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Opening of the EPR bottleneck in amorphous $Gd_xY_{0.33-x}Al_{0.67}$

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The temperature dependence of the EPR linewidth and g shift are measured in amorphous evaporated films of $Gd_xY_{0.33-x}Al_{0.67}$ with $0.0008 < x < 0.33$. Both the g shift and the Korringa slope of the linewidth-versus-temperature curve increase with decreasing x in a fashion which can be fitted to classic EPR bottleneck theory. This procedure yields the spin-lattice relaxation rate for the conduction electrons consisting of a "structural" term $(1.3-6) \times 10^{11}$ Hz and a term proportional to Gd concentration of $1 \times 10^{13}x$. The latter is within 50% of the value in the crystalline counterpart, but the former is larger by a factor of 3 to 15, showing for the first time (aside from studies on liquids) the effect of amorphous structure on this relaxation rate. Similarity of unbottlenecked g factors and Korringa slopes of amorphous and crystalline materials suggest that the conduction band is not strongly affected by structure.

I. INTRODUCTION

In this paper we report on an experimental study of the EPR (electron paramagnetic resonance) bottleneck effect in the amorphous system $Gd_xY_{0.33-x}Al_{0.67}$. This classic effect describes the increase in EPR linewidth and g factor which occurs with decreasing magnetic-impurity concentration.[1] The essential physics of the effect is that energy is absorbed from the microwave excitation by the magnetic impurities, then it relaxes to the conduction electrons and finally it relaxes to the lattice through spin-lattice relaxation. If the latter channel is too slow, the energy is bottlenecked, the lifetime of the precessing magnetic impurities increases and the linewidth is reduced. The bottleneck is opened when the impurity concentration is reduced enough to allow the bottleneck to handle the energy flow.

The effect has been studied extensively in crystalline materials and in particular in a series of Laves phase compounds[2-7] $Gd_xR_{(1/3)-x}Al_{2/3}$ with $R =$ Y, La, Lu, Sc, which are analogous in composition to our amorphous material. The structural disorder of the amorphous material can be expected to increase the spin-lattice relaxation rate in much the same way that it increases the resistivity, and a theory of this effect has already been proposed.[8] Ours is the first measurement of this effect in amorphous materials, although related measurements have been performed by conduction-electron spin resonance in liquid alkali metals.[9,10] The only previous related EPR measurements on amorphous Gd-containing metals have been on Gd-Ag and Gd-Al materials[11,12] but with Gd concentrations far above the EPR bottleneck condition. An initial report of our results, with an analysis of the low-temperature (spin-glass) effects, has been given earlier.[13] Our results here also confirm an earlier estimate for relaxation rates from data on concentrated systems.[12]

II. EXPERIMENTAL TECHNIQUES AND RESULTS

Films were prepared by coevaporation from two electron-beam sources, one containing Al and the other an arc-melted Gd-Y alloy of the composition desired in the film. The alloy evaporation was noncongruent, the concentration of Gd on the film being ~30% higher than in the source alloy. The films had 0.5 μm nominal thickness and were evaporated at 1 nm/sec onto either 10-mil glass or 3-mil Kapton polyimide film substrates at ambient temperature. The Kapton could be easily cut to allow stacking of samples for stronger EPR signals. Thickness was determined by a stylus technique, composition by electron microprobe analysis to a relative accuracy of ±5% of the given value (±10% for $x < 0.01$), and the amorphous nature of the film was established by a glancing-angle x-ray technique. Results are given in Table I. Although Al concentration varied by up to 0.12 from the target atomic concentration of 0.67, we ignore this variation in the subsequent discussion; we do not anticipate any strong effect of the Al concentration on the EPR results.

The EPR measurements were carried out in a standard X-band Varian spectrometer. Line positions were measured relative to the signal of diphenylpicrylhydrazyl (DPPH) introduced along with the sample into the microwave cavity. Microwave power was kept low to avoid heating effects. A sample of "pure" a-YAl_2 was measured to confirm that there were no background impurity signals.

Except in the spin-glass regime or for the very dilute samples, the resonance lines were Lorentzian

TABLE I. Properties of amorphous $Gd_xY_{1-x-y}Al_y$ films.

x	y	Thickness (μm)	$\frac{d\Delta H}{dT}$ (Oe/K)	Δ_g	T_g[a] (K)
0.33	0.67	1.02	2.9	-0.002 ± 0.001	12.4
0.16	0.75	~0.5	3.4	0	6.4
0.041	0.71	0.55	3.9	$+0.006 \pm 0.0002$	<1.6
0.032	0.60	0.46	4.8	+0.006	
0.016	0.58	0.50	5.4	+0.014	
0.0059	0.55	0.56	11.3	$+0.032 \pm 0.005$	
0.0027	0.69	~0.5	16	+0.071	
0.000 95	0.70	0.6	24	$+0.1 \pm 0.01$	
0.000 85	0.66	0.57	33	+0.12	
0	0.69	0.56	. . .	. . .	

[a] These values have been rechecked and are slightly corrected over those quoted in Ref. 13.

and symmetric within experimental error. In earlier studies on a-Gd_xAl_{1-x} as well as in the studies on crystalline systems, the lines are asymmetric, presumably due to the microwave skin depth effect leading to the "Dysonian line shape." In our case because of the large resistivity (of order 150 $\mu\Omega$ cm) and low thickness (see Table I), the samples are significantly thinner than the skin depth. The resulting symmetric lines are a great advantage, being easier to analyze and giving more accurate results for line position. Temperature was varied from 4.2 K to room temperature by a cooled helium gas flow using the Air Products Helitran system and was monitored both above and below the sample at the edge of the cavity by AuCo-Cu thermocouples, permitting temperature accuracy of ±0.15 K up through 40 K and ±0.5 K thereafter. The temperature control and symmetric lines permitted significantly more accurate data than in the earlier Gd-Al study.[11] These deficiencies may account for a discrepancy with the earlier work in which a positive g shift of $\Delta g = 0.006 \pm 0.004$ (above 1.992) was reported for Gd_xAl_{1-x} with $x = 0.37$ to 0.81, whereas here we find $\Delta g = -0.002 \pm 0.001$ for $x = 0.33$. It is also possible that the difference relates to the difference in sample preparation, the earlier experiments being done on sputtered samples, the present experiments on evaporated samples. However, this latter hypothesis has not been tested any further yet.

Data were taken with field both parallel and perpendicular to the sample. The peak-to-peak (p.p.) linewidths of the conventional derivative EPR signal are shown in Fig. 1 for the perpendicular orientation, the data for the parallel orientation being quite similar. $\Delta H_{\text{p.p.}}$ can be converted to the true half-power half-width ΔH of the absorption by multiplying by

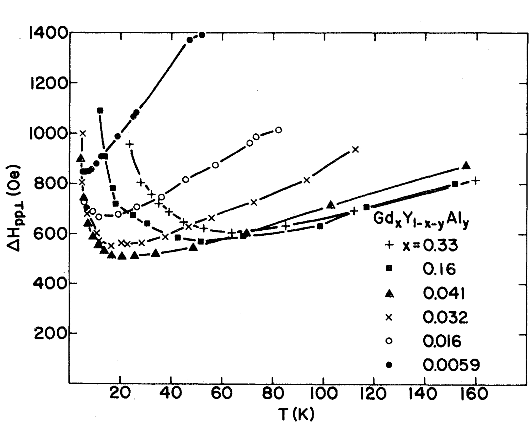

FIG. 1. Peak-to-peak linewidths $\Delta H_{\text{p.p.}\perp}$ in the perpendicular orientation for a series of amorphous GdYAl samples as a function of temperature.

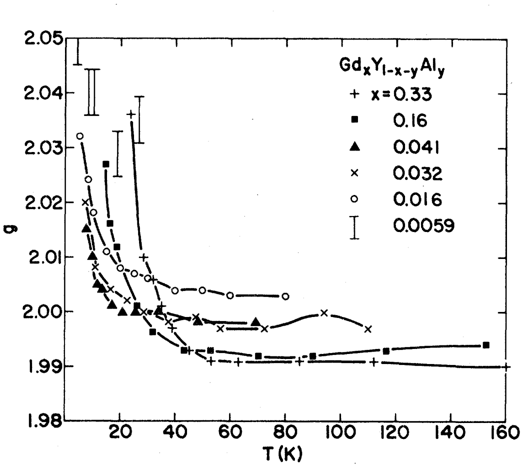

FIG. 2. g factors (corrected for demagnetizing effects) for a series of amorphous GdYAl samples as a function of temperature.

$3^{1/2}/2$ if the line is Lorentzian. The line positions $H_\perp$ and $H_\parallel$ (in Oe) yielded the g factor according to

$$g = 714.5 f H_\perp^{-1/3} H_\parallel^{-2/3} \ , \tag{1}$$

where f is the microwave frequency in GHz. A plot of g values obtained from this equation is shown in Fig. 2. Equation (1) is valid only as long as the magnetic susceptibility is linear, which breaks down at low temperatures because of spin-glass ordering.[12]

III. DISCUSSION

In this paper we discuss the high-temperature region of the results of Figs. 1 and 2, where the linewidth shows the linear Korringa dependence on temperature T and where the g factor becomes flat. The Korringa slope $d\Delta H/dT$ and the high-temperature limit of Δg have been determined in earlier work[13] and are listed in Table I (see also Appendix I). The $d\Delta H/dT$ value comes from the perpendicular orientation, and Δg is defined as $g - 1.992$, where the latter is the accepted "free-ion" value for Gd. Clearly both g and $d\Delta H/dT$ increase with decreasing Gd concentration as expected for the opening of the EPR bottleneck.

Δg and $d\Delta H/dT$ are plotted versus the logarithm of the composition x in Figs. 3 and 4, where they are compared to the earlier results of Schäfer *et al.*[3] on crystalline $Gd_xY_{0.33-x}Al_{0.67}$. In Fig. 4 the opening of the bottleneck for ΔH clearly occurs for higher concentrations in the amorphous case. In Fig. 3, the crystalline case shows no opening of the bottleneck for Δg in any of the compositions investigated. Both these comparisons indicate that the spin-lattice relaxation rate is higher in amorphous than in crystalline material, and therefore that there is a significant structural effect on the spin-lattice relaxation. In amorphous materials this structural effect is of fundamental interest because of the possibility of calculating it from a knowledge of the radial distribution function,[8] whereas in crystalline materials at low temperatures it is merely a reflection of the state of perfection of the sample (e.g., dislocations, impurities, alloy effects), as will be discussed further below.

To quantify this effect we use the conventional theory of the EPR bottleneck, including the possible effect of both s and d electrons, the effects of electron-electron enhancement and the wave-vector dependence of the exchange interaction.[5,6] Thus:

$$\Delta g = \Delta g_d + \Delta g_s \xi^2/(1+\xi)^2 \ , \tag{2}$$

$$\Delta g_s = J(0)\eta_s/[1 - U\chi(0)] \ , \tag{3}$$

$$\frac{d\Delta H}{dT} = \left(\frac{d\Delta H}{dT}\right)_d + \frac{K_s \xi}{1+\xi} \ , \tag{4}$$

$$K_s = (\pi k/g\mu_B)\langle\{J(q)/[1 - U\chi(q)]\}^2\rangle \eta_s^2 \ . \tag{5}$$

Here Δg_d and Δg_s are the g shifts due to d and s electrons, respectively; the d electrons are assumed to be unbottlenecked. $J(q)$ is the wave-vector-dependent exchange constant, between s electrons and the localized f shell, and it is defined such that the energy of one such interaction is $E = -J\vec{S}\cdot\vec{s}$. η_s is the s-electron density of states per atom per spin direction. U is the electron-electron Coulomb interaction. χ is the wave-vector-dependent s-electron susceptibility. k, g, and μ_B are the conventional Boltzmann constant, unshifted g factor and Bohr magneton. $(d\Delta H/dT)_d$ is a possible contribution to the Korrin-

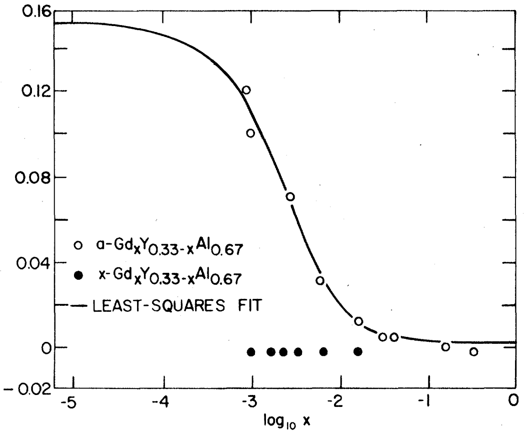

FIG. 3. Δg vs composition x for amorphous (our work) and crystalline [Schäfer *et al.* (Ref. 3)] $Gd_xY_{0.33-x}Al_{0.67}$, and least-squares fit to amorphous data ($\Delta g_s = 0.152$, $\delta_{SF}/\delta_{SLO}x = 193$ per atom fraction Gd, $\delta_{SLGd}/\delta_{SLO} = 13.4$ per atom fraction Gd).

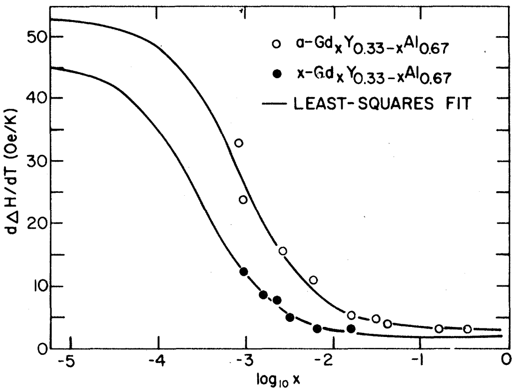

FIG. 4. $d\Delta H/dT$ vs composition x for amorphous (our work) and crystalline [Schäfer *et al.* (Ref. 3)] $Gd_xY_{0.33-x}Al_{0.67}$, and least-squares fit to data ($\Delta g_s = 53.3$ and 46 Oe/K, $\delta_{SF}/\delta_{SLO}x = 61$ and 146 per atom fraction Gd, and $\delta_{SLGd}/\delta_{SLO} = 1000$ and 3040 per atom fraction Gd, respectively).

ga slope from the d electrons. $\langle\ \rangle$ indicates an average over the Fermi surface.

ξ is the ratio of the spin-lattice relaxation rate δ_{SL} to the so-called Overhauser relaxation rate δ_{SF}. These parameters are given by

$$\xi=\delta_{\mathrm{SL}}/\delta_{\mathrm{SF}}\ , \tag{6}$$

$$\delta_{\mathrm{SL}}=\delta_{\mathrm{SLO}}+\delta_{\mathrm{SLGd}}x\ , \tag{7}$$

$$\delta_{\mathrm{SF}}=Cx\ , \tag{8}$$

$$C=(2\pi)^2\eta_s S(S+1)\langle\{J(q)/[1-U\chi(q)]\}^2\rangle \times[1-U\chi(0)]/3h\ . \tag{9}$$

Here δ_{SL} has been expanded in terms of a contribution δ_{SLO} from the $\mathrm{YAl_2}$ structure and a contribution $\delta_{\mathrm{SLGd}}x$ proportional to the concentration of Gd, because the heavy atom Gd can make a large contribution to the spin-lattice relaxation rate. The bottlenecked regime corresponds to $\xi\rightarrow 0$, the unbottlenecked regime to $\xi\rightarrow\infty$.

The two equations (2) and (4) show that Δg and $d\Delta H/dT$ depend on Gd concentration through ξ as given by Eqs. (6)–(8). We fit each of Eqs. (2) and (4) independently to the data, with a four-parameter least-squares fit. In Eq. (2) the four parameters are Δg_d, Δg_s, δ_{SLO}/C, and δ_{SLGd}/C; in Eq. (4) they are $(d\Delta H/dT)_d$, K_s, δ_{SLO}/C and δ_{SLGd}/C. Clearly, Δg_d, Δg_s, $(d\Delta H/dT)_d$, and K_s are of interest because they provide information about the band structure and exchange interactions. δ_{SLO} and δ_{SLGd} are of interest because they determine the spin-lattice relaxation rate.

The results of the fits are shown on Figs. 3 and 4 and are given in Table II, both for our amorphous data and for the crystalline data of Schäfer *et al.*[3] Both Δg_d and $(d\Delta H/dT)_d$ are found to be negligibly small. The value of Δg_s and K_s are given in parentheses and are compared to the largest values of Δg and $d\Delta H/dT$, observed directly as a function of concentration. These latter values are indicated with a $>$ symbol because apparently the concentration was not low enough to achieve a complete opening of the bottleneck. For our amorphous samples, the fits give $\delta_{\mathrm{SLO}}/C=0.0052$ and 0.0010 atom fraction Gd, and $\delta_{\mathrm{SLGd}}/C=0.069$ and 0.061 from the Δg and $d\Delta H/dT$ fits, respectively.

To get δ_{SLO} and δ_{SLGd}, the parameter C must be evaluated. To do this, we note that

$$C=4\pi g\mu_B S(S+1)K_s/3kh\eta_s^*\ , \tag{10}$$

$$\eta_s^*=\eta_s/[1-U\chi(0)]\ , \tag{11}$$

which allows us to eliminate the bulky bracket $\langle\ \rangle$ in favor of the experimentally fitted parameter K_s. Also, for convenience, we have defined an enhanced density of states η_s^*. The only unknown is η_s^*. For reasons to be discussed below, we take it to be 0.9 states per spin atom eV, giving $C=2.4\times10^{12}K_s$ Hz. For instance, in the case of the amorphous ΔH fit, this would give $\delta_{\mathrm{SF}}=1.27\times10^{14}x$ Hz per atom fraction Gd. With this value of C and the K_s values listed in parentheses in Table II, we can calculate δ_{SLO} and δ_{SLGd} as given in Table II.

It is of particular interest to compare the values in Table II for a-GdYAl (where a refers to amorphous) to the series of crystalline Laves-phase compounds x-GdRAl (where x refers to crystalline and R = Y, La, Lu, Sc) studied earlier. Unfortunately, certain problems arise in interpreting the results quoted in these earlier articles. First we consider the values for Δg_s and K_s. These are the same as quoted by the original authors, except in the case of x-GdYAl. Here our least-squares fit on the data of Schäfer *et al.*[3]

TABLE II. Comparison of parameters of amorphous and crystalline GdRAl systems (R = Sc, Y, La, Lu). x and a under "system" refer to crystalline and amorphous. Numbers in parentheses are extrapolations based on least-squares fits as described in the text.

System	Reference	Δg_s	K_s (Oe/K)	δ_{SLO} (10^{11} Hz)	δ_{SLGd} (10^{13} Hz/atom Frac. Gd)
x-Lu	6	0.085	72	2	2 ±1
x-La	5	0.11	65	0.2–0.5[a]	3 ±2
x-Y	3	>0.07	>35(46)	0.4	0.5
x-Sc	7	0.07	32	0.04	1
a-Y	This work				
	g fit	>0.12(0.15)		6.6	0.9
	ΔH fit		>33(53)	1.3	0.8

[a] Values for two different sets of samples, the higher value corresponding to as-grown samples and the lower value to a remelted set of the same samples. Large scatter in the data gives the possibility of values even outside this range.

gives slightly different results for K than what they reported (46 rather than 40). Furthermore, we note that while the data on *x*-GdLaAl (Ref. 5) and *x*-GdLuAl (Ref. 6) convincingly show a saturation in Δg_s with decreasing x, the results reported on *x*-GdYAl by Schäfer *et al.* are not so convincing (see their Fig. 6). Therefore, their value of Δg_s should be considered only a minimum value (see $>$ in our Table II). In our case of *a*-GdYAl, the largest *g*-shift observed was 0.12, slightly larger than the result of 0.11 found for *x*-GdLaAl. Our fit extrapolates to $\Delta g_s = 0.15$. Unfortunately, it was not possible to confirm this saturation value by going to lower concentrations, because the EPR signal became too weak.

In spite of these difficulties, when we compare the results for the four systems, we find they are quite similar within a factor of 2. The worst discrepancy is between Δg for *x*-GdYAl and *a*-GdYAl, but as we have noted, the result for *x*-GdYAl is only a minimum value. Since K_s and Δg_s are related to band properties according to Eqs. (2) and (4), it is plausible to assume that parameters like η_s^* and $J(0)$ are the same within a factor of 2 for all these systems. This conclusion is consistent with the surprising similarity between band parameters of many crystalline and amorphous transition-metal—metalloid systems studied earlier.

Various values for η_s^* have been used in the literature. References 3, 5, and 6 used $\eta_s^* = 0.9\ \text{eV}^{-1}$, whereas Ref. 7 (Chock *et al.*) used $0.12\ \text{eV}^{-1}$ for the same parameter. Thus, in calculating $J(0)$ from Eq. (3), using $\Delta g \sim 0.1$, we find $J(0) \sim 0.1$ eV in the first case and 0.8 eV in the second. These values bracket the values of $J(0)$ determined from magnetic measurements on Gd in metals, which usually fall in the range from 0.15 to 0.45 eV.[12] We can also use these values of η_s^* to calculate the spin-lattice relaxation rates δ. The δ values quoted in Table II are calculated with the first choice. All the δ values should be multiplied by ~ 7 to get the second choice.

The values for δ_{SLO} and δ_{SLGd} in our Table II differ slightly from the earlier values quoted by Chock *et al.*[7] (in their Table III) and Rettori *et al.*[6] (in their Table III), for reasons explained in Appendix I. Table II shows that within a factor of 6, all the results for δ_{SLGd} agree. And in particular, results for crystalline and amorphous GdYAl agree within 50%. This is a plausible result: One would expect the spin-lattice relaxation rate per Gd to be relatively independent of structure because the interaction is one of a localized Gd with an *s*-electron sea, provided the band structure is not significantly changed.

The results for δ_{SLO} are more interesting. Our results on *a*-GdYAl from the *g* fit and from the ΔH fit (Figs. 3 and 4) do not quite agree with each other. The reason for this discrepancy is not known. The result from the ΔH fit, 1.3×10^{11} Hz, is a factor of 3 larger than the results of Schäfer for *x*-GdYAl, also obtained from a ΔH fit. The average of our *g* fit and ΔH fit results is 4×10^{11} Hz and is a factor of 10 larger than the result of Schäfer *et al.*[3] This confirms the increased effect of amorphous strructure on the intrinsic spin-lattice relaxation rate.

A similar trend appears in comparing the low-temperature (residual) electrical resistivities of amorphous materials and their crystalline counterparts. Crudely, one might expect the same ratio as for electrical resistivities. The resistivity of our amorphous $\mathrm{YAl_2}$ material is about 180 $\mu\Omega$ cm which is indeed about a factor of 10 larger than the value 18 $\mu\Omega$ cm determined recently on a sample *x*-GdYAl with $x = 0.001$ actually used in the earlier EPR measurements.[14] As an aside, it is important to be sure that this value is really due to the $\mathrm{YAl_2}$ structure and is not dominated by the Gd impurities. To see that this is indeed the case, we consider the two contributions to have the conventional form:

$$\rho = \rho_0 + \rho_{\mathrm{Gd}} x \ , \tag{12}$$

which is analogous to Eq. (7). Now we expect that $\rho_{\mathrm{Gd}}/\rho_0$ will be less than $\delta_{\mathrm{SLGd}}/\delta_{\mathrm{SLO}}$ because δ is sensitive to spin-orbit coupling which is much larger on Gd than on the host atoms Y and Al. But from the values of Schäfer *et al.* for δ_{SLGd} and δ_{SLO} (see our Table II), we can show that for $x = 0.001$, $\delta_{\mathrm{SLGd}} x$ is smaller than δ_{SLO}, and so $\rho_{\mathrm{Gd}} x$ must also be much smaller than ρ_0, as expected.

Next, let us consider the origin of δ_{SLO}, which depends on atomic form factors as well as on a structure factor.[8] The form factor arises from conduction-electron spin-flip scattering, which increases with spin-orbit coupling and hence atomic weight. Thus, it predominantly occurs at rare-earth sites. However, in a perfect lattice δ_{SLO} must be zero by Bloch's theorem, just as the resistivity must be zero. Thus, in a crystalline material, δ_{SLO} depends on the state of perfection of the material, and except for the residual resistivity quoted above, no information about this state (e.g., dislocation counts) have been provided by the authors of those earlier works. In fact, Davidov *et al.*[5] have shown in their work on *x*-GdLaAl that remelting the samples led to drastic changes in g values and $d\Delta H/dT$ in an intermediate concentration range (see their Fig. 1 and the range of values for δ_{SLO} in our Table II). A rough interpretation of the data before and after remelting indicates a reduction by a factor of 2 in δ_{SLO}. But the scatter is quite large, which is not surprising. It is difficult in practice to ensure that every crystal grown has the same density of defects. What is actually surprising is that several studies, on *x*-GdYAl, *x*-GdLuAL, and *x*-GdScAl, have achieved such low scatter, indicating that defect densities were maintained the same in crystal after crystal.

All this highlights the advantage of using amorphous materials, where the scattering is presumably dominated by the structure factor which can be determined from x-ray scattering.[8] Thus, although the progression of values δ_{SLO}, increasing approximately in order of the atomic number of R in x-GdRAl, is suggestive of a dependence on spin-orbit scattering (assuming a similar dislocation density in the different materials), a more meaningful correlation with spin-orbit coupling will be obtained from studies on the amorphous counterparts. Such studies are underway.

A comment is in order about the temperature dependence of these effects. In principle the spin-lattice relaxation rate could be temperature dependent because phonons increase scattering at higher temperatures. Such an effect could be of concern in measurements like those of Schäfer *et al.* because their measurements span a range from 4 to 70 K. Our measurements also span this range, but in the amorphous case we expect the temperature dependence of the spin-lattice relaxation to be weak much as the temperature dependence of resistivity is weak in these materials. The relatively high temperatures also ensure that the "dynamical effect" arising from the Gd susceptibility[6] is negligible in the bottleneck equations.

In conclusion, this is the first study of the EPR bottleneck in an amorphous system. The results indicate a measurable but surprisingly small increase in the structural contribution to spin-lattice relaxation over the crystalline counterpart. Other band-related parameters, such as the local-moment—conduction-electron exchange interaction, enhanced density of states, and Gd contributions to spin-lattice relaxation are similar in amorphous and crystalline counterparts, confirming the similarity of the conduction bands in these two structurally different systems and supporting a free-electron picture.

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APPENDIX I.

The concentration of Gd in $R\mathrm{Al}_2$ can be defined as $\mathrm{Gd}_x R_{0.33-x}\mathrm{Al}_{0.67}$ or as $\mathrm{Gd}_y R_{1-y}\mathrm{Al}_2$. Clearly for a given material, y is three times x. Since different conventions have been used by different authors, this factor of 3, although trivial, creates problems in interpreting earlier papers on the $R\mathrm{Al}_2$ compounds and may affect calculations not only of spin-lattice relaxation rates but also of densities of states and even of exchange constants!

For example, when density of states η is quoted as states per eV, the value depends on whether you refer to a formula unit or to a per atom basis (i.e., *all* atoms treated equally). Clearly the number is three times *larger* if you used states per formula unit per eV than if you used states per atom per eV, in the case of the $R\mathrm{Al}_2$ systems. The previous literature we refer to has always quoted density of states as per atom. To avoid the ambiguity which would arise if the phrase "per atom" were interpreted as "per rare-earth atom," we have gone back to the original specific-heat data,[15] which was quoted "per gram atom" (i.e, treating rare earth and aluminum equally), and have confirmed that the density of states used by Rettori *et al.*,[6] for example, indeed also referred to the "per atom" convention, treating rare earth and aluminum equally.

Since Δg_s and K_s [Eqs. (3) and (5)] are invariant under a change of convention, the exchange constants $J(0)$ and $J(q)$ must clearly vary depending on the convention, to compensate for η. J will by three times *smaller* if you use the formula-unit convention than if you use a per atom basis. This result can also be seen directly from the properties of the localized-itinerant exchange interaction: It is clear that as the volume of a system increases, the density of conduction-electron states goes up. Since the overall exchange interaction of an isolated impurity must remain the same, the exchange to a single itinerant state must clearly go down with volume. Conventionally one drops the volume factor and just quotes J in eV. There is no ambiguity as long as one refers to a monatomic substance, but in compounds like $R\mathrm{Al}_2$ one must be careful in evaluating J from Eqs. (3) and (5) to be sure that the density of states is *per atom* if one wants to interpret J on a per atom basis. This appears to be the standard convention in the literature we refer to here.

Actually, to make the most meaningful comparison of J's between different systems, the correct convention should be decided on the basis of whether the conduction-electron density is concentrated all on the rare-earth site or whether it is spread evenly over all atoms. The use of the per atom convention implies the latter assumption about state density. If the opposite assumption holds, the J values of Laves-phase systems, calculated from Eqs. (3) or (5), will have to be corrected downwards by a factor of 3 for proper comparison, for example, to the simple case of Gd metal. We do not attempt a reanalysis of the literature values of J here but turn to the more relevant problem of relaxation rates.

In calculating the Overhauser rate [Eqs. (8) and

TABLE III. Results of least-squares fits to $\Delta H_{\mathrm{p.p.}}$ vs T data.

x	$\Theta = T_f$ (K)	n	A (Oe)	B (Oe/K)	C (Oe K^{n-1})	Comment
0.33	13	2	268	3.0	9090	
	13	1.5	52	3.3	2590	
0.16	6	2	244	3.1	10750	
	6	1.5	−60	3.9	2810	Poor fit
0.041	0	2	320	3.5	2350	
	0	1.5	75	4.5	1550	Poor fit
0.032	0	2	364	4.8	1790	
	0	1.5	181	5.6	1190	
0.016	0	2	520	6.0	920	
	0	1.5	450	6.2	530	

(9)], it is physically clear that the density of localized scattering centers per unit volume is all that is relevant. But if volume factors are dropped on the J's and η's as is conventionally done, and these are evaluated on a per atom basis, the concentration x in Eq. (8) must also be interpreted as *per atom*, i.e., as defined in $\mathrm{Gd}_xR_{0.33-x}\mathrm{Al}_{0.07}$. If you use the convention $\mathrm{Gd}_yR_{1-y}\mathrm{Al}_2$, the y is three times larger than x; so η becomes three times larger but J^2 is nine times smaller, giving the same answer for δ_{SF}. The difficulty is that several authors have used *per atom* values for η and J but the $\mathrm{Gd}_yR_{1-y}\mathrm{Al}_2$ convention for concentration, giving a factor of 3 too high an Overhauser rate. This leads to a factor of 3 too high δ_{SLO}. Since δ_{SLGd} is defined relative to concentration, its value also depends on the convention, and previous authors have been inconsistent with each other in defining it.

Going back to the raw data in each case (Fig. 2 of Ref. 3, Fig. 1 of Ref. 5, Fig. 4 of Ref. 6, and Table II of Ref. 7) we have recalculated the relaxation rates which are given in Table II, using the per-atom convention consistently, i.e., x defined by $\mathrm{Gd}_xR_{0.33-x}\mathrm{Al}_{0.67}$. Comparing to Table III of Chock *et al.*[7] and accounting for the different density of states assumed by them, or else to Table III of Rettori *et al.*,[6] we find errors of a factor of 3 in the results for δ_{SLO} on Lu and La. Chock *et al.*, in analyzing their Sc data, used the correct convention for concentration but slipped a decimal point, so their value for Sc is also wrong. Only the value of Schäfer *et al.*[3] is correct, for they distinguished between per atom and formula unit concentrations. Further, if one interprets $\delta\delta_{\mathrm{SL}}/\delta C_{\mathrm{Gd}}$ in these tables with C_{Gd} defined per formula unit, then there are factor of 3 errors for Lu, Y, and Sc. If one interprets $\delta\delta_{\mathrm{SL}}/\delta C_{\mathrm{Gd}}$ as what we have called δ_{SLGd} (i.e., on a per atom basis), then only the La entry is wrong. We hope our Table II will put an end to this bewildering array of difficulties.

APPENDIX II

Here we review the procedure used in our previous work[13] to obtain the values for $d\Delta H/dT$ and Δg quoted in Table I. The principal new points here are to show the degree of sensitivity of the results to T_f and also to show a surprising increase of the residual linewidth with decreasing Gd concentration.

In Ref. 13, the data for ΔH were fitted to

$$\Delta H_{\mathrm{p.p.}} = A + BT + C(T-\Theta)/(T-T_f)^n \ , \qquad \text{(A1)}$$

where T is temperature, Θ is the paramagnetic Curie temperature, T_f the spin-glass freezing temperature, and A, B, C, and n are constants. There were too many unknowns to achieve a reliable fit. So choices were made for T_f, Θ, and n and the least-squares fit was done for A, B, and C. Sample results are listed in Table III. It was found that mean-square deviations were high unless $\Theta \sim T_f$ and T_f were close to the value observed from the cusp in the magnetic susceptibility. Except in a few cases marked "poor fit," the mean-square deviations were comparable for all the fits in Table III.

The results show that $d\Delta H/dT$, which is proportional to the parameter B, is insensitive to the choice of n, but the residual linewidth, which is proportional to A, is very sensitive. Nevertheless, for either choice of n, the trend in A with concentration is very marked, increasing with decreasing Gd concentration. The values are much larger than those reported for the crystalline counterparts at comparable concentrations.[3] These effects are not understood.

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