Exchange and crystal field effects in the ESR spectra of Eu\textsuperscript{2+} in LaB\textsubscript{6}

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Electron spin resonance of Eu\textsuperscript{2+} (4f\textsuperscript{7}, S=7/2) in a La hexaboride (LaB\textsubscript{6}) single crystal shows a single anisotropic Dysonian resonance. From the observed negative g shift of the resonance, it is inferred that the Eu\textsuperscript{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\textsuperscript{2+} ions experience a cubic crystal field of a negative fourth order crystal field parameter (CFP), b\textsubscript{4}=-11.5(2.0) Oe, in agreement with the negative fourth order CFP, A\textsubscript{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\textsubscript{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 polaron, negative magnetoresistance, quadrupolar ordering, Jahn-Teller effect, superconductivity, heavy fermion, fluctuating valence, and Kondo lattice behavior. Particularly, LaB\textsubscript{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. Besides, for La\textsubscript{1-x}R\textsubscript{x}B\textsubscript{6} with R=Gd and Ce, spin-glass and Kondo behaviors were, respectively, reported.

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. There is now a consensus that all non-S ground state R hexaborides present a negative fourth order crystal field parameter (CFP) A\textsubscript{4}<0.\textsuperscript{16−31} Also, the experimental results in dilute (La\textsubscript{1-x}Sm\textsubscript{x},Ca\textsubscript{x},Ba\textsubscript{x},Yb\textsubscript{x})\textsubscript{1-x}R\textsubscript{x}B\textsubscript{6} (R=Pr,Er,Dy, Gd\textsuperscript{3+}) are consistent with a negative A\textsubscript{4}.\textsuperscript{17−22,25}

In this work, we report electron spin resonance (ESR) experiments of Eu\textsuperscript{2+} (S ground state) ions diluted in the metallic hexaboride of LaB\textsubscript{6}. It is generally observed that for Eu\textsuperscript{2+} and Gd\textsuperscript{3+} ions diluted in any cubic metallic/semimetallic/semiconducting/insulating hosts, the fourth order CFP, b\textsubscript{4}, for both ions, is either positive\textsuperscript{26−28} or negative,\textsuperscript{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\textsuperscript{2+} and Gd\textsuperscript{3+} (4f\textsuperscript{7}; S=7/2) ions in LaB\textsubscript{6}. Surprisingly, the analysis of our ESR data allows us to conclude that the b\textsubscript{4} parameter of Eu\textsuperscript{2+} in LaB\textsubscript{6} is negative, the same sign as that of A\textsubscript{4} for non-S Rb\textsubscript{6}, in contrast to the positive value reported by Luft et al., for Gd\textsuperscript{3+} in the same compound of LaB\textsubscript{6}.\textsuperscript{32} This discrepancy is addressed in this paper. Moreover, it is also a general observation that b\textsubscript{4} is positive in metallic hosts and negative in insulators.\textsuperscript{26,33−37} To the best of our knowledge, our finding of b\textsubscript{4}<0 for Eu\textsuperscript{2+} in LaB\textsubscript{6} represents a negative value for b\textsubscript{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\textsubscript{4} (R in an S ground state) with that of the A\textsubscript{4} (R in a non-S ground state), a comprehensive understanding of the dominant contributions to the b\textsubscript{4} parameter has not been achieved yet.\textsuperscript{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\textsuperscript{2+} and Gd\textsuperscript{3+} ions, via an exchange interaction, probe different types of conduction electrons at the Fermi level of LaB\textsubscript{6}.

II. EXPERIMENT

Single crystals of LaB\textsubscript{6} were grown as described in Ref. 3. The cubic structure (space group 221, Pn\textit{m}3\textit{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 ~1×1×0.5 mm\textsuperscript{3} 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≤T≤300 K. The Eu concentration was obtained by fitting the susceptibility data to a Curie-Weiss law assuming μ\textsubscript{eff}=7.94 μ\textsubscript{B} for the Eu\textsuperscript{2+} ions. Magnetization M(T, H) measurements for 2≤T≤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\textsubscript{6} at X and Q bands for the
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 \( \text{metallic, } \Lambda/B \approx 2.24(5) \) shape.\(^{38} \) Within the accuracy of the measurements and for this orientation, approximately the same linewidths \( \Delta H_{pp} = 72(5) \) 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), \( \Delta H_{pp} \), 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 Eu\(^{2+} \) magnetic moments.\(^{39} \)

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 \( T = 6 \) K when \( H \) is rotated in the (110) plane, respectively. A strong anisotropic behavior for \( \Delta H_{pp} \) with a minimum for \( H \) at \( \theta = 30^\circ \) 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, \( \delta H = H_r(\theta) - H_r(\theta = 30^\circ) \), between the resonance field, \( H_r(\theta) \), and that corresponding to the minimum linewidth, \( H_0(\theta = 35^\circ) = 12, 190(10) \) 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 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
host. The sign change in the $g$ shift may be understood in terms of a two band model involving the exchange interaction between the localized Eu$^{2+}$ (and Gd$^{3+}$) 4$f^7$ electrons with the conduction: (i) $R$ 5$d$-like electrons and (ii) $B$ 2$p$-like electrons. The exchange interaction with the 5$d$-like electrons is assumed to be of atomic type, $J'_{a}(q) > 0$, and that with the $B$ 2$p$-like electrons is of covalent origin, $J'_{c}(q) < 0$. Thus, the $g$ shift can be written as

$$
\Delta g = g_d + \Delta g_p = J'_{a}(q) \eta_{f}^d + J'_{c}(q) \eta_{f}^p,
$$

where $J'_{a}(q)$ and $J'_{c}(q)$ are the $q=0$ component (zero-conduction electron momentum transfer) 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 5$d$ conduction electrons of LaB$_6$ will be stronger in the case of the Eu$^{2+}$ ions. Thus, the $J'_{a}(0) \eta_{f}^d$ term may become dominant in the case of Gd$^{3+}$ and negligible in the case of Eu$^{2+}$, leading to $\Delta g = \Delta g_p = J'_{a}(0) \eta_{f}^d$ and $\Delta g = \Delta g_p = J'_{c}(0) \eta_{f}^p$ for Gd$^{3+}$ and Eu$^{2+}$ in LaB$_6$, respectively.

The linear breadth broadening of the homogeneous $\Delta H_{pp}$ [see Fig. 2(a)] indicates that the spins of the Eu$^{2+}$ ions relax to the lattice via an exchange coupling between the 4$f$ and conduction electrons (Korringa mechanism). Therefore, the so-called Korringa rate in the unbottleneck limit, $H_{pp}/\Delta T$, should be given by $b=(\pi k_B g \mu_B) \times [(\eta_{f}^d(q))_R \eta_{f}^p]$. The brackets indicate an average over the Fermi surface. Assuming that there is no $g$ dependence of the exchange interaction, i.e., $J'_{a}(q) = (J'_{a}(q))_R$, the Korringa rate becomes $b=(\pi k_B g \mu_B) [\Delta g_p]$. Using the measured $g$ shift for Eu$^{2+}$, $\Delta g_p = -0.009(2)$ [see Fig. 2(b)], and the involved constants, we find $b = 1.9(4)$ 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 2$p$-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 $R$ 5$d$-like electrons. In this case, Luft et al. have assumed that $\eta_{f}^d$ may be approximated by the total density of state at the Fermi level by $\eta_{f}^d = 0.50$ 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 $J'_{a} = 40(1)$ meV. However, band structure calculations suggest that the total density of states at the Fermi level is approximately equally distributed between the La 5$d$- and B 2$p$-like electrons. Then, assuming that $\eta_{f}^d = 0.25$ states/eV mol spin, we estimate from the experimental $g$ shifts and Korringa rates values of $J'_{a} = 80(2)$ meV and $J'_{c} = 34(3)$ 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. 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 $\Delta H_{pp}$ shows that besides the homogeneous ESR linewidth, $\Delta H_{pp}(\theta \approx 30^\circ)$, 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 $\theta \approx 30^\circ$, 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 ($\theta=29.7^\circ$). It is now well established that diluted localized magnetic moments in metallic hosts relax to the lattice via an exchange interaction, $H_{\text{int}} = J_{fs} S_f \cdot s_{ce}$, between the localized spin $S_f$ and the host conduction electron spin $s_{ce}$ (Korringa mechanism). 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. We have used this exchange narrowing theory to compute the expected ESR spectra at different angles and temperatures. Such calculation takes into account the following spin Hamiltonian:

$$
H = g \mu_B H \cdot S_f + \frac{1}{60} b_d (O_d^4 + 5 O_d^2) + J_{fs} S_f \cdot s_{ce},
$$

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 $b_d$ is always smaller than one-tenth of $b_d$ and, usually, the accuracy of the experiments does not allow one to measure reliable values of $b_d$.

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 is given by

$$
\chi'(\omega) = 1 - \omega_0 \sum_{M,M'} P_M(\Omega^{-1})_{M,M'},
$$

where $\Omega^{-1}$ is the transition matrix and the quantum numbers $M$ and $M'$ describe the various Zeeman states ($M, M' = -S, -S+1, \ldots, S-1$) associated with the $S=7/2$ Eu$^{2+}$ spin. The transition probabilities associated with the $M \rightarrow M+1$ transition can be written as
\[ P_M \approx C_M \exp(Mh \omega_0/kT) \sum_{M'} C_{M'} \exp(Mh \omega_0/kT), \] (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 \( h\omega_0 \), are expressed by

\[ \Omega_{M,M'} = \left( \frac{h}{\mu_B} - H - H_M \right) \delta_{M,M'} - \frac{i}{2} b TC_{M'}(2\delta_{M,M'} - \delta_{M,M'+1} - \delta_{M,M'-1}), \] (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 \( \Delta H_M \) the resonance field of the Eu\(^{2+} \) \( M \rightarrow M+1 \) transition in a cubic lattice, which is given by

\[ \Delta H_M = H_0 + \frac{1}{60} b \exp(\Delta M |O^0_1 + 5O^4_3|) \] (6)

where \( p \) is the angular dependence in a cubic environment 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 lines, \( a=63(5) \) Oe, and the Korringa rate \( b=1.70(2) \) Oe/K. The real part, related to the magnetic field, contains the magnetic field \( h\omega_0/\mu_B \) associated with the microwave frequency \( \omega_0 \), the external magnetic field \( H \), and the fine structure resonance fields \( \Delta H_M \).

The transition probabilities, with the appropriate Boltzmann population factors for each of the seven lines, are included in the calculation.\(^{33}\) We have considered an additional degree of freedom in the calculation that allows for a Gaussian distribution of the \( b_4 \) parameter.\(^{48}\) A distribution of \( b_4 \) was considered previously by Hardiman et al.,\(^{48}\) when studying Pt:Gd. The Gaussian distribution was symmetrically limited around \( b_4 \) to span only on \( b_4 \) values with the same sign of \( b_4 \). The solid lines shown in Figs. 3(a), 3(b), and 4 are the linewidth \( \Delta H_M(\theta,T=6 \text{ K}) \) for the field of resonance \( H_0(\theta,T=6 \text{ K}) \) and the shift of the field for resonance \( \delta H = H_0(\theta,T=6 \text{ K}) - H_0(\theta=30^\circ,T=6 \text{ K}) \), respectively. They were obtained after a Dyson analysis\(^{38}\) 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 \( b_4 \) and \( 2\sigma_{b_4} \) obtained from \( \Delta H_M(\theta,T=6 \text{ K}) \) data is \( (b_4) = 12(1) \) Oe and \( 2\sigma_{b_4} = 20(4) \) Oe, and for \( \delta H = H_0(\theta,T=6 \text{ K}) - H_0(\theta=30^\circ,T=6 \text{ K}) \) data is \( (b_4) = 11(1) \) Oe and \( 2\sigma_{b_4} = 20(4) \) Oe. Combining these results, we obtain \( (b_4) = 11.5 (2.0) \) 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 La\(_{1-x}\)Eu\(_x\)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\(_{1-x}\)Eu\(_x\)B\(_6\) and R\(_{1-x}\)Gd\(_x\)B\(_6\) (R=Ca,Sm)\(^{29,30-31}\) Therefore, there is a disagreement with the positive value for \( b_4 \) reported by Luft et al.,\(^{32}\) in La\(_{1-x}\)Gd\(_x\)B\(_6\). Using our method of calculation, including the exchange narrowing mechanism, we have reanalyzed their data for the angular dependence of the resonance \( \Delta H_\text{pp}(\theta,T) \) and shift, \( \delta H(\theta,T) \), and we obtained \( (b_4) = -6(2) \) Oe and \( 2\sigma_{b_4} = 6(2) \) Oe for La\(_{1-x}\)Gd\(_x\)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\(_{1-x}\)Eu\(_x\)B\(_6\) \( [2\sigma_{b_4} = 20(4) \text{ Oe}] \) is larger than that found for R\(_{1-x}\)Gd\(_x\)B\(_6\) \( (b_4) = 6(2) \text{ Oe} \). 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 Barnes\(^{44}\) 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,\(^{46}\) 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 (\( \sim 40 \text{ Oe} \)) 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 \( b_4 \).\(^{34,56-59}\) 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 \( A_2 \) (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 \( A_2 \) 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 \((Y, Ce)\)Pd\(_3\) and \(\text{LaAl}_2\) \(34,39-61\) semiconductors such as CeFe\(_2\)P\(_{12}\) and...
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...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\textsuperscript{56} and Williams and Hirst,\textsuperscript{57} long ago, have suggested that in metallic hosts, the presence of crystal field splitted 5$d$ 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, $A_4$.\textsuperscript{58} In addition to these Coulombic contributions, Barnes \textit{et al.}\textsuperscript{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 4$f^7$ valency fluctuation.\textsuperscript{34} Thus, the balance between all these 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$^{2+}$ and Gd$^{3+}$ 5$d$ 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 \textit{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.\textsuperscript{11,34}

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