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Nuclear Magnetic Resonance in Rare Earth Intermetallic Compounds

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The nuclear magnetic resonance (NMR) of nuclei of non-magnetic ions in rare earth intermetallic compounds (*e.g.* $GdAl_2$) has revealed that an appreciable polarization of the conduction electrons exists. A phenomenological interpretation of these results has been given assuming an exchange interaction $\mathfrak{J}\boldsymbol{S}\cdot\boldsymbol{s}$ to exist between the spins of the rare earth ions and the conduction electrons. A surprising result is that, though of the proper magnitude, $\mathfrak{J}<0$. A further study of these effects has been realized by an investigation of the broadening of the NMR in magnetically dilute compounds (*e.g.* $Gd_{0.001}La_{0.999}Al_2$) assuming that the above exchange interaction induces an oscillatory radial dependence of the conduction electron polarization. These results are consistent with the magnitudes of the effects observed in the magnetically dense compounds.

Nuclear magnetic resonance (NMR) studies have been reported[1,2] of the Al^{27} Knight shift (K^{27}) in the cubic Laves phase rare earth-aluminum intermetallic compounds RAl_2, where $R \equiv La, Ce \cdots Lu$. From the field and temperature dependence of K and χ it was deduced that the rare earth ions produce an exchange polarization of the conduction electrons. If K^{27} is the Knight shift due to the Pauli paramagnetism of the s conduction electrons (*e.g.* in nonmagnetic $LaAl_2$) then the total shift to be expected in the magnetically dense compounds for a spatially uniform polarization of the conduction electrons is

$$K^{27}=K_0^{27}\left[1+\frac{\mathfrak{J}}{gg_J\beta^2}\frac{\chi}{n_f}\frac{\langle \boldsymbol{S}\cdot\boldsymbol{J}\rangle}{J(J+1)}\right] \quad (1)$$

where $\mathfrak{J}$ is the magnitude of the exchange interaction $\mathfrak{J}\boldsymbol{S}\cdot\boldsymbol{s}$ between the spin moment $\boldsymbol{S}$ and $\boldsymbol{s}$ of the rare earth ion and conduction electron respectively, χ/n_f the susceptibility per rare earth ion and $\boldsymbol{J}=\boldsymbol{L}+\boldsymbol{S}$. Since J and J_z remain as good quantum numbers in the metals one must project $\boldsymbol{S}$ onto $\boldsymbol{J}$ to obtain the magnitude and sign of S_z, resulting in the factor $\langle \boldsymbol{S}\cdot\boldsymbol{J}\rangle/J(J+1)$. From the observed behavior of K and χ in the paramagnetic state of each metal values of $\mathfrak{J}$ were obtained which varied from -0.24 ev for $CeAl_2$ to -0.043 ev for $GdAl_2$. Though of comparable magnitude to the free ion $4f-6s$ exchange interaction the experimental values of $\mathfrak{J}$ in the metals are of opposite sign[3].

The negative sign of the derived $\mathfrak{J}$'s results from the fact that the net s spin density at the Al sites is antiparallel to the spin $\boldsymbol{S}$ of the rare earth ion. Two other quite different explanations have been given for this phenomenon. One is that the actual polarization of the conduction electrons is oscillatory, with a radial dependence as is given by the Ruderman-Kittel range function[4,5,6]. A discussion of the criteria for this consideration to be responsible for the negative spin density in the region between rare earth ions in a regular lattice, when $\mathfrak{J}>0$, is given in Ref. 2. Alternatively it has been suggested that the intra-atomic exchange polarization of the localized $5s$ and $5p$ electrons by the $4f$ spin results in a negative spin density at a distance comparable to the Gd-Al separation in $GdAl_2$, for example.

As a further step in assessing the relative importance of these, and possibly other, processes in the polarization of the conduction electrons we have studied the change in the line widths of the Al^{27} and La^{139} NMR that results from substitution of Gd for La, in varying concentrations c, in $LaAl_2$. The problem is similar in many ways to the Cu-Mn system for which detailed consideration has been given by Behringer[4] and Yosida[5]. In a nonmagnetic metal the substitution of a random distribution of paramagnetic solute ions manifests itself as a line broadening δH of the NMR of the solvent nuclei. At least four contributions to δH are to be distinguished:

(A) The purely dipolar part which is proportional to c and the thermal average $\bar{\mu}_z$ of the paramagnetic ion moment μ_J, taking the applied field H to be in the z direction. (The random demagnetizing fields resulting from the use of powdered specimens are unimportant for the small dilutions of magnetic ions used in these experiments. This is not the case for the dense RAl_2 metals.)

(B) The rare earth conduction electron exchange part[5,6] which is proportional to c, $\bar{S}_z$, and, as well, K and $\mathfrak{F}$.

(C) The rare earth conduction electron "polarization" part resulting from an interaction V which admixes localized states of the rare earth ion with those of the conduction band[8] and is proportional to c, $\bar{S}_z$, K and V.

(D) The purely [electric quadrupolar part arising out of the charge contrast of the solute ion relative to the solvent lattice[9]. This effect which is independent of $\bar{S}_z$ was found to be of negligible importance as would be expected because of the like "valence" of Gd and La ions in the RAl_2 structure.

The half width at half maximum intensity δH^{dip} of the La NMR due to (A) as given by Behringer is approximately

$$\delta H_{La}^{dip} = 9.2c\frac{\bar{\mu}_z}{\Omega_{La}} \qquad (2)$$

where Ω_{La} is the La atomic volume. The broadening expected from (A) is the same for the La and Al NMR. For example at $T=20°K$ and $H=14$ koe, we calculate $\delta H^d = 1.2c$ koe. Now it may be shown, with certain simplifying assumptions, that the contribution δH_i^{ex} resulting from (B) may be expressed as

$$\delta H_i^{ex} = \frac{3\sqrt{3}\,\Omega_i}{64\pi}\frac{K_0^i\mathfrak{F}}{g\beta^2}\delta H_i^{dip} \qquad (3)$$

The relevant measured quantities are, from $LaAl_2$; $K_0^{27}=0.13\%$, $K_0^{139}=0.65\%$, and as determined using Eq. (1) with the observed K^{27} in $GdAl_2$; $\mathfrak{F}(Gd) = -0.043$ ev. These lead to $\delta H_{Al}^{ex}/\delta H_{Al}^{dip}=0.60$ and $\delta H_{La}^{ex}/\delta H_{La}^{dip}=4.5$. Equation 3 was derived on the following bases. The radial dependence of the Ruderman-Kittel range function is of the form

$$\frac{2k_fR\cos 2k_fR - \sin 2k_fR}{(2k_fR)^4},$$

where k_f is the wave vector of the conduction electrons at the Fermi surface. Since the strength of the exchange interaction is so large that the nearest and next nearest neighbor La nuclei to a Gd spin do not contribute to the observed line profile at low temperatures and since $2k_f$ is less than, or of the order of, a_0 we make the approximations: 1) neglect the $\sin 2k_fR$ contribution and 2) take an average of the magnitude of the oscillating part of the range function.

In a similar fashion we may express the contribution δH_i^{ad} arising from (C) as

$$\delta H_i^{ad} \simeq \left(\frac{V^2}{\mathfrak{F}\Delta}\right)\delta H_i^{ex} \qquad (4)$$

where V is the matrix element of the metal crystal field potential between the localized $4f$ electrons and the conduction electrons, and Δ is the exchange self-energy of a $4f$ electron. To make a quantitative estimate V^2 and Δ would be extremely difficult, at best. However, there is a consequence of the effect of the admixture of localized $4f$ states into the conduction band on the susceptibility of the dilute alloy; namely, that the Curie constant will be decreased in direct proportion to magnitude of the admixture. Measurements of χ by Williams and Sherwood[10] on a $Gd_{0.005}La_{0.995}Al_2$ sample indicate that, if anything, the Curie constant

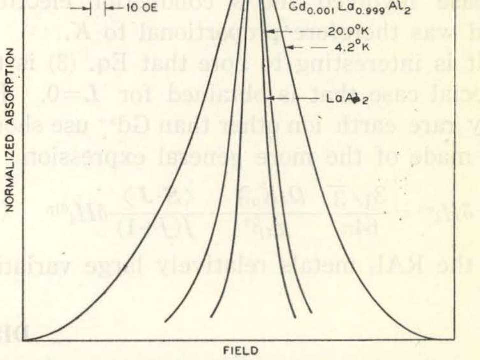

Fig. 1. The normarlized integrated line profiles of the La^{139} NMR in $LaAl_2$ and $Gd_{0.001}La_{0.999}Al_2$. Measurements were made in a field of approximately 14 koe at the temperatures indicated. The positions of maximum intensity are arbitrarily taken to be at the same external field.

Table I. Contributions to the Half-Width at Half-Maximum Intensity of the La^{139} NMR in $Gd_{0.001}La_{0.999}Al_2$ at 4.2°K and 14 koe Applied Field.

	Nuclear* dip-dip	Gd dipolar	sf exchange†	Admixture effect	Observed
$\delta H_{1/2}$(oe.)	<5	5.2	23.5		27.4

* Field and temperature independent.

† Using $\mathfrak{J}=0.043$ ev. as obtained from NMR in $GdAl_2$.

per Gd ion is *greater* than that expected for the free ion. We conclude from this that $4f$ conduction band admixture processes contribute negligibly to our NMR line broadening.

Observations of the La^{139} and Al^{27} NMR were made for samples in which $c=0.001$, 0.005 and 0.010. The La line shapes for a pure $LaAl_2$ and $Gd_{0.001}\,La_{0.999}\,Al_2$ sample are shown in Fig. 1, the latter at two temperatures 4.2°K and 20.2°K. The line shape data, when analyzed as indicated above, is in remarkably good agreement with the value of δH calculated using Eq. (3) perhaps fortuitously so when due consideration is given to the approximations involved. The relevant parameters are collected in Table I.

Since the $Al^{27}(\pm 1/2 \longleftrightarrow \pm 1/2)$ NMR is broadened by the 2nd order quadrupole interaction even in the pure $LaAl_2$ the dependence of the line width and shape on Gd concentration is difficult to determine. It was noticed, however, that the effects of Gd doping were at least five times less efficient in broadening the Al resonance indicating that the mechanism responsible for the line width increase involved the s conduction electrons and was therefore proportional to K.

It is interesting to note that Eq. (3) is the special case that is obtained for $L=0$. For any rare earth ion other than Gd^{3+} use should be made of the more general expression

$$\delta H_i^{\mathrm{ex}}=\frac{3\sqrt{3}}{64\pi}\,\frac{\Omega_i K_0 \mathfrak{J}}{g_J \beta^2}\,\frac{\langle \boldsymbol{S}\cdot\boldsymbol{J}\rangle}{J(J+1)}\,\delta H_i^{\mathrm{dip}} \qquad (5)$$

In the RAl_2 metals relatively large variation of $\mathfrak{J}$ were found[1)] and a pronounced variation is therefore to be expected in the conduction electron exchange contribution to the line widths in $LaAl_2$ doped with, say, Ce rather than Gd.

These preliminary observations lead us to conclude that an important contribution to the La NMR linewidth in Gd doped $LaAl_2$ occurs because of the exchange interaction between Gd spins and conduction electrons and that the magnitude of the interaction is not inconsistent with previous measurements on the isomorphic magnetically dense $GdAl_2$.

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DISCUSSION

S. DHARMATTI: What was the standard with respect to which the Knight shifts were measured?

V. JACCARINO: The reference for the Al^{27} Knight shifts was a solution of potassium aluminum sulphate. All chemical shifts are very small compared to our observed shifts, however.

W. MARSHALL: At Harwell calculations by J. Hubbard and D. Goodings suggest that in Fe and Co the Anderson $s-d$ mixing effect is strong enough to produce a negative polarization in the conduction electrons. These calculations refer to quite different materials, of course, in particular to ferromagnets rather than paramagnets, but it seems likely that the same mechanism could be invoked to explain the negative polarization your experiments indicate.

C. KITTEL: It would appear possible to determine the sign of the interaction from the positive and negative of the Faraday rotation associated with the exchange frequency resonance. The g-values of the s and f electrons being quite different (except with Gd), the exchange frequency resonance should be quite intense.

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Magnetic Properties of Rare Earth Aluminum Compounds with MgCu$_2$ Structure*

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The magnetic moments of some RAl$_2$ (R=rare earth element) cubic Laves phase compounds have been measured at temperatures from 1.4°K to 300°K. The measurements indicate that the spin moments of the rare earth ions are coupled ferromagnetically. The Curie points of the RAl$_2$ compounds are found to be uniformly higher than the corresponding Laves compounds, ROs$_2$, RIr$_2$ and RRu$_2$. Solid solutions of some of the compounds were also investigated. For example, in the Gd$_x$Pr$_{(1-x)}$Al$_2$ compounds, the magnetic moments of the Gd ions are antiparallel to those of the Pr ions because J is antiparallel to S in the ground state of the Pr ion. Compensation points were observed in this system.

Introduction

Recently Jaccarino *et al*[1]., have determined the magnitude and sign of the conduction electron polarization in a series of rare earth aluminum compounds having the cubic Laves structure, RA1$_2$ (R = rare earth element)[2,3]. Their measurements indicate that there is a negative (*i. e.*, antiferromagnetic) exchange interaction between the localized f electrons and conduction electrons. It is possible that the predominant rare earth exchange interaction occurs through the conduction electrons. It is therefore of interest to determine whether the coupling between the rare earths is ferromagnetic or antiferromagnetic. This paper contains the results of such a study. The structure of these compounds is shown in Fig. 1.

In the present investigation we have measured the magnetic moments and Curie temperatures of these compounds and of some solid solutions between these compounds[4]. The measurements were made with a pendulum magnetometer[5] at temperatures ranging from 1.4° to 300°K and with applied fields up to 14,000 oersteds.

Magnetic Moments of the Compounds

The magnetic moments per formula unit for the compounds CeA1$_2$, PrA1$_2$, NdA1$_2$, SmA1$_2$, GdA1$_2$, TbA1$_2$, DyA1$_2$, HoA1$_2$, ErA1$_2$, TmA1$_2$ and YbA1$_2$ are shown in Fig. 2. The shape of this curve is similar to a curve of the moments of the free trivalent ions but the measured values are always

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* Read by V. Jaccarino.