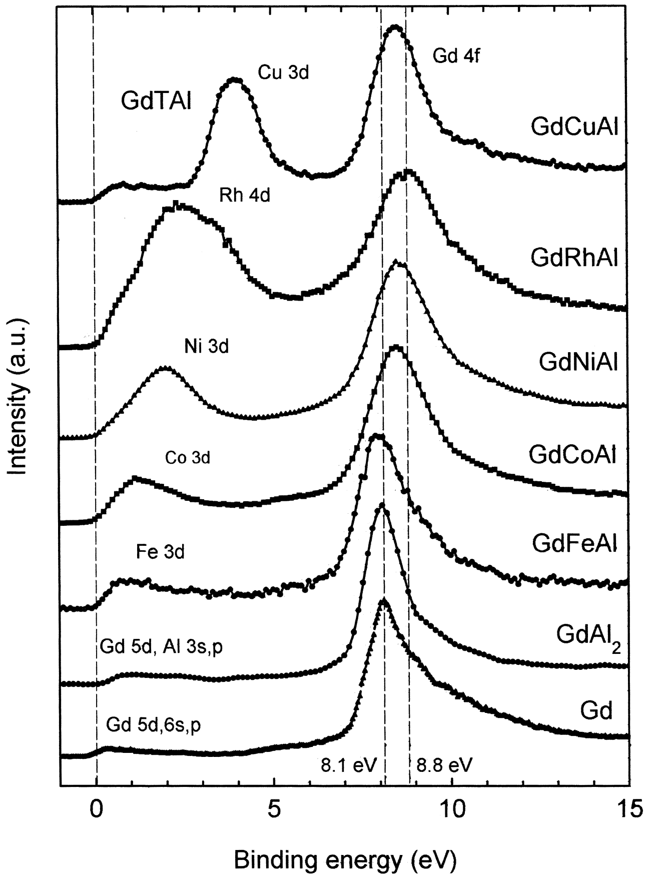

Fig. 1. The valence band XPS spectra of the GdTAl compounds (T = Cu, Rh, Ni, Co and Fe) compared with the spectra of $GdAl_2$ [7] and Gd metal.

3. Results and discussion

The XPS spectra of the valence band for GdTAl, and the $GdAl_2$ compounds together with that of the pure Gd metal are presented in Fig. 1 for the binding energy up to 15 eV. In all compounds except for the GdFeAl, the Gd 4f peak is shifted in comparison with the one for pure Gd metal to a higher binding energy. The magnitude of this shift depends on the T metal and varies between 0.3 eV for Co and 0.7 eV for Rh. A similar shift in energy of the Gd levels was observed in many Gd intermetallic compounds [4] and was related to the increase of the environmental potential due to the charge transfer (mainly 6s electrons) remote from Gd atoms. This process may lead to the increase of the d character of electrons localised at Gd atoms. The opposite shift equal to −0.2 eV was observed in GdFeAl. It seems that gadolinium gains electrons from other metal sites despite its low electronegativity.

As can be seen in GdTAl compounds the maximum of the d peak is located closer to the Fermi energy with a smaller number of d electrons of the T metal. This results in the increase of the density of states $\eta(E_F)$ at the Fermi level. The comparison of the $\eta(E_F)$ for these compounds obtained after normalising the intensity of the spectra to the Gd 4f peak is shown in Fig. 2. GdFeAl is an exception again since its density of states is smaller than for compounds with Co, Ni or even with Rh.

Owing to the fact that Gd ions are in the S state (L = 0), the energy relaxation from the Gd ions to the lattice occurs through the conduction electron (CE) system. In such

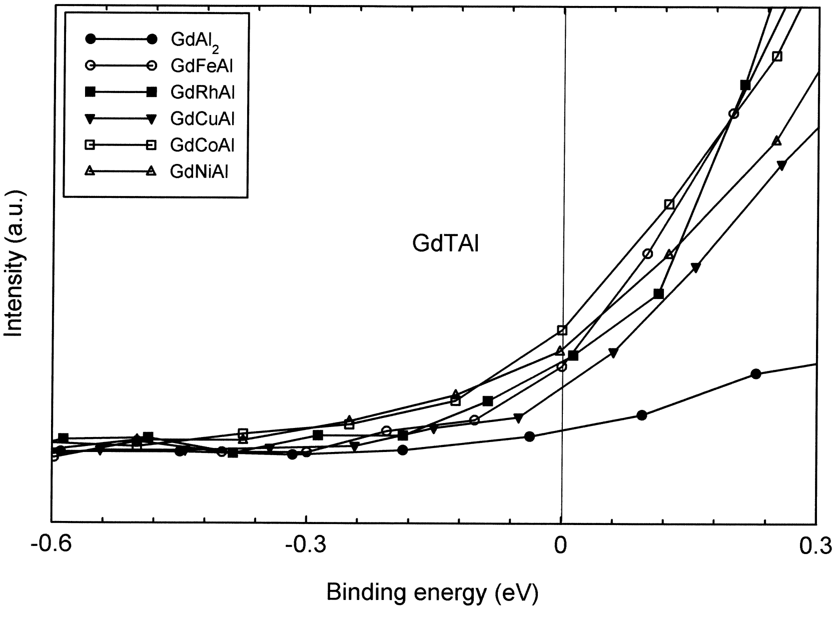

Fig. 2. The valence band XPS spectra near the Fermi level of the GdTAl compounds. Intensities are normalised using the Gd 4f peak.

conditions in a concentrated Gd system, this usually results in a bottleneck effect, depending on the parameter $A = \delta_{eL}/\delta_{ei}$, where δ_{eL} is the energy relaxation rate from the CE system to the lattice and the δ_{ei} is the relaxation rate from the CE system to the Gd ion system. One may expect that by changing the density of states at the Fermi level through involving different metals T should influence the strong bottleneck effect observed in the $GdAl_2$ compound.

Two opposite effects caused by the increase of density of states at the Fermi level require consideration.

The first effect is the increase of the δ_{ei} according to the formula given by Overhauser:

$$\delta_{ei} = (8\pi/3\hbar)\, cS(S+1)\, \eta(E_F)\, J_{Se}^2$$

where c is the Gd concentration in the compound, $S = 7/2$ the spin of Gd ion, $\eta(E_F)$ the density of states at the Fermi level and J_{Se} is the exchange coupling constant between spins of gadolinium and CE. This effect should decrease parameter A and therefore enhance the bottleneck effect.

On the other hand the d type electrons which contribute markedly to the density of states at the Fermi level have a spin–orbit scattering cross sections larger than the s or p electrons. In other words, increase of the $\eta(E_F)$ should also cause faster relaxation of CE to the lattice. This effect raises the value of parameter A and thus breaks the bottleneck.

By using the bottleneck parameter A one can describe the thermal broadening of the resonance linewidth b by means of formula [5]:

$$b \equiv \partial DH/\partial T = (\partial DH/\partial T)_{\text{unbottlenecked}}\, A/(A+1)$$

Breaking of the bottleneck is visible in the increase of the thermal broadening b in all the compounds (Fig. 3). It is evident that in GdTAl compounds, the latter mechanism is much more effective. Replacement of the Al atom in $GdAl_2$ by Cu, Rh, Ni, Co or Fe atoms causes faster increase of δ_{eL} than δ_{ei} relaxation rate. The most effective breaking of the bottleneck was observed in GdFeAl despite the fact that the density of states $\eta(E_F)$ was smaller than for compounds with Co or Ni. However, unlike Ni and Co, the Fe 3d band is not filled and, due to its magnetic moments and coupling Fe ions to the lattice, an additional relaxation path from the Gd ions to the lattice is formed and causes breaking of the bottleneck.

An unusual behaviour of the resonance linewidth of the GdNiAl and GdRhAl can be seen in Fig. 3. The magnitude of the thermal broadening b at high temperatures is smaller than that at low temperatures. The observed change takes place far above the ordering temperature and seems to be related to phase transition occurring in these compounds [1].

In order to explain the observed rapid change of the thermal broadening in GdNiAl at a temperature near 200 K, the XPS spectra near the Fermi energy were investigated at temperatures both higher and lower than the phase transition temperature. In Fig. 4 the valence band of GdNiAl for different temperatures normalised to the intensity of the Gd 4f peak are presented. The densities of states are smaller at temperatures lower than 200 K than those at higher temperatures (see Fig. 5). Despite this fact, the thermal broadening b is bigger at this temperature range and the bottleneck is weaker. It is clear that the decrease of δ_{ei} increases the parameter A and is essential in breaking the bottleneck whereas the change of δ_{eL} is unimportant. Assuming that the unbottlenecked value of b

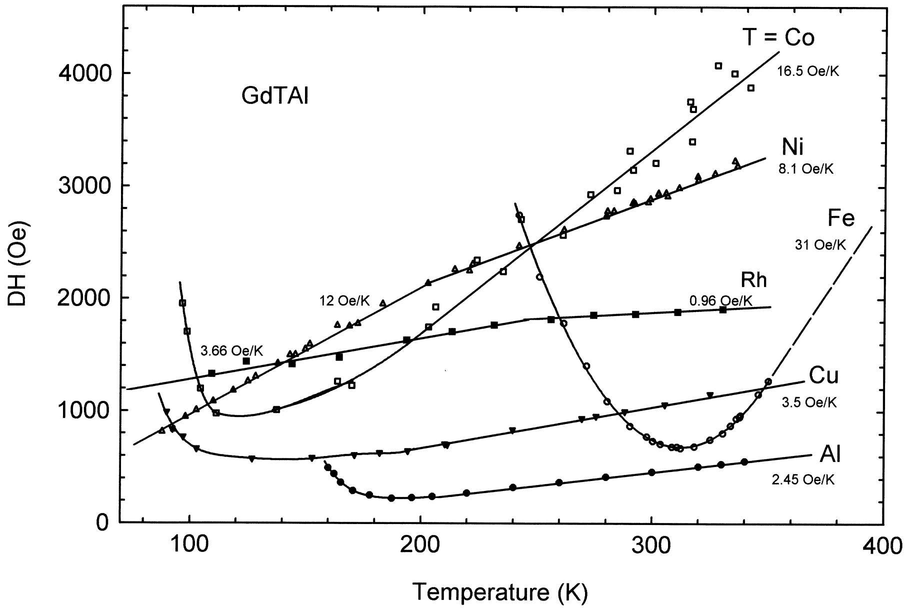

Fig. 3. The ESR resonance linewidths DH versus temperature of the GdTAl compounds (T = Co, Ni, Fe, Rh and Cu) compared to the linewidths of bottlenecked $GdAl_2$. The values of the $\partial DH/\partial T$ in the paramagnetic state are denoted.

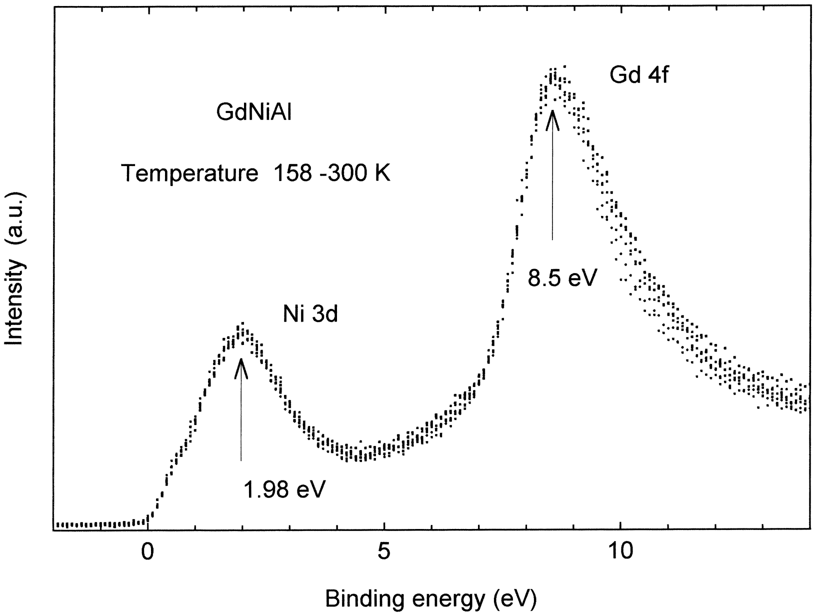

Fig. 4. The valence band XPS spectra of the GdNiAl observed at temperatures higher and lower than the phase transition temperature. Intensities are normalised using the Gd 4f peak.

equals 70 Oe K^{-1} [6] it is easy to deduce that in order to obtain the observed change in b from $b=8.1$ Oe K^{-1} to $b=12$ Oe K^{-1} the density of states has to decrease by a factor of 1.6. This value agrees very well with the changes in $\eta(E_F)$ observed in XPS. It also means that the phase transition does not affect the relaxation rate δ_{eL}. This result seems to confirm the conclusion [1] that the phase transition observed in the GdNiAl (and probably in GdRhAl) was induced by the filling of the Brillouin zone by the Fermi electrons. It results in forming a new density of states distribution with a lower density of states at the Fermi level.

Concluding, in GdTAl intermetallic compounds, increase of the density of states at the Fermi level enhances the bottleneck as long as the character of the conduction electrons remains unchanged. On the other hand increase

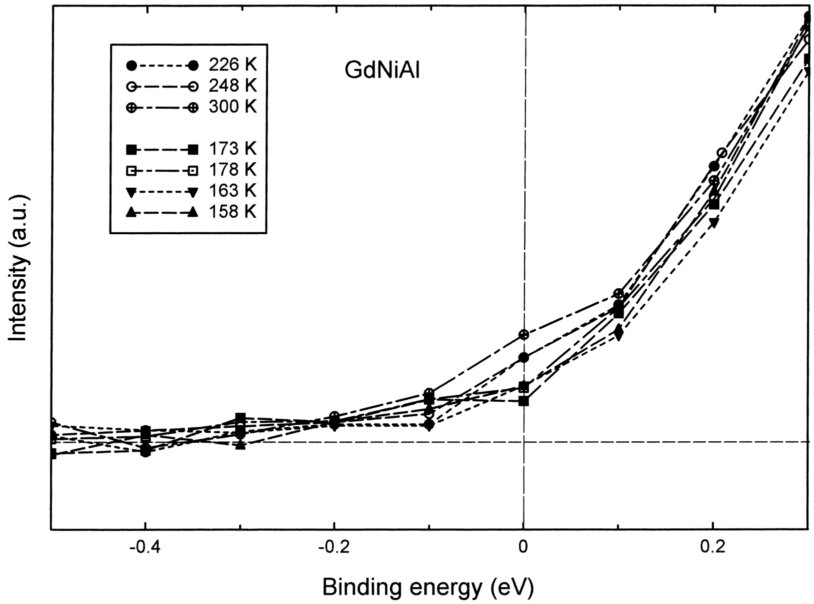

Fig. 5. Dependence of the valence band XPS spectra near the Fermi level on temperature in GdNiAl. Spectra normalised to the Gd 4f peak.

of the contribution of the d type electrons to the density of states breaks the bottleneck despite the simultaneous rise of $\eta(E_F)$.

Acknowledgements

This work was supported by KBN under project 2P 03B 124 16.

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