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### Title

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Exchange and crystal field effects in the ESR spectra of  $\text{Eu}^{2+}$  in  $\text{LaB}_6$ J. G. S. Duque,<sup>1</sup> R. R. Urbano,<sup>1,2</sup> P. A. Venegas,<sup>3</sup> P. G. Pagliuso,<sup>1</sup> C. Rettori,<sup>1</sup> Z. Fisk,<sup>4</sup> and S. B. Oseroff<sup>5</sup><sup>1</sup>Instituto de Física "Gleb Wataghin," UNICAMP, 13083-970 Campinas, SP, Brazil<sup>2</sup>Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA<sup>3</sup>Departamento de Física, Universidade Estadual Paulista-Unesp, Caixa Postal 473, 17033-360 Bauru, SP, Brazil<sup>4</sup>Department of Physics, University of California, Irvine, California 92697-4575, USA<sup>5</sup>San Diego State University, San Diego, California 92182, USA

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Electron spin resonance of  $\text{Eu}^{2+}$  ( $4f^7$ ,  $S=7/2$ ) in a La hexaboride ( $\text{LaB}_6$ ) single crystal shows a single anisotropic Dysonian resonance. From the observed negative  $g$  shift of the resonance, it is inferred that the  $\text{Eu}^{2+}$  ions are covalent exchange coupled to the B  $2p$ -like host conduction electrons. From the anisotropy of the spectra (linewidth and field for resonance), we found that the  $S$  ground state of  $\text{Eu}^{2+}$  ions experience a cubic crystal field of a *negative* fourth order crystal field parameter (CFP),  $b_4 = -11.5(2.0)$  Oe, in agreement with the negative fourth order CFP,  $A_4$ , found for the non- $S$  ground state  $R$  hexaborides. These results support covalency as the dominant contribution to the fourth order CFP for the whole  $R$  hexaboride family.

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## I. INTRODUCTION

The cubic hexaboride compounds  $\text{RB}_6$  ( $R$ =rare/alkaline earths) have been the subject of intense experimental and theoretical studies in the last decades. This is due to their variety of interesting physical properties such as magnetic ordering, weak ferromagnetism, metal-insulator transition, magnetic polarons, negative magnetoresistance, quadrupolar ordering, Jahn-Teller effect, superconductivity, heavy fermion, fluctuating valence, and Kondo lattice behavior.<sup>1-10</sup> Particularly,  $\text{LaB}_6$  is a stable and hard metal characterized by strong covalent bonds, which is used as a wavelength standard in high resolution x-ray powder diffraction and due to its very low work function,  $\sim 2.7$  eV, as electron emitters.<sup>11-13</sup> Besides, for  $\text{La}_{1-x}\text{R}_x\text{B}_6$  with  $R=\text{Gd}$  and  $\text{Ce}$ , spin-glass and Kondo behaviors were, respectively, reported.<sup>14,15</sup>

Crystal field (CF) effects are known to affect the properties of the hexaborides. For the non- $S$  ground state  $R$  (Ce, Nd, and Pr), low- $T$  anomalies, due to the CF splitting of the ground state multiplet, were observed in various experiments.<sup>16-21</sup> There is now a consensus that all non- $S$  ground state  $R$  hexaborides present a *negative* fourth order crystal field parameter (CFP)  $A_4 < 0$ .<sup>16-21</sup> Also, the experimental results in dilute  $(\text{La}, \text{Sm}, \text{Ca}, \text{Ba}, \text{Yb})_{1-x}\text{R}_x\text{B}_6$  ( $R=\text{Pr}, \text{Er}, \text{Dy}$ ) are consistent with a negative  $A_4$ .<sup>17,22-25</sup>

In this work, we report electron spin resonance (ESR) experiments of  $\text{Eu}^{2+}$  ( $S$  ground state) ions diluted in the metallic hexaboride of  $\text{LaB}_6$ . It is generally observed that for  $\text{Eu}^{2+}$  and  $\text{Gd}^{3+}$  ions diluted in any cubic metallic/semimetallic/semiconducting/insulating hosts, the fourth order CFP,  $b_4$ , for both ions, is either *positive*<sup>26-28</sup> or *negative*,<sup>23,29-31</sup> with different absolute values but always with the same sign. It is then expected that the CF acts in the same manner on the  $S$  ground state of  $\text{Eu}^{2+}$  and  $\text{Gd}^{3+}$  ( $4f^7$ ;  $S=7/2$ ) ions in  $\text{LaB}_6$ . Surprisingly, the analysis of our ESR data allows us to conclude that the  $b_4$  parameter of  $\text{Eu}^{2+}$  in  $\text{LaB}_6$  is negative, the same sign as that of  $A_4$  for non- $S$   $\text{RB}_6$ , in contrast to the positive value reported by Luft *et al.*, for

$\text{Gd}^{3+}$  in the same compound of  $\text{LaB}_6$ .<sup>32</sup> This discrepancy is addressed in this paper. Moreover, it is also a general observation that  $b_4$  is positive in metallic hosts and negative in insulators.<sup>26,33-37</sup> To the best of our knowledge, our finding of  $b_4 < 0$  for  $\text{Eu}^{2+}$  in  $\text{LaB}_6$  represents a negative value for  $b_4$  measured in a metallic host. Although many experimental and theoretical efforts were done trying to correlate the origin of the fourth order CFP  $b_4$  ( $R$  in a  $S$  ground state) with that of the  $A_4$  ( $R$  in a non- $S$  ground state), a comprehensive understanding of the dominant contributions to the  $b_4$  parameter has not been achieved yet.<sup>33-36</sup> Thus, the  $R$  hexaborides form an interesting family of insulating, semiconducting, semimetallic, and metallic systems where the CF effects can be studied. Besides, from our ESR results, we conclude that the  $\text{Eu}^{2+}$  and  $\text{Gd}^{3+}$  ions, via an exchange interaction, probe different types of conduction electrons at the Fermi level of  $\text{LaB}_6$ .

## II. EXPERIMENT

Single crystals of  $\text{LaB}_6$  were grown as described in Ref. 3. The cubic structure (space group 221,  $Pm\bar{3}m$ , CsCl type) and phase purity were checked by x-ray powder diffraction and the crystal orientation determined by Laue x-ray diffraction. The ESR spectra were taken in  $\sim 1 \times 1 \times 0.5$  mm<sup>3</sup> single crystals in a Bruker X-band (9.48 GHz) and  $Q$ -band (34.4 GHz) spectrometers, using appropriated resonators coupled to a  $T$  controller of a helium gas flux system for  $4.2 \leq T \leq 300$  K. The Eu concentration was obtained by fitting the susceptibility data to a Curie-Weiss law assuming  $\mu_{\text{eff}} = 7.94 \mu_B$  for the  $\text{Eu}^{2+}$  ions. Magnetization  $M(T, H)$  measurements for  $2 \leq T \leq 300$  K were taken in a Quantum Design Magnetic Properties Measurement System superconducting quantum interference device dc magnetometer.

## III. EXPERIMENTAL RESULTS

Figures 1(a) and 1(b) show, respectively, the low- $T$  ESR spectra for 2200 ppm of Eu in  $\text{LaB}_6$  at  $X$  and  $Q$  bands for the

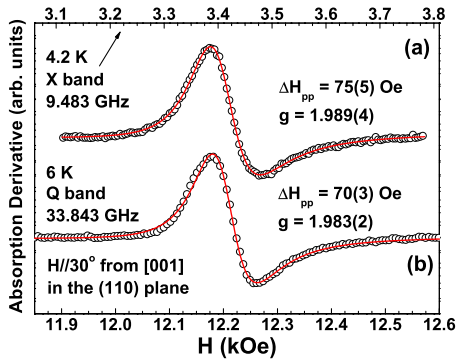


FIG. 1. (Color online) Low- $T$  ESR spectra of  $\text{Eu}^{2+}$  in a  $\text{La}_{1-x}\text{Eu}_x\text{B}_6$  ( $x=0.0022$ ) single crystal for  $H \parallel 30^\circ$  from  $[001]$  in the  $(110)$  plane: (a)  $X$  band and (b)  $Q$  band. The solid lines are the Dyson line shape analysis.

magnetic field  $H \parallel 30^\circ$  from the  $[001]$  direction when  $H$  is rotated in the  $(110)$  plane. In all our experiments, the ESR spectra showed a single resonance of Dysonian [*metallic*,  $A/B \cong 2.24(5)$ ] shape.<sup>38</sup> Within the accuracy of the measurements and for this orientation, approximately the same linewidths ( $\Delta H_{pp} \cong 72(5)$  Oe) are obtained by both frequencies. This is consistent with a negligible residual inhomogeneous broadening of the resonance. The measured  $g$  value indicates that there is a negative  $g$  shift [ $\Delta g = -0.009(2)$ ] relative to that in insulators ( $g = 1.993$ ), in contrast to the positive  $g$  shift found for  $\text{Gd}^{3+}$  in  $\text{LaB}_6$ .<sup>32</sup>

Figures 2(a) and 2(b) display the  $T$  dependence of the linewidth (peak to peak of the pure absorption),  $\Delta H_{pp}$ , and the  $g$  value of the resonance of Fig. 1(b), respectively. The thermal broadening of the linewidth can be fitted to a linear expression,  $\Delta H_{pp} = a + bT$ , with  $a = 63(5)$  Oe and  $b = 1.70(2)$  Oe/K. Similar results were obtained for the  $X$  band. Within the studied  $T$  interval and accuracy of the measurements, the  $g$  value was found to be  $T$  independent, indicating the absence of dynamic and/or interaction effects between the localized  $\text{Eu}^{2+}$  magnetic moments.<sup>39</sup>

Figures 3(a) and 3(b) show the  $Q$ -band angular dependence of the linewidth,  $\Delta H_{pp}$ , and field for resonance,  $H_r$ , at

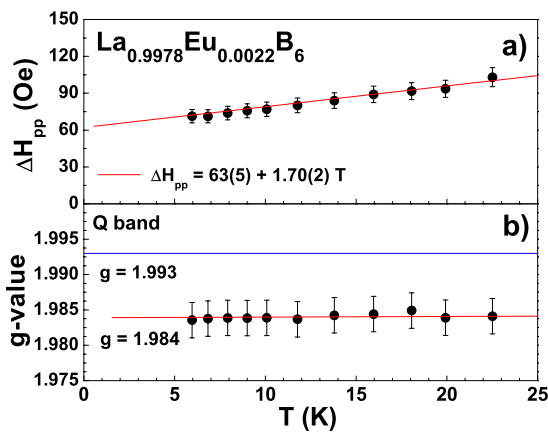


FIG. 2. (Color online)  $T$  dependence of the  $Q$ -band ESR for  $H \parallel 30^\circ$  (a) line width,  $\Delta H_{pp}$ , and (b)  $g$  value of  $\text{Eu}^{2+}$  in  $\text{La}_{1-x}\text{Eu}_x\text{B}_6$  ( $x=0.0022$ ) single crystal.

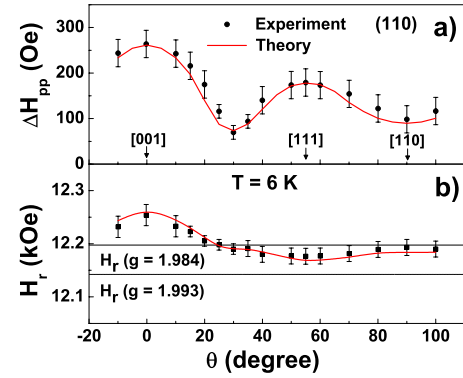


FIG. 3. (Color online) Angular dependence of the  $Q$ -band ESR (a) linewidth,  $\Delta H_{pp}(\theta)$ , and (b)  $H_r(\theta)$  for  $\text{La}_{1-x}\text{Eu}_x\text{B}_6$  ( $x=0.0022$ ) single crystal.  $H$  is rotated in the  $(110)$  plane.

$T=6$  K when  $H$  is rotated in the  $(110)$  plane, respectively. A strong anisotropic behavior for  $\Delta H_{pp}$  with a minimum for  $H$  at  $\theta \cong 30^\circ$  from the  $[001]$  direction is observed, while  $H_r$  showed a relatively small but still measurable anisotropy.

In Fig. 4, we show the angular dependence of the difference,  $\delta H = H_r(\theta) - H_0(\theta = 30^\circ)$ , between the resonance field,  $H_r(\theta)$ , and that corresponding to the minimum linewidth,  $H_0(\theta = 30^\circ) = 12,190(10)$  Oe [see Fig. 3(b)]. Although the error bars are large, it is still possible to see that the shift of the field for resonance,  $\delta H$ , changes sign around this angle, being  $\delta H > 0$  for  $\theta < 30^\circ$  and  $\delta H < 0$  for  $\theta > 30^\circ$ . The experimental and calculated (see below) spectra for  $\theta = 15^\circ$  and  $55^\circ$  are shown in the inset of Fig. 4.

## IV. ANALYSIS AND DISCUSSION

### A. Exchange field

Our results show that the  $\text{Eu}^{2+}$  resonance in  $\text{LaB}_6$  present a negative  $g$  shift [ $\Delta g = -0.009(2)$ ] in contrast to the positive  $g$  shift [ $\Delta g = 0.018(3)$ ] found for the  $\text{Gd}^{3+}$  ions in the same

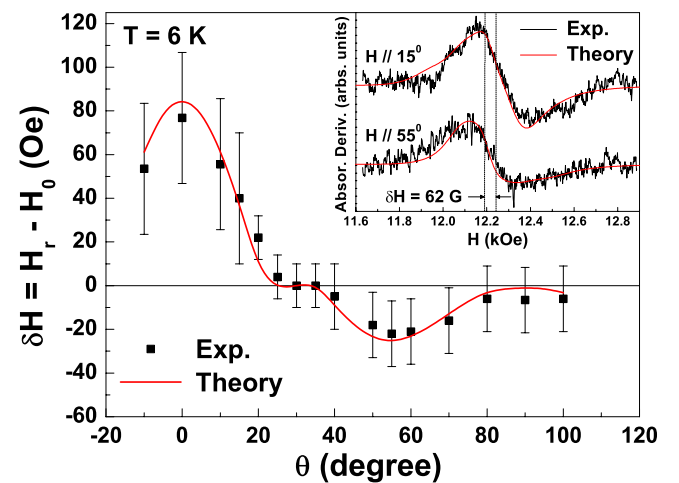


FIG. 4. (Color online)  $Q$ -band angular dependence of the  $\text{Eu}^{2+}$  resonance field shift,  $\delta H = H_r - H_0(\theta = 30^\circ)$ . Inset: experimental and calculated  $Q$ -band ESR spectra of  $\text{Eu}^{2+}$  in  $\text{La}_{1-x}\text{Eu}_x\text{B}_6$  ( $x=0.0022$ ) single crystal for  $H \parallel 15^\circ$  and  $55^\circ$  from the  $[001]$  direction in the  $(110)$  plane.

host.<sup>32</sup> The sign change in the  $g$  shift may be understood in terms of a two band model<sup>40</sup> involving the exchange interaction between the localized  $\text{Eu}^{2+}$  (and  $\text{Gd}^{3+}$ )  $4f^7$  electrons with the conduction: (i)  $R$   $5d$ -like electrons and (ii)  $B$   $2p$ -like electrons. The exchange interaction with the  $5d$ -like electrons is assumed to be of atomic type,  $J_{at}^e(q) > 0$ , and that with the  $B$   $2p$ -like electrons is of covalent origin,  $J_{cv}^h(q) < 0$ . Thus, the  $g$  shift can be written as

$$\Delta g = \Delta g_d + \Delta g_p = J_{at}^d(0) \eta_F^d + J_{cv}^p(0) \eta_F^p, \quad (1)$$

where  $J_{at}^d(0)$  and  $J_{cv}^p(0)$  are the  $q=0$  component (zero-conduction electron momentum transfer)<sup>41</sup> and  $\eta_F^d$  and  $\eta_F^p$  the local densities of states (states/eV mol spin) of  $d$  and  $p$  electrons at the Fermi level, respectively. Although both ions are in the same  $S$  ground state ( $4f^7$ ;  $S=7/2$ ), we argue that due to their different ionic charges, the local Coulomb repulsion on the  $5d$  conduction electrons of  $\text{LaB}_6$  will be stronger in the case of the  $\text{Eu}^{2+}$  ions. Thus, the  $J_{at}^d(0) \eta_F^d$  term may become dominant in the case of  $\text{Gd}^{3+}$  and negligible in the case of  $\text{Eu}^{2+}$ , leading to  $\Delta g \approx \Delta g_d = J_{at}^d(0) \eta_F^d$  and  $\Delta g \approx \Delta g_p = J_{cv}^p(0) \eta_F^p$  for  $\text{Gd}^{3+}$  and  $\text{Eu}^{2+}$  in  $\text{LaB}_6$ , respectively.

The linear thermal broadening of the homogeneous  $\Delta H_{pp}$  [see Fig. 2(a)] indicates that the spins of the  $\text{Eu}^{2+}$  ions relax to the lattice via an exchange coupling between the  $4f$  and conduction electrons (Korringa mechanism). Therefore, the so-called Korringa rate in the unbottleneck limit,  $\Delta H_{pp}/\Delta T$ ,<sup>39</sup> should be given by  $b = (\pi k_B / g \mu_B) \times [\langle J_{cv}^p(q) \rangle_F \eta_F^p]^2$ ;<sup>41</sup> the brackets indicate an average over the Fermi surface. Assuming that there is no  $q$  dependence of the exchange interaction, i.e.,  $J_{cv}^p(0) = \langle J_{cv}^p(q) \rangle_F$ , the Korringa rate becomes  $b = (\pi k_B / g \mu_B) [\Delta g_p]^2$ . Using the measured  $g$  shift for  $\text{Eu}^{2+}$ ,  $\Delta g_p = -0.009(2)$  [see Fig. 2(b)], and the involved constants, we find  $b \approx 1.9(4)$  Oe/K, in excellent agreement with the value measured experimentally. Hence, we conclude that the  $\text{Eu}^{2+}$  ions relax to the lattice basically via an exchange interaction with the  $B$   $2p$ -like electrons. Similar analysis of the data for the case of  $\text{Gd}^{3+}$  in  $\text{LaB}_6$  (Ref. 32) leads us to conclude that the  $\text{Gd}^{3+}$  ions relax to the lattice via an exchange interaction with the  $R$   $5d$ -like electrons. In this case, Luft *et al.*<sup>32</sup> have assumed that  $\eta_F^d$  may be approximated by the total density of state to be  $\eta_F^d \approx 0.50$  states/eV mol spin obtained from the electronic specific heat corrected by the electron-phonon mass enhancement of  $\text{LaB}_6$ . With that value, these authors have estimated an exchange parameter of  $J_{at}^d \approx 40(1)$  meV. However, band structure calculations suggest that the total density of states at the Fermi level is approximately equally distributed between the  $La$   $5d$ - and  $B$   $2p$ -like electrons.<sup>42</sup> Then, assuming that  $\eta_F^d = \eta_F^p \approx 0.25$  states/eV mol spin, we estimate from the experimental  $g$  shifts and Korringa rates values of  $J_{at}^d \approx 80(2)$  meV and  $J_{cv}^p \approx -34(3)$  meV for  $\text{Gd}^{3+}$  and  $\text{Eu}^{2+}$  in  $\text{LaB}_6$ , respectively. Note that in the analysis of the  $g$  shift, we used the density of states for  $\text{LaB}_6$  obtained by band structure calculation.<sup>42</sup> Moreover, we have assumed that the local density of  $d$  states at the  $\text{Eu}$  site is strongly perturbed by the Coulomb repulsion. Thus, in spite that the  $\text{Eu}$   $d$  levels will have different energies than those of the  $\text{La}$ , we argue that the negative  $g$  shift will not be much affected by it. Although

we are confident in the analysis of our data, in view of the assumptions made, the values for the exchange parameters have to be taken with care.

## B. Crystal field

The angular dependence displayed in Fig. 3(a) for  $\Delta H_{pp}$  shows that besides the homogeneous ESR linewidth,  $\Delta H_{pp}(\theta \cong 30^\circ)$ , there is a large contribution to  $\Delta H_{pp}$  from an intrinsic anisotropic inhomogeneous broadening, which reveals the presence of unresolved cubic CF effects. The minimum  $\Delta H_{pp}$  at  $\theta \cong 30^\circ$ , when  $H$  is rotated in the (110) plane, identifies the angle where the *fine structure* of the  $\text{Eu}^{2+}$  ( $4f^7$ ;  $S=7/2$ ) ESR spectra collapses ( $\theta = 29.7^\circ$ ).<sup>43</sup> It is now well established that diluted localized magnetic moments in metallic hosts relax to the lattice via an exchange interaction,  $H_{int} = J_{fs} \mathbf{S}_f \cdot \mathbf{s}_{ce}$ , between the localized spin  $\mathbf{S}_f$  and the host conduction electron spin  $\mathbf{s}_{ce}$  (Korringa mechanism).<sup>39</sup> This mechanism leads to the well known phenomenon of *exchange narrowing of the fine structure* and, as a function of  $\theta$  and  $T$ , generates a variety of ESR spectra.<sup>44,45</sup> We have used this exchange narrowing theory to compute the expected ESR spectra at different angles and temperatures.<sup>46,47</sup> Such calculation takes into account the following spin Hamiltonian:

$$H = g \mu_B \mathbf{H} \cdot \mathbf{S}_f + \frac{1}{60} b_4 (O_4^0 + 5O_4^4) + J_{fs} \mathbf{S}_f \cdot \mathbf{s}_{ce}, \quad (2)$$

where the first term is the Zeeman interaction, the second the fourth order cubic CF potential, and the third the exchange interaction between the localized magnetic moment and the conduction electrons. The sixth order term in the CF potential was not included because the sixth order CFP  $b_6$  is always smaller than one-tenth of  $b_4$  and, usually, the accuracy of the experiments does not allow one to measure reliable values of  $b_6$ .

To obtain the ESR absorption, the transverse dynamic susceptibility of the local magnetic moment coupled to the conduction electrons has to be calculated. The transverse dynamic susceptibility of the local magnetic moments can be calculated following Ref. 45. The model includes the interaction between local magnetic moments, conduction electrons, and CF. Within that model, the susceptibility is obtained using the projector formalism in the Liouville space. Our experiments are performed at concentrations where the conduction electron static susceptibility is much smaller than that of the local moments. In that limit the susceptibility for a system in the unbottleneck regime<sup>39,45,47</sup> is given by

$$\chi^+(\omega) \approx 1 - \omega_0 \left[ \sum_{M, M'} P_M(\Omega^{-1})_{M, M'} \right], \quad (3)$$

where  $\Omega_{M, M'}^{-1}$  is the transition matrix and the quantum numbers  $M$  and  $M'$  describe the various Zeeman states ( $M, M' = -S, -S+1, \dots, S-1$ ) associated with the  $S=7/2$   $\text{Eu}^{2+}$  spin. The transition probabilities associated with the  $M \leftrightarrow M+1$  transition can be written as

$$P_M = C_M \exp(M\hbar\omega_0/kT) \left/ \sum_{M'} C_{M'} \exp(M\hbar\omega_0/kT), \quad (4) \right.$$

where  $C_M = S(S+1) - M(M+1)$  and  $k$  is the Boltzmann constant. The elements of the transition matrix, for  $kT$  large compared to  $\hbar\omega_0$ , are expressed by

$$\Omega_{M,M'} = \left( \frac{\hbar\omega_0}{g\mu_B} - H - H_M \right) \delta_{M,M'} - ia\delta_{M,M'} - i\frac{1}{2}bTC_{M'}(2\delta_{M,M'} - \delta_{M,M'+1} - \delta_{M,M'-1}), \quad (5)$$

where  $\omega_0$  is the microwave frequency,  $H$  the external magnetic field,  $a=63(5)$  Oe the residual linewidth of the various fine structure lines,  $b=1.70(2)$  Oe/K the Korringa rate,  $\mu_B$  the Bohr magneton, and  $H_M$  the resonance field of the  $\text{Eu}^{2+} M \leftrightarrow M+1$  transition in a cubic lattice, which is given by

$$H_M = H_0 + \frac{1}{60}b_4p\langle M|(O_4^0 + 5O_4^4)|M\rangle, \quad (6)$$

where  $p$  is the angular dependence in a cubic environment<sup>47</sup> and the brackets are the matrix elements of the fourth order CF operator.

As we can see in Eq. (5), the transition matrix  $\Omega_{M,M'}$  is tridiagonal. The elements of the main diagonal contain the linewidth and resonance field of each resonance line. The upper and lower diagonal terms represent the fluctuation rates of the local moment between two consecutive resonance frequencies. Within the main diagonal, the linewidth that corresponds to the imaginary terms includes the residual linewidth of the various fine structure,  $a=63(5)$  Oe, and the Korringa rate  $b=1.70(2)$  Oe/K. The real part, related to the magnetic field, contains the magnetic field  $\hbar\omega_0/g\mu_B$  associated with the microwave frequency  $\omega_0$ , the external magnetic field  $H$ , and the fine structure resonance fields  $H_M$ .

The transition probabilities, with the appropriate Boltzmann population factors for each of the seven lines, are included in the calculation.<sup>43</sup> We have considered an additional degree of freedom in the calculation that allows for a Gaussian distribution of the  $b_4$  parameter ( $\langle b_4 \rangle, \sigma_{b_4}$ ). A distribution of  $b_4$  was considered previously by Hardiman *et al.*,<sup>48</sup> when studying Pt:Gd. The Gaussian distribution was symmetrically limited around  $\langle b_4 \rangle$  to span only on  $b_4$  values with the same sign of  $\langle b_4 \rangle$ . The solid lines shown in Figs. 3(a), 3(b), and 4 are the linewidth  $\Delta H_{pp}(\theta, T=6 \text{ K})$ , the field for resonance  $H_r(\theta, T=6 \text{ K})$ , and the shift of the field for resonance  $\delta H = H_r(\theta, T=6 \text{ K}) - H_0(\theta=30^\circ, T=6 \text{ K})$ , respectively. They were obtained after a Dyson analysis<sup>38</sup> of the computed ESR spectra for  $a=63(5)$  Oe,  $b=1.70(2)$  Oe/K, and  $A/B=2.24(5)$ . The best set of values for  $\langle b_4 \rangle$  and  $2\sigma_{b_4}$  obtained from  $\Delta H_{pp}(\theta, T=6 \text{ K})$  data is  $\langle b_4 \rangle = -12(1)$  Oe and  $2\sigma_{b_4} = 20(4)$  Oe, and for  $\delta H = H_r(\theta, T=6 \text{ K}) - H_0(\theta=30^\circ, T=6 \text{ K})$  data is  $\langle b_4 \rangle = -11(1)$  Oe and  $2\sigma_{b_4} = 20(4)$  Oe. Combining these results, we obtain  $\langle b_4 \rangle = -11.5(2.0)$  Oe and  $2\sigma_{b_4} = 20(4)$  Oe as the most probable set of values for the fourth order CFP and its standard deviation. The inset of Fig. 4 shows the observed experimental ESR spectra at  $T=6 \text{ K}$

for  $\theta=15^\circ$  and  $55^\circ$  and the solid lines correspond to our computed ESR spectra for the same angles and the ESR parameters found for  $\text{La}_{1-x}\text{Eu}_x\text{B}_6$ .

The negative value found for  $b_4$  in  $\text{LaB}_6$  is consistent with the negative value reported for this parameter in various  $R_{1-x}\text{Eu}_x\text{B}_6$  and  $R_{1-x}\text{Gd}_x\text{B}_6$  ( $R=\text{Ca}, \text{Sm}$ ).<sup>23,29-31</sup> Therefore, there is a disagreement with the positive value for  $b_4$  reported by Luft *et al.*,<sup>32</sup> in  $\text{La}_{1-x}\text{Gd}_x\text{B}_6$ . Using our method of calculation, including the exchange narrowing mechanism, we have reanalyzed their data for the angular dependence of the resonance  $\Delta H_{pp}(\theta, T)$  and shift,  $\delta H(\theta, T)$ , and we obtained  $\langle b_4 \rangle = -6(2)$  Oe and  $2\sigma_{b_4} = 6(2)$  Oe for  $\text{La}_{1-x}\text{Gd}_x\text{B}_6$ . Thus, their analysis in terms of the first moment of the resonance, which does not take into account the exchange narrowing mechanism, led them to a misleading conclusion. The fourth order CFP distribution found for  $R_{1-x}\text{Eu}_x\text{B}_6$  [ $2\sigma_{b_4} = 20(4)$  Oe] is larger than that found for  $R_{1-x}\text{Gd}_x\text{B}_6$  [ $2\sigma_{b_4} = 6(2)$ ]. That is presumably a consequence of the difference in ionic charge and size between  $\text{Eu}^{2+}$ ,  $\text{Gd}^{3+}$ , and  $\text{La}^{3+}$ , which may cause larger local lattice distortions at the  $\text{Eu}^{2+}$  site. In our case, the fitting shown in Fig. 4 does not come from the first moment, which is only valid in the extreme narrow regime. However, it is obtained using the field for resonance obtained by a Dyson line shape analysis of the calculated spectra, similar to the one used to fit the experimental spectra. It should be mentioned that Barnes<sup>44</sup> has developed a more complete and involved theory than Plefka.<sup>45</sup> To prove the validity of our analysis, using Plefka's approach, we compared the EPR spectra of Pt:Gd calculated with the Barnes theory,<sup>48</sup> with the one generated by Plefka, and the agreement between the spectra obtained by both theories is good. An eventual difference in the obtained parameters using both models does not compromise the main conclusion of our analysis. Thus, we conclude that the fit of the data of Luft *et al.*<sup>32</sup> using the first moment does not give the correct sign for  $b_4$ .

Most of the reported ESR data for  $\text{Eu}^{2+}$  and  $\text{Gd}^{3+}$  ( $S$  state) show that for any type of local cubic coordination (tetrahedral, octahedral, or simple cubic),  $b_4$  is positive in metallic hosts and negative in insulators and semiconductors.<sup>23,26,27,29-31,33-37,47,49</sup> Nonetheless, there are a few low carrier (semimetal/semiconducting) compounds where, still at the lowest  $T$ , no CF effects were detected. This may indicate that the maximum crystal field splitting ( $\sim 40 b_4$ ) of the ESR fine structure becomes smaller than the observed residual linewidth.<sup>51-54</sup> Possibly, this may be due to a subtle cancellation between the various contributions to  $b_4$ .<sup>34,56-58</sup> Hence, to the best of our knowledge, this paper reports a negative value of  $b_4$  for both  $\text{Eu}^{2+}$  and  $\text{Gd}^{3+}$  ( $S$  ground state) ions in a good metallic host.

Another interesting systematic observed in a few compounds of different local cubic coordinations is that the fourth order CFPs,  $b_4$  ( $S$  ground state) and  $A_4$  (non- $S$  ground state), carry the same sign. That is the case for the  $R$  hexaborides,<sup>14,16-21,23,31</sup> pnictides,<sup>22,50,51</sup> and fluorides,<sup>34</sup> where both  $A_4$  and  $b_4$  are negative, positive, and negative, respectively. However, in simple cubic metals such as Pd, Pt, and Au,<sup>34</sup> intermetallic compounds such as  $(\text{Y}, \text{Ce})\text{Pd}_3$  and  $\text{LaAl}_2$ ,<sup>34,59-61</sup> semiconductors such as  $\text{CeFe}_4\text{P}_{12}$  and

PbTe,<sup>37,49,55</sup> and insulators such as MgO (Ref. 34), that trend is not satisfied. Therefore, these results indicate that, differently from  $b_4$ ,  $A_4$  is more dependent on the type of local cubic coordination than on the metallicity of the material.

There has been already a number of efforts to explain the origin of the fourth order CFPs,  $b_4$  and  $A_4$ , and the correlation between them. Coles and Orbach<sup>56</sup> and Williams and Hirst,<sup>57</sup> long ago, have suggested that in metallic hosts, the presence of crystal field splitted  $5d$  conduction electron virtual bond state (VBS) may contribute to the screening of the ligand crystal field potential and may account for the sign of fourth order CFP,  $A_4$ . Chow has introduced the exchange interaction between the  $5f$  and the crystal field splitted  $5d$  VBS to account for the magnitude of the  $A_4$  parameter.<sup>58</sup> In addition to these Coulombic contributions, Barnes *et al.*,<sup>34</sup> in order to find a correlation between  $b_4$  and  $A_4$ , have considered the covalent contribution to the fourth order CFPs due to the  $4f^7$  valency fluctuation.<sup>34</sup> Thus, the balance between all those contributions, as others, should finally determine the sign and magnitude of these parameters. The negative  $g$  shift and negative value of  $b_4$  found for  $\text{Eu}^{2+}$  in  $\text{LaB}_6$  may indicate the importance of covalency in determining the fourth order CFPs in this metallic material.<sup>11</sup> We like to emphasize that the main purpose of this paper is to report the negative  $b_4$  in a metal doped with an  $S$ -state impurity. Also, we have addressed for the possible presence of covalent contributions to the exchange interaction and the fourth order crystal field parameter in  $\text{LaB}_6$  doped with Eu and Gd. How-

ever, it is out of the scope of this work to elucidate the role of the different covalent contributions to those parameters.

## V. CONCLUSIONS

In summary, using our data and those from others,<sup>32</sup> we have shown that in the same metallic host ( $\text{LaB}_6$ ), the  $\text{Eu}^{2+}$  and  $\text{Gd}^{3+}$  magnetic ion impurities with the same  $S$  ground state and electronic configuration ( $4f^7$ ;  $S=7/2$ ), but with different ionic charges, selectively probe, via an exchange interaction, different types of conduction electrons at the host Fermi level. We have argued that this unique behavior may be a consequence of the Coulomb repulsion potential between the ion charges and the host conduction electrons. Most importantly, we have shown that the cubic fourth order CFP  $b_4$  for both  $\text{Eu}^{2+}$  and  $\text{Gd}^{3+}$   $S$  ground state ions is negative in the metallic  $\text{LaB}_6$  compound. To the best of our knowledge, this paper reports a negative value for the  $b_4$  parameter in a metallic host. Following Barnes *et al.*, the negative value of  $b_4$  found in the metallic  $\text{LaB}_6$  compound suggests that in all the  $R$  hexaboride family, covalent contributions may play an important role in their fourth order CFPs.<sup>11,34</sup>

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