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Hyperfine interactions of ^{27}Al in paramagnetic $DyAl_2$ and $GdAl_2$

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Nuclear magnetic resonance was used to measure the parameters of the hyperfine interactions of ^{27}Al in $DyAl_2$ and $GdAl_2$. In both compounds the ^{27}Al paramagnetic shift exhibits a Curie-Weiss law behavior. The hyperfine field and the quadrupole splitting agree well with the corresponding parameters in the ferromagnetic phase.

I. INTRODUCTION

Nuclear magnetic resonance (NMR) studies in the paramagnetic phase of the ferromagnetic transition metals nickel and cobalt have proven to be valuable in measuring and understanding the hyperfine interactions in these metals in their paramagnetic state.[1] The 3*d* electrons in the ferromagnetic transition metals are only partially localized and the magnetization is largely due to polarized itinerant electronic states. It was interesting to note that the hyperfine fields in the paramagnetic phase are similar to the corresponding values in the ferromagnetic phase. The observation that the hyperfine fields did not change much with the large change of temperature from 0 K to the molten state, including the magnetic phase transition, indicates that the electronic structure is not strongly affected by these changes.[1] It is therefore of interest to investigate the hyperfine fields in the paramagnetic phases of ferromagnetic metals where the magnetization is mostly caused by local moments, as is the case for the rare-earth (RE) metals and for metallic compounds containing rare earths.[2] Since the NMR of RE nuclei could not be observed in any of these metals in the paramagnetic phase, we have chosen to study the NMR of ^{27}Al in two isostructural intermetallic ferromagnets, namely $GdAl_2$ and $DyAl_2$. These compounds have been selected because the NMR properties in the corresponding ferromagnetic phase are well known[3-5] and because they have different magnetic properties due to the $^8S_{7/2}$ state of Gd^{3+} on the one hand and the large orbital moment contribution to the magnetization in the case of $DyAl_2$.[2] NMR of ^{27}Al in these materials in the paramagnetic state was first observed by Jaccarino,[6] and the frequency shift of ^{27}Al in $GdAl_2$ at room temperature and above was measured by Jones and Budnick.[7] Here we describe a NMR study of the paramagnetic shift and the quadrupole interaction constants of ^{27}Al at room temperature and below, down towards the Curie temperature Θ_C, reaching $1.5\Theta_C$ for $DyAl_2$ ($\Theta_C = 68$ K) and $1.16\Theta_C$ for $GdAl_2$ ($\Theta_C = 170$ K). These parameters are compared with the hyperfine interaction constants in the ferromagnetic phase. A preliminary report of this work has been published.[8]

II. EXPERIMENTAL

Samples of $DyAl_2$ and $GdAl_2$ were prepared in an arc furnace, starting with 99.999% pure aluminum and 99.9% pure rare-earth metals. The samples were examined by x-ray diffraction and found to be free of phase mixing to better than 2%. The samples were ground to $\simeq 50$-μm size particles, annealed and stored in quartz ampoules in silicone oil.

The spin echo of ^{27}Al was observed using a pulsed NMR apparatus in the range 4–22 MHz. Magnetic fields H_0 were in the range of $0 \leq H_0 \leq 22.5$ kOe. The spectra of ^{27}Al in powder samples of $DyAl_2$ were measured in the range 96 K $\leq T \leq$ 340 K and those of $GdAl_2$ in the range 200 K $\leq T \leq$ 350 K. The sample was heated by the rf power of the NMR pulses and cooled by flowing cold nitrogen gas around the sample. The combined effect of this heating-cooling cycle determined the temperatures. Temperatures were controlled using a thermocouple element embedded in the sample. The temperature at that point was stable to better than 1 K. We estimate the overall temperature gradient on the sample to be less than 5K.

III. THE POWDER PATTERN

The spin-echo amplitude for ^{27}Al in DyAl$_2$ powder is shown in Fig. 1 as a function of the magnetic field for the resonance frequency $\nu=17.000$ MHz at $T=339$ K. This spectrum is typical for DyAl$_2$ and GdAl$_2$ at room temperature and above. On cooling the samples towards Θ_C, the lines broaden. The spectrum exhibits well-resolved quadrupole splitting with structure which is typical of an $I=\frac{5}{2}$ spin in powder samples.[9,10]

For a site with axial symmetry (this axis is denoted as the z direction), the expression for the transition frequency, correct to second order, is given by[10]

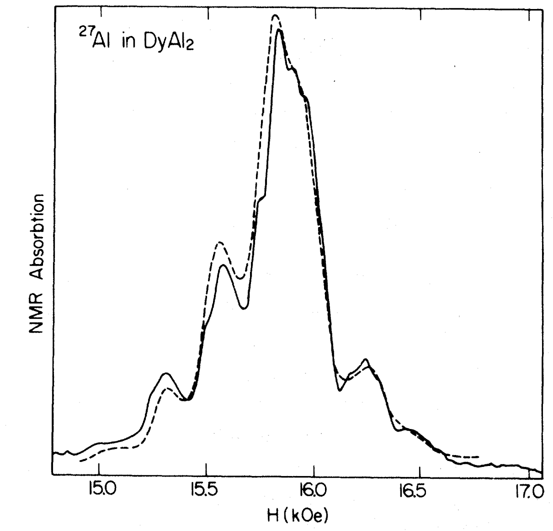

FIG. 1. Spectrum of ^{27}Al in DyAl$_2$ powder for $\nu=17$ MHz and $T=339$ K. The broken line represents the calculated curve with $\nu_Q=557$ kHz, $K_p=-0.033$, $K_{\rm ax}=-0.004$, and $\Delta H_{1/2}=107$ Oe.

$$\nu(m\leftrightarrow m-1)=\nu_0+\tfrac{1}{2}\nu_Q(3\mu^2-1)(m-\tfrac{1}{2}) + \frac{\nu_Q^2}{32\nu_0}(1-\mu^2)\{[102m(m-1)-18I(I+1)+39]\mu^2-[6m(m-1)-2I(I+1)+3]\}\;, \tag{1}$$

where $\nu_Q=3e^2qQ/2I(2I-1)h$, $eq=V_{zz}$ is the value of the electric field gradient in the z direction. eQ is the quadrupole moment of the nucleus, $\mu=\cos\theta$, where θ is the angle between the z direction and $\vec{\rm H}_0$, and

$$\nu_0=\gamma H_0[(1+K_p)+K_{\rm ax}(3\mu^2-1)]/2\pi\;, \tag{2}$$

where γ is the gyromagnetic ratio $\gamma_{^{27}\rm Al}/2\pi=1109.4$ Hz/Oe.[11] K_p is the isotropic part of the shift, which will be shown to be associated with the paramagnetic susceptibility χ, and $K_{\rm ax}$ is the axial part of the shift.

The powder pattern spectrum is determined from Eq. (1) with the parameters ν_Q, K_p, and $K_{\rm ax}$ and a linewidth $\Delta H_{1/2}$ with a Gaussian or a Lorentzian line shape. We used the HEQSIM2 program[12] for simulation of the spectra. The program was limited to small values of K_p and $K_{\rm ax}$ and had some distortion for large ν_Q values when converting the spectrum for constant field (frequency sweeping) to the spectrum for constant frequency, the condition in our experiments. We therefore modified the program for our larger parameter values. The broken line in Fig. 1 gives the computed spectrum for the parameters

$$\nu=17.000\text{MHz},\quad K_p=-0.033\;,$$
$$K_{\rm ax}=-0.004,\quad \nu_Q=557\text{kHz}$$

and a Gaussian line shape for all the lines with a width at half-intensity $\Delta H_{1/2}=107$ Oe.

IV. HYPERFINE INTERACTIONS

A. Hyperfine field of ^{27}Al in DyAl$_2$

Barbara and Rossignol[13] measured χ for 80 K $\le T \le$ 280 K and found that the susceptibility obeys a Curie-Weiss law

$$\chi=\frac{C}{T-\Theta_C}\;, \tag{3}$$

with $C=0.065\pm0.002$ emu/g and $\Theta_C=68\pm2$ K.

The polarization of the RE electronic spins, associated with the susceptibility, gives rise to a transferred hyperfine field on the aluminum nuclei, causing the shift K_p. It is thus expected that K_p will obey a Curie-Weiss law

$$K_p = \frac{C_k}{T - \Theta_C} . \tag{4}$$

Figure 2 shows that indeed $-1/K_p$ vs T is a straight line with $\Theta_C = 68 \pm 2$ K, and $C_k = -8.47 \pm 0.13$ K. It is possible to calculate the hyperfine field in the paramagnetic state H_{hf}^{p} from the value of C_k. However, a more critical approach would be to apply the Clogston-Jaccarino[14] plot (K_p vs χ), using the measured susceptibility. This is done in Fig. 3, and the paramagnetic hyperfine field is obtained from the relation

$$H_{\text{hf}}^{p} = \frac{\partial K_p}{\partial \chi} N \mu_B , \tag{5}$$

where N is the number of spins per gram (2.782×10^{21} for $DyAl_2$) and μ_B is the Bohr magneton. From Fig. 3 we find $H_{\text{hf}}^{p} = -3.24 \pm 0.06$ kOe/n_B, where n_B is the polarization of each dysprosium ion in Bohr magnetons.

NMR of ^{27}Al in ferromagnetic $DyAl_2$ at 4.2 K and zero external field shows one line[3] with $\nu = \gamma_{^{27}\text{Al}} H_{\text{eff}} / 2\pi = 29.8$ MHz. The effective field at the site of the aluminum nucleus is given by

$$\vec{H}_{\text{eff}} = \vec{H}_{\text{int}} + \vec{H}_d + \vec{H}_L + \vec{H}_D . \tag{6}$$

$\vec{H}_L = 4\pi \vec{M}/3$ is the Lorentz field where $\vec{M}$ is the volume magnetization (M is taken in units of emu/cm^3) and H_{int} is the isotropic part of the transferred hyperfine field (i.e. $\vec{H}_{\text{int}}$ is collinear with $\vec{M}$). $\vec{H}_D$ is the shape-dependent demagnetizing field, and it vanishes in a multidomain sample at zero field. $\vec{H}_d$ is the dipolar field at the site of the Al and it may also include, in addition to the classical contribution from the RE dipole moment, dipolarlike hyperfine contributions.[3,4]

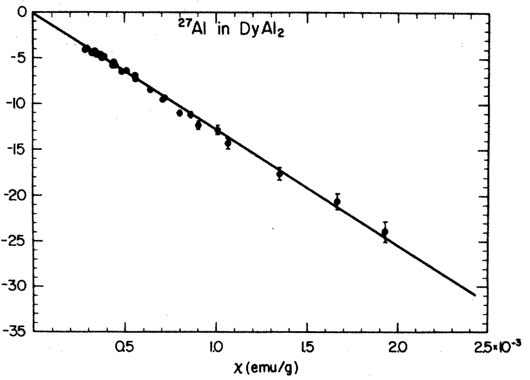

FIG. 3. K_p-χ plot of ^{27}Al in paramagnetic $DyAl_2$. The slope yields $H_{hf}^{p} = -3.24 \pm 0.06$ kOe/n_B.

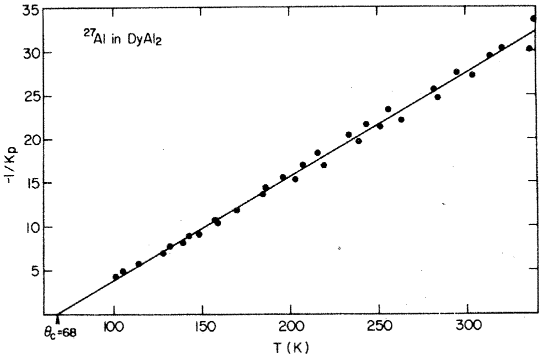

FIG. 2. Reciprocal of the paramagnetic shift of ^{27}Al in $DyAl_2$ as a function of temperature.

Denoting the unit vector along $\vec{M}$ by $\vec{n}$, $\vec{H}_d$ is given by[5]

$$\vec{H}_d = H_d^0 \tilde{D} \vec{n} \quad \text{with } \tilde{D} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{bmatrix} . \tag{7}$$

For each aluminum site the principal axis (z') for $\tilde{D}$ is the three-fold symmtery axis of this site, i.e., one of the equivalent [111] directions. The other principal axes (x' and y') are any two axes which are perpendicular to z' and to each other. H_d^0 is found by lattice sum and adjusted to the experimental results. Since the easy axis in $DyAl_2$ is parallel to one of the cubic ⟨100⟩ directions, we shall take $\vec{M} \| [001]$.

Using $a_0 = 7.82$ Å,[15] $n_B = 9.89$,[16] and $n = 8$ for the number of Dy atoms in the unit cell, we obtain $M = n n_B \mu_B / a_0^3 = 1534$ emu/cm^3 for the saturation magnetization (at 0 K). Thus $H_{\text{int}} = H_{\text{hf}}^{f} n_B$, where $\vec{H}_{\text{hf}}^{f}$ is the hyperfine field (per Bohr magneton) in the ferromagnetic phase and is antiparallel to $\vec{M}$.[3] According to Eq. (7) the dipolar field is in the [110] direction. Assuming that the dipolar field is enhanced by a factor of $e = 1.3$,[3] we find $|H_d| = \sqrt{2} H_d^0 = 9507$ Oe. With these values we obtain $H_{\text{hf}}^{f} = -3.2 \pm 0.1$ kOe/n_B, where most of the error comes from the uncertainty in the value of e.

For $|H_{\text{int}}| >> H_d^0$ we find from Eqs. (6) and (7) that

$$H_{\rm eff} \approx H_{\rm int} - H_d^0(3\cos^2\theta - 1) + H_L + H_D ,$$

where θ is the angle between $\vec{\rm M}$ and [111]. In the paramagnetic state the volume magnetization is $M = \chi_v H_0$, where χ_v is the volume susceptibility. In a powder sample the demagnetization field on a nucleus might have a value between $H_D = 0$ and $H_D = 4\pi M$. The distribution of the demagnetization fields between these two values depends on the shape of the particles and the magnetic interaction between the particles of the sample.[17] In view of the NMR results in ferromagnetic EuO powder,[18] we consider a Gaussian distribution with a maximum at about $H_D = 2\pi M$ and width of $\Delta H_{1/2} \approx 4\pi M/3$.[18] Thus, around this maximum $H_L + H_D \approx 0$ and the effective field is given by

$$H_{\rm eff} = H_0 + \chi H_0[H_{\rm int} - H_d^0(3\cos^2\theta - 1)]/M_0 ,$$

where $H_{\rm int}$ and H_d^0 are the values for saturated magnetization. [If, however, $H_L + H_D \neq 0$, this sum is still proportional to M, $H_L + H_D = \alpha M$, and our calculation of the hyperfine field from the paramagnetic shift, Eq. (5), will yield $H_{\rm hf}^p + \alpha M_0/n_B$, rather than $H_{\rm hf}^p$. This adds to the uncertainty in determining H_{hf}^p.] H_d^0 is positive and for ^{27}Al in DyAl$_2$ and GdAl$_2$, $H_{\rm int}$ is negative. Comparing this expression for $H_{\rm eff}$ with Eq. (2) we find that K_p in the paramagnetic state corresponds to $H_{\rm int}$ in the ferromagnetic state, as discussed above, and that $K_{\rm ax}$ corresponds to the local dipolar field. $K_{\rm ax}$ (as well as K_p) is negative. We also have $K_{\rm ax}/K_p = -H_d^0/H_{\rm int}$. This gives $K_{\rm ax} = -0.0065$, for ^{27}Al in DyAl$_2$ at 339 K, while our best fit in Fig. 1 is with $K_{\rm ax} = -0.004 \pm 0.002$. The large error bar is due to the linewidth since both the anisotropic shift, $K_{\rm ax}H_0$, and $\Delta H_{1/2}$ have values close to $4\pi M/3$.

As discussed above, the linewidth comes mainly from the distribution of demagnetization fields. The linewidth is given by

$$\Delta H_{1/2} = 4\pi M/3 = 4\pi H_0 M_0 K_p / 3H_{\rm int} .$$

For the conditions in Fig. 1 this gives $\Delta H_{1/2} = 106$ Oe which explains the experimental value of 107 Oe. When cooling the samples the magnetization grows and $\Delta H_{1/2}$ becomes excessively large (of the order of 1 kOe for $K_p = -25\%$), obscuring the quadrupole structure below room temperature and preventing observation of the signal close to T_C. A way around this problem would be to use well-shaped, spherical single-crystal samples, but none were available to us.

B. Hyperfine field of ^{27}Al in GdAl$_2$

Figure 4 shows $-K_p$ vs $(T - \Theta_C)^{-1}$ for ^{27}Al in GdAl$_2$, where Θ_C was chosen as 170 K (with uncertainty of ± 5 K) for the best linear fit. The plot includes the data of Jones and Budnick.[7] We prefer this way of representation (over $-1/K_p$ vs T) since we have succeeded in measuring K_p in temperatures much closer to Θ_C than in DyAl$_2$. Figure 4 gives more weight to K_p of these temperatures. For the parameter C_k in the Curie-Weiss law [Eq. (4)], we obtained $C_k = 10.3 \pm 0.2$ K. For GdAl$_2$ where the Gd^{3+} is in the S state one can take the Curie constant of the free ion

$$C = \frac{N(g_J \mu_B)^2 J(J+1)}{3k_B} . \tag{8}$$

With $g_J = 2$, $J = \frac{7}{2}$, Eqs. (3)–(5) and (8) yield

$$H_{\rm hf}^p = \frac{3k_B C_k}{g_J^2 J(J+1)\mu_B} , \tag{9}$$

which gives $H_{\rm hf}^p = 7.3 \pm 0.2$ kOe/n_B. As we could not find any susceptibility measurements in the literature which are appropriate for our range of measurements, we could not deduce $H_{\rm hf}^p$ directly from a $K_p - \chi$ plot, as was done for DyAl$_2$.

In the ferromagnetic phase the hyperfine field was measured very precisely by NMR of a spherical single crystal of GdAl$_2$ in an external magnetic field.[4] The measured value of the isotropic contribution to the hyperfine field (taking into account $7\mu_B$ per Gd^{3+} ion) is $H_{\rm hf}^f = 7.494 \pm 0.015$ kOe/n_B.

C. The quadrupole splitting

From the powder spectra of DyAl$_2$ (Fig. 1) and GdAl$_2$ we find $\nu_Q = 557 \pm 5$ kHz for DyAl$_2$ and

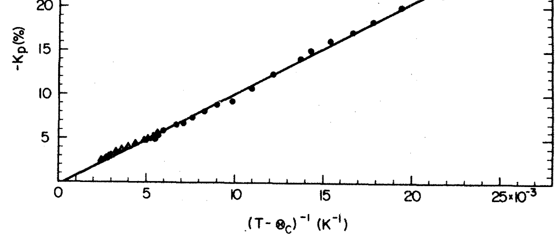

FIG. 4. $-K_p$ vs $(T - \Theta_C)^{-1}$ for ^{27}Al in GdAl$_2$, with $\Theta_C = 170$ K. ● present data, Δ Jones and Budnick.[7]

$\nu_Q=600\pm10$ kHz for $GdAl_2$ at 340 K. Our values are close to what was found for other paramagnetic RE Al_2 compounds.[19] Our ν_Q value for $GdAl_2$ is, however, lower than that measured by Jones and Budnick ($\nu_Q=641$ kHz). It is of interest to compare our results with those in the ferromagnetic state. For $DyAl_2$ there are no data. For ferromagnetic $GdAl_2$ the ν_Q of ^{27}Al was measured as a function of temperature and found to be linear with the magnetization,[20] in the range $M/M_0\approx1$, yielding

$$\nu_Q^f(T)=629\pm8-(87\pm8)M(T)/M_0 \qquad (10)$$

expressed in kHz. Extrapolation of relation (10) to the paramagnetic phase with the low value of $M=\chi H_0$ of our present experiments predicts ν_Q in the range 620–628 kHz, which is about 6% above our experimental value. The influence of thermal expansion on ν_Q can be estimated from $\nu_Q\propto a_0^{-3}$. Thus, ν_Q changes like the reciprocal of the volume expansion, which is very small, i.e., about 1% between 0 K and room temperature.[15]

DISCUSSION AND CONCLUSION

The parameters for the hyperfine interaction of ^{27}Al in $DyAl_2$ and $GdAl_2$ were measured in the paramagnetic phase and found to agree well with the corresponding parameters in the ferromagnetic state of these materials. The parameter values are compared in Table I. In both materials the paramagnetic shift obeys a Curie-Weiss law. This behavior is clear for $GdAl_2$ with an S state for Gd^{3+}, where the crystal-field splitting of the $^8S_{7/2}$ state is very small. On the other hand, for $DyAl_2$ Curie-Weiss behavior is not obvious since the crystal-field parameters are quite large, $W=-0.16$ K and $x=0.475$,[13] and the crystal field splits the $J=\frac{15}{2}$ state of Dy^{3+}. The ground state is Γ_8 and the first excited state is Γ_6 at $\Delta\approx15$ K above Γ_8. The overall splitting is about 62 K.[21] However, this splitting is not sufficient to cause a noticeable deviation of the paramagnetic susceptibility from a Curie-Weiss law since for cubic crystals such a deviation is expected only at temperatures much lower than Δ.[22] In the paramagnetic state of $DyAl_2$, $T>\Theta_C>>\Delta$. Indeed, susceptibility measurements give an isotropic Curie constant

$$C=0.065\pm0.002 \text{ emu/g} \quad \text{(Ref. 13)}$$

which is very close to the value for the free ion,

$$C=0.0655 \text{ emu/g} .$$

Local deviations from the average crystal-field splitting of the $J=\frac{15}{2}$ state of Dy^{3+} due to local imperfections (impurities, vacancies), will cause a distribution of the paramagnetic shifts around the average value K_p. Though it is difficult to estimate this distribution, it might give rise to additional NMR line broadening which increases with decreasing temperature. This mechanism might further limit observation of the NMR close to Θ_C.

TABLE I. The parameters of $DyAl_2$ and $GdAl_2$ and comparison between the hyperfine constants in the paramagnetic state and the ferromagnetic state.

	$DyAl_2$	$GdAl_2$
RE^{3+} state	$^6H_{15/2}$	$^8S_{7/2}$
n_B	9.89 ± 0.1[a]	7.2 ± 0.05[a]
a_0 at 4.2 K (Å)	7.82 ± 0.01[b]	7.87 ± 0.01[b]
M_0 (emu/cm^3)	1534 ± 15	1096 ± 10
Θ_C (K)	68 ± 2	170 ± 5
H_{hf}^p (kOe/n_B)	-3.24 ± 0.06	-7.3 ± 0.2
H_{hf}^f (kOe/n_B)	-3.2 ± 0.1	-7.494 ± 0.015[c]
$\nu_Q{}^p$ (kHz)	557 ± 5	600 ± 10
ν_Q^f (kHz)	no data	625[d]

[a] Reference 16.
[b] Reference 15.
[c] Reference 4.
[d] Reference 20.

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