

Exchange and crystal field effects in the ESR spectra of Eu^{2+} in LaB_6

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Electron spin resonance of Eu^{2+} ($4f^7$, $S=7/2$) in a La hexaboride (LaB_6) single crystal shows a single anisotropic Dysonian resonance. From the observed negative g shift of the resonance, it is inferred that the 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 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 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.¹⁻¹⁰ Particularly, 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, ~ 2.7 eV, as electron emitters.¹¹⁻¹³ Besides, for $\text{La}_{1-x}\text{R}_x\text{B}_6$ with $R=\text{Gd}$ and Ce , spin-glass and Kondo behaviors were, respectively, reported.^{14,15}

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.¹⁶⁻²¹ There is now a consensus that all non- S ground state R hexaborides present a *negative* fourth order crystal field parameter (CFP) $A_4 < 0$.¹⁶⁻²¹ 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 .^{17,22-25}

In this work, we report electron spin resonance (ESR) experiments of Eu^{2+} (S ground state) ions diluted in the metallic hexaboride of LaB_6 . It is generally observed that for Eu^{2+} and Gd^{3+} ions diluted in any cubic metallic/semimetallic/semiconducting/insulating hosts, the fourth order CFP, b_4 , for both ions, is either *positive*²⁶⁻²⁸ or *negative*,^{23,29-31} 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 Eu^{2+} and Gd^{3+} ($4f^7$; $S=7/2$) ions in LaB_6 . Surprisingly, the analysis of our ESR data allows us to conclude that the b_4 parameter of Eu^{2+} in LaB_6 is negative, the same sign as that of A_4 for non- S RB_6 , in contrast to the positive value reported by Luft *et al.*, for

Gd^{3+} in the same compound of LaB_6 .³² 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.^{26,33-37} To the best of our knowledge, our finding of $b_4 < 0$ for Eu^{2+} in 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.³³⁻³⁶ 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 Eu^{2+} and Gd^{3+} ions, via an exchange interaction, probe different types of conduction electrons at the Fermi level of LaB_6 .

II. EXPERIMENT

Single crystals of 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 $\sim 1 \times 1 \times 0.5$ mm³ 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 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 LaB_6 at X and Q bands for the

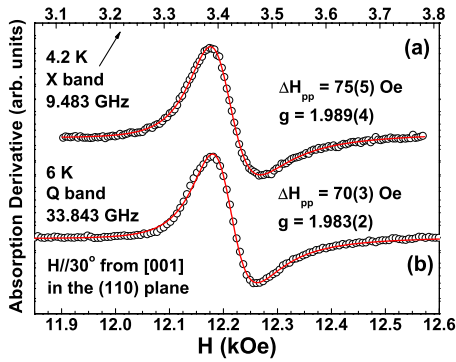


FIG. 1. (Color online) Low- T ESR spectra of Eu^{2+} in a $\text{La}_{1-x}\text{Eu}_x\text{B}_6$ ($x=0.0022$) single crystal for $H \parallel 30^\circ$ from $[001]$ in the (110) plane: (a) X band and (b) Q band. The solid lines are the Dyson line shape analysis.

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.³⁸ 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 Gd^{3+} in LaB_6 .³²

Figures 2(a) and 2(b) display the T dependence of the linewidth (peak to peak of the pure absorption), ΔH_{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 Eu^{2+} magnetic moments.³⁹

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

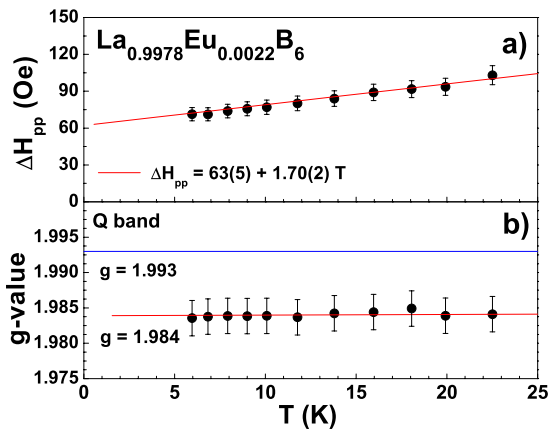


FIG. 2. (Color online) T dependence of the Q -band ESR for $H \parallel 30^\circ$ (a) line width, ΔH_{pp} , and (b) g value of Eu^{2+} in $\text{La}_{1-x}\text{Eu}_x\text{B}_6$ ($x=0.0022$) single crystal.

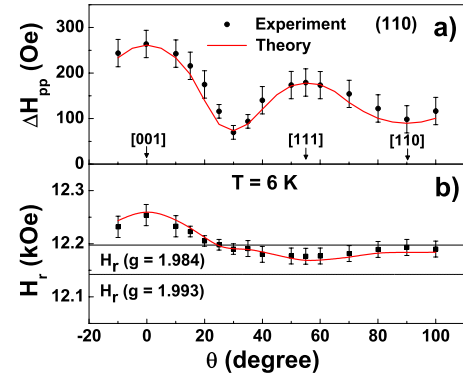


FIG. 3. (Color online) Angular dependence of the Q -band ESR (a) linewidth, $\Delta H_{pp}(\theta)$, and (b) $H_r(\theta)$ for $\text{La}_{1-x}\text{Eu}_x\text{B}_6$ ($x=0.0022$) single crystal. H is rotated in the (110) plane.

$T=6$ K when H is rotated in the (110) plane, respectively. A strong anisotropic behavior for ΔH_{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, δH , 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° are shown in the inset of Fig. 4.

IV. ANALYSIS AND DISCUSSION

A. Exchange field

Our results show that the Eu^{2+} resonance in 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 Gd^{3+} ions in the same

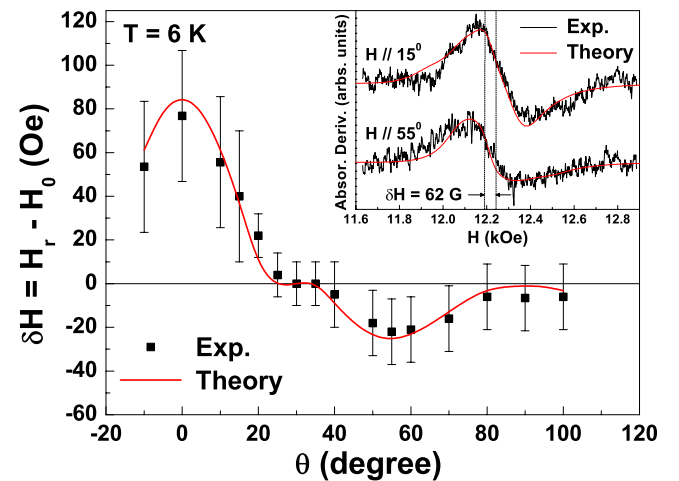


FIG. 4. (Color online) Q -band angular dependence of the Eu^{2+} resonance field shift, $\delta H = H_r - H_0(\theta = 30^\circ)$. Inset: experimental and calculated Q -band ESR spectra of Eu^{2+} in $\text{La}_{1-x}\text{Eu}_x\text{B}_6$ ($x=0.0022$) single crystal for $H \parallel 15^\circ$ and 55°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

host.³² The sign change in the g shift may be understood in terms of a two band model⁴⁰ involving the exchange interaction between the localized Eu^{2+} (and 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)⁴¹ and η_F^d and η_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 LaB_6 will be stronger in the case of the Eu^{2+} ions. Thus, the $J_{at}^d(0) \eta_F^d$ term may become dominant in the case of Gd^{3+} and negligible in the case of 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 Gd^{3+} and Eu^{2+} in LaB_6 , respectively.

The linear thermal broadening of the homogeneous ΔH_{pp} [see Fig. 2(a)] indicates that the spins of the 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, $\Delta H_{pp}/\Delta T$,³⁹ should be given by $b = (\pi k_B / g \mu_B) \times [\langle J_{cv}^p(q) \rangle_F \eta_F^p]^2$;⁴¹ 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 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 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 Gd^{3+} in LaB_6 (Ref. 32) leads us to conclude that the Gd^{3+} ions relax to the lattice via an exchange interaction with the R $5d$ -like electrons. In this case, Luft *et al.*³² have assumed that η_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 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.⁴² 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 Gd^{3+} and Eu^{2+} in LaB_6 , respectively. Note that in the analysis of the g shift, we used the density of states for LaB_6 obtained by band structure calculation.⁴² Moreover, we have assumed that the local density of d states at the Eu site is strongly perturbed by the Coulomb repulsion. Thus, in spite that the Eu d levels will have different energies than those of the 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 ΔH_{pp} shows that besides the homogeneous ESR linewidth, $\Delta H_{pp}(\theta \cong 30^\circ)$, there is a large contribution to ΔH_{pp} from an intrinsic anisotropic inhomogeneous broadening, which reveals the presence of unresolved cubic CF effects. The minimum ΔH_{pp} at $\theta \cong 30^\circ$, when H is rotated in the (110) plane, identifies the angle where the fine structure of the Eu^{2+} ($4f^7$; $S=7/2$) ESR spectra collapses ($\theta = 29.7^\circ$).⁴³ 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).³⁹ This mechanism leads to the well known phenomenon of *exchange narrowing of the fine structure* and, as a function of θ and T , generates a variety of ESR spectra.^{44,45} We have used this exchange narrowing theory to compute the expected ESR spectra at different angles and temperatures.^{46,47} 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^{39,45,47} 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 $S=7/2$ Eu^{2+} spin. The transition probabilities associated with the $M \leftrightarrow M+1$ transition can be written as

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

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 ω_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, μ_B the Bohr magneton, and H_M the resonance field of the 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 environment⁴⁷ 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 ω_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.⁴³ 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.*,⁴⁸ 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 $\Delta H_{pp}(\theta, T=6$ K), the field for resonance $H_r(\theta, T=6$ K), and the shift of the field for resonance $\delta H = H_r(\theta, T=6$ K) $- H_0(\theta=30^\circ, T=6$ K), respectively. They were obtained after a Dyson analysis³⁸ 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 $\Delta H_{pp}(\theta, T=6$ K) data is $\langle b_4 \rangle = -12(1)$ Oe and $2\sigma_{b_4} = 20(4)$ Oe, and for $\delta H = H_r(\theta, T=6$ K) $- H_0(\theta=30^\circ, T=6$ 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 $T=6$ K

for $\theta=15^\circ$ and 55° 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 LaB_6 is consistent with the negative value reported for this parameter in various $R_{1-x}\text{Eu}_x\text{B}_6$ and $R_{1-x}\text{Gd}_x\text{B}_6$ ($R=\text{Ca}, \text{Sm}$).^{23,29-31} Therefore, there is a disagreement with the positive value for b_4 reported by Luft *et al.*,³² 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 Eu^{2+} , Gd^{3+} , and La^{3+} , which may cause larger local lattice distortions at the 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 Barnes⁴⁴ has developed a more complete and involved theory than Plefka.⁴⁵ To prove the validity of our analysis, using Plefka's approach, we compared the EPR spectra of Pt:Gd calculated with the Barnes theory,⁴⁸ 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.*³² using the first moment does not give the correct sign for b_4 .

Most of the reported ESR data for Eu^{2+} and 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.^{23,26,27,29-31,33-37,47,49} 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 (~ 40 b_4) of the ESR fine structure becomes smaller than the observed residual linewidth.⁵¹⁻⁵⁴ Possibly, this may be due to a subtle cancellation between the various contributions to b_4 .^{34,56-58} Hence, to the best of our knowledge, this paper reports a negative value of b_4 for both Eu^{2+} and 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,^{14,16-21,23,31} pnictides,^{22,50,51} and fluorides,³⁴ where both A_4 and b_4 are negative, positive, and negative, respectively. However, in simple cubic metals such as Pd, Pt, and Au,³⁴ intermetallic compounds such as $(\text{Y}, \text{Ce})\text{Pd}_3$ and LaAl_2 ,^{34,59-61} semiconductors such as $\text{CeFe}_4\text{P}_{12}$ and

PbTe,^{37,49,55} 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 Orbach⁵⁶ and Williams and Hirst,⁵⁷ 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.⁵⁸ In addition to these Coulombic contributions, Barnes *et al.*,³⁴ 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.³⁴ 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 Eu^{2+} in LaB_6 may indicate the importance of covalency in determining the fourth order CFPs in this metallic material.¹¹ 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 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,³² we have shown that in the same metallic host (LaB_6), the Eu^{2+} and 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 Eu^{2+} and Gd^{3+} S ground state ions is negative in the metallic 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 LaB_6 compound suggests that in all the R hexaboride family, covalent contributions may play an important role in their fourth order CFPs.^{11,34}

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