

Dynamic behavior of paramagnetic ions and conduction electrons in intermetallic compounds: $\text{Gd}_x\text{Lu}_{1-x}\text{Al}_2$ [†]

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Electron-spin resonance of Gd in $\text{Gd}_x\text{Lu}_{1-x}\text{Al}_2$ intermetallic compounds exhibits significant changes in the g shift and thermal broadening upon (i) varying the Gd concentration, (ii) adding a second nonmagnetic impurity Th, and (iii) varying the temperature. These behaviors indicate the presence of the "bottleneck" and "dynamic" effects in the relaxation mechanism. The results were analyzed using a recent band calculation. The q dependence of the exchange interaction and the spin-flip scattering rates of the conduction electrons caused by the Gd and Th impurities were extracted. Our data are compared with previous results on isoelectronic systems LaAl_2 and YAl_2 doped with the same impurities.

I. INTRODUCTION

Electron-spin resonance is a powerful technique for studying the dynamic behavior of the conduction electrons (CE) and paramagnetic impurities in metals.^{1,2} These two spin systems (impurities and CE) are coupled by the exchange interaction. Its isotropic part can be expressed by the formula

$$\mathcal{H} = J\vec{S} \cdot \vec{s}. \quad (1)$$

Here \vec{S} and \vec{s} are the spins of the paramagnetic impurities and the CE, respectively, and J is the exchange interaction between the paramagnetic ions and the CE. As a result of this interaction one expects³ a " g shift" (analogous to a Knight shift) and a "Korringa-like"⁴ thermal broadening in the ESR of the localized moment. Hasegawa² was the first to present quantitative expressions for the observation of the g shift caused by Eq. (1) in terms of the conduction electron's spin-lattice relaxation time. He described the dynamical behavior of the spin systems by means of two coupled Bloch equations of motion. His theory clearly demonstrates the existence of the bottleneck effect,^{5,6} resulting from the fact that the electron-gas spin system is not an infinite heat reservoir, and from the so-called "dynamic effects"⁷ caused by the proximity of the field for resonance of the paramagnetic ions to that of the conduction electrons. The molecular-field approach of Hasegawa suffers, however, from several disadvantages.

(a) As a phenomenological theory it fails to calculate from first principles the various relaxation rates appearing in the equations.

(b) Ambiguity is present concerning the destination of the relaxing magnetization. Hasegawa distinguishes between relaxation toward a time-averaged thermal equilibrium (his case A), and toward

instantaneous local equilibrium (case B).

(c) Electron-electron Coulomb interaction responsible for the exchange enhancement was not taken into account.

The first two difficulties were settled (at least partially) by several microscopic theories describing the two spin systems. The theory of Orbach and Spencer^{8,9} and Barnes and Zitkova¹⁰ supports Hasegawa's case B, while, that of Sasada and Hasegawa¹¹ supports his case A. Recently, Schultz *et al.*^{12,13} have claimed to show the equivalence of the two approaches. The problem of "relaxation destination" has been treated also by Cottet *et al.*¹⁴ and Giovannini¹⁵ using the phenomenological theory. These authors have shown that a positive-definite energy absorption in the resonance condition requires relaxation toward the instantaneous local field. The extension of the theory to include electron-electron interaction (responsible for the CE exchange-enhanced susceptibility) has been recently published by Zitkova-Wilcox.¹⁶

In the present work we report ESR measurements of Gd in LuAl_2 . Our results indicate an appreciable change of the g shift and thermal broadening as a function of Gd concentration and temperature. This behavior illustrates the presence of both bottleneck and dynamic effects in $\text{LuAl}_2:\text{Gd}$. The experimental data were analyzed using Giovannini's approach (relaxation destination to the instantaneous local field) modified by the Zitkova-Wilcox (electron-electron interaction) results.

The bottleneck effect has been observed previously in many systems including $\text{Ag}:\text{Mn}$,⁶ $\text{Cu}:\text{Mn}$,^{5,17} $\text{Cu}:\text{Cr}$,¹⁸ $\text{LaAl}_2:\text{Gd}$,^{1,19} $\text{Ca}:\text{Eu}$,²⁰ $\text{YAl}_2:\text{Gd}$,²¹ and $\text{YAg}:\text{Gd}$.²² The so-called dynamic effects, however, are verified experimentally only in $\text{Yb}:\text{Eu}$,²⁰ with some evidence for its presence in $\text{LaNi}_5:\text{Gd}$.⁷ The observation of this effect in

$\text{LuAl}_2:\text{Gd}$ provides important additional information. This observation is also extremely interesting since previous experiments on the isoelectronic systems $\text{YAl}_2:\text{Gd}^{21}$ and $\text{LaAl}_2:\text{Gd}^{1,19}$ "failed" to show dynamic effects. Our understanding of the dynamic behavior in $\text{LuAl}_2:\text{Gd}$ enables us to interpret this "failure." Indeed, new experiments performed by us on $\text{YAl}_2:\text{Gd}$ in a different range of Gd concentration reveal the existence of dynamic effects here too, as expected. Finally, the CE spin-flip scattering rate caused by Gd and Th impurities in LuAl_2 was measured, and compared to those found in the isoelectronic systems YAl_2 and LaAl_2 .

II. MODEL

Following Cottet *et al.*,¹⁴ Schmidt,²⁰ and Davidov and Shaltiel,⁷ the g shift Δg and thermal broadening $\Delta H/T$ can be written as follows:

$$\Delta g = \frac{(\delta_{eL}/\delta_{e1})^2}{(1 + \delta_{eL}/\delta_{e1})^2 + (\gamma\lambda\chi_i H/\delta_{e1})^2} \Delta g_0, \quad (2)$$

$$\frac{\Delta H}{T} = \frac{(1 + \delta_{eL}/\delta_{e1}) + (\gamma\lambda\chi_i H/\delta_{e1})^2}{(1 + \delta_{eL}/\delta_{e1})^2 + (\gamma\lambda\chi_i H/\delta_{e1})^2} \frac{\delta_{eL}}{\delta_{e1}} \left(\frac{\Delta H_K}{T} \right), \quad (3)$$

where γ is the electronic and ionic gyromagnetic ratio (we assume $g_e = g_i$); λ is the exchange (molecular-field) coupling constant between the paramagnetic ions and the conduction electrons; δ_{e1} and δ_{eL} are the spin-flip relaxation rates of the conduction electrons to the paramagnetic impurities and lattice, respectively, δ_{ie} is the spin-flip relaxation rate of the paramagnetic impurities to the conduction electrons; χ_i and χ_e are the spin susceptibilities of the paramagnetic ions and the conduction electrons, respectively; H is the external magnetic field; and Δg_0 and ΔH_K are the unbottleneck g shift and linewidth, respectively.

In the absence of electron-electron interactions all the parameters appearing in Eqs. (2) and (3) are the unenhanced values. In the presence of such an interaction Eqs. (2) and (3) still hold,¹⁶ but the various parameters must be replaced by their enhanced values. Taking the q dependence of the exchange into consideration, as well as electron-electron interactions, the various parameters can be written¹⁶

$$\delta_{ie} = \frac{\pi}{\hbar} \left\langle \left(\frac{J(q)}{1 - U\chi(q)} \right)^2 \right\rangle \eta^2 K_B T, \quad (4)$$

$$\chi_e = \frac{2\mu_B^2 \eta}{1 - U\chi(0)} = \frac{\chi_e^{(0)}}{1 - U\chi(0)}, \quad (5)$$

$$\delta_{e1} = \frac{2\pi}{3\hbar} \eta C N_0 S(S+1) \left\langle \left(\frac{J(q)}{1 - U\chi(q)} \right)^2 \right\rangle [1 - U\chi(0)], \quad (6)$$

$$\lambda = \frac{J(0)}{g^2 \mu_B^2 N_0}, \quad (7)$$

$$\chi_i^{(0)} = \frac{g^2 \mu_B^2 C N_0 S(S+1)}{3K_B T}, \quad (8)$$

$$\Delta g_0 = \frac{J(0) \eta}{1 - U\chi(0)}, \quad (9)$$

$$\Delta H_K / T = \delta_{ie} / \gamma T, \quad (10)$$

where U is the electron-electron Coulomb interaction, η is the density of states for one spin direction at the Fermi surface, the brackets $\langle \rangle$ indicate an average over the Fermi surface, μ_B is the Bohr magneton, C is the concentration of the paramagnetic ions, K_B is the Boltzmann constant, $J(q)$ is the Fourier transform of the spatially varying exchange, $J(0)$ is the $\vec{q}=0$ component of the exchange interaction, $\chi(q)$ is the q -dependent susceptibility of the CE, and $\chi(0)$ is the $\vec{q}=0$ component.

If $J(q)$ is replaced by a parameter J_0 , independent of q , Eq. (4) reduces to

$$\begin{aligned} \delta_{ie} &= \frac{\pi}{\hbar} J_0^2 \eta^2 K_B T \left\langle \left(\frac{1}{1 - U\chi(q)} \right)^2 \right\rangle \\ &= \delta_{ie}^{(0)} \frac{K(\alpha)}{(1 - \alpha)^2}, \end{aligned} \quad (11)$$

where $\delta_{ie}^{(0)}$ is the unenhanced value of δ_{ie} , $\alpha = U\chi(0)$, and $K(\alpha)$ is defined in Ref. 23. Similarly, it can be shown [assuming $J(q) \equiv J_0$] that¹⁶

$$\delta_{e1} = \delta_{e1}^{(0)} [K(\alpha)/(1 - \alpha)]. \quad (12)$$

Equations (4)–(8) indicate the existence of the detailed-balance condition (in the presence of electron-electron interaction) given by

$$\chi_i \delta_{ie} = \chi_e \delta_{e1}. \quad (13)$$

This was shown also by Zitkova from the first principles and by Cottet *et al.*¹⁴ using phenomenological theory.

It is clearly seen from Eqs. (2) and (3) that if the inequalities $\delta_{eL} \gg \delta_{e1}$ and $\delta_{eL} \gg \gamma\lambda\chi_i H$ do not hold, one expects both the g shift and thermal broadening to be dependent on the concentration of the magnetic impurity (bottleneck effect) as well as on temperature and external magnetic field (dynamic effect).

III. EXPERIMENT AND RESULTS

The ESR measurements were performed using a standard Varian X-band spectrometer equipped with ^3He cold-finger cryostat.²⁴ The temperature was varied continuously from $T=0.52$ K up to 25 K. The intermetallic compounds of LuAl_2 , GdAl_2 , and ThAl_2 were first prepared in an ultra-high-purity-argon arc furnace. The purities of the starting elements used are: Al(99.9999%), Gd(99.9%), Lu(99.9%), and Th(99.99%). LuAl_2 tends to shatter violently upon heating with the arc. Series of

dilute Gd solutions from 2 at. % to 50 ppm were subsequently made by successive dilutions. Even for the "pure" LuAl_2 the ESR signal of Gd was detected, the intensity of the signal corresponding to approximately 10 ppm of Gd present in the samples. Great care was taken to assure reasonable reliability in concentration and homogeneity. X-ray diffraction analysis showed that the samples were single phase. Each sample (~ 0.04 g) was remelted eight times, each time from a different side. They were then ground in an agate mortar, and the powder dispersed in paraffin wax in 2.8-mm quartz tubes for the spectrometer.

Our experimental results are partially shown in Figs. 1–3 and Table I. These results can be summarized as follows:

(a) The linewidth in the high-temperature range

($T > 5$ K) increases linearly with increasing temperature. Its slope, $d(\Delta H)/dT$, depends appreciably on Gd concentration. The thermal broadening increases with decreasing concentration down to 2000 ppm [Fig. 1(a)]. Below this concentration the high-temperature thermal broadening is independent of Gd concentration and equal to 73 G/K (Fig. 2). At low temperatures ($T < 5$ K), and for Gd concentrations below 1 at. %, $d(\Delta H)/dT$ decreases with lowering temperature. For higher Gd concentrations the total linewidth increases with decreasing temperature (for $T \leq 6$ K) [Fig. 1(a)].

(b) For Gd concentration above 2000 ppm the g shift varies appreciably with Gd concentration [Fig. 1(b)], being almost temperature independent above 6 K. Below this temperature a sharp decrease in Δg with decreasing temperature is clearly seen

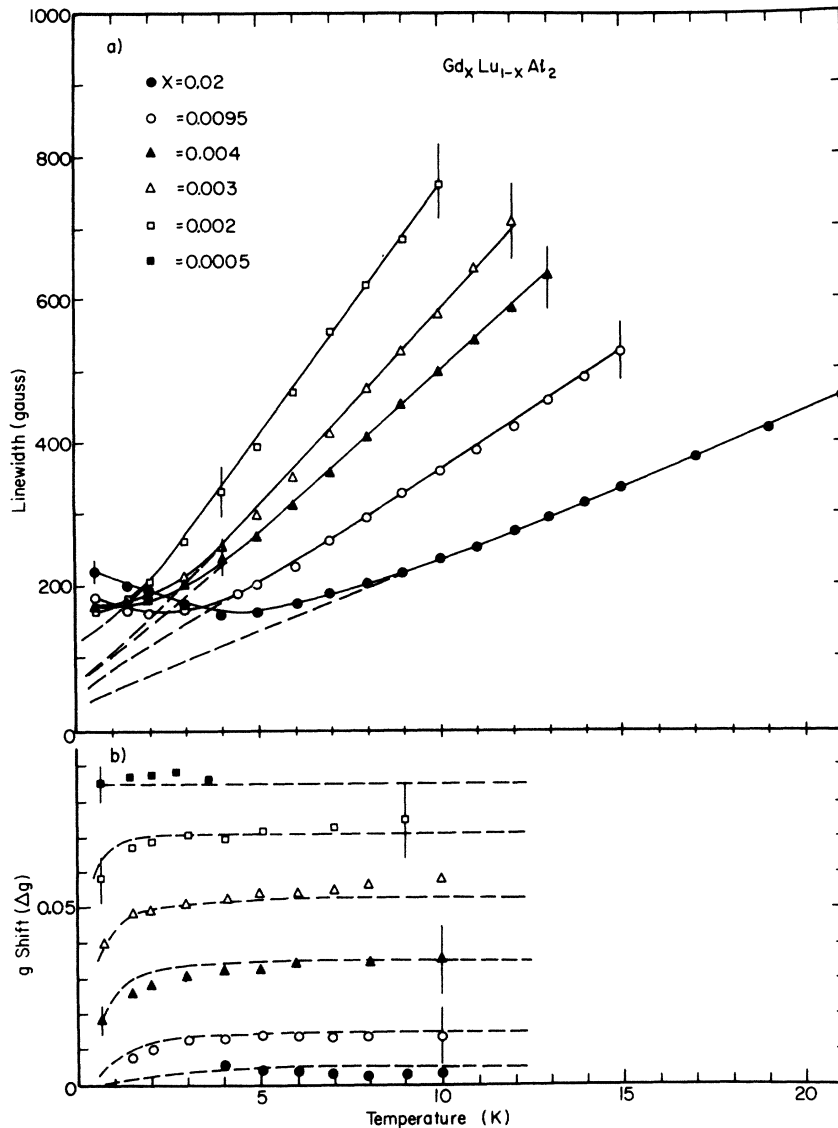


FIG. 1. (a) EPR linewidth; (b) g shift of Gd in $\text{Gd}_x\text{Lu}_{1-x}\text{Al}_2$ as a function of temperature for various Gd concentrations. The dashed lines are fitting of the experimental result to theory [Eq. (3)]. The values of $\delta_{\text{eL}}/\delta_{\text{eI}}$ extracted from this measurement are: $\delta_{\text{eL}}/\delta_{\text{eI}} = 0.4$ ($x = 0.02$), $\delta_{\text{eL}}/\delta_{\text{eI}} = 0.8$ ($x = 0.0095$), $\delta_{\text{eL}}/\delta_{\text{eI}} = 1.8$ ($x = 0.004$), $\delta_{\text{eL}}/\delta_{\text{eI}} = 3.5$ ($x = 0.003$), and $\delta_{\text{eL}}/\delta_{\text{eI}} = 10$ ($x = 0.002$, 2000 ppm). The EPR g shift was measured with respect to $g = 1.993$.

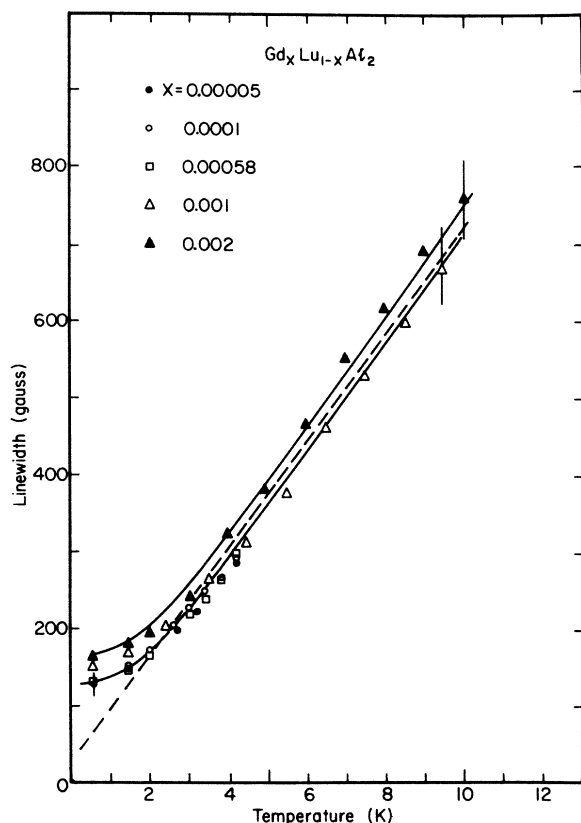


FIG. 2. EPR linewidth of Gd in $\text{Gd}_x\text{Lu}_{1-x}\text{Al}_2$ as a function of temperature. All the results shown here are for small Gd concentration and correspond to the unbottlenecked limit.

[Fig. 1(b)]. For Gd concentrations less than 2000 ppm, Δg is temperature and concentration independent, $\Delta g = +0.085$.

(c) The effect of a second nonmagnetic impurity (Th) is shown in Fig. 3 as well as in Table I. It is clearly seen that the addition of Th increases Δg and $d(\Delta H)/dT$. In the high-temperature range, and for Th concentration above 6 at.%,²⁵ the g shift and $d(\Delta H)/dT$ approach the values $\Delta g \approx +0.085$ and $d(\Delta H)/dT = 73 \text{ G/K}$ as can be clearly seen in Fig. 3.

(d) At relatively high Gd concentration ($C \geq 1 \text{ at. \%}$), both the g shift and the thermal broadening show an increase with decreasing temperature in the low-temperature range. This behavior is indicative of ordering effects, and will not be discussed in the present work.

IV. ANALYSIS

The experimental results above can be interpreted by the existence of the magnetic resonance bottleneck and the dynamic effect. Equation (6) indicates that decreasing the Gd concentration de-

creases δ_{e1} ; δ_{eL} is much less affected (see below). Furthermore, at the high-temperature range the term $\gamma\lambda\chi_i H/\delta_{e1}$ is negligible. Thus the high-temperature g shift and thermal broadening are affected only by the ratio δ_{eL}/δ_{e1} [see Eqs. (2) and (3)]. This ratio increases with decreasing Gd concentration, leading to an increase of both the high-temperature Δg and $d(\Delta H)/dT$. Their values, $\Delta g = +0.085$ and $\Delta H_K/T = 73 \text{ G/K}$, observed for very low Gd concentrations, correspond to unbottlenecked values of Δg and $d(\Delta H)/dT$. This explains qualitatively the high-temperature results in Figs. 1–2. The low-temperature results are clearly related to the term $\gamma\lambda\chi_i H/\delta_{e1}$ in Eqs. (2) and (3).

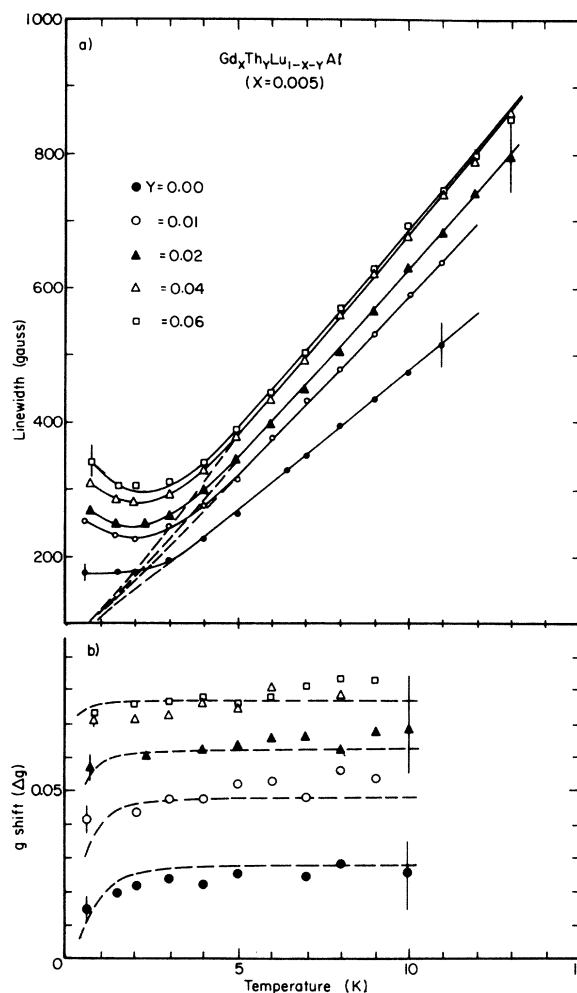


FIG. 3. (a) EPR linewidth; (b) g shift of Gd in $\text{Gd}_x\text{Th}_y\text{Lu}_{1-x-y}\text{Al}_2$ as a function of temperature for various Th concentrations (the Gd concentration is constant and equals $x = 0.005$). The dashed lines are the fitting of the experimental data to the theory [Eq. (3)] using the following values of δ_{eL}/δ_{e1} as parameters: $\delta_{eL}/\delta_{e1} = 1 \pm 0.5$ ($y = 0$), $\delta_{eL}/\delta_{e1} = 2 \pm 1$ ($y = 0.01$), $\delta_{eL}/\delta_{e1} = 3 \pm 2$ ($y = 0.02$), and $\delta_{eL}/\delta_{e1} = 10 \pm 7$ ($y = 0.04$).

TABLE I. High-temperature g value and thermal broadening of Gd in $\text{Gd}_x\text{Th}_{1-x}\text{Lu}_{1-x-y}\text{Al}_2$. The low-temperature results of these samples clearly show "bordering effects"; i. e., both the g value and linewidth increase with decreasing temperature.

x	y	g value	$d(\Delta H)/dT$
0.01 (1%)	0.00	2.023 ± 0.005	28 ± 5
	0.02	2.04 ± 0.010	41 ± 6
	0.04	2.05 ± 0.012	50 ± 7
	0.08	2.07 ± 0.015	57 ± 7
0.02 (2%)	0.00	2.008 ± 0.005	22 ± 3
	0.02	2.02 ± 0.01	31 ± 3
	0.04	2.032 ± 0.012	40 ± 5
	0.08	2.048 ± 0.015	48 ± 6

At very low temperatures this term becomes comparable to $(1 + \delta_{eL}/\delta_{e1})$, causing a reduction of Δg and $d(\Delta H)/dT$ with decreasing T . The decrease in $d(\Delta H)/dT$ (or even the increase of the total linewidth at low temperatures in Figs. 1 and 2) occurs even for very low Gd concentrations, (Fig. 2) where the temperature independence of the g shift indicates the absence of dynamic effects. We attribute this behavior to large "residual width" (unresolved fine structure or the presence of stresses and dirt in the sample) and to interaction effects for the higher-concentration samples.

Adding Th to $\text{LuAl}_2:\text{Gd}$ "opens" the bottleneck by virtue of increasing the CE spin-flip relaxation rate to the lattice, δ_{eL} . For relatively low Gd concentration, the unbottlenecked limit can be reached (Fig. 3). For Gd concentrations of 1 at. % or higher, however, the bottleneck was not able to be broken completely (Table I). This is because of the very high Th concentration needed (more than 10-at. % Th) in order to reverse the inequality $\delta_{eL} < \delta_{e1}$. At such high Th concentration, the residual width is very large, making the determination of $d(\Delta H)/dT$ nearly impossible.

We now carry the analysis through quantitatively. The term $\gamma\lambda\chi_i H/\delta_{e1}$ in Eqs. (2) and (3) can be written in the form

$$\frac{\gamma\lambda\chi_i H}{\delta_{e1}} = \frac{\Delta g_0 H}{2\Delta H_K}.$$

Thus, this term is proportional to the ratio of two measured quantities [Δg_0 and ΔH_K] and can be evaluated independent of any model. Since all the quantities in Eqs. (2) and (3) are known experimentally (except the parameter δ_{eL}/δ_{e1}), we can fit the theory to the experimental data (Figs. 1-3) with only one unknown parameter. This enables us to estimate δ_{eL}/δ_{e1} . The dashed lines in Figs. 1-3 represent our best fit with values of δ_{eL}/δ_{e1} written in the captions of the same figures.

The determination of δ_{eL} requires the knowledge

of δ_{e1} . Estimation of δ_{e1} [see Eq. (6)] is slightly complicated because of the absence of other independent experimental information about the enhancement factor $[1 - U\chi(0)]$. The enhancement factor is usually determined by the ratio of the susceptibility and specific heat.¹ The specific heat of LuAl_2 was measured by Hungsberg *et al.*,²⁶ yielding a density of states $\eta = 0.35$ states/atom spineV. As for the determination of the susceptibility, this is difficult to measure by a standard macroscopic measurement because of the "dirt" present in commercially available Lu. The presence of such dirt makes the separation of χ_e nearly impossible. Indeed, susceptibility measurements on the isoelectronic system LaAl_2 and YAl_2 measured in several laboratories exhibit contradictory results.²⁷

In the absence of the above important information the value of δ_{e1} can be determined under the following alternative assumptions: (a) We can neglect the enhancement factor $[1 - U\chi(0)]$ in Eq. (6) but assuming still that the exchange interaction is q dependent; (b) we can neglect the q dependence of the exchange [i. e., assume $\langle J^2(q) \rangle = J^2(0) = J_0^2$] and consider only electron-electron interaction.

For the estimation of δ_{e1} we shall adopt the approach (b), primarily because previous analysis of the bottleneck effect in LaAl_2 ¹ and YAl_2 ²¹ had also neglected the q dependence of the exchange. Afterwards, we shall calculate $J(q)$ and estimate an upper limit for possible errors in our analysis.

Assuming that the exchange interaction J does not depend heavily on the CE momentum transfer, Eqs. (9) and (11) yield

$$\Delta H_K/T = (\pi K_B/g\mu_B) (\Delta g_0)^2 K(\alpha) \quad (14)$$

Substituting the experimental values of Δg_0 and $\Delta H_K/T$ into (14), gives $K(\alpha)$ to be 0.45. Now, from the work of Shaw and Warren²³ and the value of $K(\alpha)$, we can estimate α ($\alpha = 0.6$) and hence also the enhancement factor $(1 - \alpha)$. This enables us to estimate an exchange parameter, J_0 , using relation (9), to be $J_0 = 0.1$ eV. It enables us also to calculate the value of δ_{e1} using Eqs. (6) or (12). We find $\delta_{e1} = 2 \times 10^{14}$ C_{Gd} for $\text{LuAl}_2:\text{Gd}$, C_{Gd} being the Gd concentration in atomic fraction. Thus, the values of δ_{eL} in Figs. 1-3 and Table I can be determined. Figure 5 exhibits the values of δ_{eL} as a function of Th concentration. These values of δ_{eL} were estimated using the data in Table I.

According to Eq. (3) we expect only small deviations from linearity of the linewidth at very low temperatures. The experimental points (Fig. 2) show, however, noticeable deviations outside any error bar. This behavior was observed also at very low concentrations (i. e., in the unbottlenecked limit) and therefore is not entirely associ-

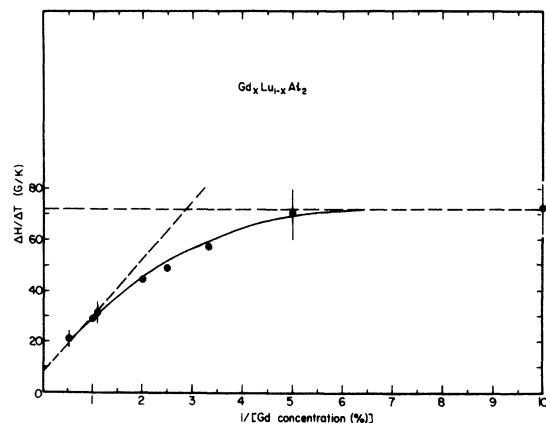


FIG. 4. Thermal broadening of Gd in $Gd_xLu_{1-x}Al_2$ as a function of $1/C_{Gd}$ (C_{Gd} being the Gd concentration). The horizontal dashed line is the unbottlenecked value of $\Delta H_K/T$. The other dashed line represents the initial slope and gives $\delta_{eL}^{(0)}$ according to Eq. (21); its intersection with the vertical axis yields $\partial\delta_{eL}^{(1)}/\partial C_{Gd}$ according to the same equation.

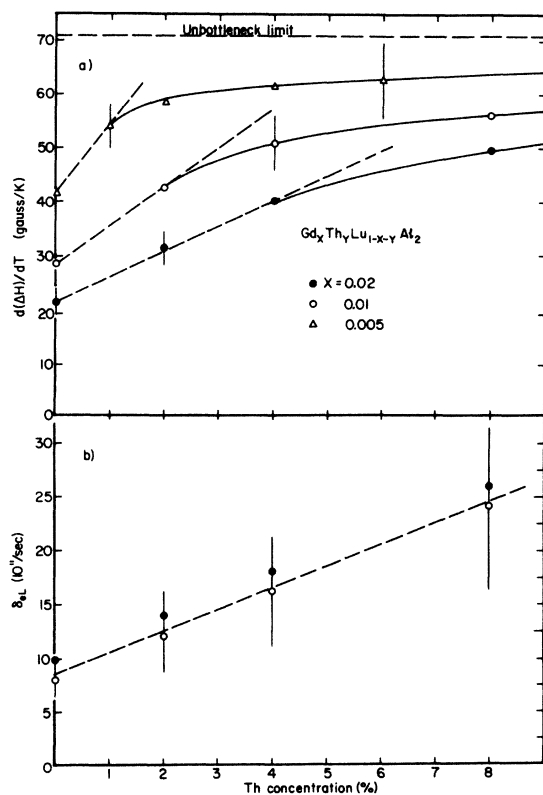


FIG. 5. (a) Thermal broadening as a function of thorium concentration (for constant Gd concentrations). The dashed lines represent the initial slopes and yield $\partial\delta_{eL}^{(2)}/\partial C_{Th}$ according to Eq. (21); (b) the total spin-flip scattering rate, δ_{eL} , as derived from (a) vs the concentration of Th.

ated with interaction effects. Partial support for this interpretation is provided by the plot of the absolute linewidth versus Gd concentration at 0.52 K (Fig. 6). It is clearly seen in Fig. 6 that below concentrations of 600 ppm the linewidth is concentration independent leading us to the above conclusion. As was stressed above, we attribute the deviation of the linewidth from linearity (at very low Gd concentrations) to a possible unresolved fine structure, stresses, and other impurities being present in the samples.²⁸ At higher Gd concentrations (above 1000 ppm) ordering effects, obviously, play a role.

V. DISCUSSION

In this section we shall discuss and compare the system $LuAl_2:Gd$ with the analog systems $YAl_2:Gd$ and $LaAl_2:Gd$. This will be done with emphasis on the following subjects: (a) dynamic effects, (b) band structure, (c) the q dependence of the exchange interaction, and (d) the CE spin-flip scattering due to impurities.

A. Dynamic effects

The analysis above clearly demonstrates that the temperature dependence of the g shift is due to the dynamic effects according to the theory of Giovannini and Hasewaga. These dynamic effects are associated with the term $\gamma\lambda\chi_i H/\delta_{eL}$ in Eq. (2). It has been stressed above that this term can be estimated from the experimental results alone [i.e., Δg_0 and ΔH_K] independent of the choice of any particular model. Since Δg_0 and ΔH_K do not vary appreciably from $Gd_xLu_{1-x}Al_2$ to $Gd_xLa_{1-x}Al_2$ and $Gd_xY_{1-x}Al_2$, we expect dynamic effects to exist in all three systems. However, only $Gd_xLu_{1-x}Al_2$ exhibits such an effect clearly. As will be shown below, δ_{eL} is larger in $LuAl_2$ than

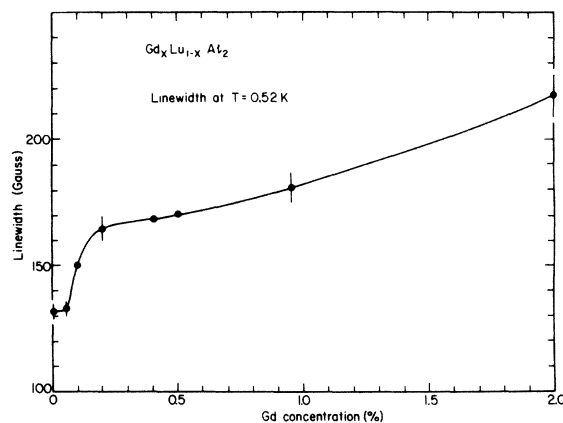


FIG. 6. EPR linewidth of Gd in $Gd_xLu_{1-x}Al_2$ at $T = 0.52$ K as a function of Gd concentration.

in LaAl_2 and YAl_2 . Therefore, the bottleneck in $\text{Gd}_x\text{Lu}_{1-x}\text{Al}_2$ is opened up (i.e., $\delta_{eL} \approx \delta_{eI}$) at relatively higher Gd concentration than in the other two systems. This makes the dynamic effects more easily observable for the LuAl_2 . Our estimates indicate that the optimum Gd concentration for successful observation of this effect in $\text{Gd}_x\text{La}_{1-x}\text{Al}_2$ and $\text{Gd}_x\text{Y}_{1-x}\text{Al}_2$ is around 0.05 at. %. In the case of LaAl_2 , the superconducting absorption at the critical field interferes with the EPR signal at low temperatures (for such a concentration) making meaningful measurements almost impossible.¹ For YAl_2 :Gd, there is no report about measurements at such low concentrations and temperatures.²¹ Consequently, we performed measurements on two samples of $\text{Gd}_x\text{Y}_{1-x}\text{Al}_2$. One of them definitely shows dynamic effects (Fig. 7).

This success encourages one to look more deeply into various systems where the observation of bottleneck effect has been reported, whereas dynamic effects have not. Some of these systems (e.g., $\text{Gd}_x\text{Y}_{1-x}\text{Cu}$) are still not very well understood. High-field measurements are necessary for better interpretation of the data.

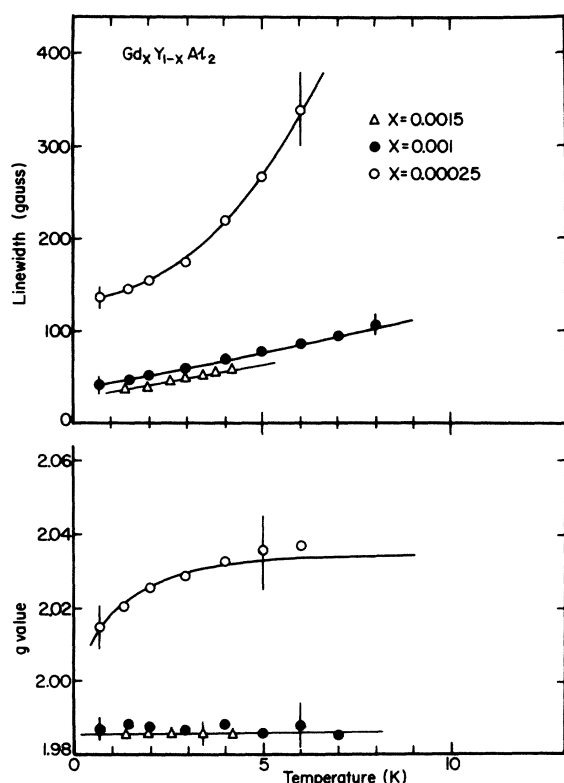


FIG. 7. EPR linewidth and g value of Gd in YAl_2 as a function of temperature for two different Gd concentrations. The solid lines represent the fitting to Eqs. (2) and (3).

B. Band structure

In our band-structure analysis we shall distinguish between (i) conduction electrons originating with the Gd site, having mainly 6s character and forming s band,²⁹ and (ii) conduction electrons originating at both the Al and X site ($X = \text{La}, \text{Lu}$, and in XAl_2).

The band calculation of Switendick³⁰ deals with (ii). It demonstrates the existence of significant density of states of p and d characters on the Al and X sites, respectively, with negligible s -electron densities on both sites. Generally speaking, the band structure in all the three XAl_2 systems is very similar, except for additional contributions due to f -like character at the La site in LaAl_2 . This f character, admixed into the CE wave function at the Fermi level, substantiates the interpretation of Hungsberg *et al.*²⁶ for the larger specific heat in LaAl_2 in comparison to YAl_2 and LuAl_2 . It also supports recent NMR Knight-shift measurements of $^{139}\text{LaAl}_2$.³¹ It is, however, in some disagreement with the interpretation of recent EPR measurements of Gd in $\text{Gd}_x\text{La}_{1-x}\text{Al}_2$.¹ This EPR experiment was analyzed using two band models: s band (originating with the 6s electrons on the Gd site) and d band (originating with the La site). The second band was verified in our EPR experiment by observation of small negative g shift. This g shift appears only when the J_{f-s} interaction is bottlenecked completely.

It was argued that the J_{f-d} interaction (rather than the J_{f-p} or J_{f-f}) between the 4f shell and the d electrons on the La site is responsible for this shift. This is in complete analogy to the situation in transition metals³² where the J_{f-d} interaction is negative (because of the orthogonality condition³²) and unbottlenecked (because of the rapid relaxation of the d electrons to the lattice).

The interpretation of the EPR experiment is supported, however, by preliminary EPR measurements on $\text{Gd}_x\text{Y}_{1-x}\text{Al}_2$ (Fig. 7). The EPR spectra of Gd in YAl_2 exhibit a small negative g shift, although the f character in the conduction band is not present here.

It should be mentioned that our data on $\text{Gd}_x\text{Lu}_{1-x}\text{Al}_2$ do not exhibit a negative g shift. This may be caused by the relatively large $\delta_{eL}^{(0)}$, such that an appreciable amount of Gd is needed to reach the extreme bottleneck condition. For such high Gd concentrations, interaction effects might play a role, eliminating the possibility of seeing this effect.

C. q dependence of the exchange interaction

Watson, Freeman, and Koide³³ have demonstrated that the exchange coupling $J(\vec{q})$ can be expressed by partial-wave expansion. Davidov *et al.*²² use

this expansion to express the g shift [proportional to $J(0)$] and the thermal broadening [proportional to $\langle J^2(q) \rangle$] in terms of these partial waves.

In the presence of electron-electron interaction U , responsible for exchange enhancement, the analysis of Davidov *et al.*²² can be immediately extended. We write

$$\frac{J(q)}{1 - U\chi(q)} = J_{\text{eff}}(q) \quad (15)$$

and

$$J_{\text{eff}}(q) = \sum_L (2L+1) J_{\text{eff}}^{(L)} P_L(\cos\theta), \quad (16)$$

where \vec{q} is the momentum transfer $\vec{q} = \vec{K} - \vec{K}'$. Both \vec{K} and \vec{K}' lie on the spherical Fermi surface. Thus, $|\vec{q}| = K_F [2(1 - \cos\theta)]^{1/2}$ where θ is the angle between \vec{K} and \vec{K}' . $J_{\text{eff}}^{(L)}$ represents the effective exchange (in the presence of electron-electron interaction) associated with the L partial wave.

Following Davidov *et al.*,²² we can write (see Appendix)

$$J_{\text{eff}}(0) = \frac{J(0)}{1 - U\chi(0)} = J_{\text{eff}}^{(0)} + 3J_{\text{eff}}^{(1)} + 5J_{\text{eff}}^{(2)} + \dots, \quad (17)$$

$$\begin{aligned} \langle [J_{\text{eff}}(q)]^2 \rangle &= \left\langle \left(\frac{J(q)}{1 - U\chi(q)} \right)^2 \right\rangle \\ &= [J_{\text{eff}}^{(0)}]^2 + 3[J_{\text{eff}}^{(1)}]^2 + 5[J_{\text{eff}}^{(2)}]^2 + \dots \end{aligned} \quad (18)$$

$J_{\text{eff}}(0)$ and $\langle [J_{\text{eff}}(q)]^2 \rangle$ are related to the g shift and thermal broadening according to Eqs. (4) and (6), respectively.

Because of the stability of the $4f^7(\text{Gd}^{+3})$ configuration, we shall neglect any contribution to the exchange interaction originating from covalent mixing, considering only atomic-like exchanges. For this case, it has been demonstrated that the magnitude of $J_{\text{eff}}^{(L)}$ (always positive) decreases with increasing L . This enables us to consider only the first two terms in Eqs. (17) and (18). Solution of these equations yields for LuAl_2 :Gd

$$J_{\text{eff}}^{(0)} = +0.15 \text{ eV and } J_{\text{eff}}^{(1)} = +0.03 \text{ eV}.$$

The q dependence of the exchange is given in this approximation by

$$J_{\text{eff}}(q) = J_{\text{eff}}^{(0)} + 3J_{\text{eff}}^{(1)} (1 - q^2/2K_F^2).$$

Table II exhibits the values of $J_{\text{eff}}^{(0)}$ and $J_{\text{eff}}^{(1)}$ for the various XAl_2 systems. For comparison, we also give the exchange parameter J_0 . This parameter was calculated above by neglecting the q dependence of the exchange interaction [case (i) above].

D. Conduction electrons spin flip due to impurities

The spin-flip scattering rate of the CE to the lattice, δ_{eL} , is due to three different contributions: (i) scattering in pure LuAl_2 due to imperfections or other impurities (other than Gd and Th) which we shall denote by $\delta_{\text{eL}}^{(0)}$; (ii) scattering due to Gd ions, $\delta_{\text{eL}}^{(1)}$; (iii) scattering due to Th impurities, $\delta_{\text{eL}}^{(2)}$. In the first approximation we can assume the following expansion to be valid:

$$\delta_{\text{eL}} = \delta_{\text{eL}}^{(0)} + \frac{\partial \delta_{\text{eL}}^{(1)}}{\partial C_{\text{Gd}}} C_{\text{Gd}} + \frac{\partial \delta_{\text{eL}}^{(2)}}{\partial C_{\text{Th}}} C_{\text{Th}}, \quad (19)$$

where C_{Gd} and C_{Th} are the concentrations of Gd and Th, respectively. In order to separate δ_{eL} into its three contributions, we adopt the following procedure: at the higher temperature range and in the extreme bottleneck regime ($\delta_{\text{eL}} \ll \delta_{\text{e1}}$), the thermal broadening [Eq. (2)] is reduced to

$$\frac{d(\Delta H)}{dT} = \frac{\delta_{\text{eL}}}{\delta_{\text{e1}}} \cdot \frac{\Delta H_K}{T}. \quad (20)$$

Substituting Eq. (19) into (20) and using the estimated value of δ_{e1} , we obtain

$$\left[\frac{d(\Delta H)}{dT} \right]_{\text{exp}} = \frac{\Delta H_K/T}{2 \times 10^{14}} \left[\frac{\delta_{\text{eL}}^{(0)}}{C_{\text{Gd}}} + \frac{\partial \delta_{\text{eL}}^{(1)}}{\partial C_{\text{Gd}}} + \left(\frac{\partial \delta_{\text{eL}}^{(2)}}{\partial C_{\text{Th}}} \right) \frac{C_{\text{Th}}}{C_{\text{Gd}}} \right]. \quad (21)$$

Thus by plotting (i) the experimental values of $[d(\Delta H)/dT]_{\text{exp}}$ from Figs. 1 and 2 as a function of $1/C_{\text{Gd}}$ (taking $C_{\text{Th}} = 0$) and (ii) the experimental value of $[d(\Delta H)/dT]_{\text{exp}}$ from Fig. 3 and Table I versus C_{Th} (but for constant C_{Gd}), the three terms $\delta_{\text{eL}}^{(0)}$, $\partial \delta_{\text{eL}}^{(1)}/\partial C_{\text{Gd}}$, and $\partial \delta_{\text{eL}}^{(2)}/\partial C_{\text{Th}}$ can be estimated.

These procedures have been carried out in Figs. 4 and 5(a). The values observed are tabulated in Table III. Table III also gives a comparison with the analog systems LaAl_2 and YAl_2 .

TABLE II. Exchange interaction as calculated by (i) neglecting the q dependence of the exchange interaction and (ii) assuming Eqs (17) and (18) to be valid. We assumed the same density of state ($\eta = 0.35$ states/atom spineV) for all the XAl_2 systems.

	Experimental		Case (i)		Case (ii)	
	Δg_0	$\Delta H_K/T$ (G/K)	Enhancement factor α	J_0 (eV)	$J_{\text{eff}}^{(0)}$ (eV)	$J_{\text{eff}}^{(1)}$ (eV)
$\text{Gd}_x\text{Lu}_{1-x}\text{Al}_2^a$	+0.085	72 ± 10	0.6	+0.1	+0.15	+0.03
$\text{Gd}_x\text{Y}_{1-x}\text{Al}_2^b$	+0.07	40 ± 5	0.6	+0.08	+0.11	+0.03
$\text{Gd}_x\text{La}_{1-x}\text{Al}_2^c$	+0.11	65 ± 10	0.56	+0.13	+0.145	+0.055

^aThis work.

^bReference 21.

^cReference 1.

TABLE III. Spin-flip relaxation rate of the CE due to Gd ions, Th ions, and "pure" XAl_2 ($X=Lu, Y, La$). The analysis was carried out assuming J to be q independent.

	$\delta_{eL}^{(0)}$ (10^{10} sec $^{-1}$)	$\partial\delta_{eL}^{(1)}/\partial C_{Gd}$ (10^7 sec $^{-1}$ /ppm)	$\partial\delta_{eL}^{(2)}/\partial C_{Th}$ (10^7 sec $^{-1}$ /ppm)
$Gd_xLu_{1-x}Al_2^a$	60 ± 20	2 ± 1	2 ± 1
$Gd_xY_{1-x}Al_2^b$	4	0.36	2.2
$Gd_xLa_{1-x}Al_2^c$	17 ± 5	1 ± 0.6	5 ± 2

^aThis work.

^bReference 21.

^cReference 1.

It is clearly seen that the CE spin-flip scattering rates caused by Th impurity are consistently larger than those due to the Gd. Asik, Ball, and Slichter³⁴ have demonstrated that the spin-flip scattering rate depends appreciably on the overlap integral between the CE wave function and the orbital core states responsible for this scattering. It is determined, also, by the contrast of the spin-orbit coupling between the impurity and that of the host. The difference in valence between the Th (+4) and that of the host (+3) causes a strong attractive potential leading to an increase of the overlap integral. Also, a larger contrast in the spin-orbit coupling is expected for Th in XAl_2 because of the larger difference in atomic numbers. This can explain the faster spin-flip scattering rate found for $XAl_2:Th$ relative to $XAl_2:Gd$ ($X=Lu, La, Y$).

In summary, we have demonstrated the existence of dynamic effects in $Gd_xLu_{1-x}Al_2$ and extracted several parameters of profound importance. The decrease in the thermal broadening at low temperatures (for low Gd concentrations) is not completely understood yet. A possible approach for studying more deeply this low-temperature phenomena, as well as some other features of the coupled spin systems, is by a computation of the complete solution of Hasegawa-Giovannini equations [Eqs. (2) and (3) are first approximation only]. This is done, at the present, with the cooperation of G. Dublon (from the Nuclear Research Center, Negev, Israel). Further experimental work on single crystal and high-field measurements are also needed.

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APPENDIX

Note added in proof. Equations (17) and (18) were derived in complete analogy with those in Ref. 22. Thus, formally they are correct and the exchange enhancement is already included (in some complicated manner) in the coefficients $J_{eff}^{(L)}$. There is no simple way, however, to relate these coefficients to the exchange interaction as measured by means of other techniques (resistivity, magnetoresistance, ...). It is advantageous, therefore, to separate the exchange enhancement from the partial-wave amplitudes $J^{(L)}$. Such a calculation was carried out by R. Walstedt (private communication) as follows: The exchange interaction $J_{eff}(q)$ can be written as

$$J_{eff}(q) = \sum_L (2L+1) J^{(L)} \left[\frac{P_L(\cos\theta)}{1 - U\chi(\cos\theta)} \right], \quad (A1)$$

where U is the Coulomb electron-electron interaction responsible for the exchange enhancement and $J^{(L)}$ are the unenhanced partial-wave amplitudes. Thus, $J_{eff}(0)$ is immediately obtained as

$$J_{eff}(0) = \frac{1}{1-\alpha} (J^{(0)} + 3J^{(1)} + 5J^{(2)} + \dots), \quad (A2)$$

where α is equal to $U\chi(0)$. The value of $\langle [J_{eff}(q)]^2 \rangle$ can be expressed using (A1) as

$$\begin{aligned} \langle [J_{eff}(q)]^2 \rangle &= \sum_{L,L'} (2L+1)(2L'+1) J^{(L)} J^{(L')} \\ &\times \left\langle \frac{P_L(\cos\theta) P_{L'}(\cos\theta)}{[1 - U\chi(\cos\theta)]^2} \right\rangle \\ &= \sum J^{(L)} J^{(L')} K_{LL'}(\alpha). \end{aligned} \quad (A3)$$

The value of $K_{LL'}(\alpha)$ is defined by (A3). It is expected that for $\alpha=0$ (zero exchange enhancement), $K_{LL'}(0)$ is equal to 1, 3, and 5 for $L=L'=0$, $L=L'=1$, and $L=L'=2$, respectively, and $K_{LL'}(0)=0$ for $L \neq L'$. For $\alpha \neq 0$, however, the cross terms ($L \neq L'$) do not vanish. Walstedt has calculated the values of $K_{LL'}(\alpha)$ for various values of α . For instance, assuming $\alpha=0.6$ Walstedt found $K_{00}=0.6269$, $K_{01}=0.325$ and $K_{11}=1.9223$. We restricted ourselves to partial-wave amplitudes up to $L=1$ because of reasons given in the text. The existence of cross terms in this analysis increases the number of the unknown parameters and with our limited experimental information, we were not able to use Walstedt analysis. We would like to thank Professor R. Orbach and Dr. R. Walstedt for this important information.

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