

## Electron spin resonance of $\text{Nd}^{3+}$ and $\text{Gd}^{3+}$ in $d$ -band intermetallic compounds

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We report on the ESR of the rare-earth ions  $\text{Nd}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Er}^{3+}$ , and  $\text{Yb}^{3+}$  on powdered samples of various intermetallic compounds of  $AB_2$  cubic structure where  $B$  is a transition-metal ion belonging to the group VIII of the Periodic Table, and  $A$  is a nonmagnetic ion (La, Ce, Y). The resonance of the  $\text{Nd}^{3+}$  in these compounds originates within a  $\Gamma_6$  crystal-field ground level and exhibits resolved hyperfine satellites for the  $^{143}\text{Nd}$  and  $^{145}\text{Nd}$  isotopes. The  $\text{Gd}^{3+}$  spectra show a single isotropic line. Using our data for  $\text{Gd}^{3+}$  and  $\text{Nd}^{3+}$  together with results previously published for the  $AB_2$  cubic compounds, we were able to show a correlation between the observed  $g$  shifts and the position of the  $B$  ion in the Periodic Table. This variation is explained qualitatively using a simple multiband model, as well as band-structure arguments. The hyperfine constants for the  $^{143}\text{Nd}$  and  $^{145}\text{Nd}$  isotopes were found smaller in magnitude with respect to the values in insulators; this effect is attributed to  $s$ -electron self-polarization due to the Nd localized-moment- $s$ -electron exchange coupling. The ESR linewidths of  $\text{LaIr}_2\text{Nd}$  and  $\text{LaRh}_2\text{Nd}$  exhibit an exponential thermal dependence at high temperatures which is attributed to the presence of a  $\Gamma_8$  excited level at  $\Delta = 90 \pm 20$  K.

### I. INTRODUCTION

The sign of the effective exchange coupling between rare-earth impurities and the conduction electrons in transition-metal hosts and intermetallic compounds is still an unsolved issue of central importance.<sup>1</sup> It is well known that the exchange interaction experienced by a Gd ion in transition metals varies considerably in both sign and magnitude, depending on the position of the host transition metal in the Periodic Table.<sup>1</sup> For example, the effective exchange interaction is negative in transition metals like Pd,<sup>2</sup> and Pt,<sup>2</sup> but positive in La.<sup>3</sup> Also in intermetallic compounds like  $\text{LaRu}_2$ ,  $\text{CeRu}_2$ ; and  $\text{ThRu}_2$ , a negative exchange is observed for  $\text{Gd}^{3+}$  in contrast to the positive one in  $\text{LaPt}_2$ .<sup>1</sup> The exchange coupling between other rare-earth ions and the conduction electrons exhibits similar behavior: very recently<sup>4</sup> we were able to observe the resonance of  $\text{Nd}^{3+}$  in  $\text{LaRu}_2$ ,  $\text{CeRu}_2$ , and  $\text{ThRu}_2$ .<sup>4</sup> We found that the effective exchange coupling between the Nd localized moment and the conduction electrons is negative, consistent with the observation for Gd in these compounds. For further information on the sign of the exchange in the various  $d$ -band metals the reader is referred to the review paper by Taylor.<sup>1</sup>

Because of the stability of the  $4f$  shell in many of

these rare-earth ions, the negative sign of the exchange could not be attributed to a covalent mixing mechanism.<sup>5</sup> Orbach and his coworkers<sup>5</sup> have suggested that the negative sign of the effective exchange for rare-earth impurities in some  $d$ -band metals is associated with the lack of orthogonality between the  $4f$  and the  $d$  orbitals on the neighbor sites. This idea was developed very recently by Troper *et al.*<sup>6</sup> These authors have shown that the effective exchange interaction changes sign as a function of the  $d$ -band filling across the transition-metal series. They were able to explain qualitatively some of the observed trends of the measured  $g$  shifts as a function of the position in the Periodic Table of the transition-metal hosts. It is the purpose of this paper to provide experimental ESR data on rare-earth impurities ( $\text{Nd}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Er}^{3+}$ ), in transition-metal intermetallic compounds of  $AB_2$  structure and to correlate these data as well as data of others<sup>1,4</sup> with the existing models for exchange coupling and band-structure concepts.

Another interesting problem is associated with the contribution of conduction-electrons to the hyperfine field. Recently, the hyperfine constants appropriate to the  $^{143}\text{Nd}$  and  $^{145}\text{Nd}$  isotopes in  $\text{LuIr}_2$  and  $\text{LuRh}_2$  compounds were measured and found to be smaller in magnitude with respect to the insulating values.<sup>7</sup>

This is in contrast to the larger hyperfine constant found for  $\text{Dy}^{3+}$ ,  $\text{Er}^{3+}$ , and  $\text{Yb}^{3+}$  in various metallic hosts.<sup>1</sup> However an explanation as to why this occurs, was given without a detailed mechanism.<sup>8</sup> In this paper we hope to provide further experimental information and to suggest a satisfactory mechanism.

There is also much interest in the relaxation mechanisms of  $\text{Nd}^{3+}$  in intermetallic compounds of  $AB_2$  structure. Recently, Dodds *et al.*<sup>9</sup> have noted, in the case of  $\text{LaRh}_2\text{Nd}$ , that the nonlinear thermal broadening above 12 K is too rapid to be accounted by the Hirst mechanism.<sup>10,11</sup> This mechanism is associated with relaxation via the excited crystalline-field levels due to exchange interaction with the conduction electrons. They have attributed this effect to a phonon-relaxation process (Orbach process) similar to those found in insulators.<sup>12,13</sup> The work of Dodds *et al.*<sup>9</sup> is the first report on the phonon-relaxation mechanism in the ESR of impurities in any metal and it is interesting to find out whether such a mechanism exists also in other metallic hosts.

We report a detailed ESR study of the rare-earth ions  $\text{Nd}^{3+}$  and  $\text{Gd}^{3+}$  in the cubic intermetallic compounds  $\text{LaIr}_2$ ,  $\text{LaRh}_2$ ,  $\text{YIr}_2$ ,  $\text{YRh}_2$ ,  $\text{CeIr}_2$ ,  $\text{CeRh}_2$ ,  $\text{YPt}_2$ , and  $\text{LaPt}_2$ . In addition we report on the observation of a resonance in  $\text{CePt}_2\text{Er}$  and  $\text{LaRh}_2\text{Yb}$ . The resonance of  $\text{Nd}^{3+}$  in the  $AB_2$  intermetallic compounds arises from a  $\Gamma_6$  ground-state crystalline-field splitting; that of  $\text{Er}^{3+}$  in  $\text{CePt}_2$  originates from a  $\Gamma_7$  ground state. The resonance properties of  $\text{Nd}^{3+}$  and  $\text{Gd}^{3+}$  in  $\text{LaRh}_2$  have been reported previously,<sup>9</sup> but no study about the  $\text{Nd}^{3+}$  resonance in the rest of the host compounds exists, except a preliminary report on some of the compounds.<sup>7</sup> Our experimental data indicate that the Korringa relaxation rates vary significantly from host to host and are generally much larger for samples containing  $\text{Nd}^{3+}$  than with respect to those containing  $\text{Gd}^{3+}$ . Also, the magnitude of Gd  $g$  shifts was found to be much smaller than the magnitude of the Nd  $g$  shift (negative). In one particular host ( $\text{LaIr}_2$ ), the effective exchange parameter changes its sign upon going from  $\text{Nd}^{3+}$  to  $\text{Gd}^{3+}$ . The hyperfine constants  $A$  ( $^{143}\text{Nd}$ ) and  $A$  ( $^{145}\text{Nd}$ ) were extracted from the low-temperature resolved spectra. We found the magnitude of the hyperfine constant to be smaller than in insulators which is consistent with previous observations.<sup>7</sup> Finally, we found that the ESR linewidth versus temperature increases exponentially for  $\text{LaRh}_2\text{Nd}$  and  $\text{LaIr}_2\text{Nd}$  at high temperatures, but no such an effect was observed for  $\text{YB}_2\text{Nd}$  ( $B = \text{Rh, Ir}$ ) studied, however, over a smaller temperature range. Our results for  $\text{LaRh}_2\text{Nd}$  are roughly consistent with those of Dodds *et al.*<sup>9</sup>

Section II of our paper describes the experimental results and gives an analysis of the results. The discussion is given in Sec. III. In Sec. III, we mainly emphasize the following subjects: (a) The sign of the exchange as manifested by the ESR  $g$ -shift study.

We demonstrate that the sign of the exchange for both  $\text{Nd}^{3+}$  and  $\text{Gd}^{3+}$  in the  $AB_2$  compounds can be understood in terms of the position in the Periodic Table of the  $B$  atom. This can be explained qualitatively by existing models together with band-structure arguments. (b) The hyperfine field of rare-earth ions in metallic environments. We shall demonstrate that the conduction-electron contribution to the hyperfine field is most probably associated with  $6s$  electrons. (c) The crystalline-field effects as manifested by the high-temperature exponential thermal broadening. Section IV yields our conclusions with respect to the significance of our results.

## II. EXPERIMENT AND ANALYSIS

The samples were prepared by arc melting of the stoichiometric amounts of the corresponding elements without further annealing. X-ray analysis indicated a single phase for all the samples studied. The ESR measurements were performed mostly at X-band frequency on powdered samples. The temperature range studied was between 1.4 and 50 K, limited by the signal intensity. Above  $T = 4$  K, temperatures were obtained by helium flow inside a three-wall quartz tail Dewar. The temperature of the sample inside the tail was measured using a Au-Fe versus Cr thermocouple.

### A. $AB_2\text{Nd}$ ( $A = \text{Y, La, Ce}$ ; $B = \text{Rh, Ir, Pt}$ )

Figure 1 exhibits a typical  $\text{Nd}^{3+}$  ESR absorption-derivative spectrum (in the particular case of  $\text{YRh}_2$ ). As seen, the spectrum consists of a central line corresponding to the  $I = 0$  isotope of Nd surrounded by many hyperfine satellites corresponding to  $^{143}\text{Nd}$  isotope ( $I = \frac{7}{2}$ , 12.3% abundance) and  $^{145}\text{Nd}$  isotope ( $I = \frac{7}{2}$ , 8.3% abundance). The central line properties were analyzed using the method of Peter *et al.*<sup>14</sup> We found the  $g$  values of the  $\text{Nd}^{3+}$  central line to be close to  $g = 2.667$ , appropriate to a  $\Gamma_6$  ground-state crystalline-field splitting (Tables I–III). The value of  $g(\Gamma_6) = 2.667$  is calculated using the Lea-Leask-Wolf tabulated wave functions<sup>15</sup> and assuming ideal Russell-Saunders coupling. This might be incorrect. However, in the absence of any information about  $g(\Gamma_6)$  for  $\text{Nd}^{3+}$  in insulators, we adopt this number to calculate the  $g$  shifts in the various hosts. Table IV exhibits the  $g$  shift of Nd,  $\Delta g_{\text{Nd}}$ , for the various hosts studied. It indicates that the Nd  $g$  shift is negative. This is in contrast to our previous observation of the  $\text{Nd}^{3+}$  resonance in  $\text{ARu}_2$  compounds<sup>4</sup> where a positive  $g$  shift was observed. In a single-band model the  $g$  shift is proportional to the effective exchange interaction with proportionality constant of  $g(\Gamma_6)(g_J - 1)/g_J$ , where  $g_J$  is the Landé  $g$  factor. For

TABLE I. Experimental ESR data for Nd<sup>3+</sup> and Gd<sup>3+</sup> in YIr<sub>2</sub>, YRh<sub>2</sub>, and YPt<sub>2</sub>. All the samples presented in Table I (except the starred ones) were measured in the temperature range 1.4 ≤ *T* ≤ 4.2 K.

Alloy	Concentration (%)	<i>a</i> (G) <i>T</i> = 0	<i>b</i> (G/K)	<i>g</i> value ( <i>T</i> = 1.5 K)
YIr <sub>2</sub> :Nd	1	270 ± 20	16 ± 6 <sup>a</sup>	2.646 ± 0.010
	0.3	68 ± 7	14 ± 4	2.640 ± 0.006
	0.1	60 ± 5	17 ± 7	2.645 ± 0.008
	0.05	46 ± 4	13 ± 3	2.630 ± 0.010
	0.01	50 ± 5	15 ± 5	2.630 ± 0.010
YIr <sub>2</sub> :Gd	0.35	127 ± 15	2.2 ± 0.5	† 1.994 ± 0.010
	0.08	155 ± 15	1.8 ± 0.5 <sup>b</sup>	1.990 ± 0.010
	0.05	153 ± 15	2.0 ± 0.5	1.995 ± 0.010
	0.04	130 ± 20	2.5 ± 0.5	1.998 ± 0.010
	0.02	120 ± 20	2.6 ± 0.5	1.993 ± 0.010
YRh <sub>2</sub> :Nd	1	277 ± 20	5.2 ± 1	2.655 ± 0.010
	0.1	35 ± 4	6.1 ± 0.7 <sup>a</sup>	2.640 ± 0.005
	0.05	30 ± 3	6.4 ± 0.8	2.640 ± 0.005
	0.02	35 ± 4	6.1 ± 0.7	2.640 ± 0.005
YRh <sub>2</sub> :Gd	0.2	110 ± 10	2 ± 0.2 <sup>b</sup>	1.993 ± 0.007
	0.05	46 ± 5	1.9 ± 0.2	1.999 ± 0.005
	0.01	40 ± 4	2.1 ± 0.2	1.999 ± 0.005
YPt <sub>2</sub> :Nd	1	250 ± 30	17 ± 5 <sup>a</sup>	2.61 ± 0.02
	0.5	300 ± 30	13 ± 5	2.62 ± 0.02
	0.1	230 ± 30	16 ± 5	2.62 ± 0.03
YPt <sub>2</sub> :Gd	1	290 ± 30	3.5 ± 0.5 <sup>c</sup>	2.022 ± 0.010
	0.5	275 ± 30	4.0 ± 0.5 <sup>c</sup>	2.019 ± 0.010
	0.1	260 ± 30	3.5 ± 0.5 <sup>b</sup>	2.025 ± 0.010

<sup>a</sup>Measured in the temperature range 1.4 ≤ *T* ≤ 15 K.

<sup>b</sup>Measured in the temperature range 1.5 ≤ *T* ≤ 20 K.

<sup>c</sup>Measured in the temperature range 1.5 ≤ *T* ≤ 40 K.

Nd<sup>3+</sup>  $g_J = \frac{8}{11}$ , and the above proportionality constant equals  $-1$ . Thus, the negative *g* shifts observed for Nd<sup>3+</sup> in the various hosts are consistent with a positive effective exchange interaction; the positive *g* shift, observed for Nd in LaRu<sub>2</sub>, CeRu<sub>2</sub>, and ThRu<sub>2</sub>,<sup>4</sup> is consistent with a negative effective exchange. In Sec. III we shall argue that the Nd *g* shift in the various AB<sub>2</sub> intermetallic compounds can be understood in terms of the position of the *B* element in the Periodic Table. We have tabulated, therefore, the experimental *g* shifts as well as those observed previously<sup>4</sup> in Table V, according to the position of the *B* element in group VIII of the Periodic Table. The group VIII of transition-metal elements in the Period-

ic Table consists of three different columns which are denoted by VIIIA, VIIIB, and VIIC in Table V. One can clearly see from Table V that the positive shift observed for samples at the beginning of the group VIII tends to decrease with the increase of the *d* occupation number.

At low temperatures, 1.4 K ≤ *T* ≤ 4.2 K, the ESR linewidth of the Nd<sup>3+</sup> central line could be fitted with the formula  $a + bT$ . Tables I–III, exhibit the values of *a* and *b* for Nd<sup>3+</sup> in the various hosts. As clearly seen the thermal broadening *b* varies significantly from one host to another. For the same host, *b* is almost independent of the Nd concentration for low concentrations. At high temperatures a large de-

TABLE II. Experimental ESR data for  $\text{Nd}^{3+}$ ,  $\text{Gd}^{3+}$ , and  $\text{Yb}^{3+}$  in  $\text{LaIr}_2$ ,  $\text{LaRh}_2$ , and  $\text{LaPt}_2$ . All samples presented in Table II (except the starred ones) were measured in the temperature range  $1.4 \leq T \leq 4.2$  K.

	Concentration (%)	$a$ (G) $T=0$	$b$ (G/K)	$g$ value ( $T=1.5$ K)
$\text{LaIr}_2\text{:Nd}$	2	$120 \pm 25$	$10 \pm 2^a$	$2.643 \pm 0.010$
	1	$52 \pm 5$	$9 \pm 2^b$	$2.638 \pm 0.005$
	0.1	$31 \pm 10$	$10 \pm 2$	$2.637 \pm 0.005$
	0.05	$22 \pm 5$	$10 \pm 2$	$2.633 \pm 0.005$
	0.01	$17 \pm 8$	$10 \pm 2$	$2.633 \pm 0.005$
$\text{LaIr}_2\text{:Gd}$	0.5	$37 \pm 8$	$2.6 \pm 0.4^a$	$1.983 \pm 0.005$
	0.05	$16 \pm 2$	$2.2 \pm 0.2$	$1.979 \pm 0.004$
	0.005	$12 \pm 1$	$2.4 \pm 0.2$	$1.979 \pm 0.003$
	0.0025	$11 \pm 1$	$2.5 \pm 0.2$	$1.979 \pm 0.003$
$\text{LaRh}_2\text{:Nd}$	2	$115 \pm 10$	$4 \pm 1^b$	$2.639 \pm 0.010$
	1	$64 \pm 5$	$4.3 \pm 0.7^c$	$2.646 \pm 0.008$
	0.5	$46 \pm 3$	$4.4 \pm 0.5^b$	$2.636 \pm 0.005$
	0.3	$50 \pm 4$	$4.7 \pm 1.0$	$2.643 \pm 0.008$
	0.1	$25 \pm 3$	$4.5 \pm 0.5$	$2.636 \pm 0.005$
	0.01	$27 \pm 3$	$5.0 \pm 0.6$	$2.639 \pm 0.005$
$\text{LaRh}_2\text{:Gd}$	0.3 <sup>a</sup>	$49 \pm 5$	$1.1 \pm 0.2$	$1.994 \pm 0.005$
	0.1	$18 \pm 2$	$0.8 \pm 0.3$	$1.993 \pm 0.005$
	0.02	$17 \pm 2$	$0.7 \pm 0.3$	$1.993 \pm 0.005$
	0.01	$18 \pm 2$	$0.8 \pm 0.3$	$1.994 \pm 0.005$
$\text{LaRh}_2\text{:Yb}$	1	$100 \pm 5$	$36 \pm 5$	$4.45 \pm 0.06$
$\text{LaPt}_2\text{:Nd}$	1	$350 \pm 50$	$8 \pm 3$	$2.630 \pm 0.015$
$\text{LaPt}_2\text{:Gd}$	1	$500 \pm 60$	$<2$	$2.040 \pm 0.015$

<sup>a</sup>Measured in the temperature range  $1.5 \leq T \leq 50$  K.

<sup>b</sup>Measured in the temperature range  $1.5 \leq T \leq 20$  K.

<sup>c</sup>Measured in the temperature range  $1.5 \leq T \leq 30$  K.

viation from linear thermal broadening was observed for  $\text{LaIr}_2\text{:Nd}$  and  $\text{LaRh}_2\text{:Nd}$ . Figures 2 and 3 show the linewidth, after subtraction of the residual width  $a$  for  $\text{LaIr}_2\text{:Nd}$  and  $\text{LaRh}_2\text{:Nd}$  over the entire temperature range ( $1.4 \text{ K} \leq T \leq 30 \text{ K}$ ). As clearly seen, there is an exponential increase of the linewidth versus temperature for temperatures above 15 K. In addition we have studied the Nd ESR thermal broadening in  $\text{YRh}_2\text{:Nd}$  and  $\text{YIr}_2\text{:Nd}$ . We were not able to measure above 16 K for the former sample and 10 K for the latter sample because of small signal-to-noise ratio above these temperatures. Within the temperature range studied, the linewidth increases linearly with temperature and no evidence

for exponential thermal broadening was observed.

The positions of the hyperfine satellites were determined experimentally by taking the second derivative of the spectra. Table VI exhibits the hyperfine constants  $A(^{143}\text{Nd})$  and  $A(^{145}\text{Nd})$  appropriate to the  $^{143}\text{Nd}$  and  $^{145}\text{Nd}$  isotopes as extracted from our observed spectra using the Breit-Rabi formula.<sup>16</sup> For comparison the values of  $A(^{143}\text{Nd})$  and  $A(^{145}\text{Nd})$  found for the insulator  $\text{CeO}_2\text{:Nd}$  (Ref. 17) are also given. It is seen that the magnitude  $A(^{143}\text{Nd})$  and  $A(^{145}\text{Nd})$  is much reduced in the metallic host with respect to the insulating values. To emphasize this point we have also tabulated in Table VI the hyperfine changes  $\Delta A(^{143}\text{Nd})$  and  $\Delta A(^{145}\text{Nd})$ .

TABLE III. Experimental ESR data for Nd<sup>3+</sup> and Gd<sup>3+</sup> in CeIr<sub>2</sub> and CeRh<sub>2</sub>. All the samples presented in Table III (except the starred ones) were measured in the temperature range 1.4 ≤ T ≤ 4.2 K.

Alloy	Concentration (%)	a (G) T = 0	b (G/K)	g value (T = 1.5 K)
CeIr <sub>2</sub> :Nd	0.06	195 ± 30	85 ± 20	2.57 ± 0.03
CeIr <sub>2</sub> :Gd	1	180 ± 10	18 ± 2 <sup>a</sup>	1.998 ± 0.005
	0.3	145 ± 10	22 ± 4 <sup>b</sup>	1.996 ± 0.006
	0.1	130 ± 10	23 ± 4	2.006 ± 0.006
	0.043	90 ± 10	28 ± 8	2.005 ± 0.008
CeRh <sub>2</sub> :Nd	1.1	152 ± 20	110 ± 30	2.61 ± 0.02
	0.6	130 ± 20	95 ± 20	2.59 ± 0.02
	0.4	120 ± 20	110 ± 30	2.60 ± 0.02
	0.2	100 ± 20	90 ± 20	2.60 ± 0.02
CeRh <sub>2</sub> :Gd	1	50 ± 5	19 ± 2 <sup>a</sup>	1.996 ± 0.004
	0.3	75 ± 10	17 ± 2 <sup>b</sup>	1.993 ± 0.004
	0.1	55 ± 5	18 ± 2	1.998 ± 0.004
	0.04	46 ± 5	20 ± 2	1.998 ± 0.004

<sup>a</sup>Measured in the temperature range 1.4 ≤ T ≤ 30 K.

<sup>b</sup>Measured in the temperature range 1.4 ≤ T ≤ 12 K.

### B. AB<sub>2</sub>:Gd (A = Y, La, Ce; B = Rh, Ir, Pt)

The Gd<sup>3+</sup> ESR spectra exhibit a single isotropic line. The resonance properties as analyzed by the method of Peter *et al.*<sup>14</sup> indicate a slightly positive *g* shift with respect to the insulator value *g* = 1.993 for most of our samples, except for the case of LaIr<sub>2</sub>:Gd,

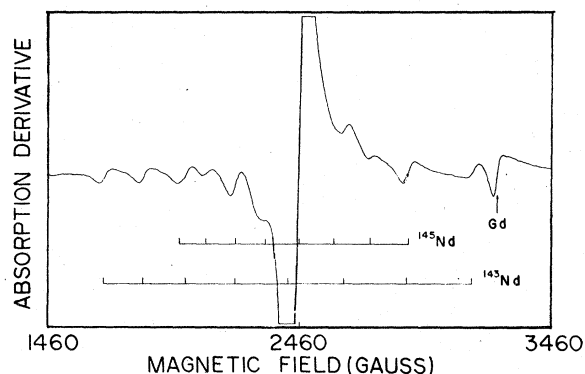


FIG. 1. ESR spectrum of 1000 ppm of Nd in YRh<sub>2</sub> at T = 1.5 K. The resonance of natural impurities of Gd is also indicated. The vertical lines indicate the positions of the various hyperfine satellites appropriate to the <sup>143</sup>Nd and <sup>145</sup>Nd isotopes.

where a clear negative *g* shift of  $-0.013 \pm 0.005$  is observed. The thermal broadening of the ESR linewidth was fitted to the formula  $a + bT$ . The *g* value, *a* and *b* for Gd in the various hosts are given in Tables I, II, and III; the *g* shifts with respect to *g* = 1.993 are given in Table IV. It is seen that the value of *b* (as well as the *g* value) are concentration independent at low concentrations, indicating the absence of bottleneck in the relaxation mechanism. Table IV indicates, that the magnitude of both the *g* shift and thermal broadening are smaller for samples containing Gd, with respect to the same hosts with Nd. In Table IV we also give the ratio of  $b_{Nd}/b_{Gd}$  for the various hosts. In a frame of a single-band model this ratio is related to the exchange ratio  $\langle J^2 \rangle_{Nd} / \langle J^2 \rangle_{Gd}$ .<sup>1</sup> The exchange ratio for the various hosts studied are also given in Table IV. Similar exchange ratios were observed in other hosts.<sup>4,7</sup>

Table VII exhibits the Gd *g* shifts in various AB<sub>2</sub> compounds, where *B* belongs to the group VIII of the Periodic Table. Similarly to Table V, we have tabulated the various *g* shifts for Gd in the AB<sub>2</sub> compounds according to the position of the *B* atom in the Periodic Table. One can clearly see that the magnitude of the negative *g* shift observed at the beginning of the 3*d* series decreases with increasing *d* occupation number or with increasing *n* (*n* = 3, 4, 5). This is a similar tendency to that observed for the Nd *g*

TABLE IV. A comparison between the  $g$  shifts and thermal broadenings of  $\text{Nd}^{3+}$  and  $\text{Gd}^{3+}$  in the various  $AB_2$  hosts. The  $g$  shifts were measured with respect to 2.667 and 1.993 for  $\text{Nd}^{3+}$  and  $\text{Gd}^{3+}$ , respectively.

host	$\Delta g_{\text{Nd}}$	$\Delta g_{\text{Gd}}$	$b_{\text{Nd}}/b_{\text{Gd}}$	$\langle J^2 \rangle_{\text{Nd}}/\langle J^2 \rangle_{\text{Gd}}$
$\text{YIr}_2$	$-0.029 \pm 0.010$	$0.001 \pm 0.010$	$6.5 \pm 2$	$8.7 \pm 3.0$
$\text{YRh}_2$	$-0.023 \pm 0.005$	$0.004 \pm 0.005$	$3 \pm 1$	$4.0 \pm 1.0$
$\text{YPt}_2$	$-0.047 \pm 0.020$	$0.027 \pm 0.010$	$4 \pm 1$	$5.3 \pm 1.5$
$\text{LaIr}_2$	$-0.030 \pm 0.005$	$-0.013 \pm 0.005$	$4 \pm 1$	$5.3 \pm 1.0$
$\text{LaRh}_2$	$-0.027 \pm 0.005$	$0.001 \pm 0.005$	$5 \pm 1$	$6.7 \pm 1.5$
$\text{LaPt}_2$	$-0.038 \pm 0.015$	$0.047 \pm 0.015$	$>4$	$>5$
$\text{CeIr}_2$	$-0.097 \pm 0.030$	$0.008 \pm 0.005$	$4 \pm 1$	$5.3 \pm 1.5$
$\text{CeRh}_2$	$-0.067 \pm 0.020$	$0.003 \pm 0.004$	$5.5 \pm 1$	$7.4 \pm 1.5$

shifts in Table V (only the sign of the  $g$  shift is reversed because of the  $\text{Nd}^{3+}$   $g_J - 1$  factor). This is a striking feature and will be discussed later.

### C. $\text{CePt}_2:\text{Er}$ and $\text{LaRh}_2:\text{Yb}$

We were able to observe a resonance originated with  $\Gamma_7$  ground state for  $\text{Er}^{3+}$  in  $\text{CePt}_2$ . The resonance properties were analyzed similar to the  $AB_2:\text{Nd}$

data. We found the  $g$  value to be equal to  $g = 6.78 \pm 0.05$ ,  $b < 0.5$  G/K, and  $a \approx 80$  G. The relatively large error bar and the small  $g$  shift with respect to  $g = 6.77$  reported in insulators (see Ref. 16), does not allow any conclusion with respect to the sign of the exchange. It is believed that the exchange is positive as for Gd in  $\text{YPt}_2$  and  $\text{LaPt}_2$  hosts (see Table IV). We were not able to observe the resonance of  $\text{Nd}^{3+}$  and  $\text{Gd}^{3+}$  in  $\text{CePt}_2$ .

We were able to observe also the resonance of  $\text{Yb}^{3+}$  in  $\text{LaRh}_2$  (Table II). The  $g$  value observed is not understood at present but the hyperfine splitting of 570 G ( $I = \frac{1}{2}$  isotope) allows for positive identification.

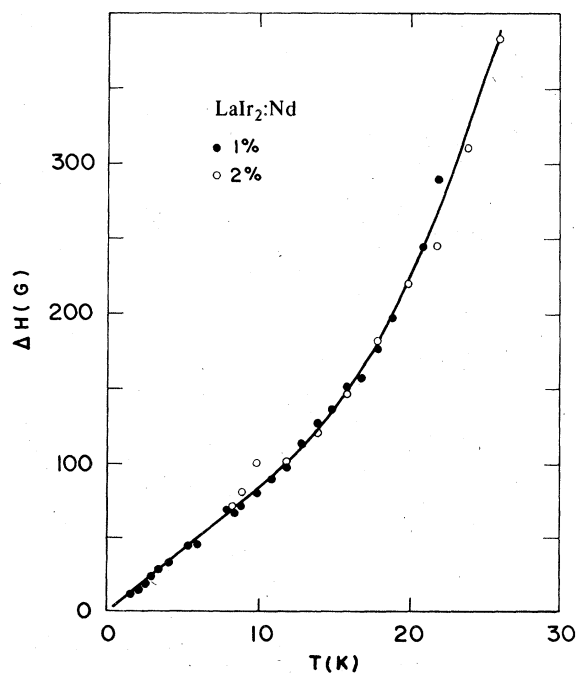


FIG. 2. ESR linewidth of Nd in  $\text{LaIr}_2$  vs temperature. The solid line is the best fit of Eq. (6a) to the experimental data. This fit yields  $\Delta = 94$  K,  $C = 6530$  G.

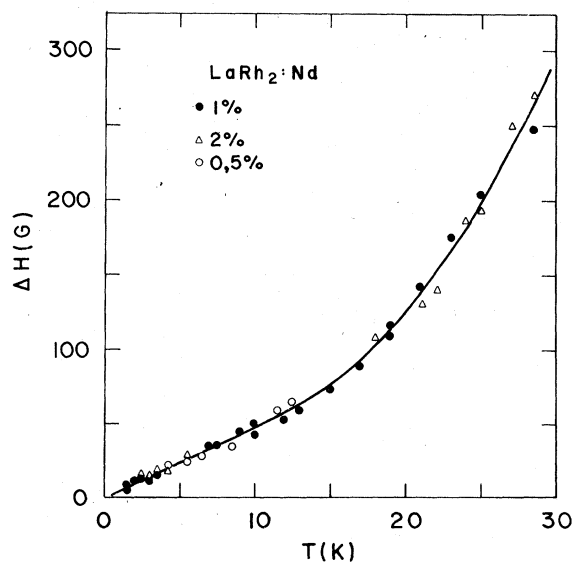


FIG. 3. ESR linewidth of Nd in  $\text{LaRh}_2$  vs temperature. The solid line is best fit of Eq. (6a) to the experimental data. This fit yields  $\Delta = 93$  K,  $C = 3310$  G.

TABLE V. Comparison of the Nd<sup>3+</sup> *g* shifts (measured with respect to 2.667) in some AB<sub>2</sub> hosts. The *g* shifts are tabulated according to the position of the *B* element in the group VIII of the Periodic Table.

	VIII A	VIII B	VIII C
3 <i>d</i>	Fe	Co	Ni
4 <i>d</i>	Ru +0.18 ± 0.10 (LaRu <sub>2</sub> ) <sup>a</sup> +0.033 ± 0.010 (CeRu <sub>2</sub> ) <sup>a</sup> +0.023 ± 0.010 (ThRu <sub>2</sub> ) <sup>a</sup>	Rh -0.031 ± 0.005 (LaRh <sub>2</sub> ) <sup>b</sup> -0.067 ± 0.020 (CeRh <sub>2</sub> ) <sup>b</sup> -0.027 ± 0.005 (YRh <sub>2</sub> ) <sup>b</sup>	Pd
5 <i>d</i>	Os	Ir -0.034 ± 0.005 (LaIr <sub>2</sub> ) <sup>b</sup> -0.097 ± 0.030 (CeIr <sub>2</sub> ) <sup>b</sup> -0.034 ± 0.005 (YIr <sub>2</sub> ) <sup>b</sup>	Pt -0.038 ± 0.015 (LaPt <sub>2</sub> ) <sup>b</sup> -0.047 ± 0.020 (YPt <sub>2</sub> ) <sup>b</sup>

<sup>a</sup>G. E. Barberis, D. Davidov, J. P. Donoso, F. G. Gandra, C. Rettori, and J. F. Suassuna, Solid State Commun. **28**, 427 (1979).

<sup>b</sup>The present work.

### III. DISCUSSION

In this section we shall discuss our experimental results with emphasis on the following three subjects:

A. exchange interaction between the localized moments (Nd, Gd) and the conduction electrons, especially its sign, as reflected by our *g*-shift study, B. the hyperfine interaction, and C. crystalline-field effects.

#### A. Exchange-interaction parameters

An interesting feature of our results in Tables I – III is the very large Korringa thermal broadening *b*, but the small *g* shift for some of the Gd containing

TABLE VI. Hyperfine constants and the hyperfine changes for some of the systems studied. For comparison the hyperfine constants of the insulating cubic CeO<sub>2</sub>:Nd are given.

system	<i>A</i> ( <sup>143</sup> Nd)(G)	<i>A</i> ( <sup>145</sup> Nd)(G)	Δ <i>A</i> ( <sup>143</sup> Nd)(G)	Δ <i>A</i> ( <sup>145</sup> Nd)(G)
LaIr <sub>2</sub> :Nd	209 ± 3	131 ± 2	-12 ± 3	-7 ± 2
LaRh <sub>2</sub> :Nd	209 ± 2	131 ± 2	-12 ± 2	-7 ± 2
YIr <sub>2</sub> :Nd	208 ± 2	131 ± 4	-13 ± 4	-7 ± 4
YRh <sub>2</sub> :Nd	209 ± 2	132 ± 2	-12 ± 2	-6 ± 2
CeO <sub>2</sub> :Nd	221	138	0	0

hosts like YIr<sub>2</sub>:Gd, LaRh<sub>2</sub>:Gd, CeIr<sub>2</sub>:Gd, and CeRh<sub>2</sub>:Gd. Following Seipler and Elschner,<sup>18</sup> one can define a parameter *R* as follows:

$$R = \frac{g \mu_B}{\pi k_B} \frac{b}{(\Delta g)^2}, \quad (1)$$

where *g* is the Gd *g* value,  $\mu_B$  is the Bohr magneton, and  $k_B$  is the Boltzman factor. In the absence of  $\bar{q}$  dependence of the exchange and the exchange enhancement,<sup>1</sup> *R* gives the ratio of the exchange parameters as extracted from the linewidth and the *g* shift and it is expected to be equal to 1 (*R* = 1). In the presence of the  $\bar{q}$  dependence of the exchange and exchange enhancement, a much smaller value of *R* (*R* < 1) is expected for a single-band model. Indeed the experimental values for *R* in many *d*-band metals and intermetallic compounds<sup>18</sup> have indicated that *R* < 1. Our own experimental results have shown, however, that the value of *R* for the samples quoted above is larger than 10. This indicates that our results can not be described by a single-band model and one has to invoke a multiband model with different competing mechanisms having different signs, such that the *g* shift is almost cancelled out, but the thermal broadening is not.

In the present section we shall introduce a simple multiband model similar to that of Troper *et al.*<sup>6</sup> and Davidov *et al.*<sup>5</sup> We shall demonstrate that this model can explain qualitatively the tendency of the *g* shift in our results as well as those of others<sup>1</sup> for transition-metal intermetallic compounds of AB<sub>2</sub> structure,

TABLE VII. Comparison of the  $Gd^{3+}$   $g$  shifts (measured with respect to 1.993) in some  $AB_2$  hosts. The  $g$  shifts are tabulated according to the position of the  $B$  element in the group VIII of the Periodic Table.

	VIIIA	VIIIB	VIIIC
3d	Fe	Co	Ni
		$-0.25 \pm 0.1$ (YCo <sub>2</sub> ) <sup>a</sup>	
4d	Ru	Rh	Pd
	$-0.172 \pm 0.005$ (LaRu <sub>2</sub> ) <sup>b</sup>	$0.001 \pm 0.005$ (LaRh <sub>2</sub> ) <sup>d</sup>	$+0.05$ (LaPd <sub>3</sub> ) <sup>e</sup>
	$-0.050 \pm 0.005$ (CeRu <sub>2</sub> ) <sup>b</sup>	$0.003 \pm 0.004$ (CeRh <sub>2</sub> ) <sup>d</sup>	$+0.03$ (CePd <sub>3</sub> ) <sup>f</sup>
	$-0.06$ (YRu <sub>2</sub> ) <sup>c</sup>	$0.004 \pm 0.005$ (YRh <sub>2</sub> ) <sup>d</sup>	$+0.028 \pm 0.003$ (YPd <sub>3</sub> ) <sup>f</sup>
	$-0.035 \pm 0.004$ (ThRu <sub>2</sub> ) <sup>b</sup>		
5d	Os	Ir	Pt
	$-0.06$ (LaOs <sub>2</sub> ) <sup>g</sup>	$-0.013 \pm 0.005$ (LaIr <sub>2</sub> ) <sup>d</sup>	$+0.047 \pm 0.015$ (LaPt <sub>2</sub> ) <sup>d</sup>
		$0.008 \pm 0.005$ (CeIr <sub>2</sub> ) <sup>d</sup>	
		$0.001 \pm 0.010$ (YIr <sub>2</sub> ) <sup>d</sup>	$+0.027 \pm 0.010$ (YPt <sub>2</sub> ) <sup>d</sup>

<sup>a</sup>Measured by E. Valach and D. Shaltiel (private communication).

<sup>b</sup>Measured by Davidov *et al.*, Phys. Rev. B **9**, 147 (1974).

<sup>c</sup>YRu<sub>2</sub> is hexagonal, quoted by R. H. Taylor, Ad. Phys. **24**, 681 (1975).

<sup>d</sup>Present work.

<sup>e</sup>LaPd<sub>2</sub> is unstable and we give the results for LaPd<sub>3</sub> as measured by Kim and Karra, Phys. Rev. B **15**, 2538 (1977).

<sup>f</sup>CePd<sub>2</sub> and YPd<sub>2</sub> are unstable and we give the results for CePd<sub>3</sub> and YPd<sub>3</sub> as measured by Gambke *et al.*, Phys. Rev. Lett. **40**, 1290 (1978).

<sup>g</sup>Measured by Schrittenlacher *et al.*, Solid State Commun. **16**, 923 (1975).

where  $B$  is a transition-metal atom belonging to the group VIII in the Periodic Table. We shall define three different exchange parameters  $J_A^{(d)}$ ,  $J_B^{(d)}$ , and  $J^{(s)}$ ;  $J_A^{(d)}$  is the exchange coupling between the Gd 4f electrons (substituting for the  $A$  atom) and the  $d$  electrons in the same  $A$  site,  $J_B^{(d)}$  is the exchange coupling between the Gd 4f electrons (substituting for the  $A$  site) and the  $d$  electrons on the next-neighbors  $B$  sites in the  $AB_2$  compounds, and  $J^{(s)}$  is the coupling between the 4f electrons and the average  $s$  electrons in both the  $A$  and  $B$  sites.  $J_B^{(d)}$  and  $J_A^{(d)}$  are identical to the intersite and intrasite exchange parameters, respectively, suggested by Troper *et al.*<sup>6</sup> According to Troper *et al.*<sup>6</sup> and Davidov *et al.*,<sup>5</sup> the intersite exchange  $J_B^{(d)}$  can be negative because of lack of orthogonality between wave functions originating with different sites. The exchange parameters  $J_A^{(d)}$  and  $J^{(s)}$  are always positive. Numerical estimations<sup>6</sup> have shown that  $J_A^{(d)}$  is of the order of magnitude of  $J^{(s)}$ . Both these exchange parameters, however, have much larger magnitude than  $J_B^{(d)}$ .<sup>6</sup> The  $d$  electrons originating with the  $B$  site can

form a narrow  $d$  band at the Fermi level for  $AB_2$  compounds with  $B$  belonging to the group VIII. The appropriate density of states at the Fermi level is  $\eta_B^{(d)}$ . The  $d$  band associated with the  $A$  site and the  $s$  bands are probably much more broader. The corresponding density of states at the Fermi level will be denoted by  $\eta_A^{(d)}$  and  $\eta^{(s)}$ . It is believed that  $\eta_B^{(d)}$  is much larger than  $\eta_A^{(d)}$  and  $\eta^{(s)}$ , at least for  $AB_2$  compounds, with  $B$  belonging to the VIIIA column in Tables V and VII. In terms of these notations the  $g$  shifts can be expressed in a multiband model as follows:

$$\Delta g = \Delta g_A^{(d)} + \Delta g_B^{(d)} + \Delta g^{(s)} = g(g_J - 1/g_I) \times (J_A^{(d)}\eta_A^{(d)} + J_B^{(d)}\eta_B^{(d)} + J^{(s)}\eta^{(s)}) \quad (2)$$

where we have neglected for simplicity the  $\bar{q}$  dependence of the exchange interaction as well as the Coulomb interaction leading to exchange enhancement. According to our understanding,  $\Delta g_B^{(d)}$  is negative, and  $\Delta g_A^{(d)}$  and  $\Delta g^{(s)}$  are positive for Gd, and the reverse is true for Nd. In the following we shall restrict ourselves to the discussion of the Gd  $g$



shift in Table VII simply because of the more data available on this impurity. As stressed above, the tendency in Tables V and VII is the same.

In terms of Eq. (2), the variation of the *g* shift can be understood by the competition between the inter-site exchange mechanism and the intrasite exchange mechanism. Both mechanisms are largely dependent on the local density of states which can be shown to vary significantly across the *AB*<sub>2</sub> compounds. This will be demonstrated using simple band-structure arguments as well as several experimental facts observed by others using different experimental techniques. Our discussion is based on the paper of Troper *et al.*<sup>6</sup> and private communication with A. A. Gomes. Let us denote by  $\epsilon_B^{nd}$  ( $n = 3, 4, 5$ ) the "atomic" energy of the  $nd$  ( $n = 3, 4, 5$ ) electrons on the *B* site;  $\epsilon_A^{5d}$  is the "atomic" energy of the *5d* electrons on the rare-earth site (*A* site). Clearly,  $|\epsilon_B^{nd} - \epsilon_A^{5d}|$  decreases with increasing *n*. One expects, therefore, a larger amplitude of *d* states originating from the *B* site at the rare-earth site (*A* site), with increasing *n* or equivalently less localization of *d* electrons with increasing *n* ( $n = 3, 4, 5$ ) in intermetallic compounds of *AB*<sub>2</sub> structure. This means broadening of the *d* levels and consequently a decrease of  $\eta_B^{(d)}$  [and  $\Delta g_B^{(d)}$ ] with increasing *n* ( $n = 3, 4, 5$ ). It should be noted that a transfer of *d* electron from the *B* site to the *A* site must be accompanied by a reverse charge transfer (probably of *s* electrons) in order to keep the charge neutrality in metals according to the Friedel sum rule. This tends to reduce the amplitude of the *s* electrons on the *A* site. However, because of the very broad *s* band at the Fermi level, we don't expect appreciable change in  $\eta^{(s)}$ . Thus we expect a decrease of  $\Delta g_B^{(d)}$ , no significant change in  $\Delta g_A^{(s)}$ , and a possible increase in  $\Delta g_A^{(d)}$  upon increasing *n* ( $n = 3, 4, 5$ ) in Table VII. Indeed, this was observed experimentally. Table VII clearly indicates that the negative *g* shift decreases with increasing *n* ( $n = 3, 4, 5$ ) for compounds having the same *A* element (see for example, the much smaller negative shift observed in LaOs<sub>2</sub>:Gd with respect to LaRu<sub>2</sub>:Gd or the much smaller shifts observed for YRh<sub>2</sub>:Gd with respect to YCo<sub>2</sub>:Gd in Table VII). Another remarkable feature of our results in Table VII is that the *g* shift is always negative for hosts in column VIII A, nearly zero for hosts in column VIII B (except YCo<sub>2</sub>:Gd) and definitely positive for hosts in column VIII C. Similar behavior (with opposite sign) can be clearly recognized also in Table V. These decrease of the negative *g* shift across the *d* series was interpreted previously by filling the *d* band associated with the *B* site.<sup>1</sup> No explanation as to why this occurs was given. We suggest here some experimental evidence that this is indeed the case. We argue that this effect is consequence of a significant broadening of the *d* band for intermetallic compounds with large *d* occupation number. This argument is based on experimental observation on

the systems YFe<sub>2</sub>, YCo<sub>2</sub>, and YNi<sub>2</sub> as well as on GdFe<sub>2</sub>, GdCo<sub>2</sub>, and GdNi<sub>2</sub>. It is known that the Fe in YFe<sub>2</sub> exhibits a well defined localized moment. The intermetallic compound YCo<sub>2</sub>, however, is a strongly exchange enhanced itinerant paramagnet, whereas in YNi<sub>2</sub>, a less localization of the Ni *d* states is expected.<sup>19</sup> Thus, the magnetic properties of the YFe<sub>2</sub>, YCo<sub>2</sub>, and YNi<sub>2</sub> systems can be easily understood by delocalization of the *d* electrons on the *B* site upon going from YFe<sub>2</sub> to YNi<sub>2</sub>.<sup>19</sup> Using the same argument as before, such a delocalization (or broadening of the *d* band) would lead to a decrease of  $|\Delta g_B^{(d)}|$  and consequently a decrease of the negative shift in Eq. (2) with increasing the *d* occupation number. Thus, the large negative *g* shift in LaRu<sub>2</sub>:Gd, for example, is probably associated with narrow *4d* band at the Fermi level. The almost zero shift for LaRh<sub>2</sub>:Gd is due to competition between the positive shifts  $\Delta g_A^{(d)}$  and  $\Delta g^{(s)}$ , and the negative shift  $\Delta g_B^{(d)}$ . We note that in LaRh<sub>2</sub> the *4d* band is much broader (and probably partially filled) such that  $\Delta g_B^{(d)}$  has a smaller magnitude with respect to that in LaRu<sub>2</sub>. In the case of YPt<sub>2</sub>, the Pt *5d* band is very broad (and may be filled) and one can not distinguish any more between the host *5d* electrons and those of the impurity. One expects, in this case, a positive exchange interaction due to the *6s* and *5d* electrons on the impurity site. This is indeed the tendency observed in Tables V and VII.

Our data in Table V indicate that the magnitude of  $\Delta g_{Nd}$  is larger than the magnitude of  $\Delta g_{Gd}$ . Using Eq. (2), one can show that this implies that the term

$$J_A^{(d)}\eta_A^{(d)} + J_B^{(d)}\eta_B^{(d)} + J^{(s)}\eta^{(s)}$$

is more positive for the Nd<sup>3+</sup> ion than for the Gd<sup>3+</sup> ion in the same host. This can be explained in the framework of our model by the larger value of  $J_A^{(d)}$  (positive) for Nd<sup>3+</sup>, noting that the radius of its *4f* shell is also much larger with respect to that of Gd<sup>3+</sup>. It is difficult to estimate the effect of a larger *4f* shell on  $J_B^{(d)}$  but it is believed that  $J_B^{(d)}$  is also more positive for Nd<sup>3+</sup> with respect to Gd<sup>3+</sup>.<sup>6</sup> The larger values of  $J_A^{(d)}$  and  $J^{(s)}$  for Nd<sup>3+</sup> with respect to Gd<sup>3+</sup> are probably responsible also for the larger thermal broadening of the former ion in the various hosts (Table IV). Unfortunately the absence of knowledge about the electronic properties of the host compounds like density of state, enhancement factors, and the degeneracy at the Fermi level does not permit the separation between the various exchange mechanisms. Band-structure calculation and further experimental study certainly will give information about some of these missing parameters.

## B. Hyperfine interaction

A remarkable feature of our data in Table VI is the smaller magnitude of  $A(^{143}Nd)$  and  $A(^{145}Nd)$  with

respect to the insulator value (see the negative value of  $\Delta A$  in Table VI). This is in contrast to the slightly larger magnitude of the hyperfine constant observed for  $\text{Er}^{3+}$ ,  $\text{Dy}^{3+}$ , and  $\text{Yb}^{3+}$  (with respect to insulators) in various metallic hosts.<sup>8,16</sup> In analogy with previous work,<sup>16</sup> we attribute this change in the hyperfine constant to the effect of conduction electrons. We argue that the rare-earth ion polarizes the conduction electrons which, interact with the rare-earth nucleus to produce an additional hyperfine contribution (in our case a negative contribution). Similar to our  $g$ -shift analysis we shall distinguish between three different contributions:

(a) Conduction electrons of  $d$  character (mainly  $5d$ ) on the rare-earth site ( $A$  site). These electrons in-

$$\Delta A = g \left( \frac{g_J - 1}{g_J} \right) \left( \frac{g_I \mu_I}{g_e \mu_e} \right) \left( \frac{A_{\text{cp}}^{(d)}}{g_I \mu_I} J_A^{(d)} \eta_A^{(d)} + \frac{A_{\text{cp}}^{(d)} + A_{\text{con}}^{(d)}}{g_I \mu_I} J_B^{(d)} \eta_B^{(d)} + \frac{A_{\text{con}}^{(s)}}{g_I \mu_I} J^{(s)} \eta^{(s)} \right) \quad (3a)$$

$$= \frac{g_I \mu_I}{g_e \mu_e} \left( \frac{A_{\text{cp}}^{(d)}}{g_I \mu_I} \Delta g_A^{(d)} + \frac{A_{\text{cp}}^{(d)} + A_{\text{con}}^{(d)}}{g_I \mu_I} \Delta g_B^{(d)} + \frac{A_{\text{con}}^{(s)}}{g_I \mu_I} \Delta g^{(s)} \right) \quad (3b)$$

Clearly, because of the negative value of  $g_J - 1$ , we expect the first term in Eqs. (3) to be positive [ $A_{\text{cp}}^{(d)} < 0$ ,  $J_A^{(d)} > 0$ , and  $g_J - 1 < 0$ ], the second term to be either positive or negative depending on the dominant mechanism for the hyperfine interaction and the third term to be definitely negative [ $A_{\text{con}}^{(s)} > 0$ ,  $J^{(s)} > 0$ , but  $g_J - 1 < 0$ ]. Numerical estimations have shown that the hyperfine field  $A_{\text{con}}^{(s)}/g_I \mu_I \approx 10^6 - 10^7$  G for  $6s$  electrons<sup>16</sup> while  $A_{\text{cp}}^{(d)}/g_I \mu_I$  is of the order of  $10^4 - 10^5$  G. In addition we have already shown that for  $\text{Nd}^{3+}$  in the various  $AB_2$  compounds (except in the Ru compounds) we have

$$|\Delta g^{(s)} + \Delta g_A^{(d)}| > |\Delta g_B^{(d)}|,$$

see Table IV. Thus, the second term in Eqs. (3) can be neglected. The first term in Eqs. (3) is probably unimportant as well, because it leads to positive hyperfine contribution to  $\Delta A$  in disagreement with our experimental observation. We conclude that the  $6s$  electrons are responsible to the observed negative contribution to the hyperfine field. This is because of the large value of  $A_{\text{con}}^{(s)}/g_I \mu_I$  [much larger than  $A_{\text{cp}}^{(d)}/g_I \mu_I$  to overcome the small value of  $\eta^{(s)}$ ].

### C. Crystalline-field effects

We turn, now, to the high-temperature measurements of  $\text{LaRh}_2\text{Nd}$  and  $\text{LaIr}_2\text{Nd}$  (Figs. 2, 3). Following Dodds *et al.*,<sup>9</sup> we shall write the linewidth  $\Delta H$  as the sum of three contributions as follows:

$$\Delta H = bT + \frac{C' \Delta}{\exp(\Delta/T) - 1} + \frac{C'' \Delta^3}{\exp(\Delta/T) - 1} \quad (4)$$

interact with the rare-earth nucleus via the core polarization mechanism only (zero probability on the nucleus). The appropriate hyperfine constant is  $A_{\text{cp}}^{(d)}$  which is negative.

(b) Conduction electrons of  $d$  character on the  $B$  site. These electrons can produce hyperfine field either by the direct contact term,  $A_{\text{con}}^{(d)}$  (positive), or by polarization of the rare-earth core electrons,  $A_{\text{cp}}^{(d)}$  (negative).

(c) Conduction electrons with  $s$  character on the  $A$  site. These electrons interact directly with the nucleus via the Fermi-contact term,  $A_{\text{con}}^{(s)}$  which is positive.

In terms of these contributions one can express the hyperfine change  $\Delta A$  as follows:

The first term in Eq. (4) represents the Korringa relaxation rate associated with modulation and transitions within the  $\Gamma_6$  ground-state levels due to the  $\text{Nd}^{3+}$  localized-moment conduction-electrons exchange coupling. The second term in Eq. (4) is the Hirst mechanism which involves relaxation via higher-crystalline-field levels induced by conduction-electrons exchange coupling. The last term is the Orbach process in which the relaxation via the excited-crystalline-field levels is induced by the host phonons. We have considered in Eq. (4) only the first excited  $\Gamma_8$  level with energy splitting  $\Delta$  ( $\Delta = \Gamma_8 - \Gamma_6$ ), as numerical calculations have shown that the higher-excited levels are not important. The coefficient  $b$  is defined by others<sup>16</sup>;  $C'$  and  $C''$  can be expressed as

$$C' = \frac{1}{2} b M_H^2; \quad C'' = \frac{3 k_B^2}{2 \pi \hbar^4 \rho v^5} M_0^2 \quad (5)$$

where  $\rho$  is the host density and  $v$  is the velocity of sound in the host. The symbols  $M_H^2$  and  $M_0^2$  represents sum of the square of matrix elements of the  $\text{Nd}^{3+}$  total angular momentum and of the dynamic crystal-field potential, respectively. Explicit expressions for  $M_H^2$  and  $M_0^2$  can be found in the paper of Davidov *et al.*<sup>11</sup> and Bierig and Weber<sup>12</sup>, respectively. Since the relative contributions of the Hirst mechanism<sup>10</sup> and the Orbach phonon process<sup>12,13</sup> to the  $\text{Nd}^{3+}$  relaxation rate (Figs. 2, 3) is unknown, it is preferable to express Eq. (4) as follows:

$$\Delta H = bT + \frac{C}{\exp(\Delta/T) - 1} \quad (6a)$$

with

$$C = C'\Delta + C''\Delta^3 \quad (6b)$$

Such an expression leaves us with only two parameters, namely,  $C$  and  $\Delta$  to be determined by fitting Eq. (6a) to the experimental data. The best fit (solid lines in Figs. 2 and 3) yields  $\Delta = 94$  K;  $C = 6530$  G for LaIr<sub>2</sub>, and  $\Delta = 93$  K;  $C = 3310$  G for LaRh<sub>2</sub>. The values of  $\Delta$  observed are independent of the relative importance of the various relaxation mechanisms. The error bar in the determination of  $\Delta$  is  $\pm 20$  K. Our value for  $\Delta$  in LaRh<sub>2</sub>:Nd is smaller with respect to that found by Dodds *et al.*<sup>9</sup> ( $\Delta = 125$  K) for the same system.

The paper of Dodds *et al.*<sup>9</sup> and the present paper are the only examples where a strong evidence for phonon relaxation in the ESR of impurities in metals was observed. It is interesting, therefore, to compare the phonon contribution with that found in insulators.<sup>12</sup> This requires, however, a separation between the two mechanisms mentioned above, which is impossible in the absence of knowledge about the Lea-Leask-Wolf parameter,  $x$ .<sup>15</sup> We have calculated, therefore, the value of  $C'$  for various  $x$  values and have estimated  $C''$  using Eq. (6b), and our own experimental results for  $C$ . The values of  $C''\Delta^3$  (phonon contribution) were found to be between  $1.1 \times 10^{11}$  sec<sup>-1</sup> and  $1.5 \times 10^{11}$  sec<sup>-1</sup> for LaIr<sub>2</sub>:Nd. The value of  $C''\Delta^3$  (for large range of  $x$  values) is larger by factor of 2, only with respect to the value of  $\approx 5 \times 10^{10}$  sec<sup>-1</sup>, found by Bierig *et al.*<sup>12</sup> for CaF<sub>2</sub>:Nd.

#### IV. CONCLUSIONS

(a) In this paper, we have measured the ESR properties of Gd and Nd in cubic  $AB_2$  compounds, where  $B$  is either  $3d$ ,  $4d$  or  $5d$  transition-metal element belonging to the group VIII of the Periodic Table. We have studied more than 18 different systems (150 samples approximately!) and by doing so we have established an almost complete picture of the resonance properties (as far as the  $g$  shift and the thermal broadening are concerned) in the cubic  $AB_2$  series. Our experimental results indicate that the Gd and Nd  $g$  shifts (in most cases having opposite signs) vary in a systematic manner and depend on the position of the host in the Periodic Table. Especially, we have shown that for two different impurities (namely, Gd and Nd) the exchange interaction changes its sign going from the Ru compounds (VIII A column in Tables V and VII) to Pt compounds (VIII C column in Tables V and VII). The systematics observed could be explained by simple band-structure and charge-transfer arguments. The charge transfer leads to  $d$  band filling.

The ability to relate the  $g$  shift to charge transfer of electrons having  $d$  character is very important, as

there is at least one important physical parameter, namely, the heat of formation  $\Delta G$  which depends also on charge transfer. We argue that the larger amount of  $d$  electrons transfer from the  $B$  site into bonding orbitals on the  $A$  site, the larger will be the stability of the compound, i.e.,  $\Delta G$  is more negative. The same situation would lead also to a less negative  $g$  shift. Indeed we can show the existence of some correlation between  $\Delta G$  and  $\Delta g$  as follows: The heat of formation of the compound LaRu<sub>2</sub> and LaRh<sub>2</sub> was extracted recently<sup>20</sup> from thermodynamic study of the corresponding hydrides. (The heat of formation of the hydrides was measured and by using the "rule of reverse stability" of Miedema,<sup>21</sup> the heat of formation of the parents compound LaRu<sub>2</sub> and LaRh<sub>2</sub> could be estimated<sup>20</sup>). It was found that the stability of LaRh<sub>2</sub> is much higher with respect to that of LaRu<sub>2</sub> [i.e.,  $|\Delta G(\text{LaRu}_2)| > |\Delta G(\text{LaRh}_2)|$ ]. This indicates a larger charge transfer of  $d$  electrons into bonding orbitals on the  $A$  site in LaRh<sub>2</sub>, and consequently smaller negative shift in this compound, as observed experimentally (Table IV). This idea of correlating  $\Delta G$  and  $\Delta g$  is presently being checked on other compounds.

(b) The hyperfine constants for <sup>143</sup>Nd and <sup>145</sup>Nd isotopes were extracted from the low temperature resolved spectra. We find the hyperfine constants to be always smaller in magnitude with respect to the insulator value. This is in contrast to the situation in the second half of the rare-earth series, where the magnitude of the hyperfine constant for Er<sup>3+</sup>, Dy<sup>3+</sup>, and Yb<sup>3+</sup> is always larger than those in insulators.<sup>16,8</sup> We argue that this is probably due to electrons of  $6s$  character<sup>16,8</sup> and the sign reversal of  $\Delta A$  reflects the sign reversal of  $g_j - 1$  in the second half with respect to the first half of the rare-earth series.<sup>8</sup>

(c) The fit of the high-temperature ESR linewidth of Nd in LaIr<sub>2</sub> and LaRh<sub>2</sub> with combined Orbach and Hirst processes, enables us to extract the energy of the first excited  $\Gamma_8$  level of Nd<sup>3+</sup> in LaIr<sub>2</sub> and LaRh<sub>2</sub> to be  $\Delta = 90 \pm 20$  K. The strength of the orbit-lattice coupling is twice as large for LaIr<sub>2</sub>:Nd than for LaRh<sub>2</sub>:Nd. The Debye temperature  $\Theta_D$  of the transition-metal intermetallic compounds LaPt<sub>2</sub>, LaRu<sub>2</sub>, and CeRh<sub>2</sub> have been measured by Joseph *et al.*<sup>22</sup> Surprising low values for  $\Theta_D$  between 150 and 250 K were observed. Following the procedure suggested by these authors, we have estimated the value of  $\Theta_D$  for our compounds to be roughly in the same temperature range. Thus, we believe that the possibility of a relatively small  $\Theta_D$  (but not too small such that the inequality  $\Theta_D > \Delta$  is satisfied) may be the reason for the large phonon effect found in our materials.

(d) Recently Gambke *et al.*<sup>23</sup> have argued that interconfigurational fluctuations act to reduce the relaxation rate of impurities. As an evidence they have shown that the Gd relaxation rate in the interconfi-

guration fluctuation host CePd<sub>3</sub> is three times smaller than in the isostructural host YPd<sub>3</sub>. There is some evidence that the compounds CeRh<sub>2</sub> and CeIr<sub>2</sub> are intermediate valence compounds.<sup>24</sup> If these compounds also exhibit interconfiguration fluctuations, then probably the very large thermal broadening observed (see Table III) is associated with coupling between the rare-earth impurity and the host fluctuating configuration. This would be contrary to the prediction of Gambke.<sup>23</sup> Work on CeRh<sub>2</sub> and CeIr<sub>2</sub> is underway to find out if these are interconfiguration fluctuation compounds.

(e) Finally, it is difficult to demonstrate a systematic variation in the value of  $b$  across the group VIII of the Periodic Table. This is because in any calculation of the Korringa relaxation rate, one has to take into consideration the enhancement factors as well as the degeneracy of the  $d$  electrons at the Fermi level.<sup>1,5</sup> These factors are different for the different

types of electrons, a fact which further complicates any analysis. It is interesting to note, however, that the values of  $b_{Nd}$  and  $b_{Gd}$  yield a very large exchange ratio,  $\langle J^2 \rangle_{Nd} / \langle J^2 \rangle_{Gd}$ , (see Table IV) for all the samples studied, in a framework of a single-band model. This large exchange ratio is consistent with the large exchange ratio as extracted from the depression of the superconducting transition temperature of LaAl<sub>2</sub>, by alloying with Nd and Gd ions.<sup>25</sup>

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