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bottleneck in $Gd(Al_{1-x}M_x)_2$ Laves phases

The influence of non-magnetic M ≡ Pd, Cu, Ag, In, Sn impurities on the bottleneck in Gd(Al₁₋ₓMₓ)₂ Laves phases

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Abstract. The ESR investigation was performed in the paramagnetic region of the Gd(Al₁₋ₓMₓ)₂ inter-metallic compounds where M ≡ Pd, Cu, Ag, Ga, In and Sn. Using the measured thermal broadening of the linewidth the bottleneck parameter $X = \delta_{eL}/\delta_{ei}$ was calculated as a function of concentration x. An explicit dependence of the behaviour of the investigated compounds on the conduction electron (CE) concentration was ascertained. When the Al atoms were replaced by Pd, Cu or Ag atoms (a decrease in the number n of the CEs per unit cell), breaking of the bottleneck was observed; when the Ga or In atoms were substituted (the same n for all x), the bottleneck did not change; substituting the Sn atoms (an increase in n) caused strengthening of the bottleneck existing in the initial GdAl₂ compound. All these changes described by the bottleneck parameter X against n lie along the same (identical for all non-magnetic M) curve. The observed effects are related to the changes in the relaxation rates between the systems of CEs and localised spins. These changes are stimulated by the changes in the density of states at the Fermi level, which can be understood on the basis of band-structure calculations.

1. Introduction

Inter-metallic compounds of a rare earth with Al, forming Laves phases of cubic C15 crystal structure have been investigated for many years. Much attention has been paid to the pseudo-binary compounds obtained from GdAl₂ by substituting a number of Al atoms by magnetic or non-magnetic metals [1–7].

In this paper the results of an ESR investigation of Gd(Al₁₋ₓMₓ)₂ compounds are presented where M is a non-magnetic metal such as Pd, Cu, Ag, Ga, In or Sn. In these compounds a dramatic decrease in the Curie temperature against x was observed [1, 6]; this was caused by a decrease in the density of states at the Fermi level as a consequence of the change in the conduction electron (CE) concentration together with an increase in the M concentration. The metals which replaced Al atoms introduce different numbers of CEs (Pd, none; Ag, Cu, one; Ga, In, three; Sn, four) in place of the three Al electrons which change the number n of CEs per unit cell. Considering the essential role played by CEs in relaxation processes in metals, one may expect these changes to appear also in the ESR study. GdAl₂ is a compound exhibiting a strong bottleneck effect. Gd ions are in the S state ($L = 0$); so direct relaxation from the Gd ion system i to the lattice L may be neglected. The only means of relaxation is indirect relaxation through the CE system but the relaxation rate δ_{eL} from CE to the lattice is smaller than the relaxation rate δ_{ei}

Table 1. Atomic radii of elements forming the investigated Laves phases $Gd(Al_{1-x}M_x)_2$ in the metallic state.

Element	r_{at} (Å)
Gd	1.78
Al	1.43
Cu	1.28
Ga	1.25
Pd	1.37
Ag	1.44
In	1.62
Sn	1.58

from CE to the Gd spin system, thereby causing accumulation of the energy in the CE system and creating the bottleneck effect. Increasing the relaxation rate δ_{eL} or decreasing δ_{ei} allows the bottleneck to be broken; this is manifested in a g-shift and an increase in the temperature slope of the resonance linewidth $\partial \Delta H / \partial T$.

2. Experiment

The polycrystalline samples of $Gd(Al_{1-x}M_x)_2$ compounds were prepared by arc melting under an Ar atmosphere using Gd of purity 99.9% and the other metals of purity 99.999%. Some samples were heated at a temperature of 1100 K for a few days. The x-ray study showed that the samples were single phase for x up to 0.2 and had a cubic C15 structure. For the highest M concentrations the presence of additional reflections in the diffraction diagrams was observed, revealing the presence of the impurity phase. The lattice constant investigations indicated that it depends on the ratio of the radius of the M atom introduced to the Al radius (table 1). For Pd, Cu and Ga the lattice constant decreased with increase in M content, for Ag the lattice constant did not change and for In and Sn it increased.

To prepare the samples for ESR measurements, they were ground to powder in methyl alcohol in order to obtain a suspension which was then sedimented in such a way that samples with a particle size smaller than the skin depth for the applied frequency were obtained. Such samples enabled us to record a signal proportional only to the imaginary part of the complex susceptibility; in other words it was very convenient to analyse the symmetrical resonance line [8]. The ESR measurements were performed in the X band, in the paramagnetic temperature range of the compounds investigated.

3. Results and discussion

Introducing a non-magnetic metal M into $GdAl_2$ does not change the relaxation scheme as radically as it does for $Gd_{1-x}RE_xAl_2$, in which the introduction of rare-earth (RE) atoms formed an additional path of relaxation from CES to the lattice through an exchange interaction with RE ions. These ions were strongly coupled to the lattice ($L \neq 0$) and so

the effective δ_{eL} considerably increased [9, 10]. Decreasing the Gd ion concentration was a supplementary effect and it led to a decreasing relaxation rate:

$$\delta_{ei} = (8\pi/3\hbar)cS(S + 1)\rho_{EF} J^2_{s-f} \tag{1}$$

where c is the Gd ion concentration in the compound, S the spin of the Gd ion, ρ_{EF} the density of states at the Fermi level and J_{s-f} the exchange coupling constant.

In such a system an appreciable increase in the temperature slope of linewidth and a relatively large g-shift were observed with respect to RE ion concentration.

For Gd(Al$_{1-x}$M$_x$)$_2$ compounds, neither of these two mechanisms can be involved and so considerable changes in $\partial\Delta H/\partial T$ and the g-factor against x were not expected. The measured dependences of the $g(T)$-factor and the linewidth $\Delta H(T)$ (figure 1) were typical of ferromagnets and were similar for all the compounds under investigation. The $g(T)$-factor was independent of T far from the para–ferromagnetic transition temperature and rapidly increased near T_c where the linewidth $\Delta H(T)$ had its minimum; it then increased linearly with T. However, the changes in the g-factor for different M concentrations were within the limit of experimental error and only the changes in the slope $\partial\Delta H/\partial T$, reflecting the changes in the bottleneck, could be estimated using the measured dependences of $\Delta H(T)$. To calculate the bottleneck parameter the formula for $\partial\Delta H/\partial T$ in concentrated Gd alloys [11] was employed:

$$\partial\Delta H/\partial T = [X/(X + 1)](\partial\Delta H/\partial T)_0 \tag{2}$$

where $X = \delta_{eL}/\delta_{ei}$ is the bottleneck parameter and $(\partial\Delta H/\partial T)_0$ is the Korringa value for systems with no bottleneck. On the assumption that $(\partial\Delta H/\partial T)_0 \simeq 70$ G K^{-1} [9] the X-parameters were calculated as a function of M content in Gd(Al$_{1-x}$M$_x$)$_2$ compounds for all M (figure 2).

In fact, substituting Al atoms by M atoms caused not very large but distinct changes in X and the direction of these changes evidently depended on the metal introduced. The use of Pd breaks the bottleneck with respect to x. A similar but weaker effect is caused by Cu and Ag atoms and, additionally, for Cu and Ag when $x > 0.20$ the parameter X decreases again. A different result is obtained on replacing Al atoms by In or Ga atoms. In the whole concentration x range the parameter X is constant and there are no changes in the bottleneck. Contrary to the case for Pd, Cu and Ag, increasing the Sn content caused a decrease in X and strengthened the bottleneck existing in the GdAl$_2$ compound. Such a behaviour indicates that the bottleneck is determined by the CE concentration in the compounds investigated. Decreasing the CE concentration (substituting Pd, Cu or Ag atoms) breaks the bottleneck while increasing the CE concentration (Sn) makes it stronger and when it remains constant (In, Ga) the bottleneck also does not change. Replacing some atoms by atoms with a different atomic radius changes the lattice constant and causes an increase in the crystalline lattice imperfections. This process always increases the relaxation rate δ_{eL} from the CE system to the lattice which should cause a slight breaking of the bottleneck. However, the behaviour of the series with Ga and In indicates that despite a marked difference between the atomic radii of Ga, In and Al in the metallic state (table 1) the imperfections introduced do not increase δ_{eL} sufficiently to produce any visible changes in the experiment.

An essential influence of the CE concentration on the observed changes in the resonance linewidth and relaxation processes in the compounds investigated manifests itself more clearly when one considers the observed δ_{eL}/δ_{ei} changes as a function of the number of free CEs per unit cell of Gd(Al$_{1-x}$M$_x$)$_2$. (One unit cell of GdAl$_2$ contains eight
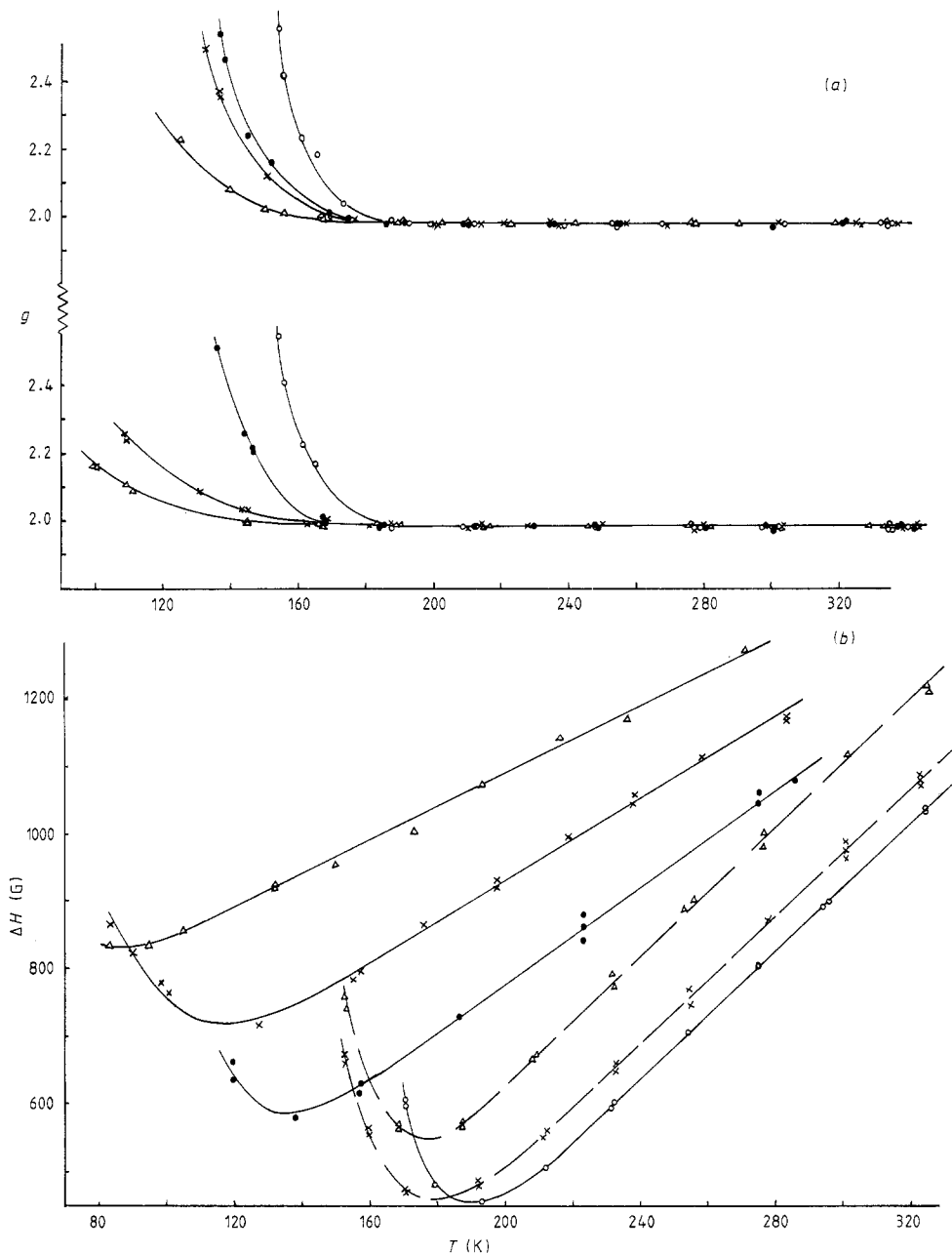
Figure 1. An example of the dependences of (a) the spectroscopic splitting factor g on temperature (upper curves for $Gd(Al_{1-x}In_x)_2$, lower curves for $Gd(Al_{1-x}Sn_x)_2$) and (b) the resonance linewidth ΔH in compounds $Gd(Al_{1-x}Sn_x)_2$ (———) and $Gd(Al_{1-x}In_x)_2$ (‒‒‒); $\bigcirc$, $x = 0$; $\bullet$, $x = 0.10$; $\times$, $x = 0.15$; $\triangle$, $x = 0.20$.

Gd and sixteen Al atoms.) All the values of δ_{eL}/δ_{ei} for the compounds investigated, independently of M, lie along the same curve (figure 3) which has a parabolic shape.

The dependence of the bottleneck parameter on the CE concentration n in the compounds under investigation is related to the changes in density of states at the Fermi
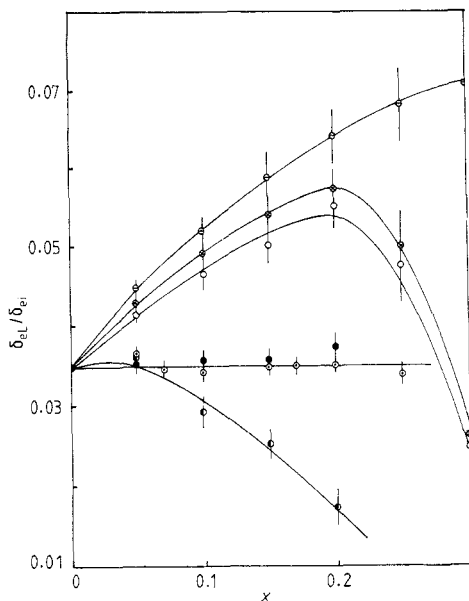
Figure 2. Dependence of the bottleneck parameter $X = \delta_{eL}/\delta_{ei}$ on M content x in Gd(Al$_{1-x}$M$_x$)$_2$ compounds: $\ominus$, Pd; $\otimes$, Cu; $\bigcirc$, Ag; $\bullet$, Ga; $\odot$, In; $\mathbb{O}$, Sn.
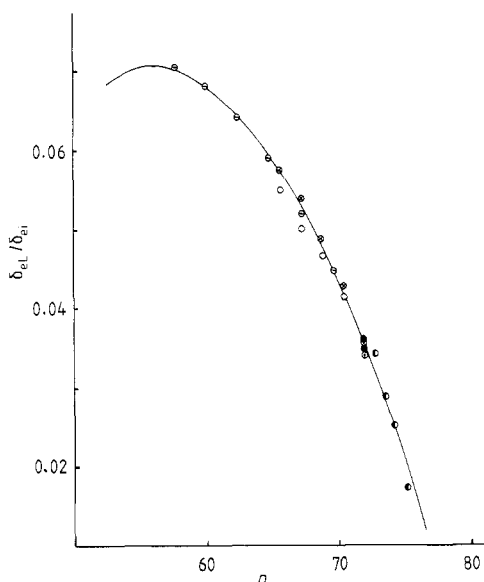
Figure 3. The bottleneck parameter $X = \delta_{eL}/\delta_{ei}$ as a function of the number of free CEs per unit cell of Gd(Al$_{1-x}$M$_x$)$_2$ compounds: $\ominus$, Pd; $\otimes$, Cu; $\bigcirc$, Ag; $\bullet$, Ga; $\odot$, In; $\mathbb{O}$, Sn; ——, parabola described by the equation $X = -0.00013733n^2 + 0.015392n - 0.361010$.

level which determine the relaxation rate from the CE to the localised Gd spin system (see equation (1)). The band-structure calculations for YAl$_2$, LaAl$_2$ and LuAl$_2$ [12–14] indicated that these structures are similar for all these compounds and the Fermi level

lies near the peak of the density of states. Assuming that the energy band structure is also similar in the $GdAl_2$ compound, one may expect that the changes in the Fermi energy related to the changes in the CE concentration in $Gd(Al_{1-x}M_x)_2$ will cause marked changes in the density of states at the Fermi level. In such a situation the observed decrease in δ_{eL}/δ_{ei} against CE concentration could indicate that the Fermi level in these compounds lies below the top of the peak of the density of states. Increasing the CE concentration brings this level closer to the top but it is not attained in the investigated range of n.

The observed decrease in the parameter X in compounds doped with a high concentration x of Cu and Ag seems to be related to the modification of the band structure and means that the rigid-band assumption is no longer valid for these compounds. Nevertheless, it seems that the parabolic dependence of δ_{eL}/δ_{ei} on n shown in figure 3 (which has a phenomenological character) could describe the influence of non-magnetic metals on the relaxation rates in $Gd(Al_{1-x}M_x)_2$ Laves phases, at least in a limited concentration range.

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