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# Crystalline field effects in intermetallic compounds

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Electron-spin resonance of the rare-earth ions $Ce^{+3}$, $Dy^{+3}$, $Er^{+3}$, and $Yb^{+3}$ has been observed in various cubic intermetallic compounds. Our experimental results indicate the ground states to be (a) $\Gamma_7$ for $Yb^{+3}$ in $LaPd_3$ ($Cu_3Au$ structure), (b) $\Gamma_8^{(1)}$ for $Er^{+3}$ in LaSb, LuSb, LaBi, and LuBi (NaCl structure), (c) $\Gamma_7$ for $Ce^{+3}$ in LaSb, (d) $\Gamma_6$ for $Dy^{+3}$ in LaSb, (e) $\Gamma_6$ for $Yb^{+3}$ in LaSb, and (f) $\Gamma_6$ for Er in $LaB_6$ ($CaB_6$ structure). These data represent the first observations of anisotropic resonance and hyperfine structure in intermetallic compounds as well as the first observation of EPR of $Ce^{+3}$ in any metal. The observations are consistent with crystalline field parameters deduced from measurements of concentrated spin systems with the same structure, by means of other experimental techniques. Analysis of the crystalline field parameters in terms of the point-charge model, the virtual-bound-state model, and possible $f$-like contributions is given.

## I. INTRODUCTION

The observation of crystalline field effects in the electron paramagnetic resonance (EPR) of localized moments (rare-earth ions) in dilute alloys has been reported previously.[1-3] The success of these measurements is probably associated with the extreme stability of the rare earth's $4f$ configuration, such that the amount of admixture with the conduction electrons is relatively small. This also yields small relaxation rates and exchange interactions. Because of this tendency of the rare-earth ions to preserve their free ionic configuration in metals, we may use crystal-field theories initially developed for the case of rare-earth ions in insulators. For the case of rare-earth ions in cubic metal the crystalline field Hamiltonian can be written[4]

$$\mathcal{H}_{c.f.} = \beta A_4 \langle r^4\rangle [O_4^0(J) + 5O_4^4(J)] + \gamma A_6 \langle r^6\rangle [O_6^0(J) - 21\, O_6^4(J)] , \qquad (1)$$

where the $O_n^m$ are Stevens operator equivalents and $\beta$ and $\gamma$ are reduced matrix elements.[4] $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$ are fourth-order and sixth-order crystalline field parameters. Following Lea, Leask, and Wolf[4] (hereafter denoted LLW) it is convenient to introduce new parameters $W$ and $x$ defined by

$$\beta A_4 \langle r^4\rangle F(4) = Wx ,$$
$$\gamma A_6 \langle r^6\rangle F(6) = W(1 - |x|) , \qquad (2)$$

where $-1 < x < 1$ and $F(4)$ and $F(6)$ are numerical factors given by LLW.[4] The physical significance of $W$ and $x$ is as follows: $W$ is proportional to the over-all splitting and $x$ is a measure of the ratio of the fourth-order parameter and the sixth-order parameters, i.e., $x$ is given by

$$\frac{x}{1-|x|} = \frac{\beta F(4) A_4 \langle r^4\rangle}{\gamma F(6) A_6 \langle r^6\rangle} . \qquad (3)$$

In this ionic model the exchange interaction of the type $J\vec{S}\cdot\vec{s}$ between the localized $4f$ electrons and the conduction electrons is considered as a small perturbation on the crystalline field Hamiltonian.

In the case of $Er^{+3}$ or $Dy^{+3}$ the $J = \frac{15}{2}$ ground multiplet is split by the crystalline field into three quartets ($\Gamma_8^{(i)}$, $i = 1, 2, 3$) and two doublets ($\Gamma_6$ and $\Gamma_7$); $Yb^{+3}$ ($J = \frac{7}{2}$) in the presence of the cubic crystalline field exhibits one quartet $\Gamma_8$ and two doublets $\Gamma_7$ and $\Gamma_6$. As for $Ce^{+3}$ ($J = \frac{5}{2}$), only one quartet ($\Gamma_8$) and one doublet ($\Gamma_7$) are expected. The crystalline field ground state and the energy-level ordering are determined by the sign and magnitude of $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$. The wave functions and the energy levels as a function of $x$ for the various $4f$ configurations are tabulated in LLW.[4]

The experiments on dilute alloys indicated that $A_4\langle r^4\rangle$ is negative and $A_6\langle r^6\rangle$ is positive. It should be mentioned that the point-charge (PC) model, for fcc structure and positive charges on the ligands, predicts positive values for both $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$. A virtual-bound-state (VBS) model was suggested[5] to explain this discrepancy. This model takes into consideration the contribution of the screening $5d$ electron to $A_4\langle r^4\rangle$ in metals.

In the present work we extend our measurements on rare-earth ions to various cubic intermetallic compounds exhibiting the following structures: (a) $Cu_3Au$ phase ($LaPd_3$), (b) NaCl structure (LaSb, LaBi, LuSb, LuBi, (c) $CaB_6$-type structure ($LaB_6$). The present research was motivated mainly by recent success in observation of crystalline field effects in concentrated spin systems having the same structures by means of different experimental techniques.[6-10] This success can be attributed to the following reasons: (i) It has been found that inelastic neutron scattering[6,7] or a modified Mössbauer[10] technique can yield valuable information about crystalline fields. (ii) The ordering temperature of these compounds (in the concentrated limit) is extremely low, such that single-ion excitations, i.e., crystalline field splittings, may be observed. (iii) If the crystalline field produces a singlet ground state, an appreciable Schottky anomaly in the specific heat is expected.[11]

These experiments indicate reasonable agreement with the PC model. It was therefore of interest to check the validity of such a model in the very dilute case (real single-ion excitation!) This was especially necessary in view of the different conclusion regarding the crystalline field reached in dilute alloys, i.e., the necessity of including $d$- and $f$-like screening.

We have observed a $\Gamma_7$ ground state for Yb in $LaPd_3$, a $\Gamma_8^1$ ground state for Er in LaSb, LaBi, LuSb, and LuBi $\Gamma_7$ ground state for $Ce^{+3}$ in LaSb (the first observation of $Ce^{+3}$ in a metal), a $\Gamma_6$ ground state for Yb and Dy in LaSb and also a $\Gamma_6$ ground state for Er in $LaB_6$. All our observations are consistent with the experiments on concentrated systems measured by means of other techniques. It should be stressed that these techniques (neutron scattering, etc.) are insensitive to the sixth-order parameter, i.e., the error in the determination of $A_6\langle r^6\rangle$ is very large. Therefore no attempt has been made to interpret the magnitude (and usually not even the sign) of $A_6\langle r^6\rangle$. In this paper we shall reanalyze the data, taking into consideration both $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$. We find that we cannot always explain the crystalline field parameter by the PC model and we have to extend the discussion to include the VBS model as well as the $f$-like contributions. Moreover, in the case of a $\Gamma_8$ ground state, the EPR technique can determine the ratio $A_4\langle r^4\rangle/A_6\langle r^6\rangle$ very accurately. Therefore, knowledge of $A_4\langle r^4\rangle$ enables one to extract $A^6\langle r^6\rangle$ and, thus, to check the various contributions to the crystalline field in a critical manner.

In Sec. II of this paper we describe our experimental results and analyze them. A comparison with the available experimental data on concentrated systems is also given in the same section. In Sec. III we discuss the expected contributions (sign only) of the various mechanisms (PC, 5$d$ VBS, $f$-like mixing) to the crystalline field and analyze our data accordingly. We shall concentrate mainly on the crystalline field aspect of the above systems. Detailed information about the exchange interactions will be published elsewhere.

## II. EXPERIMENTAL RESULTS AND ANALYSIS

### A. $Cu_3Au$ system: $LaPd_3$:Yb

The magnetic resonance of powdered samples of Yb in $LaPd_3$ with nominal Yb concentrations of 5000, 1000, and 500 ppm was observed at $X$ band. A few samples with $Yb^{170}$-enriched isotope (4000 and 2000 ppm) were also checked. Figure 1 exhibits the spectrum observed for a 2000-ppm Yb (nominal concentration) with natural abundance. This spectrum is very similar to that observed previously for Au:Yb dilute alloys.[12] A central line, corresponding to Yb isotopes with $I=0$, is surrounded by two hyperfine satellite lines (originating from the $Yb^{171}$ isotope with $I=\frac{1}{2}$). The $g$ value of the central line is $g=3.34\pm0.01$. This value is very close to $g=3.42$, expected for a $\Gamma_7$ ground state of $Yb^{+3}$ in a cubic site.[12] The difference is attributed to a (negative) shift induced by the conduction electrons. The negative shift may be due to an almost filled $d$ band in $LaPd_3$[13] or to covalent mixing between the 4$f$ electrons and the conduction band.[12] The observation of a small positive shift ($g\simeq2.01$) in a preliminary EPR experiment on Gd in $LaPd_3$, however, eliminates the first possibility. Thus we believe that covalent mixing is the main source of the negative shift observed for Yb. The hyperfine constant was found to be $A(Yb^{171})=570\pm15$ G. This value is somewhat enhanced with respect to that expected in an insulating host (548) as in the case of Au:Yb[12] where a possible physical mechanism consistent with the $f$ mixing was suggested.

The crystalline field parameters of Yb in $YbPd_3$ have been measured previously by Nowik *et al.*[10] using the Mössbauer technique. Their results exhibit a $\Gamma_7$ ground state for the $Yb^{+3}$ ions with crystalline field parameters $A_4\langle r^4\rangle=(-12\pm1)\ cm^{-1}$ and $A_6\langle r^6\rangle=+0.6\pm0.6\ cm^{-1}$. These parameters yield,

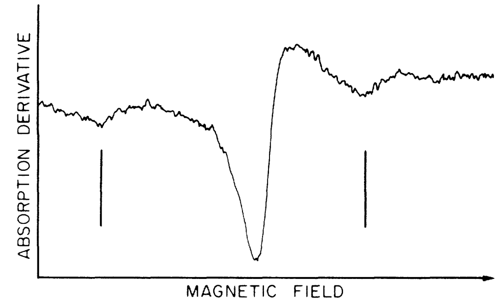

FIG. 1. The electron-spin-resonance spectrum (absorption derivative) of 2000-ppm Yb in $LaPd_3$ at 1.4 K. The two hyperfine satellites (vertical lines) corresponding to the isotope with $I=\frac{1}{2}$ are clearly seen in the figure. The hyperfine constant (the magnetic field difference between the vertical lines) is 575 G.

in the notations of LLW, a positive value for $W$ with $x=+0.91$. Nowik *et al.*[10] suggested an explanation for the magnitude and the sign of $A_4\langle r^4\rangle$ in terms of a point-charge model. Assuming almost zero charge on the twelve Pd first neighbors and charges of $+3$ on the six $Yb^{+3}$ second-nearest neighbors, the point-charge model of Nowik *et al.* yields $A_4\langle r^4\rangle=-10.7$ cm$^{-1}$ and $A_6\langle r^6\rangle=-0.06$ cm$^{-1}$. In the notation of LLW these correspond to a negative value of $W$ and $x=-0.90$. It should be stressed that according to the LLW tabulation both cases ($W>0$, $x=+0.91$ and $W<0$, $x=-0.90$) yield the level sequence $\Gamma_7-\Gamma_8-\Gamma_6$ with $\Gamma_7$ as the ground state and are therefore consistent with our observations. The positive value for $A_6\langle r^6\rangle$ observed by Nowik *et al.*[10] can not be explained, however, by the PC model.

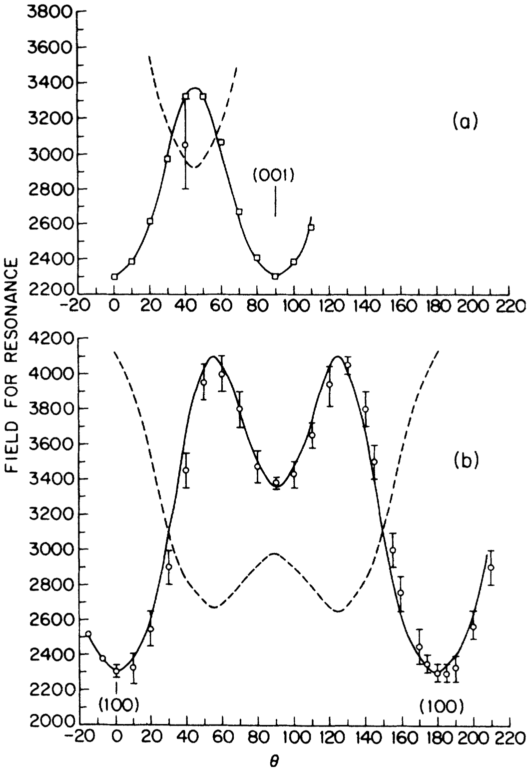

FIG. 2. The angular variation of the field for resonance of (a) 500-ppm Er in LaSb, (b) 2000-ppm Er in LaSb. In (a) the magnetic field was rotated in the (100) plane; in (b) the magnetic field was rotated in the (110) plane. $\theta$ is the angle between the [001] direction and the magnetic field in the plane of rotation (containing that direction). Expressing the direction cosines as ($\alpha=\cos\theta$, $\beta=\sin\theta\sin\varphi$, $\gamma=\sin\theta\cos\varphi$), x-ray indicates that for case (a), $\varphi=0$, and for case (b), $\varphi=45°$. The solid line in Fig. 2 is a theoretical fit with Eq. (4), assuming that this line is the $\frac{1}{2}\rightarrow-\frac{1}{2}$ transition (in the spin-Hamiltonian notation). This fit is for $P=-4.88$, and $Q=-2.30$ corresponds to $x=0.78$. The dashed line is the theoretical angular variation expected for the $\pm\frac{3}{2}\rightarrow\pm\frac{1}{2}$ transition for the same value of $x$. The circle in (a) represents the experimental field for resonance for the bump (see text) observed.

On the assumption that the crystalline field parameters are almost independent of the $4f$ occupation number, our observation is in agreement with the prediction of $\Gamma_5$ ground state for $Pr^{+3}$ in $PrPd_3$.[11] According to LLW a $\Gamma_5$ ground state for $Pr^{+3}$ in a cubic site is possible only in the following cases: (a) $W>0$ and $x>0$, (b) $W<0$ and $x<0$. Case (a) yields $A_4\langle r^4\rangle<0$ and $A_6\langle r^6\rangle>0$; case (b) requires negative values for both $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$. Both cases are consistent with a $\Gamma_7$ ground state for $Yb^{+3}$. It should be mentioned also that EPR experiments on Er and Dy in $LaPd_3$ (powdered samples) fail to reveal any resonance indicative of either a $\Gamma_7$ or a $\Gamma_6$ ground state. This supports case (b) as more likely for $Yb^{+3}$ in $LaPd_3$.

## B. Rock-salt structure

### *1. LaSb : Er, LaBi : Er, LuSb : Er, LuBi : Er*

Electron-spin-resonance measurements of Er in LaSb, LaBi, LuSb, and LuBi were conducted on single-crystal samples at 1.5-cm wavelength. The nominal Er concentrations were 2000 and 500 ppm. The single crystals were cleaved such that the cleavage planes were always the (001) planes and were attached to the wall of the rectangular cavity used for these measurements. The spectra for all the samples measured exhibit the same character: At least one anisotropic line is observed. This line has a metallic shape with $A/B$ ratio (in the notation of Feher and Kip[14]) between 2 and 2.5. The field for resonance as a function of angle between the magnetic field and one of the cubic axes is shown in Fig. 2 for a typical spectrum in LaSb : Er. For some of the crystals (LuBi : Er) we also observed the hyperfine lines associated with the $Er^{167}$ iostope ($I=\frac{7}{2}$)(Fig. 3). The extracted hyperfine constant $A(Er^{167})=75.5\pm1$ G is in agreement with previous measurements[12] and gives us complete confidence that the anisotropy observed is associated with $Er^{+3}$ in a cubic site. We analyze our spectra by assuming a $\Gamma_8$ ground state for Er in Lu$X$ and La$X$ ($X$ = Sb, Bi). Bleaney[15] has formulated a spin Hamiltonian to describe the Zeeman splitting of an isolated $\Gamma_8$ quartet in the presence of a magnetic field. The four energy levels of the effective spin $S=\frac{3}{2}$ were obtained by direct diagonalization of the $4\times4$ matrix associated with the spin Hamiltonian. Following Ayant *et al.*,[16,17] the Zeeman energy is given in the form $E_i=y_i g_J \mu_B H$, where $y_i$ are the roots of the biquadratic equation

$$y^4-(P^2+Q^2)y^2+P^2Q^2+\tfrac{3}{16}(P-3Q)(3P-Q)(P+Q)^2$$
$$\times[\alpha^2\beta^2+\alpha^2\gamma^2+\beta^2\gamma^2]=0, \qquad (4)$$

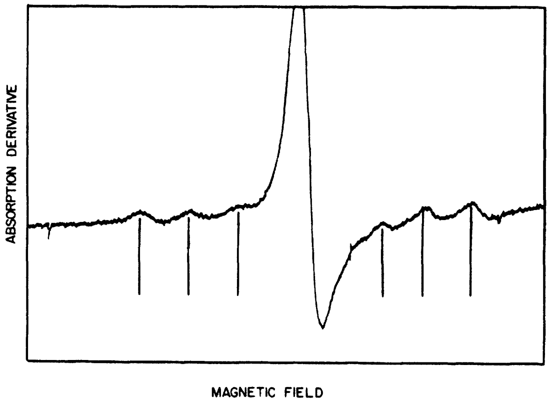

FIG. 3. The EPR spectra of LuBi : Er (2000 ppm of Er). Some of the hyperfine satellites associated with $Er^{167}$ isotope ($I=\frac{7}{2}$) are clearly seen in the figure (vertical line). The spectra was measured at 1.5-cm wavelength at $T=1.4$ K. The hyperfine constant is 75 G.

where $g_J$ and $\mu_B$ are the Landé $g$ factor and the Bohr magneton, respectively. For $Er^{+3}$ we used $g_J=1.18$ slightly smaller than the ionic value $g_J = \frac{6}{5}$.[17] $\alpha$, $\beta$, and $\gamma$ are the direction cosines of the magnetic field with respect to the cubic axes. $P$ and $Q$ are matrix elements given by

$$\begin{aligned} P &= \langle \Gamma_8, \tfrac{3}{2} | J_z | \Gamma_8, \tfrac{3}{2} \rangle = - \langle \Gamma_8, -\tfrac{3}{2} | J_z | \Gamma_8, -\tfrac{3}{2} \rangle , \\ Q &= \langle \Gamma_8, \tfrac{1}{2} | J_z | \Gamma_8, \tfrac{1}{2} \rangle = - \langle \Gamma_8, -\tfrac{1}{2} | J_z | \Gamma_8, -\tfrac{1}{2} \rangle . \end{aligned} \tag{5}$$

The wave functions $|\Gamma_8, i\rangle$ ($i=-\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$ in the notation of the effective spin space) are dependent on $x$ and are partially given by LLW.[4] We identify the sharp resonance line in our spectrum as the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition. Intensity calculations indicate that the transition probabilities for the $\frac{1}{2} \rightarrow -\frac{1}{2}$ line and the $\pm\frac{3}{2} \rightarrow \pm\frac{1}{2}$ line are roughly the same (but much larger than that of the $+\frac{3}{2} \rightarrow -\frac{3}{2}$ transition). As demonstrated by Descamps *et al.*[17] and by Davidov *et al.*,[1] the $\pm\frac{3}{2} \rightarrow \pm\frac{1}{2}$ transitions are extremely sensitive to any strains in the crystals which shift the $\pm\frac{3}{2}$ levels relative to the $\pm\frac{1}{2}$ levels. X rays of our crystals indicate that most of them are twinned with distortions of 2° to 3°. Such an effect can easily broaden the $\pm\frac{3}{2} \rightarrow \pm\frac{1}{2}$ transition appreciably. Similar behavior has been observed by Davidov *et al.*[1] for Au : Dy where crystalline field splitting of the $Dy^{+3}$ ion also results in a $\Gamma_8$ ground state. In addition, near the turning points we observed a very broad line associated presumably with the $\pm\frac{3}{2} \rightarrow \pm\frac{1}{2}$ transition.

Assuming that the sharp line observed is the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition we are ready to fit our data with Eqs. (4) and (5). The solid line in Fig. 2 is our theoretical fit for the case of LaSb. We were able to fit the spectra of two different samples (2000-ppm Er and 500-ppm Er), examined in different orientation with respect to the magnetic field with the same values of $P$ and $Q$. The best fit yielded $P=-4.88$ and $Q=-2.30$, consistent with the unique value $x=0.78$. This is consistent with a $\Gamma_8^1$ level lowest. Similar procedures have been carried out for the other samples and the values of $x$ are tabulated in Table I. It should be mentioned that the observed EPR line is extremely anisotropic and therefore any misorientation of the crystal can lead to dangerous errors in the determination of the value of $x$. Fortunately all the samples cleave along the (001) plane. Thus we can accurately measure the field for resonance with the external magnetic field along the [001] direction. At this position [the turning point in Fig. 2(a) and 2(b)], the field for resonance is almost independent of small misorientations. It is clearly seen from Eq. (4) that for the external magnetic field parallel to the [001] direction the roots corresponding to the $\frac{1}{2}$ and $-\frac{1}{2}$ energy levels are $Q$ and $-Q$ respectively. The field for resonance for the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition, $H_{001}(\frac{1}{2} \rightarrow -\frac{1}{2})$, is given by

$$H_{001}(\tfrac{1}{2} \rightarrow -\tfrac{1}{2}) = \frac{h\nu}{2 g_J \mu_B Q} .$$

Thus by performing measurements along the [001] direction the value of $Q$ and therefore $x$ can be determined easily. Table I exhibits the field for resonance $H_{001}(\frac{1}{2} \rightarrow -\frac{1}{2})$, the value of $Q$ as well as $x$ for Er in the various compounds measured. In the above discussion we neglect any possible shift due to the exchange interaction with the conduction electrons. This is justified by the following argument: The thermal broadening (measured in the [001] direction) yields an exchange parameter $J \approx 0.1$ eV. The density of states has been measured previously[8] and roughly corresponds to 1 electron per formula unit. Thus an upper limit to the shift was estimated to be $\approx 15$ G. This value is within the limit of our "error bars."

It is worthwhile at this stage to compare our EPR measurements with neutron scattering data on the

TABLE I. The field for resonance $H_{001}(\frac{1}{2} \rightarrow -\frac{1}{2})$, the value of $Q$ and $x$ as well as the ratio of the crystalline field parameters for the various LuX : Er and LaX : Er ($x$ = Sb, Bi) samples measured. $H_{001}(\frac{1}{2} \rightarrow -\frac{1}{2})$ is the field for resonance with the magnetic field along the [001] direction.

| | $a_0$ (Å) | $H_{001}(\frac{1}{2} \rightarrow -\frac{1}{2})$ (G) | $\lvert Q \rvert$ | $x$ | $A_4 \langle r^4 \rangle / A_6 \langle r^6 \rangle$ |
|---|---|---|---|---|---|
| LaSb | 6.49 | 2300 ± 30 | 2.309 | 0.783 | 39 |
| LaBi | 6.58 | 2130 ± 30 | 2.488 | 0.83 | 54 |
| LuSb | 6.055 | 2408 ± 30 | 2.20 | 0.77 | 34 |
| LuBi | 6.156 | 2201 ± 30 | 2.40 | 0.81 | 46 |

TABLE II. The crystalline field ground state for Er (as well as the sign of $W$ and of $x$) as extrapolated from crystalline field parameters measured by neutron scattering. In this extrapolation we assume that the crystalline field parameters do not vary across the $4f$ series.

| | $A_4\langle r^4\rangle$ (meV) | $A_6\langle r^6\rangle$ (meV) | Extrapolated values for $Er^{+3}$ Sign of $W$ | $x$ | ground state |
|---|---|---|---|---|---|
| Tm : TmSb[a] | $6.81\pm0.1$ | $0.44\pm0.04$ | + | 0.60 | $\Gamma_8^{(1)}$ |
| Pr : PrSb[b] | $8.3\pm0.3$ | $0.17\pm0.04$ | + | 0.81 | $\Gamma_8^{(1)}$ |
| Pr : PrBi[b] | $6.9\pm0.3$ | $0.24\pm0.06$ | + | 0.72 | $\Gamma_8^{(1)}$ |
| Er : ErP[c] | $11.3\pm0.6$ | $0.35\pm0.2$ | + | 0.75 | $\Gamma_8^{(1)}$ |

[a] Reference 9. [b] Reference 7. [c] Reference 8.

concentrated systems: TmSb, PrSb, PrBi, and ErP. The crystalline field parameters for these systems are given in Table II. In the same table, we also estimated the expected value of $x$ as well as the ground state for $Er^{+3}$, assuming that the crystalline field parameters do not vary much across the $4f$ series. This assumption is supported by recent neutron scattering measurements by Birgeneau *et al.*[8] It is clearly seen from Table II that a $\Gamma_8^1$ ground state is expected for all the cases in complete agreement with our EPR observation.

#### 2. *LaSb : Ce, LaSb : Dy, LaSb : Yb*

The EPR of Ce, Dy, and Yb in LaSb have been observed at $X$ band in the temperature range $1.4 \leq T \leq 4.2$ K. We used $Yb^{174}$ and $Dy^{164}$ isotope ($I = 0$), but Ce with natural abundance. The nominal concentrations were 4000 and 2000 ppm. In all the cases, a single line has been observed. Table III exhibits the $g$ values deduced from the field for resonance of this single line. For comparison, the $g$ values expected theoretically for the isotropic resonances originating with either a $\Gamma_7$ or $\Gamma_6$ ground state are given. It is clearly seen that the observed resonance corresponds to a $\Gamma_7$ ground state for $Ce^{+3}$ in LaSb, $\Gamma_6$ ground state for $Yb^{+3}$ and $Dy^{+3}$ in LaSb. These observations are consistent with positive values for both $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$.

This is another indication that the crystalline field parameters do not vary much across the $4f$ series in these compounds, and at least retain their sign and magnitude. To the best of our knowledge this is the first report of $Ce^{+3}$ resonance in metals.

### C. Hexaboride phase: $LaB_6$ : Er

The EPR measurements were performed on powdered samples at $X$ band frequencies. The Er nominal concentrations were 4000, 2000, and 500 ppm. The spectra exhibit a single line with a field for resonance appropriate to a $g$ value of 5.90. This is very close to a $g = 5.85$, expected for a $\Gamma_6$ ground state for $Er^{+3}$ in a cubic site. The thermal broadening measured in the temperature range $1.4 \leq T \leq 4.2$ K is $\Delta H/T = 14 \pm 5$ G/K. The large thermal broadening is attributed partially to the low-lying $\Gamma_8$ level, as can be seen from the tabulated data of LLW. It has been demonstrated previously[18] that the presence of low-lying crystalline field levels can result in violation of the simple Korringa relation with appreciable increase of the thermal broadening even at temperatures much smaller than the crystalline field energy separation.

According to LLW, the $\Gamma_6$ ground state is consistent with (a) $W > 0$, $x < 0$ or (b) $W < 0$, $x > 0$. Case (a) requires $A_6\langle r^6\rangle > 0$ and $A_4\langle r^4\rangle < 0$; case (b) yields $A_6\langle r^6\rangle < 0$ and $A_4\langle r^4\rangle < 0$. These values are in agree-

TABLE III. The experimental $g$ value observed for $Ce^{+3}$, $Dy^{+3}$, and $Yb^{+3}$ in LaSb. For comparison the theoretical $g$ values expected for $\Gamma_7$ or $\Gamma_6$ ground state as well as the $g$ value observed in CaO (insulator) are given.

| | Experimental $g$ value | Crystalline field ground state | Theoretical $g$ value |
|---|---|---|---|
| LaSb : Ce (metal) | $1.43\pm0.02$ | $\Gamma_7$ | $g(\Gamma_7) = 1.42$ |
| CaO : Ce[a] (insulator) | 0.7963[b] | $\Gamma_7$ | $g(\Gamma_7) = 1.42$ |
| LaSb : Dy (metal) | $6.70\pm0.1$ | $\Gamma_6$ | $g(\Gamma_6) = 6.67$ |
| CaO : Dy[c] (insulator) | 6.60 | $\Gamma_6$ | $g(\Gamma_6) = 6.67$ |
| LaSb : Yb (metal) | $2.50\pm0.02$ | $\Gamma_6$ | $g(\Gamma_6) = 2.63$ |
| CaO : Yb[c] (insulator) | 2.585 | $\Gamma_6$ | $g(\Gamma_6) = 2.63$ |

[a] R. W. Reynolds, Y. Chen, L. A. Boatner, and M. M. Abrahams, Phys. Rev. Lett. 29, 18 (1972).

[b] This $g$ value is assumed to originate from $\Gamma_7$ ground state. The large deviation was explained by mixing with the higher $J = \frac{7}{2}$ levels (energy separation of 2200 $cm^{-1}$) by the large crystalline field. Such an effect is negligible for LaSb : Ce because of the much smaller crystal field. We thank R. Birgeneau for clarifying this point to us.

[c] W. Low and R. S. Rubins, Phys. Rev. 131, 2527 (1963).

ment with specific-heat measurements by Bucher *et al.* which indicate a $\Gamma_5$ ground state for Pr in the concentrated system $PrB_6$.[11] The tabulated data of LLW give the same sign for the crystalline field parameters as quoted above.

## III. DISCUSSION

The PC model "successfully"[8,11] explains the sign and even the magnitude of the crystalline field parameter $A_4\langle r^4\rangle$ in the concentrated spin systems. In metals where conduction electrons might play a role, the "success" of such a naive model is very surprising. This is especially true in view of recent EPR measurements on dilute alloys which indicate a large contribution to $A_4\langle r^4\rangle$ from the virtual bound state (VBS) on the rare-earth site. It will, therefore, be extremely interesting to analyze our data in terms of the VBS model. This model was suggested primarily to explain the negative value of the fourth-order crystalline field parameter $A_4\langle r^4\rangle$ in dilute alloys. It successfully explains qualitatively and even sometimes quantitatively the ground state properties of the following alloys: Ag : Er,[12] Ag : Dy,[3] Au : Er,[12] Au : Dy,[1] Au : Yb,[12] Al : Er,[19] Al : Dy,[19] Th : Er,[20] Th : Dy,[20], Ir : Er,[21] Ir : Dy,[21] Rh : Er,[22] Rh : Dy,[22] and Pt : Er.[13] In all of these alloys the observed ground state is consistent with negative $A_4\langle r^4\rangle$ and positive $A_6\langle r^6\rangle$. Exceptional cases are Pd : Er and Pd : Dy[2] in which both $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$ are negative. It should be mentioned that the point-charge model for fcc symmetry with positive charges (+1) on the ligands predicts positive values for both $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$. The arguments in favor of the VBS model are as follows[5]: Because of the difference in valence between the trivalent rare earth and that of the host, there will be screening charge around the rare-earth ion to satisfy the Friedel rule. The screening electrons must be in states orthogonal to the rare-earth core. It can be shown that the low-lying state which satisfies this requirement is the 5*d* state. This 5*d* electron is nonmagnetic and, in metal, can be considered as a virtual bound state. The positive charge on the ligands (in the case of cubic noble metals) can split this 5*d* VBS into three so-called $d\epsilon$ orbitals ($xy$, $yz$, $zx$) and two $d\gamma$ orbitals ($x^2-y^2$, $z$). This crystalline field splitting produces an aspherical charge distribution that can affect the crystalline field experienced by the 4*f* electrons. An aspherical charge distribution associated with the 5*d* VBS is possible if the width of the VBS is smaller than the crystalline field splitting of the VBS.

The over-all charge distribution associated with the $d\epsilon$ orbitals has fcc-like symmetry; that associated with the $d\gamma$ has octahedral symmetry. Thus for fcc metals with positive charges on the ligands, we expect $d\epsilon$ orbitals to lie lowest and their contribution to $A_4\langle r^4\rangle$ will be the same as expected from fcc-like summetry with a negative charge distribution, i.e., negative $A_4\langle r^4\rangle$. If, however, the charge on the ligands is negative, the $d\gamma$ will lie lowest. Then the contribution to $A_4\langle r^4\rangle$ for the VBS will be positive as expected from octahedral-like charge distribution with negative charge (electrons). In a similar way, one can analyze the contribution of the VBS to $A_4\langle r^4\rangle$ in the other cubic hosts (NaCl and CsCl structures with different charges on the ligands). Table IV exhibits the values of $A_4\langle r^4\rangle$ for the VBS model. For comparison the crystalline field parameters expected according to the PC model are also given. It is clearly seen that the contribution of the VBS to $A_4\langle r^4\rangle$ is always opposite in sign to that of the PC model. This behavior is nothing but another example of the well-known law of physics: the external crystalline field (originating with the ligands) splits the VBS in such a way as to diminish its own effect on the 4*f* electrons. Similar "antishielding" effects due to conduction electrons have been observed in the electric field gradients of ordered metals by Watson, Gossard, and Yafet.[23] It should be stressed that our analysis is qualitatively correct as long as the crystalline field splitting of the VBS is much larger than the width of the VBS, so that only the ground state is populated. Symmetry considera-

TABLE IV. The sign of $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$ for the various cubic structures as expected according to the point-charge model, and 5*d*- and *f*-like virtual bound states.

| Structure | Effective charge on ligands | Point charge model | | 5*d* virtual bound state model | | | *f* mixing contribution |
|---|---|---|---|---|---|---|---|
| | | sign of $A_4\langle r^6\rangle$ | sign of $A_6\langle r^6\rangle$ | VBS ground state | symmetry of VBS charge distribution | sign of $A_4\langle r^4\rangle$ | sign of $A_6\langle r^6\rangle$ |
| fcc (12) | + | + | + | $d\epsilon$ | fcc | – | – |
| fcc (12) | – | – | – | $d\gamma$ | octahedron | + | + |
| Octahedral, NaCl (6) | + | – | – | $d\gamma$ | octahedron | + | + |
| Octahedral, NaCl (6) | – | + | + | $d\epsilon$ | fcc | – | – |
| Simple cubic, CsCl (8) | + | + | – | $d\epsilon$ | fcc | – | + |
| Simple cubic, CsCl (8) | – | – | + | $d\gamma$ | octahedron | + | – |

tions indicate that 5$d$ VBS *cannot* contribute to $A_6\langle r^6\rangle$. As demonstrated by Dixon and by Dupree[24] the $f$-like component in the conduction electron's wave function can contribute to $A_6\langle r^6\rangle$; its contribution to $A_4\langle r^4\rangle$ is much less than that of the 5$d$ VBS and we shall neglect it at the moment. The orthogonalization theorem of Cohen and Heine[25] suggests that in the vicinity of the atomic core, the conduction electrons will assume a radial dependence not unlike the atomic valence electrons. Therefore we do not expect any 4$f$ character in the conduction electrons in the vicinity of the rare-earth core unless there is a mixing with the 4$f$ localized electrons.

Recently, Dixon and Dupree[24] calculated the contribution of the 5$d$ and 4$f$ partial-wave components of the conduction electron's wave function to $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$, respectively. Their approach is completely equivalent to the VBS model as represented by William and Hirst[5] and the present work. It should be mentioned that the 5$f$ contribution to $A_6\langle r^6\rangle$ is small because the energy of this state might be quite high. Nevertheless, this 5$f$ contribution may be dominant due to the smallness of $A_6\langle r^6\rangle$. In Table IV we also give the contribution to $A_6\langle r^6\rangle$ due to this $f$ character. This is an "antishielding" mechanism and we expect its contribution to $A_6\langle r^6\rangle$ to be opposite in sign to that of the PC model.

We would like now to analyze our experimental results in terms of the VBS model. Unfortunately, quantitative calculations are impossible at this stage and we shall restrict ourselves, therefore, to a discussion of the sign only. Intuitively one expects much larger contributions of the VBS to $A_4\langle r^4\rangle$ in dilute alloys than in intermetallic compounds. This is mainly due to the much smaller screening effect of the rare-earth ions in the latter. As a result the crystalline field in intermetallic compounds should behave more like what is expected from the PC model.

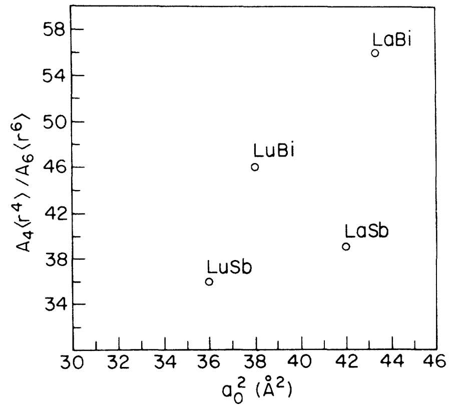

FIG. 4. The ratio of the fourth-order and sixth-order crystalline field parameter as a function of the square of the lattice constant. This ratio was extracted from our measurements on Er in LaSb, LaBi, LuSb, and LuBi.

### A. Cu$_3$Au structure: YbPd$_3$, LaPd : Yb

The experimental results of Nowik *et al.*[10] indicate $A_4\langle r^4\rangle < 0$ and $A_6\langle r^6\rangle > 0$.[26] According to Table III the sign of $A_4\langle r^4\rangle$ can be explained by the PC model, assuming negative charge on the twelve Pd first neighbors and positive charge (+3) on the six Yb$^{+3}$ second-nearest neighbots. A negative sign for $A_6\langle r^6\rangle$ is inconsistent with the PC model, but can be explained by assuming an $f$-like mixing contribution (Table III). Evidence for such an admixture is provided by our $g$ shift measurement on LaPd$_3$ : Yb. A large negative shift $\Delta g \cong -0.08$ has been observed which indicates appreciable 4$f$-5$f$ covalent mixing.

### B. NaCl structure (La$X$, Lu$X$)

The measurements on the concentrated systems, as well as our EPR measurements in the dilute limit, indicate positive values for $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$, in agreement with the PC model for octahedral symmetry with a negative charge on the ligands. The charges on the Sb or Bi are between $-2$ and $-3$ (probably close to $-3$, depending on their location in the Periodic Table). Because of the large electronegativity of the $X$ ions, we do not expect screening effects on the rare-earth ions. This might explain the failure of the VBS model as well as the "success" of the PC model in this case.

Recently, Birgeneau *et al.*[8] have demonstrated that the fourth-order crystalline field parameters for rare-earth pnictides and phosphides obey the effective point-charge model for the light rare-earths, but deviate for the heavy rare earths. It is therefore of extreme importance to check the validity of the point-charge model using a heavy rare earth such as Er.

Our EPR results can give us information about the value of $x$, i.e., the ratio $A_4\langle r^4\rangle/A_6\langle r^6\rangle$. The point-charge model gives for this ratio.

$$\frac{A_4\langle r^4\rangle}{A_6\langle r^6\rangle} = 9.33\,\frac{\langle r^4\rangle_{\mathrm{Er}}}{\langle r^6\rangle_{\mathrm{Er}}}\,a_0^2\,. \tag{6}$$

Assuming that $\langle r^4\rangle_{\mathrm{Er}}/\langle r^6\rangle_{\mathrm{Er}}$ is independent of the host matrix, the ratio $A_r\langle r^4\rangle/A_6\langle r^6\rangle$ depends only on $a_0$ (the lattice parameter). Thus the point-charge model can be checked in a critical manner. Figure 4 exhibits $A_4\langle r^4\rangle/A_6\langle r^6\rangle$ as a function of $a_0^2$. Although there is no simple linear relation between these two quantities, our results certainly show a tendency for $A_4\langle r^4\rangle/A_6\langle r^6\rangle$ to increase with increasing $a_0^2$. Further experiments on insulators of rock-salt structure may explain the success of the PC model here.

Finally, neutron scattering experiments provide us with an accurate measure of $A_4\langle r^4\rangle$ (the accuracy in $A_6\langle r^6\rangle$ is poor). EPR, however, gives us very good numbers for the ratio of these two parameters. Therefore, simultaneous measurements using both these experimental techniques are necessary for complete determination of the crystalline field parameters.

### C. CsCl structure: $LaB_6$ : Er

Our experimental results ($\Gamma_6$ ground state) for Er in $LaB_6$ are consistent with one of the following possibilities: (a) $A_4\langle r^4\rangle < 0$ and $A_6\langle r^6\rangle > 0$ or (b) $A_4\langle r^4\rangle < 0$ and $A_6\langle r^6\rangle < 0$. According to Table III, for eightfold coordination the VBS model is consistent with (b), while the PC model is in agreement with (a). Further experimental work (i.e., exact knowledge of the level scheme) is needed to resolve the problem completely.

In conclusion, the main issue of this work was to point out the complete agreement in the sign of the crystalline field parameters as measured by EPR on very dilute systems with those measured by other techniques (neutron diffraction, Mössbauer, specific heat) on concentrated systems. This is a step towards a better knowledge of the difficult problem of crystalline fields in metals.

Three contributions were considered to account for the origin of crystalline fields in metals. Unfortunately quantitative fitting at this stage is impossible because the PC model is too naive to explain such complicated phenomena and because no satisfactory calculation of the VBS model is available yet. However, the sign of the crystalline field observed can give information about the dominant mechanisms in metals. It was found that the weaker screening in intermetallic compounds implies appreciably reduced VBS contribution to $A_4\langle r^4\rangle$ in comparison with dilute alloys. Nevertheless this contribution cannot be neglected completely.

*Note added in proof.* In a recent experiment performed on LaSb : Dy single crystal, with the cooperation of J. Susss from the Soreq Nuclear Research Center (Yavne, Israel), a slight angular variation around $g \cong 6.7$ has been observed. It is not yet clear if this anisotropy is due to mixing of the excited $\Gamma_8$ level into the $\Gamma_6$ ground state or if it is due to distortions or clusters. This point is being examined at present. Measurements on other compounds (LaSb : Er) agree with the results quoted in the paper.

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