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Paramagnetic and electron spin resonance investigation of the $Gd(Al_{1-x}Bi_x)_2$ Laves phase compounds

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Abstract. The lattice constant, magnetic susceptibility and the bottleneck parameter of the $Gd(Al_{1-x}Bi_x)_2$ intermetallic compounds were measured in the paramagnetic temperature range. Fundamental disagreement was found between the concentration dependences of the density of states at the Fermi level estimated on the basis of magnetic measurements on the one hand and ESR measurements on the other hand.

1. Introduction

Many papers have been devoted to the investigation of the pseudobinary Laves phase compounds with the cubic crystal structure of the C15 type obtained by introducing a non-magnetic or 3d-type metal in the place of Al in the initial $GdAl_2$ compound [1–7]. The magnetic susceptibility, lattice constant, electrical conductivity and ESR investigations revealed that the properties of these compounds notably depend on the conduction electron (CE) concentration related to the size and amount of the introduced metal. No exact calculations of the band structure of the investigated compounds are available but some assumptions have been made [1, 6] on the relative position of the Fermi energy in the density of states versus energy curve.

In this paper the results of a magnetic and ESR investigation of $Gd(Al_{1-x}Bi_x)_2$ compounds are presented in the Bi concentration x range up to 0.25. We expect to obtain information about the change in the density ρ_{E_F} of states at the Fermi level both from the paramagnetic Curie temperature Θ_p and from the bottleneck parameter X. The bottleneck parameter is equal to δ_{eL}/δ_{ei}, where δ_{eL} describes the relaxation rate from the CEs to the lattice and δ_{ei} is the relaxation rate from the CEs to the localised Gd spin system. The information about ρ_{E_F} could be extracted from X because, as Bi is the non-magnetic metal and is introduced in the place of Al atoms, it does not give any additional possibility for relaxation to the lattice.

2. Experiment

The polycrystalline samples of the $Gd(Al_{1-x}Bi_x)_2$ compounds with x up to 0.25 were prepared by arc melting under a pure Ar atmosphere. Because of the relatively low boiling point of Bi the samples were prepared using as a basis one sample with the maximum Bi content ($x = 0.25$). This sample was divided into parts and then melted

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Table 1. The lattice constants and paramagnetic data for $Gd(Al_{1-x}Bi_x)_2$ compounds.

x	a (Å)	Θ_p (K)	μ_{eff} (μ_B)
0	7.900	171	7.91
0.025	7.900	166.9	8.17
0.05	7.898	160.3	8.03
0.07	7.897	129	7.87
0.20	7.898	123.8	8.26

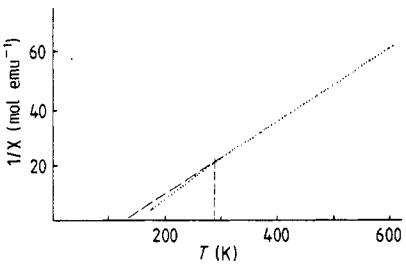

Figure 1. The dependence of the inverse susceptibility on temperature for $Gd(Al_{0.93}Bi_{0.07})_2$.

again with appropriate amounts of Al and Gd in order to obtain all the desired Bi concentrations.

The x-ray analysis showed single-phase samples within the usual resolution of 6%. For $GdAl_2$ and for all the investigated compounds we found the cubic $MgCu_2$ structure [8]. For alloys with $x > 0.2$, weak lines were observed in the diffraction pattern, and these could not be identified.

The lattice constants were investigated at room temperature by the Debye–Scherrer method with Fe Kα radiation by extrapolation of $a_{hkl}(\cos^2\theta)$ to the value $\cos^2\theta = 0$. The values of the lattice constants obtained for the $Gd(Al_{1-x}Bi_x)_2$ compounds for various x listed in table 1 and are independent of Bi content.

The susceptibilities of the Bi alloys and of the matrix were measured between the Curie temperature and 600 K by the Faraday method in an external field of 0.075 T and in a pure He atmosphere. In all the samples containing Bi atoms a small deviation from linearity was observed in the plot of the inverse susceptibility versus temperature (figure 1). In all cases this deviation occurs below 290 K and depends on the Bi concentration. The temperature range in which the effect was found could indicate that this effect is related to the small clusters of Gd atoms. The presence of these clusters, however, was not observed in the x-ray analysis.

In table 1 we collected together the paramagnetic temperatures Θ_p of the ferromagnetic samples and their effective moments which were derived from the slope of the inverse susceptibility versus temperature well above 350 K. We observed a strong decrease in Θ_p with increasing Bi concentration and a slight increase in the effective paramagnetic moment.

The ESR investigation was performed within the X band in the paramagnetic temperature range of the investigated compounds. The samples used for these measurements were prepared in such a way that the particle size was smaller than the skin depth for the applied frequency. The resonance lines obtained in this case were symmetrical and easy to analyse [9].

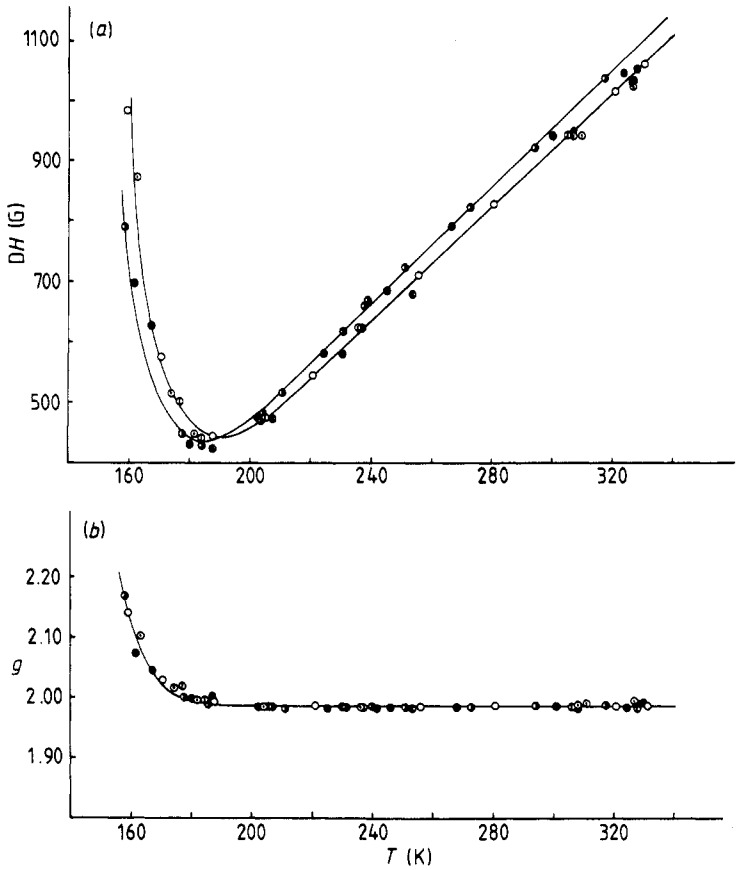

Figure 2. The dependence of (*a*) the resonance linewidth DH and (*b*) the spectroscopic splitting factor on temperature for $Gd(Al_{1-x}Bi_x)_2$ compounds: ○, $x = 0$; ⊙, $x = 0.05$; ◑, $x = 0.10$; ⊗, $x = 0.15$; ◑, $x = 0.20$; ●, $x = 25$; ——, curves in (*a*) for $x = 0$ and $x = 0.20$.

The measured dependences of the $g(T)$-factor and linewidth D$H(T)$ (figure 2) were typical of ferromagnets and exhibit a behaviour very similar to that observed in $Gd(Al_{1-x}M_x)_2$ compounds with various non-magnetic metals M such as Pd, Cu, Ag, Ga, In, Sn and Pb introduced [6]. In the $Gd(Al_{1-x}Bi_x)_2$ compounds as in the case of all the compounds investigated earlier the changes in paramagnetic value of the g-factor with concentration x were within the limit of the experimental error. However, the values of thermal broadening $dDH/dT(x)$ obtained using the measured D$H(T)$ dependences, occurred independent of Bi concentration as was observed in the series with Ga and In.

3. Discussion

The strong dependence of the Curie temperature of $Gd(Al_{1-x}Bi_x)_2$ compounds on x is characteristic of Laves phases of the $Gd(Al_{1-x}M_x)_2$ type where M is a metal without a magnetic moment (such as Cu [3], Ni [3, 4], Pd, Ag, In, Sn [1] and Pb [7] or M is a metal which has a partly filled d shell (such as Mn, Fe and Co [5]) and in a low concentration

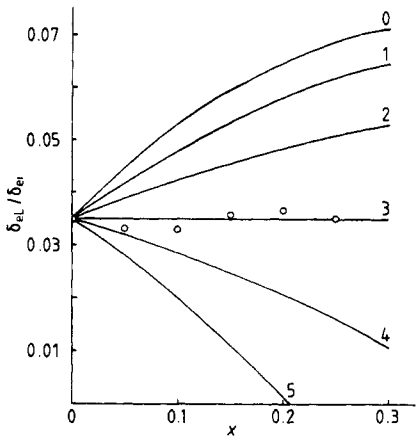

Figure 3. Dependence of the bottleneck parameter $X = \delta_{eL}/\delta_{ei}$ (○) on the Bi content in $Gd(Al_{1-x}Bi_x)_2$ compounds, and dependence of δ_{eL}/δ_{ei} (——) on x in $Gd(Al_{1-x}M_x)_2$ Laves phase compounds for different numbers (from 0 to 5) of CEs provided by the M atom. These curves were obtained on the basis of the universal phenomenological dependence of δ_{eL}/δ_{ei} on the concentration of CEs in the unit cell of $Gd(Al_{1-x}M_x)_2$ [6].

of it (approximately lower than 20%), there is no M–M magnetic interaction. The drastic decrease in the Curie temperature and the change in the lattice parameters versus M concentration are largest for Sn and clearly depend on the number of conduction electrons per M atom [1].

The lattice parameters for $Gd(Al_{1-x}Bi_x)_2$ almost do not depend on the Bi concentration below $x = 0.25$ and suggest that the Bi radius is the same as the Al radius in $GdAl_2$, i.e. 1.396 Å, independent of its concentration. It is not possible to determine the valence of Bi in these compounds from the value of its radius but it could indicate that this valence is less than five. The independence of the lattice constant of the Bi concentration suggests a constant value for the density of states at the Fermi energy. This suggestion is supported by the ESR investigation results.

The independence of the thermal broadening dDH/dT of x observed in $Gd(Al_{1-x}Bi_x)_2$ indicated that the bottleneck existing in the initial $GaAl_2$ material did not change despite introduction of Bi atoms. The bottleneck parameters $X = \delta_{eL}/\delta_{ei}$ (presented in figure 3 as a function of x) were calculated using the formula for the thermal broadening in a concentrated Gd alloy [10]:

$$dDH/dT = [X/(X+1)]\,(dDH/dT)_0 \tag{1}$$

where $(dDH/dT)_0$ is the Korringa value for the systems with no bottleneck, assumed to be equal 70 G K^{-1} [11]. The values obtained for δ_{eL}/δ_{ei} were the same for all concentrations x and the same as for the $GdAl_2$ compound.

According to the previous band-structure calculations for Laves phase dialuminates [12] and ESR investigations of $Gd(Al_{1-x}M_x)_2$ compounds [6, 7] it is most probable that the Fermi energy is placed on the left side of a maximum in the density of states versus energy curve (figure 4). On reducing or increasing the number of free electrons the Fermi energy shifts to lower or higher energy, respectively, giving rise to a change in the density of states. Any changes in ρ_{E_F} must be reflected in the relaxation rate δ_{ei} from

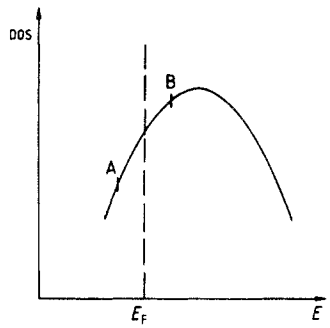

Figure 4. Position of the Fermi energy in relation to the peak of the density of states (DOS) in the $Gd(Al_{1-x}M_x)_2$ compounds. A ($Gd(Al_{0.7}Pd_{0.3})_2$) and B ($Gd(Al_{0.75}Sn_{0.25})_2$) respectively are the points at which the lowest and highest ρ_{E_F} are obtained experimentally from the ESR in the compounds under investigation [6].

the CE system to the localised Gd spin system (Overhauser relaxation rate) which may be given as

$$\delta_{ei} = (8\pi/3\hbar)c_{Gd}S(S+1)\rho_{E_F}J^2 \tag{2}$$

where c_{Gd} is the concentration of Gd atoms, S is the spin of the Gd^{3+} ion (the magnetic moment of M is zero) and J is the exchange coupling constant between localised Gd electrons and the conduction band.

The constant value of the bottleneck parameter in the whole Bi concentration range indicates that there are not any marked changes in the density of states at the Fermi energy with x. This is the same situation as observed in the case of $Gd(Al_{1-x}Ga_x)_2$ and $Gd(Al_{1-x}In_x)_2$ compounds. On the assumption of the rigid-band model this result suggests that Bi atoms provide only three p electrons to the conduction band while the 6s electrons occupied localised states below the conduction band. However, there are also other possible explanations of the constant ρ_{E_F} versus x. Of course, the energy distribution of the density of states could change in such a way that ρ_{E_F} remains unchanged. To answer this question, band calculations or XPS experiments are necessary.

The results obtained from the magnetic measurements contrast greatly the band structure speculations near the Fermi energy made on the basis of the ESR data. Using Lindgard's [13] formula for Θ_p (note the similarity to equation (2)) given by

$$\Theta_p(x) = (4/3k_B)\rho_{E_F}c_{Gd}J^2S(S+1) \tag{3}$$

we expect a rapid decrease in ρ_{E_F} together with a strong decrease in Θ_p with increasing Bi content, contrary to the ESR result. We suppose that this disagreement in the $\rho_{E_F}(x)$ dependences which are estimated from two different experimental results, i.e. Θ_p and the parameter X must arise from essential imperfections in the theory. Similar disagreements were observed when Al was substituted by Ga, In and Sn [1, 6] and for M ≡ Ag, Cu, Pd and Pb [1, 6, 7] the results were consistent.

One of the mechanisms which ought to be taken into account is the change in the mean free path of the CEs with composition. If we consider this problem in the frame of the modified RKKY model with assumed dumping of the Ruderman–Kittel function [14], the decrease in Θ_p with increasing Bi content could be related to the decrease in the mean free path. Quantitative information could be obtained from the resistivity data

(which are not available at present); however, it could be expected that the decrease in Θ_p related to this mechanism is much smaller than observed. The observed small increase in the effective paramagnetic moment with increasing x is most probably related to the polarisation of the CES.

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