

## Conduction-electron spin and orbital polarization effects in rare-earth $Al_2$ compounds

Y. Berthier, R. A. B. Devine,\* and E. Belorizky

Laboratoire de Spectrométrie Physique, † Université Scientifique et Médicale Grenoble, Boîte Postale 53, 38041 Grenoble Cédex, France

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Nuclear magnetic resonance of the rare-earth nuclei in rare-earth  $Al_2$  compounds ( $R = Nd, Dy, Tb, Er$ ) is reported. Separation of the hyperfine field into its various components is made and we deduce the variation of the self-polarization field with rare earth. The observed behavior indicates strong dependence on rare-earth orbital moment, this is accounted for including both spin and orbital polarization of the conduction bands. From comparison with the transferred hyperfine field at the Al nuclei we conclude that the orbital polarization does not extend to these sites. The consequences of these results in terms of the magnetic coupling in  $R Al_2$  compounds are considered.

### I. INTRODUCTION

The origin of magnetic coupling in rare-earth intermetallic compounds has become the subject of much recent interest with the discovery of such phenomena as cooperative Jahn-Teller effects<sup>1</sup> and anisotropic exchange terms in the magnetization.<sup>2</sup> Inherent in such work is an understanding not only of the ion-ion coupling but of the local ion-conduction-electron exchange and its consequences in terms of the more classical Ruderman-Kittel-Kasuya-Yosida (RKKY) approach to magnetism. Most conventional techniques for the study of magnetism are sensitive to the macroscopic environment and do not reflect, except indirectly, effects local to the magnetic ion. Nuclear magnetic resonance is a technique which, in principle, is more sensitive to the local rather than general internal magnetic field in a magnetic system and is thus a microscopic probe. We have endeavored to study, via NMR, the local rare-earth  $4f$ -electron-conduction-electron exchange in magnetically ordered  $RAl_2$  compounds. A study has already been made<sup>3</sup> of the local hyperfine field at the nonmagnetic Al site and through combination of the two sets of results we hope to present some picture of the processes of magnetic coupling in these compounds.

The hyperfine field at the nucleus of a rare-earth ion in an ordered system is usually assumed composed of three terms,

$$H_N = H_{4f} + H_{sp} + H_{nn}. \quad (1)$$

$H_{4f}$  represents the field created by the  $4f$  electrons and is proportional to the magnetic moment of these electrons. In consequence this term is sensitive to the crystalline electric field and the molecular field in the environment.<sup>4</sup>  $H_{nn}$  is the so-called transferred hyperfine field arising from polarization of the conduction electrons<sup>5</sup> (spin and orbital) by neighbor and distant magnetic ions

transferred to the nucleus under study. The spatial variation of this polarization is generally assumed to follow the RKKY model.<sup>6</sup>  $H_{sp}$  is the "self-polarization" field arising from polarization of the conduction electrons by  $4f$ -electron-conduction-electron exchange which consequently reflects itself through such mechanisms as the contact hyperfine field ( $s$  electrons), core polarization and/or orbital field ( $d$  or  $p$  electrons), etc.<sup>7</sup> It is this term which reflects the character of the localized  $4f$ -electron-conduction-electron exchange. In terms of order of magnitude, as we will discuss in some detail later, the  $4f$  field is typically several megagauss, the transferred hyperfine field is some tens of kilogauss and  $H_{sp}$  is several hundreds of kilogauss. Given that the self-polarization field is typically 10% of the total hyperfine field, only a technique such as NMR gives sufficient precision to permit accurate determination of  $H_{sp}$ . Other microscopic techniques such as the Mössbauer effect are typically an order of magnitude less precise in hyperfine-field determination.

In the following we report the results of nuclear-magnetic-resonance measurements at the rare-earth ( $R$ ) nucleus in  $RAl_2$  compounds. We separate out the various terms given in Eq. (1) and show that it is necessary to introduce orbital polarization effects in  $H_{sp}$ . The transferred hyperfine field at the Al sites is found to be explained assuming a purely spin polarization of the conduction band. The consequences of these two results are discussed in terms of the magnetic coupling in  $RAl_2$  compounds.

### II. RESULTS AND METHOD OF INTERPRETATION

Samples were prepared following the method outlined previously.<sup>4</sup> The rare-earth compounds prepared and studied were  $NdAl_2$ ,  $DyAl_2$ ,  $TbAl_2$ , and  $ErAl_2$ .  $GdAl_2$  has been studied previously.<sup>7</sup>

TABLE I. Experimental resonance frequencies (MHz) and equivalent hyperfine field  $H_N$  (kOe) for Pr, Nd, Gd, Dy, Tb, and Er in  $Al_2$  compounds (Pr obtained from specific-heat measurement). Values of hyperfine parameter  $A$  from Ref. 9 [kOe/(unit of  $J_Z$ )].  $H_{nn}$  is the transferred hyperfine field in kOe, and  $H_{4f}$  the  $4f$  hyperfine field (see text). The self-polarization field is obtained by subtracting  $H_{nn}$  and  $H_{4f}$  from  $H_N$ . The values in parentheses are those obtained for  $PrAl_2$  and  $NdAl_2$  with a spin-exchange model (see text).

|             | $PrAl_2$                            | $NdAl_2$                           | $GdAl_2$         | $DyAl_2$         | $TbAl_2$       | $ErAl_2$       |
|-------------|-------------------------------------|------------------------------------|------------------|------------------|----------------|----------------|
| $\nu_{res}$ |                                     | $-786 \pm 0.5$                     | 20.6             | $1183.5 \pm 0.5$ | $3248 \pm 1$   | $-890 \pm 1$   |
| $H_N$       | 2918                                | $3373 \pm 2$                       | $-160.9 \pm 0.3$ | $5917.5 \pm 1$   | $3215.8 \pm 1$ | $7295 \pm 8$   |
| $A$         | $841 \pm 8$                         | $946 \pm 9$                        | -94              | $762 \pm 15$     | $525 \pm 5$    | $1027 \pm 9.8$ |
| $H_{4f}$    | $2632 \pm 24$<br>( $3140 \pm 24$ )  | $2568 \pm 24$<br>( $3366 \pm 24$ ) | $-332 \pm 6$     | $5285 \pm 102$   | $2949 \pm 28$  | $6246 \pm 60$  |
| $H$         | 5.6                                 | 7.2                                | -26.7            | -18.5            | -22.2          | -10.0          |
| $H_{sp}$    | $282 \pm 180$<br>( $-228 \pm 108$ ) | $798 \pm 203$<br>( $0 \pm 90$ )    | $198 \pm 50$     | $651 \pm 247$    | $289 \pm 86$   | $1050 \pm 268$ |

Spin-echo spectra of the  $^{143}Nd$ ,  $^{163}Dy$ ,  $^{159}Tb$ , and  $^{167}Er$  were observed at 1.4 K for the resonance frequencies given in Table I. These frequencies are appropriate to the  $\frac{1}{2} \leftrightarrow -\frac{1}{2}$  nuclear transition.

The resonance frequencies were converted into magnetic field using the gyromagnetic ratios published in NBS tables<sup>8</sup>—it should be noted that these values can differ significantly from those most commonly used, which are given by the Varian Company. The resultant hyperfine fields are also quoted in Table I. In order to deduce  $H_{sp}$  from the total hyperfine field we must evaluate  $H_{4f}$  and  $H_{nn}$ . Bleaney<sup>9</sup> has shown that  $H_{4f}$  is related to the saturation moment of the  $4f$  electron,  $g_J \mu_B \langle J_Z \rangle$ , through

$$H_{4f} = A \langle J_Z \rangle, \quad (2)$$

where the values of  $A$ , the “hyperfine parameter,” have been given for insulators in Ref. 9. The parameter  $A$  is in fact the hyperfine splitting parameter measured directly in electron paramagnetic resonance experiments where the effect of the nucleus on the  $4f$  electron is studied rather than the inverse as in the case of NMR. In Fig. 1 we present the results available in the literature<sup>10</sup> for Er and Dy in metallic and insulator hosts (values for Nd and Tb are not available). It can be seen that  $A$  is remarkably constant independent of both lattice parameter of the host and character of the environment, e.g., metal or insulator. These results, we believe, justify the use of the values of  $A$  given in Ref. 9 equally for the case of our intermetallic compounds.

In order to apply Eq. (2) it is necessary to have

values for  $\langle J_Z \rangle$ . If one admits the presence of orbital and spin polarization of the conduction-band electrons, these terms will be included in the magnetic moment measured by magnetization experiments. The “bare” value of  $\langle J_Z \rangle$  required for Eq. (2) must thus be deduced in a self-consistent manner. Since Gd carries no orbital moment, the saturation moment must include only the pure  $\langle J_Z \rangle$  value plus the results of spin polarization of the conduction electrons. This latter is thus estimated<sup>2</sup> to be  $(+0.2 \pm 0.05) \mu_B$ . There exists no rare earth with purely orbital moment so that one cannot obtain a value for the orbital polarization of the conduction bands. However, by polarized neutron diffraction, Boucherle<sup>11</sup> has found a total polarization of  $(0.66 \pm 0.15) \mu_B$  in  $HoAl_2$ . Assuming that the spin polarization is

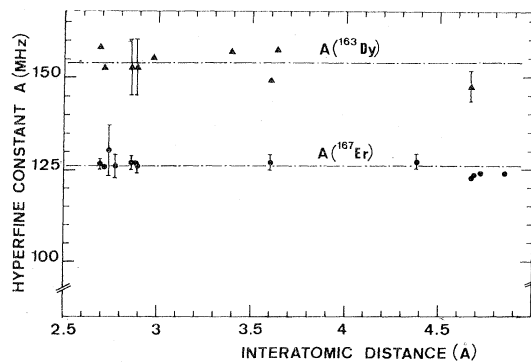


FIG. 1. Values of  $A$  (Ref. 9) for  $Dy^{3+}$  and  $Er^{3+}$  in various metallic and insulating materials.

proportional to  $\langle S_z \rangle$  one can estimate the spin polarization for  $\text{HoAl}_2$  and thus, by subtraction, the orbital contribution. Combining these two results we write the measured rare-earth saturation moment in the  $R\text{Al}_2$  series ( $\langle \mu_s \rangle$ ) in terms of the purely  $4f$  value ( $g_J \langle J_z \rangle$ ) in the form

$$\langle \mu_s \rangle = \langle J_z \rangle [g_J + \frac{0.2}{3.5} (g_J - 1) + (2 - g_J) \times 0.0826] \mu_B, \quad (3)$$

where the second term in the square brackets represents the spin polarization proportional to  $\langle S_z \rangle$  [ $\langle S_z \rangle = (g_J - 1) \langle J_z \rangle$ ] and the third represents the orbital polarization proportional to  $\langle L_z \rangle$  [ $\langle L_z \rangle = (2 - g_J) \langle J_z \rangle$ ].

A problem arises for the light rare-earth compounds. For  $\text{NdAl}_2$ , polarized neutron results<sup>11</sup> suggest a polarization of  $(-0.14 \pm 0.04) \mu_B$ . This result is inconsistent with the prediction of the above formula and could be explained consistently with  $\text{GdAl}_2$  (assuming spin only exchange terms) by an exchange constant for  $\text{NdAl}_2$  approximately 2.6 times the value for  $\text{GdAl}_2$ . We have chosen to take both values into account in the following so that the predictions of a spin and orbital model and a pure spin model for  $\text{PrAl}_2$  and  $\text{NdAl}_2$  will be considered.

In Table II we show the measured saturation moment values, the values deduced for  $\langle J_z \rangle$  and hence  $\langle L_z \rangle$  and  $\langle S_z \rangle$ . For  $\text{NdAl}_2$  and  $\text{PrAl}_2$  we include the values found if we ignore orbital effects and assume spin polarization of  $-0.14 \mu_B$  for  $\text{NdAl}_2$ . These values are shown in parentheses in both tables. Using values of  $\langle J_z \rangle$  given in Table II we have evaluated the  $4f$  hyperfine fields  $H_{4f}$  given in Table I.

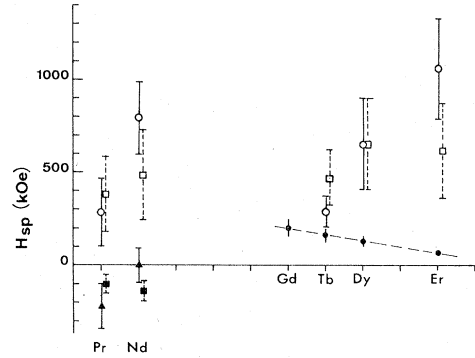


FIG. 2. Plot of the values deduced for  $H_{sp}$ , as given in Table I (O). □ Fit obtained assuming orbital and spin contributions to  $H_{sp}$  (fitting points  $\text{DyAl}_2$  and  $\text{GdAl}_2$ ). ● Fit following a spin polarization only model. Δ experimental and ■ fit for  $\text{PrAl}_2$  and  $\text{NdAl}_2$  assuming spin-only polarization and exchange 2.6 times the  $\text{GdAl}_2$  value (see text).

The transferred hyperfine field  $H_{nn}$  can be generally obtained by measuring the hyperfine field at the nucleus of a nonmagnetic rare-earth ion (e.g., La, Y, Lu) substituted for a magnetic ion.<sup>12</sup> A detailed study has been made of  $H_{nn}$  in various intermetallic Gd-based compounds<sup>5</sup> from which one can estimate the value to be 27 kOe for  $\text{GdAl}_2$ . The values for other rare-earths can be estimated by assuming  $H_{nn}$  varies, following the molecular field model,<sup>4</sup> as  $\langle S_z \rangle$ , they are given in Table I. Although the simplified assumption of proportionality to  $\langle S_z \rangle$  ignores orbital effects<sup>13</sup> the magnitude of the values of  $H_{nn}$  is, in all cases, small with respect to the errors induced by lack of precise knowledge of  $A$ .

TABLE II. The Landé  $g$  factors and measured saturation moments for the various compounds.  $\langle J_z \rangle$  values were calculated using Eq. (3). Values for  $\text{PrAl}_2$  and  $\text{NdAl}_2$  in parentheses are those obtained assuming only spin polarization of the band.

|                       | $\text{PrAl}_2$                       | $\text{NdAl}_2$                        | $\text{GdAl}_2$  | $\text{DyAl}_2$  | $\text{TbAl}_2$   | $\text{ErAl}_2$ |
|-----------------------|---------------------------------------|--|------------------|------------------|-------------------|-----------------|
| $g_J$                 | $\frac{4}{5}$                         | $\frac{8}{11}$                         | 2                | $\frac{4}{3}$    | $\frac{3}{2}$     | $\frac{6}{5}$   |
| $\mu_s (\mu_B)$       | $2.88 \pm 0.05^a$                     | $2.45 \pm 0.02^b$                      | $7.2 \pm 0.05^c$ | $9.89 \pm 0.1^c$ | $8.90 \pm 0.05^d$ | $7.9 \pm 0.1^e$ |
| $\langle J_z \rangle$ | $3.13 \pm 0.19$<br>( $3.74 \pm 0.1$ ) | $2.72 \pm 0.19$<br>( $3.56 \pm 0.07$ ) | 3.5              | $6.94 \pm 0.19$  | $5.62 \pm 0.11$   | $6.08 \pm 0.2$  |
| $\langle L_z \rangle$ | 3.76<br>(4.48)                        | 4.70<br>(6.16)                         | 0                | 4.65             | 2.81              | 4.86            |
| $\langle S_z \rangle$ | -0.63<br>(-0.75)                      | -0.74<br>(-0.97)                       | 3.5              | 2.31             | 2.81              | 1.22            |

<sup>a</sup> Reference 22.

<sup>b</sup> Reference 23.

<sup>c</sup> Reference 24.

<sup>d</sup> Reference 25.

<sup>e</sup> Reference 26.

Values of  $H_{sp}$  determined by subtraction of  $H_{4f} + H_{nn}$  from the measured total hyperfine field are given in Table I. It should be noted that the result for  $\text{PrAl}_2$  does not come from NMR measurement, we have used the value for the total hyperfine field deduced from measurement of the nuclear specific heat.<sup>14</sup> For the sake of later discussion and to emphasize pictorially the behavior, the deduced values of  $H_{sp}$  are shown graphically in Fig. 2.

### III. DISCUSSION

#### A. Classical model

In the simplest model,<sup>15</sup> assuming  $s$  and  $d$  conduction bands polarized by the spin-only part of the exchange interaction, the self-polarization field is given by

$$H_{sp} = A(Z) \frac{J_s \chi_s}{g_e \mu_B} \langle S_Z \rangle - \alpha_d \frac{J_d \chi_d}{g_e \mu_B} \langle S_Z \rangle, \quad (4)$$

where  $J_s$  and  $J_d$  are the  $4f$ -electron- $s$ -electron and  $4f$ -electron- $d$ -electron exchange parameters,  $\chi_s$  and  $\chi_d$  are the band susceptibilities, and  $A(Z)$  and  $\alpha_d$  are the contact and core-polarization hyperfine fields per unit polarization of the conduction band.<sup>16</sup> This form neglects  $d$ -electron-nucleus dipole-dipole terms which have been shown via transferred hyperfine field studies to be small.<sup>13</sup> From Eq. (4) it can be seen that the self-polarization field should vary across the rare-earth series as  $\langle S_Z \rangle$ . In Fig. 2 we show the behavior of  $H_{sp}$  predicted using values of  $\langle S_Z \rangle$  from Table II and fitting to the hyperfine field at the Gd nucleus in  $\text{GdAl}_2$  (any possible nonspin effects will be absent for Gd). The predicted behavior deviates significantly from experimental results. It should be emphasized that we have ignored variations in  $A(Z)$ ,  $\alpha_d$ ,  $J_s$ , and  $J_d$  across the rare-earth series; we justify this on the basis that there does not appear to exist in the published literature any evidence for dramatic variations.

The form of  $H_{sp}$  given in Eq. (4) arises through consideration of only the spin part of the exchange interaction. When considering  $d$  electrons and non- $S$ -state rare-earth ions one must take into account orbital polarization.<sup>13</sup> Orbitaly polarized  $d$  electrons will give rise to an orbital field at the nucleus in exactly the same way as we assume  $4f$  electrons do<sup>9</sup>; this field can be the dominant field for  $4f$  electrons. We therefore assume that  $H_{sp}$  can be written

$$H_{sp} = A' \langle S_Z \rangle + B \langle l_Z \rangle, \quad (5)$$

where  $A'$  and  $B \langle l_Z \rangle$  are determined from experiment.  $\langle l_Z \rangle$  is the average orbital polarization of the  $d$  band arising from an exchange energy of

the type

$$E = J_d \langle L_Z \rangle \mathcal{N}_Z,$$

and hence one expects the term  $B \langle l_Z \rangle$  to vary as  $\langle L_Z \rangle$ . In Fig. 2 we have plotted the results of fitting Eq. (5) to experimental results for  $\text{GdAl}_2$  ( $\langle l_Z \rangle$  equals zero since  $\langle L_Z \rangle$  equals zero) and  $\text{DyAl}_2$ . Allowing for the experimental errors, the fit between theory and experiment is good. The principal terms neglected in obtaining this fit, we repeat, are spin-spin<sup>13</sup> and anisotropic-exchange effects<sup>17</sup> from the  $d$  and  $s$  electrons. Development of a detailed theory including these terms is in progress.<sup>18</sup> Also included in Fig. 2 are the results for Nd and Pr, neglecting orbital polarization as mentioned previously. The results for the light rare earths Nd and Pr fit a pure spin model [Eq. (4)] with Gd if we allow the exchange to be enhanced by a factor of approximately 2.5. This factor is identical to that required to bring the results for the transferred hyperfine field at the Al site into agreement for the light rare earths (Sec. III C). The implications of this and the apparent absence of orbital polarization for Nd and Pr will be discussed in a further publication.

#### B. Estimation of $\langle l_Z \rangle$ for the $d$ band

The orbital field produced at the rare-earth nucleus by a polarized  $d$  band can be written<sup>9</sup>

$$\langle H_d \rangle = -2\beta \langle r_i^{-3} \rangle \langle l_Z \rangle. \quad (6)$$

In fitting to results in Fig. 2 in Sec. III A we assumed  $\langle l_Z \rangle$  proportional to  $\langle L_Z \rangle$  by considering the orbital part of the  $4f$ -electron-conduction-electron exchange. From knowledge of  $\langle H_d \rangle$  for each ion we can use Eq. (6) to determine the equivalent value of  $\langle l_Z \rangle$ . We have calculated a value for  $\langle r_i^{-3} \rangle$  for the  $5d$  electron of Gd using a Hartree-Fock-Slater atomic wave function.<sup>19</sup> The sensitivity of  $\langle r_i^{-3} \rangle$  to the wave function close in to the nucleus suggests that this value will not vary much in going to the metallic environment. Furthermore, since  $5d$  wave functions are not available for ions other than Gd we assume that  $\langle r_i^{-3} \rangle$  varies as does  $\langle r^{-3} \rangle$  for the  $4f$  electron across the rare-earth series.<sup>20</sup> As an example, using  $\langle H_d \rangle$  deduced for Er in  $\text{ErAl}_2$ , we find  $\langle l_Z \rangle$  equal to  $0.53 \pm 0.17$ . Scaling via proportionality of  $\langle L_Z \rangle$  and  $\langle r_i^{-3} \rangle$  we estimate  $\langle l_Z \rangle$  for Ho in  $\text{HoAl}_2$  to be  $0.6 \pm 0.18$  to be compared with the value of  $0.55 \pm 0.15$  obtained from polarized neutron diffraction<sup>11</sup> after subtraction of spin polarization.

The general conclusion which must be drawn from measurements of the hyperfine field at the rare-earth nucleus is that, despite some problems associated with the absolute magnitude of the

orbital polarization present, a model assuming spin polarization alone is grossly inadequate (Fig. 2).

### C. Transferred hyperfine field

If the RKKY model can be assumed to apply equally to spin and orbital polarization in ordered ferromagnetic compounds, one expects the orbital polarization to be "transmitted" to neighboring atoms around the rare-earth ion. Dunlap *et al.*<sup>13</sup> have suggested that in order to understand the hyperfine field at the Al nucleus in  $RAl_2$  compounds, orbital contributions must be taken into account. This is a good test for such an effect since Al, carrying no intrinsic electron magnetic moment, finds itself purely in a transferred hyperfine field ( $H_T$ ). Since the transferred hyperfine field is sensitive to both spin and orbital terms, a plot of  $H_T$  measured at the Al nucleus as a function of rare earth should not *a priori* vary simply as  $\langle S_z \rangle$  for the rare earth. The measured behavior<sup>3</sup> is shown in Fig. 3. Unfortunately, in fitting to these results Dunlap *et al.* assumed the magnetic moment for the rare-earth ion to be given by  $g_J \langle J \rangle \mu_B$ , i.e., the maximum value in the absence of crystal-field and molecular-field effects. The actual values can be significantly reduced<sup>2</sup> and using the correct values of  $\langle J_z \rangle$  one obtains, using a spin-polarization-only model [ $\langle S_z \rangle$  equals  $(g_J - 1) \langle J_z \rangle$ ] the fit shown in Fig. 3; considering only the heavy rare earths initially one sees little deviation from experiment suggest-

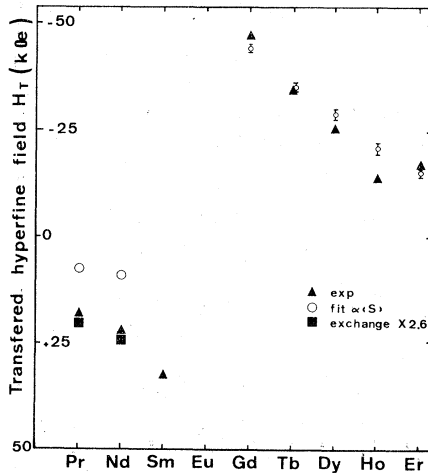


FIG. 3. Measured transferred hyperfine field  $H_T$  at the Al sites in  $RAl_2$  compounds (▲), results taken from Ref. 3. The open circles represent the results of fitting a model involving rare earth ( $\langle S_z \rangle$ ) only. Values for  $\langle S_z \rangle$  taken from Table II. For  $PrAl_2$  and  $NdAl_2$  the solid squares give the results obtained if the exchange is enhanced by a factor of 2.6 (see text).

ing that the transferred hyperfine field at the Al nucleus depends essentially on spin polarization of the conduction electrons. It is significant that for the lighter rare earths the spin model does not seem to work (at least assuming polarization only proportional to  $\langle S_z \rangle$ ). An orbital contribution, being of opposite sign, would further destroy the agreement and one is tempted to suggest that a plausible explanation would be absence of orbital, but increase of  $s$  exchange effect. Such a conclusion would also be consistent with the neutron-diffraction results<sup>11</sup> and one of the interpretations possible of the self-polarization field for the light rare earths. However, it is hard to see a simple justification for the neglect of orbital polarization for the light rare earths and its inclusion for the heavy rare earth.

The apparent validity of the spin-only model for the transferred hyperfine field despite the presence of significant orbital polarization at the rare-earth sites appears to demonstrate a breakdown of the RKKY model. However, in justice to the RKKY approach, it is unfair to try to apply it to a spatially nonuniform  $d$ -banded material. A semiquantitative explanation of the transferred hyperfine field can be advanced if we study the results of band structure calculations<sup>21</sup> for dialuminide compounds. Results for  $LaAl_2$  and  $LuAl_2$  clearly indicate the absence of  $d$  electrons in the Wigner-Seitz sphere around the Al site, but predominance of their character at the rare-earth site. Thus, conclusion that orbital polarization is absent at the Al nucleus is completely consistent with the absence of  $d$  electrons in the local-band character.

Before concluding this section, we will compare the results of the transferred hyperfine field at the Al nucleus and the field at the Gd nucleus in  $GdAl_2$ . Since orbital polarization is absent in  $GdAl_2$  there should presumably be correlation between these two fields. At the Gd nucleus the field is +198 kOe and -47 kOe at the Al nucleus. In the absence of  $d$  electrons around the Al we have

$$H_T(Al) \approx A_{Al}(Z) \langle \sigma_{Al} \rangle, \quad (7)$$

where  $\langle \sigma_{Al} \rangle$  represents the  $s$ -electron polarization at the Al site. The ratio is then

$$\frac{H_{sp}(Gd)}{H_T(Al)} \approx \frac{A_{Gd}(Z) \langle \sigma_{Gd} \rangle - \alpha_d \langle \sigma'_{Gd} \rangle}{A_{Al}(Z) \langle \sigma_{Al} \rangle}, \quad (8)$$

where  $\langle \sigma'_{Gd} \rangle$  is used to denote the spin polarization of the  $d$  band. The  $d$  term is of opposite sign to  $A_{Gd}(Z) \langle \sigma_{Gd} \rangle$  and hence reduces  $H_{sp}(Gd)$ . To obtain an upper limit we can ignore the  $d$  terms to yield

$$\frac{H_{sp}(Gd)}{H_T(Al)} \approx \frac{A_{Gd}(Z) \langle \sigma_{Gd} \rangle}{A_{Al}(Z) \langle \sigma_{Al} \rangle}. \quad (9)$$

In a uniform polarization model<sup>15</sup>  $\langle\sigma_{\text{Gd}}\rangle/\langle\sigma_{\text{Al}}\rangle \cong n_s(E_F)_{\text{Gd}}/n_s(E_F)_{\text{Al}}$ , where  $n_s(E_F)$  are the local  $s$  densities of states. Taking values for  $A(Z)$  from Campell<sup>16</sup> together with  $n_s(E_F)$  from band calculations<sup>21</sup> gives  $|H_{\text{sp}}(\text{Gd})/H_{\text{sp}}(\text{Al})| \sim 14$ . The measured value is  $-4.2$ . Comparison of this result suggests: (a) Spin polarization of the  $d$  band at the Gd nucleus cannot be neglected; and (b) The  $s$  polarization at the Al nucleus has reversed sign—this is consistent with the neutron-diffraction results.<sup>11</sup> It should be noted that the RKKY model ignoring density of states variation, could certainly predict  $\langle\sigma_{\text{Gd}}\rangle > \langle\sigma_{\text{Al}}\rangle$  leading to a larger ratio than  $-14.0$ . However, although  $\alpha_d \approx 0.1A_{\text{Gd}}(Z)$ ,  $n_d(E_F)_{\text{Gd}}$  is approximately three times  $n_s(E_F)_{\text{Gd}}$  so that, if the  $s$  and  $d$  exchange parameters are essentially equal, significant reduction of the Gd contact term will arise due to the core polarization ( $\alpha_d$ ) term. The latter cancellation effect presumably accounts for the experimental ratio being much less than the  $s$ -electron-only model.

#### IV. CONCLUSIONS

The conclusions drawn from the hyperfine-field experiments can be essentially summarized as

follows: (a) The self-polarization field at the rare-earth nuclei in  $\text{RAl}_2$  compounds cannot be explained unless one includes orbital polarization effects; (b) The orbital polarization of the  $5d$  band at the rare-earth site is considerable; and (c) The transferred hyperfine field at the Al nucleus shows no evidence for the orbital polarization effect; however, the spin polarization is reversed in sign from that found at the rare-earth site.

It remains to be concluded that the next, and perhaps most interesting step, would be to measure the transferred hyperfine field between rare-earth nuclei and observe whether or not the magnetic coupling is primarily via  $s$  or  $d$  electrons. It would also be of interest to analyze the transferred hyperfine field at nonmagnetic sites in compounds with more spatially uniform  $d$  bands. From these results it should be possible to see if indirect orbital coupling via the  $d$ -band electrons is important in ordered rare-earth systems.

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\*Also at Laboratoire Louis Néel, Centre National de la Recherche Scientifique B. P. 166 X, 38 042 Grenoble Cédex, France.

†Laboratoire associé au Centre National de la Recherche Scientifique.

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