# Effect of local environment on the magnetic state of cerium in $(Ce_{1-c}Gd_c)Rh_2$

M. S. Kariapper and A. Tari

Department of Physics, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia (Received 19 March 1990)

We have investigated the cubic Laves-phase compounds  $(Ce_{1-c}Gd_c)Rh_2$  across the entire concentration range by means of magnetic measurements and lattice-parameter studies. The magnetic data show that only those cerium atoms having at least three nearest-neighbor gadolinium atoms are magnetic and in the ordered state they couple antiparallel to the gadolinium sublattice. With use of the Ruderman-Kittel-Kasuya-Yosida model and the lattice-parameter data, a value of 0.58 eV is obtained for the effective exchange integral. The x-ray data do not show the change of valency for cerium across the series.

#### I. INTRODUCTION

The  $RRh_2$  compounds, where R is a rare earth, have received little attention. They crystallize in the cubic Laves phase and order ferromagnetically with low Curie temperatures except for LaRh<sub>2</sub>, YRh<sub>2</sub>, and CeRh<sub>2</sub>, which are not magnetic.

Of the  $RRh_2$  compounds,  $EuRh_2$  and  $CeRh_2$  are in the class of so-called intermediate-valence compounds.  $EuRh_2$  and the pseudobinary compounds  $Eu(Rh_{1-c}Pt_c)$  and  $(Eu_{1-c}La_c)Rh_2$  were investigated more than a decade ago by Bauminger and co-workers<sup>1,2</sup> and Novik *et al.*<sup>3</sup> by use of the Mössbauer effect and x-ray photoemission spectroscopy, respectively, because of the intermediate-valence state of Eu. These studies and the work of Wortmann *et al.*<sup>4</sup> on  $(Eu_{0.25}La_{0.75})Rh_2$  showed that in these pseudobinary compounds the valency of Eu depends strongly on its local environment.

Ce is in an intermediate-valence state in a number of intermetallic compounds.<sup>5</sup> This is the result of the hybridization or mixing between the conduction electrons of the host and the 4f electrons of Ce,<sup>6,7</sup> and the difference in the properties of these compounds is closely related to the strength of this mixing. The hybridization is expected to be strong in compounds with a high density of the *d* electrons. Indeed, this appears to be the case.<sup>6</sup>

Recent  $L_{\rm III}$  experiments carried out by Wohlleben and Rohler<sup>8</sup> and Mihalisin *et al.*<sup>9</sup> put the valency of Ce in CeRh<sub>2</sub> at between 3.13 and 3.21. From their hightemperature susceptibility data, Weidner *et al.*<sup>5</sup> put an upper limit of 3.4 for the valency of Ce in CeRh<sub>2</sub> at T = 1200 K.

Harrus and co-workers<sup>10,11</sup> investigated the change in the valency of Ce in (Ce, R)Rh<sub>2</sub>, R = La, Y, and Ce(Rh<sub>1-c</sub>Pt<sub>c</sub>)<sub>2</sub> by means of susceptibility, specific heat, resistivity, and lattice-spacing measurements. They found that the substitution of Y for Ce in CeRh<sub>2</sub> decreases the valency of cerium, contrary to the expectation that Y with a smaller ionic radius should lower spacing and thereby lead to the lattice pressure on Ce and, hence, cause an increase in its valency. However, they found  $(Ce, Y)Rh_2$  to behave much the same as  $(Ce, La)Rh_2$ , although La has a considerably larger ionic radius and, hence, does not cause any lattice pressure on cerium. Their work, therefore, supports the view that lattice-pressure effects are not always the dominant factor in determining the valency of cerium in the intermetallic compounds.

The series  $(Ce_{1-c}Gd_c)Rh_2$  is expected to be interesting. The effects of the substitution of Gd for Ce are many. On the one hand, this substitution is expected to, somewhat, increase the lattice pressure on cerium and thereby drive it toward Ce<sup>4+</sup>, since in its behavior CeRh<sub>2</sub> resembles  $\alpha$ -Ce.<sup>12</sup> On the other hand, the strong exchange field produced by gadolinium should drive the cerium atoms toward a  $Ce^{3+}$  state. This, however, should lead to a situation where the effect of the local environment on cerium should be important. Furthermore, gadolinium is an S-state ion and is, therefore, free from the complications of crystal-field effects. The value of its moment, both in the ordered state and in the paramagnetic phase, is known sufficiently accurately. It is thus possible to obtain the value of the cerium moment in this series when and if it becomes magnetic.

We have, therefore, been investigating the series  $(Ce_{1-c}Gd_c)Rh_2$  over the entire concentration range by means of (i) x-ray scattering, (ii) magnetic measurement, (iii) electron-spin resonance, (iv) nuclear magnetic resonance of <sup>165</sup>Ho at the gadolinium-rich end of the series as a dilute substitutional impurity, and (v) specific-heat measurements. In this paper we report the results of the magnetic measurements and the lattice-spacing studies.

## II. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES

Eight samples of  $(Ce_{1-c}Gd_c)Rh_2$  with c = 0.01, 0.03, 0.10, 0.15, 0.30, 0.45, 0.60, and 0.80 were made and investigated. A further three samples were prepared, but only their saturation magnetizations are included in this paper.

The samples were made by melting together the

stoichiometric amount of 99.99%-pure rare earths and 99.9%-pure rhodium in a cold-crucible induction furnace at the Laboratoire Louis Néel, Grenoble, France. The sample with c = 0.45 and those with  $c \ge 0.80$ , however, were made in an argon arc furnace. All the samples were melted and remelted a minimum of four times under a high-purity argon atmosphere for good homogeneity. There was practically no weight loss during the melts.

The samples were heat treated at 800 °C for 3 days under an argon pressure of  $P \le 10^{-7}$  Torr. The cubic Laves structure of the compounds was confirmed, and the lattice parameters were determined to a precision of  $\le 0.003$  Å by the conventional x-ray diffractometry using the Nelson-Riley method.

Magnetization measurements were made at various temperatures between 2 and 300 K and in fields of up to 50 kOe, using a vibrating-sample magnetometer. The temperature measurements were made using a GaAs diode for temperatures between 2 and 60 K and a copper-Constantan thermocouple for the temperature interval 30-300 K. The "Curie temperatures" of the samples with c = 0.03 and 0.10 were obtained from the graph of magnetization squared  $M^2$  against (H/M), the socalled Arrott plots, and of the remaining samples from the inflection points of the low fields (H=0.2 kOe)magnetization-versus-temperature graphs. The saturation magnetizations were obtained from the usual extrapolation procedure using the high-field data.

#### **III. RESULTS AND DISCUSSION**

The variation of the magnetization with temperature for the compounds with c = 0.30, 0.45, 0.60, and 0.80 are



FIG. 1. Variation of the magnetization with temperature for the compounds with  $(\nabla, \mathbf{\nabla})c=0.3$ ,  $(\triangle, \mathbf{\Delta}) c=0.45$ ,  $(\Box, \mathbf{\Box}) c=0.6$ , and  $(\bigcirc, \mathbf{\Theta}) c=0.8$ . The open and solid data points correspond to H=0.2 and 2 kOe, respectively.

shown in Fig. 1 for two magnetic field values, namely, H = 0.2 and 2 kOe. As the figure shows, the behavior of the compounds with c = 0.45 and 0.60 is different from those with c = 0.30 and 0.80. The effect of the 2-kOe field on the former two compounds is guite pronounced. The reasonably sharp transitions observed in the low-field *M*-*T* graphs are almost completely wiped out by the field. It is also clear from the figure that the Curie temperatures of all four compounds are somewhat reduced by the 2-kOe field. We attribute the behavior of the samples with 0.3 < c < 0..8 to the distribution of cerium atoms with a different valent state in these compounds. As will be shown presently, in the region c < 0.3 the number of magnetic cerium atoms is, on average, less than 5% of their total number. In this region, therefore, the magnetic properties of the samples are dominated by the gadolinium ions with their much larger moment. A similar situation exists for the region  $c \ge 0.8$ , where the compounds are highly concentrated in gadolinium. In the concentration interval 0.3 < c < 0.8, however, an important fraction of the cerium atoms are magnetic, and different valent cerium atoms are distributed randomly. The compounds in this concentration region, therefore, behave like an inhomogeneous alloy with a distribution of the ordering temperatures and, hence, cannot display a sharp transition at their ordering temperatures.

The anisotropy of the compounds in this series is weak. The magnetization of all the samples approaches saturation at about 5 kOe. This is due to the fact that at the cerium-rich end of the series few of the cerium atoms are magnetic, while at the gadolinium-rich end there are too few magnetic cerium atoms to contribute to the magnetocrystalline anisotropy. Gd being an S-state ion does not contribute to the anisotropy to any significant degree.

The inverse susceptibilities  $\chi^{-1}$  of the three most dilute samples are plotted against temperature in Fig. 2. It is seen that for the two most dilute samples the inverse susceptibility  $\chi^{-1}$  decreases (and hence  $\chi$  increases) rapidly below about 100 K. Above this temperature  $\chi^{-1}$  varies linearly with temperature. A simple computation shows that the susceptibility of gadolinium, assumed to follow



FIG. 2. Temperature variation of the inverse susceptibility  $\chi^{-1}$  for the compounds with ( $\bigcirc$ ) c = 0.01, ( $\blacktriangle$ ) c = 0.03, and ( $\bigcirc$ ) c = 0.10.

4395

the Curie law, gradually dominates the host CeRh<sub>2</sub> susceptibility below 100 K. This situation leads to a large negative, apparent, asymptotic temperature  $\Theta$ , which, however, is not the true paramagnetic Curie temperature  $\Theta_p$ , in the sense that it does not reflect the magnitude of the interaction between the magnetic ions. The thermal variation of the inverse susceptibility of the samples with  $c \ge 0.10$  is typical of the remaining compounds. It intercepts the temperature axis on the positive side and varies linearly with temperature.

In Fig. 3 the variation of  $T_c$  and  $\Theta_p$  against c is plotted.  $\Theta_p$  passes through zero at about c = 0.08. The variation of  $T_c$  with c is linear up to about c = 0.15. Above this concentration it rises rapidly, the rate of increase being the largest at about c = 0.30.

Figure 4 shows the variation of the experimentally determined average molar Curie constant  $\overline{C}_m$  and the effective moment  $\mu_{\text{eff}}$ /f.u. against c (f.u. indicates formula unit). The Curie constants, and hence  $\mu_{\text{eff}}$ , were determined for each compound from the graph of the inverse differential susceptibility  $\chi^{-1}$  against temperature. As the figure shows, the experimental values of  $\overline{C}_m$  fall below the straight line representing the average of  $C_m = 8$  emu/mol for Gd<sup>3+</sup> and  $C_m = 0.8$  emu/mol for Ce<sup>3+</sup>. This clearly shows that in this series not all the cerium atoms are magnetic; i.e., they are not all in the Ce<sup>3+</sup> state even when the gadolinium concentration reaches 80%.

The variation of the effective moment  $\mu_{\text{eff}}$  with c is linear for  $c \ge 0.30$  and extrapolates to  $\mu_{\text{eff}}=2.5\mu_B/\text{f.u.}$ , the value of the effective moment for  $\text{Ce}^{3+}$ , as  $c \rightarrow 0$ .



FIG. 3. Variation of  $T_c$  and  $\theta_p$  with gadolinium content.



FIG. 4. Change of the average molar Curie constant  $\overline{C}_m(\bullet)$  and of the effective moment  $\mu_{\text{eff}}/\text{f.u.}(\circ)$  with godolinium concentration.

This is difficult to reconcile with the deficiency in  $\overline{C}_m$  discussed immediately above as it implies that above c = 0.30 all the Ce atoms are in the Ce<sup>3+</sup> state. It is clear, however, that the experimental value of  $\mu_{\text{eff}}$  goes to zero as one approaches the CeRh<sub>2</sub> end of the series.

It is found by Murae and Matsubara<sup>13</sup> that the crystalline-electric-field ground state of Ce in La-based compounds is represented by an effective moment  $\mu_{\text{eff}} = g'[S(S+1)]^{1/2} = 1.24\mu_B$ , where g' = 1.43 and  $S = \frac{1}{2}$  are the modified Landé factor and the effective spin, respectively, for Ce in these compounds. This may be the reason for the large deficiency in  $\overline{C}_m$  close to the gadolinium-rich end of the series.

In Fig. 5 the variation of the saturation magnetization per formula unit,  $\mu$  against c, is shown. The solid line in this figure represents the magnetization of gadolinium alone, i.e., assuming that Ce is not magnetic. The experimental points deviate from this line around c = 0.30, implying that above this concentration the cerium atoms become magnetic and align antiparallel to gadolinium atoms. This deviation is largest in the interval



FIG. 5. Variation of the saturation magnetization  $\mu$  per formula unit with godolinium concentration.

0.3 < c < 0.80. Above c = 0.80 the experimental points approach the straight line. Here the concentration of Ce is very low and all the cerium atoms are not yet magnetic as will be discussed presently. This deviation, therefore, gradually becomes less and eventually disappears on reaching the GdRh<sub>2</sub> end as expected.

The effect of the local environment in this series is important as one would expect from such a system. This is displayed clearly in Fig. 6, where  $P_N(n,c)$ , the probability that a given cerium atom will have n = 2, 3, or 4 nearest-neighbor Gd atoms out of a total of 4 nearest-neighbor R atoms, is plotted against c. Also plotted in this graph is the variation of the experimentally determined reduced moment,  $\overline{\mu} = \mu/\mu_0$  ( $\mu_0 = 2.14\mu_B$  for Ce<sup>3+</sup>), against c. As the figure shows, n = 3 gives the best fit, and the choice is unique. This explains why the experimental values of  $\mu$ ,  $\mu_{\text{eff}}$ , and  $\overline{C}_m$  fall below the straight lines as discussed above.

Except for the saturation magnetization and the lattice-parameter determination, the compounds with c > 0.80 were not investigated, and the reduced magnetization of Ce in these compounds is not computed and, hence, is not shown in Fig. 6 for the following reasons: (i) The uncertainty in  $\mu$  is given by  $\Delta \overline{\mu} = A \Delta \mu$ , where  $A = [2.14(1-c)]^{-1}$ . Therefore, as  $c \rightarrow 0$ ,  $A \rightarrow \infty$ , and hence the uncertainty in  $\overline{\mu}$  becomes very large for a very small uncertainty in the saturation magnetization. (ii) These compounds contain 1 at % Ho, and the value of the Ho moment is not known accurately in these compounds. For instance, an uncertainty of 0.01 in the Ho moment will introduce an uncertainty of 0.16 in the reduced moment  $\overline{\mu}$  for the compound containing 97 at. % Gd.



FIG. 6. Change of the mean effective moment of cerium normalized to  $\mu_0 = 2.14\mu_B$  and of  $P_N(n,c)$  with the godolinium concentration.  $P_N(n,c)$  is the probability of finding *n* nearestneighbor Gd atoms to a given Ce atom out of a total N=4rare-earth atoms for a given concentration *c*.

The change of the lattice spacing  $a_0$  with c is shown in Fig. 7. Our values of  $a_0$  for CeRh<sub>2</sub> are in very good agreement with the values reported in the literature.<sup>9,14</sup> The dashed line is the variation expected if the valency of Ce were constant. It is clear from the figure that the change of  $a_0$  with C is approximately linear. This is surprising, since it implies that the valency of cerium remains the same on going from CeRh<sub>2</sub> to GdRh<sub>2</sub>, contrary to the conclusion reached above on the basis of the magnetic data. However, since the valency of cerium is close to 3 in CeRh<sub>2</sub> and the change in the lattice spacing is only 0.026 Å over the entire concentration range, it is hard to detect any variation with the precision of our xray facilities. Therefore, no firm conclusion can be drawn from the variation of lattice spacing in this series regarding the change in the valency of cerium.

In the Ruderman-Kittel-Kasuya-Yosida (RKKY) approximation the effective exchange integral,  $J(0)=J_0$ , between the conduction electrons and a localized spin is related to the lattice sum  $\sum_n F(2k_FR_n)$  via

$$J^{2}(0) = -\frac{k_{B}\theta_{p}E_{F}}{3\pi Z^{2}G\sum_{n}F(2k_{F}R_{n})}, \qquad (1)$$

where  $G = (g-1)^2 J (J+1)$  is the de Gennes factor,  $F(X) = X^{-4} (X \cos X - \sin X)$ , with  $X = 2k_F R_n$ , and  $R_n$  is the distance of a given rare earth to a chosen central ion. The summation in Eq. (1) is over all the local moment sites. Z in the above equation is the number of the effective conduction electrons per atom. The other terms have their usual meanings.

For the concentration range  $c \ge 0.6$ , we have computed the lattice sum  $\sum_{n} F(2k_FR_n)$  for various values of  $R_n$  in the interval 30 Å < R < 2000 Å and have found little difference in its variation with  $k_F$ .

From Eq. (1) it is seen that the sign of  $\theta_p$  depends on  $F(2k_FR_n)$ . In order that  $\theta_p$  be positive, the lattice sum must be negative. For our compounds this occurs in the interval 0.75 Å  $< k_F < 0.86$  Å, with a minimum at  $k_F = 0.80$  Å, which corresponds approximately to one



FIG. 7. Variation of the lattice constant across  $CeRh_2$ -GdRh<sub>2</sub>. The dashed line is the result expected if the valence of Ce were constant. The data point for GdRh<sub>2</sub> is from Ref. 14.

electron per formula unit, and 1.23 Å  $< k_F < 1.64$  Å, with a minimum at  $k_F = 1.38$  Å, corresponding to approximately five electrons per formula unit. This last would be the case if each Gd and Rh atom contributed three electrons and one, respectively, to the conduction band.

In their detailed investigations of  ${}^{155,157}$ Gd in GdRh<sub>2</sub> and of  ${}^{139}$ La and  ${}^{155,157}$ Gd in the series (Gd<sub>1-c</sub>La<sub>c</sub>)Rh<sub>2</sub>, Dormann and co-workers<sup>15-18</sup> did not find clear evidence for holes in the 4*d* band of Rh.

From this and the fact that rhodium is much more electronegative than gadolinium, they asserted that of the three electrons released by each gadolinium into the conduction band, two are taken by its two rhodium partners to acquire the stable  $4d^{10}$  configuration. They concluded, therefore, that in GdRh<sub>2</sub> the effective number of conduction electrons per formula unit is one. This gives a  $k_F$  of 0.823 Å, corresponding to an  $E_F$  of 2.62 eV. Using this value of  $E_F$  in (1), we have obtained a value of |J(0)| = 0.58 eV. This is large, but is of the right order of magnitude. A reasonable value of J(0) in  $GdX_2$ , X = Rh, and Ir appears to be about 0.16 eV.<sup>7</sup> The main source of uncertainty in the computation of J(0) is the value of Z. If we set Z = 1, i.e., if we assume three conduction electrons per formula unit, then the value of |J(0)| is computed to be 0.19 eV.

We have also computed  $\overline{J}(0)$ , the average exchange integral for the compounds with c > 0.6 using the concentration-weighted de Gennes factor  $\overline{G}(c)$  for Gd and the magnetic Ce atoms:

$$\overline{G}(c) = cG_{\rm Gd} + (1-c)G_{\rm Ce}[P(3,c) + P(4,c)] .$$
(2)

The value of |J(0)| thus computed appears to remain al-

- <sup>1</sup>E. R. Bauminger, I. Felner, D. Froindlich, D. Levron, I. Novik, S. Offer, and R. Yanewski, J. Phys. (Paris) Colloq. 35, C6-61 (1974).
- <sup>2</sup>E. R. Bauminger, I. Felner, D. Levron, I. Nowik, and S. Ofer, Solid State Commun. **18**, 1073 (1976); Phys. Rev. Lett. **33**, 890 (1974).
- <sup>3</sup>I. Nowik, M. Campagna, and G. K. Wertheim, Phys. Rev. Lett. **38**, 43 (1977).
- <sup>4</sup>G. Wortmann, J. Moser, and U. F. Klein, Phys. Lett. **55A**, 486 (1976).
- <sup>5</sup>P. Weidner, B. Wittershagen, B. Roden, and D. Wohlleben, Solid State Commun. **48**, 915 (1983).
- <sup>6</sup>A. Yanase, J. Magn. Magn. Mater. 52, 403 (1985).
- <sup>7</sup>D. Gunnarsson, N. E. Christensen, and O. K. Andersen, J. Magn. Magn. Mater. 76-77, 30 (1988).
- <sup>8</sup>D. Wohlleben and J. Rohler, J. Appl. Phys. 55, 1904 (1984).
- <sup>9</sup>T. Mihalisin, A. Harrus, S. Raaen, and R. D. Parks, J. Appl. Phys. 55, 1966 (1984).
- <sup>10</sup>A. Harrus, T. Mihalisin, and B. Batlogg, J. Appl. Phys. 55,

most constant. This is surprising, since one expects a weakening of the exchange interaction with the increasing number of nonmagnetic cerium atoms and the increased negative contribution due to the Anderson mixing term from the magnetic cerium atoms.

## **IV. SUMMARY AND CONCLUSION**

We conclude that in the series  $(Ce_{1-c}Gd_c)Rh_2$  the valence state of cerium depends on the number of its nearest-neighbor gadolinium ions. Cerium atoms become magnetic only when they posses at least three nearest-neighbor gadolinium atoms. At c = 0.3 the cerium, sub-lattice reaches the magnetic percolation limit whereby a continuous chain of magnetic nearest-neighbor cerium atoms is established throughout the sample. The effective exchange integral in this series is computed using the RKKY model and the lattice spacings, and is found to be  $\approx 0.58$  eV for  $c \geq 0.6$ .

### ACKNOWLEDGMENTS

The authors gratefully acknowledge support of the KFUPM. We thank Dr. R. Lemaire and Dr. D. Guignoux of the Laboratoire Louis Néel, Grenoble, France, for access to their sample preparation facilities and Professor E. Dormann for a private communication regarding the effective number of conduction electrons in  $GdRh_2$ . We also thank Dr. N. M. Abbas of the Research Institute, King Fahd University of Petroleum and Minerals for access to the x-ray facilities and Dr. R. P. Khatri for obtaining the x-ray spectra of our samples.

1993 (1984).

- <sup>11</sup>A. Harrus, T. Mihalisin, and E. Kemly, J. Magn. Magn. Mater. 47&48, 93 (1985).
- <sup>12</sup>R. Mock, B. Hillebrands, H. Schmidt, G. Guntherodt, Z. Fisk, and A. Mayer, J. Magn. Magn. Mater. 47&48, 312 (1985).
- <sup>13</sup>T. Murae and T. Matsubara, Prog. Theor. Phys. Osaka 18, 215 (1957).
- <sup>14</sup>A. Iandelli and A. Palenzona, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneider, Jr. and L. Eyring (North-Holland, Amsterdam, 1979), Chap. 13.
- <sup>15</sup>E. Dormann, J. Magn. Magn. Mater. 6, 87 (1977).
- <sup>16</sup>D. Dressel, U. Meister, E. Dormann, and K. H. J. Buschow, J. Magn. Magn. Mater. 74, 91 (1988).
- <sup>17</sup>E. Dorman, M. Huck, and K. H. J. Buschow, J. Magn. Magn. Mater. 4, 47 (1977).
- <sup>18</sup>E. Dormann and K. H. J. Buschow, Phys. Status Solidi B 59, 411 (1973).