Direct determination of the crystal field parameters of Dy, Er and Yb impurities in the skutterudite compound CeFe$_4$P$_{12}$ by Electron Spin Resonance.

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Despite extensive research on the skutterudites for the last decade, their electric crystalline field ground state is still a matter of controversy. We show that Electron Spin Resonance (ESR) measurements can determine the full set of crystal field parameters (CFPs) for the $T_h$ cubic symmetry ($Im3$) of the Ce$_{1−x}$R$_x$Fe$_4$P$_{12}$ ($R =$ Dy, Er, Yb, $x < 0.003$) skutterudite compounds. From the analysis of the ESR data the three CFPs, $B'_0$, $B'_1$ and $B'_2$ were determined for each of these rare-earths at the Ce$^{3+}$ site. The field and temperature dependence of the measured magnetization for the doped crystals are in excellent agreement with the one predicted by the CFPs $B'_n$ derived from ESR.

INTRODUCTION

The filled skutterudite compounds RT$_4$X$_{12}$, where R is a rare-earth or actinide, T is a transition metal (Fe, Ru, Os) and X is a pnictogen (P, As, Sb) crystallize in the LaFe$_4$P$_{12}$ structure with space group $Im3$ and local point symmetry $T_h$ for the R ions. Also recently a new skutterudite family, (Sr,Ba)Pt$_4$Ge$_{12}$, was found.\[1] The R ion is surrounded by eight transition metal ions forming a cube, and twelve pnictogen ions that form a slightly deformed icosahedron.\[2] These materials exhibit a broad range of strongly correlated electron phenomena.\[3, 4, 5] In addition, the antimonite members, are potential thermoelectric materials due to their enhanced Seebeck coefficient.\[6, 7] It has been assumed for a long time that the description of the electric crystalline field (CF) of the cubic point groups, T, $T_h$, O, $T_d$, and $O_h$ is the same for all of them. Recently, Takegahara et al.\[8] studied the CF for cubic point groups using group theory and a simple point charge model and found that the above was not correct. Takegahara et al. noticed that due to the absence of two symmetry operations in the T and $T_h$ groups, namely the $C_4$ and $C_4'$ rotations, the CF Hamiltonian ($H_{CF}$) allows for additional sixth order terms with an extra crystal field parameter (CFP), $B'_6$. Therefore, for $T_h$ symmetry, in terms of the Steven’s operators\[10] $H_{CF}$ should be written as

$$H_{CF} = B'_0 (O_4^0 + 5O_4^1) + B'_0 (O_6^0 - 21O_4^1) + B'_6 (O_6^2 - O_6^0),$$

where the last term is absent in the ordinary cubic symmetry $O_h$. Its presence does not affect the degeneracy of each sublevel when compared with that of the $O_h$ group, but some eigenfunctions and eigenvalues may be appreciably different.\[8] The knowledge of the CF levels, especially the ground state, is essential to understand the role of the 4f-electrons in these compounds. However, in spite of the large amount of work invested, the CF ground state is still unclear in several of these systems.\[11, 12]

Electron spin resonance (ESR) has been used for more than half a century to examine a wide variety of compounds.\[10] It is a very useful and highly sensitive technique to study spin correlations. It provides information about CF effects, site symmetry, valence of the paramagnetic ions, $g$-value, fine and hyperfine parameters, etc. Besides, the sample size required for ESR is typically less than $\sim 4 \text{ mm}^3$, i.e., much smaller than that needed for most other techniques. When the compound is not paramagnetic, ESR can still provide useful information by doping the matrix with a small amount of paramagnetic ions such as Nd$^{3+}$, Gd$^{3+}$, Dy$^{3+}$, Er$^{3+}$, Yb$^{3+}$, etc. The ESR spectra of the impurities allow not only to learn about the impurity, but also to study the properties of the host lattice. In cases where the first excited state is separated from the ground state by an energy of the order of the temperature at which the data is taken, a field induced change of the $g$-value\[13] and an exponentially activated $T$-dependence of the linewidth\[14, 15] may be expected. Moreover, the ESR of an excited state could also be observed.\[16] Thus, by measuring the ESR at different frequencies and temperatures of various R impurities, one may obtain an accurate determination of their ground state and, in some cases, the full set of CFPs determining the overall splitting of the ground J-multiplet.

Mesquita et al.\[17] measured the ESR spectra of Ce$_{1−x}$R$_x$Fe$_4$P$_{12}$ ($R =$ Nd, Dy, Er, Yb; $x < 0.005$) up to 4.2 K. Our data, taken in the same range of $T$, agree with those published previously. The data in Refs.\[17, 18] was analyzed assuming $H_{CF}$ for the cubic group, i.e., Eq.\[11] without the $B'_6$-term. In particular, the unexpected $g$-value of 6.408(3) measured for the Kramers doublet ground state of Er$^{3+}$ in CeFe$_4$P$_{12}$ can-

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not be explained if the term $B_0^x(O_0^x - O_0^y)$ is not included in $H_{CF}$. By using the $H_{CF}$ given in Eq. (1) and measuring up to $T \approx 50$ K to populate the excited states, the ESR data for the various R impurities can be explained and the full set of CFPs determined.

The last term in Eq. (1) is usually of secondary importance. ESR is the second technique known to us where this term cannot be ignored. The other examples are the crystalline field potential of PrOs$_4$Sb$_{12}$ and PrFe$_2$Sb$_{12}$ measured by inelastic neutron scattering.[23, 24] In those compounds the $B_0^x$-term rules out the non-Kramers doublet $\Gamma_3$ as the ground state, in favor of the $\Gamma_1$ singlet.

**EXPERIMENTAL**

Single crystals of Ce$_{1-x}$R$_x$Fe$_4$P$_{12}$ (R = Nd, Dy, Er, Yb; $x \lesssim 0.003$) were grown in a molten Sn flux according to the method described in Ref. 21. Within the accuracy of microprobe analysis the crystals studied are found to be uniform. The R concentrations were determined from the $H$ and $T$-dependence of the magnetization, $M(H, T)$. $M(H, T)$ measurements were taken in a Quantum Design MPMS SQUID dc-magnetometer.

The crystals used were about $2 \times 2 \times 2$ mm$^3$ with perfect natural crystallographic grown faces. The cubic structure (space group $I\overline{4}3$) is not included in Table I. The low-$T$ metallic character of the compound is associated to the thermally activated conductivity ($\sim 10^{-3}$ (Ωcm)$^{-1}$) reported for this material at low-$T$. [21]

**RESULTS**

Fig. 1 shows the $T$-dependence of the X-Band ESR linewidth, $\Delta H$, for the Kramers doublet ground state of Dy$^{3+}$ and Er$^{3+}$ in CeFe$_2$P$_{12}$. Within the experimental accuracy, the linear $T$-term is negligible at low-$T$, in agreement with previous measurements.[17] This indicates that there is no spin-lattice relaxation via an exchange interaction with the conduction-electrons (ce) (Korringa relaxation).[23, 24] Q-Band data (not shown here) are similar to the data presented in Fig. 1 with slightly larger ($\lesssim 15\%$) residual linewidth, $\Delta H(T = 0$ K), i.e., no inhomogeneous broadening is observed. Thus, the exponential increase of $\Delta H$ at high-$T$ results from an homogeneous line broadening due to a phonon spin-lattice relaxation process involving the excited CF levels (see below). For Yb$^{3+}$ in CeFe$_2$P$_{12}$ a $T$-independent (not shown) resonance of $\Delta H = 8(2)$ Oe corresponding to a Kramers doublet ground state was observed up to $T \gtrsim 40$ K. Fig. 2 displays $M(H, T)$ for the same samples.

**ANALYSIS AND DISCUSSION**

We now add the Zeeman term $g_J\mu_B H \cdot J$ to Eq. (1), where $g_J$ is the Lande g-factor, $\mu_B$ the Bohr magneton, $J$ the total angular momentum for each R ion and $H$ is the dc-magnetic field. Following Lea, Leask and Wolf...
TABLE I: ESR and CFPs for Ce_{1-x}R_xFe_4P_{12} (R = Nd, Dy, Er, Yb). Ground state degeneracy is abbreviated “gsd” and “Anis” denotes anisotropic ground state. The symbol ( ) denotes a result obtained from Dy^{3+} data.

| R^{3+} | g_{gsd} | g_{exp.} | g_{calc.} | x | y | W [K] | B_2 [mK] | B_6 [mK] | B_8 [mK] |
|--------|---------|---------|-----------|---|---|-----|--------|--------|--------|
| Nd^{3+} | 4 | Anis. | Anis. | -0.566 | 0.00 | < 0 | > 0 | < 0 | 0.00 |
| Dy^{3+} | 2 | 7.43(7) | 7.43(3) | 0.32 | 0.40 | 0.92(16) | 2.9(6) | 0.027(6) | 0.28(6) |
| Er^{3+} | 2 | 6.408(3) | 6.40(6) | -0.16 | 0.45 | 1.6(3) | -2.3(5) | 0.053(10) | 0.54(10) |
| Yb^{3+} | 2 | 2.575(2) | 2.6(1) | 0.54 | 0.08 | 7(2)^* | 58(17) | 2.3(7) | 24(7) |

FIG. 2: $M(H,T)$ for Dy^{3+}, Er^{3+} and Yb^{3+} in Ce_{1-x}R_xFe_4P_{12} (R = Dy, Er, Yb). The dashed curves are the calculated $M(H,T)$ from Eq. (3) using the CFPs from Table I. The contribution of the sample holder and host lattice to the measured magnetization has been subtracted.

(LLW) the Hamiltonian can be parametrized as

$$H_{CFZ} = W \left\{ (1-|y|) \left[ x \frac{O_{F_4}^0 + 5O_{F_4}^4}{F_4} + (1-|x|) \frac{O_{F_6}^6}{F_6} \right] + y \frac{O_{F_8}^8}{F_8} \right\} + g\mu_B H \cdot J,$$

(2)

where we denoted $O_{F_4}^0 + 5O_{F_4}^4$ by $O_F^4$ and similarly the sixth order terms by $O_F^6$ and $O_F^8$, respectively. The coefficients of Eq. (1) are rewritten as $B_2^2 = (1-|y|) x W / F_4^0$, $B_6 = (1-|y|) (1-|x|) W / F_6^0$, and $B_8 = y W / F_8^0$. The coefficients $F_n^m$ are tabulated in Ref. [20] for various values of $J$. The above is a generalization of the LLW Hamiltonian that includes the $O_F^6$-term.[8, 25] Our parametrization is slightly different from that in Ref. [8] and has the advantage that the entire range of the CFPs is accounted for within the finite intervals (-1 ≤ x ≤ 1) and (-1 ≤ y ≤ 1).

By diagonalizing $H_{CFZ}$ we obtained the CF wave functions and energies for each of the R in units of W as a function of x and y. Then, for a small H the doublet ground state ($\Gamma_i$, i = 5, 6 or 7) the g-value can be calculated ($g = 2g_J |\langle \Gamma_i|S_z|\Gamma_i\rangle|$). For finite field and at resonance $g$ can be obtained from the Zeeman splitting of the doublet, $\Delta E(H) = h\nu = g\mu_B H$. Fig. 3 shows the x and y dependence of the g-value for the ground state of Er^{3+} ($J = 15/2$; $g_1 = 6/5$; W > 0) in a color scale. For y = 0 and variable x, we obtain the expected g-value of 6.000 (orange) for the $\Gamma_6$ and 6.800 (yellow) for the $\Gamma_7$ doublets.[23] The white region in Fig. 3 corresponds to the quadruplet ground states. Thus, a g-value of 6.408 corresponds neither to a $\Gamma_6$ nor to a $\Gamma_7$ ($y = 0$). For y ≠ 0 the g-value decreases and approaches to zero for large values of y (black region). Hence, the measured g-value of ~ 6.4 for Er^{3+} corresponds to a doublet ground state with y ≠ 0. Such a g-value is obtained for the set of (x,y) values indicated by the dashed blue line in Fig. 3. The results shown in Fig. 3 do not depend on the sign of y.

FIG. 3: (color online) The color scale shows the ground state theoretical g-values for Er^{3+} ($J = 15/2$; $g_1 = 6/5$, W > 0) as a function of (x,y). The blue dashed line indicates the set of (x,y)-values corresponding to the experimental $g$. The red line correspond to the (x,y)-values for Dy^{3+} ($J = 15/2$; $g_1 = 4/3$, W > 0) and measured $g = 7.438$ (the experimental uncertainty of the g-value is about the width of those lines).

The same procedure was followed with the measured g-values for Dy^{3+} ($J = 15/2$; $g_1 = 4/3$) and Yb^{3+} ($J = 7/2$; $g_1 = 8/7$) impurities. To be able to present the
g-values of Dy$^{3+}$ in Fig. 3, we re-scaled them by the $g_I$ ratio between Dy$^{3+}$ and Er$^{3+}$ ($g_D^3/y_D^{10} = 10/9$). The (x,y) values corresponding to the experimental $g$-value for Dy$^{3+}$ are given by the red curve in Fig. 3. The results for Yb$^{3+}$ are similar, but not shown in Fig. 3.

The $B_n^m$ parameters are angular momentum effective values of the actual CFP $A_n^m$ defined in real space. The $B_n^m$ and $A_n^m$ are related by $B_n^m = \langle r^n(r) \rangle \theta_n A_n^m$. Here $\theta_n$ is a geometrical factor arising from the addition of angular momenta. The substitution of a weakly intermediate valence Ce ion by a R$^{3+}$ impurity may distort the electron density in the neighborhood of the defect. However, the host perturbation by the R$^{3+}$ impurities should be comparable for Er$^{3+}$, Dy$^{3+}$ and Yb$^{3+}$ ions, therefore, the actual CFPs $A_n^m$ should not depend much on the ion R. Thus, if $R_1$ and $R_2$ denote two rare earth impurities, it is possible to relate their CFPs $B_n^m$ (3).

$$
\frac{B_n^m(R_1)}{(r^n(R_1))\theta_n(R_1)} = \frac{B_n^m(R_2)}{(r^n(R_2))\theta_n(R_2)}.
$$

Defining

$$
\beta = \frac{\langle r^4(R_2) \rangle \langle r^6(R_1) \rangle}{\langle r^6(R_2) \rangle \langle r^4(R_1) \rangle},
$$
$$
\delta = \frac{\langle r^6(R_1) \rangle}{\langle r^6(R_2) \rangle},
$$
$$
\xi = \theta_4(R_2) \theta_6(R_1) F_0^6(R_1) F_0^4(R_2) \theta_4(R_1) \theta_6(R_2) F_0^6(R_2) F_0^4(R_1),
$$
$$
\gamma = \frac{F_0^6(R_1) F_0^2(R_2)}{F_0^4(R_2) F_0^6(R_1)},
$$
$$
\eta = \frac{F_0^2(R_1) \theta_6(R_1)}{F_0^6(R_2) \theta_6(R_2)},
$$

we obtain the following relations among the sets of parameters $(x_2,y_2,W_2)$ and $(x_1,y_1,W_1)$ for the two ions

$$
x_2 = \frac{\xi \beta}{1 - (1 - |\xi \beta|) |x_1|} x_1.
$$
$$
y_2 = \left[ 1 + \frac{(1 - |x_1|)(1 - y_1)}{\gamma \gamma_1 (1 - |(1 - |\xi \beta|)|x_1|)} \right]^{-1}
$$

and

$$
W_2 = \eta \delta W_1 \left[ y_1 + \frac{(1 - |x_1|)(1 - y_1)}{\gamma \gamma_1 (1 - |(1 - |\xi \beta|)|x_1|)} \right]^{-1}
$$

where $\xi$, $\gamma$ and $\eta$ are geometrical parameters that only depend on $\theta_n$ and $F_0^m$ (their values are tabulated in Ref. 20). On the other hand, $\beta$ and $\delta$ depend on the expectation values $\langle r^n(R) \rangle$. $\beta$ enters the expression for $x_2$ and $y_2$, while in order to obtain $W_2$ also $\delta$ is needed. The values for $\langle r^n(R) \rangle$ have been computed in Ref. 21 for the free (unperturbed) rare earth ions. In general, the $\langle r^n(R) \rangle$ values depend on the host, in particular whether it is an insulating 28 or a metallic 29 environment. Their values may be obtained from ab-initio calculations, which are beyond the scope of this work. Nonetheless, $\beta$ and $\delta$ depend on the $\langle r^n(R_1) \rangle/\langle r^n(R_2) \rangle$ ratios that, for Dy$^{3+}$, Er$^{3+}$ and Yb$^{3+}$, in a given lattice (whether insulator 21, 28 or metals 29) present differences smaller than 5%. In other words, the changes of $\langle r^n(R) \rangle$ from the free ion values are about the same for the various R when located in the same environment. As CeFe$_4$P$_{12}$ is a small gap semiconductor, for $\beta$ and $\delta$ we shall assume values close to those for an insulator. Here we assume that the values are within $\pm 10\%$ of the insulating ones.

The blue curve in Fig. 4 again shows the (x,y) parameters for Er$^{3+}$ (see Fig. 3). Using Eq. 4 the set of (x,y) values for Dy$^{3+}$ and Yb$^{3+}$ that satisfy the measured ground state g-values may be transformed to the (x,y) space corresponding to Er$^{3+}$. The results for Yb$^{3+}$ and Dy$^{3+}$ are shown in Fig. 4 by the red and black lines, respectively. The width of these lines includes the uncertainty of $\beta$ and experimental error bars of the measured g-values. Notice that the lines for Dy$^{3+}$, Er$^{3+}$ and Yb$^{3+}$ all intersect at a single point (x $\approx$ −0.16(3), y $\approx$ 0.45(3)). The three ions have the same charge and a similar size, therefore, we may assume that the actual CFPs are about the same for these impurities in CeFe$_4$P$_{12}$. This suggests that the ratios involving the actual CFPs are $A_n^2(\langle r^4(R) \rangle)/A_0^6(\langle r^6(R) \rangle) \approx$ −2.0 and $A_6^6/A_0^6 \approx$ 10 for the three impurities. Now these Er$^{3+}$ (x,y)-values are transformed back to obtain the (x,y)-values for Dy$^{3+}$ and Yb$^{3+}$, which are listed in Table I. Notice that the (x,y)-values for Dy$^{3+}$ and Yb$^{3+}$ are obtained by using their experimental g-values and the assumption of similar crystal fields.

![FIG. 4: (color online) Set of (x,y)-values, satisfying the ground state g-values of the studied R$^{3+}$ ions, transformed into the Er$^{3+}$ (x,y)-space by eq. 4. The open circle indicates the point where Dy$^{3+}$, Er$^{3+}$ and Yb$^{3+}$ share the same ratios, A_n^2(\langle r^4(R) \rangle)/A_0^6(\langle r^6(R) \rangle) \approx$ −2.0 and $A_6^6/A_0^6 \approx$ 10 (see text).](image-url)
The above is valid independently of the energy scaling parameter $W$. The values of $W$ for all three impurities can be determined if the $W$ for one of them is known (see Eq. 1). $W$ can be estimated from the $T$-dependence of $\Delta H$ data. The solid lines seen in Fig. 1 are the best fit of the measured $\Delta H$ for Dy$^{3+}$ and Er$^{3+}$ in CeFe$_4$P$_{12}$ to the expression

$$\Delta H = a + c_1 \frac{\Delta_1^3}{[e^{\Delta_1/kT} - 1]} + c_2 \frac{\Delta_2^3}{[e^{\Delta_2/kT} - 1]} \quad (6)$$

where $a$ is the residual linewidth. The relaxation is through phonon modes and requires the coupling of phonons between the ground and excited CF states. We consider here the two lowest excited CF states with non-vanishing matrix elements from the ground state and denote the excitation energies with $\Delta_{1,2}$, respectively. The coefficients $c_{1,2}$ are given by $(3k_B^2/2\pi\hbar^2\rho v^2)M_{1,2}^2$ ($\rho$ is the host density, $v$ the sound velocity and $M_{1,2}^2$ the sum of the squares of the matrix elements of the dynamic-crystal field potential). [14, 15] The parameter values resulting from the fits are given in the caption of Fig. 1.

By using the values of $(x,y)$, $\Delta_1$ and $\Delta_2$ (see Fig. 1) we obtain $W_{Dy} = 0.92(16)$ K and $W_{Er} = 1.6(3)$ K. The resulting energy levels for Dy$^{3+}$ and Er$^{3+}$ ions are shown in Fig. 5. On the other hand, using $W_{Dy}$ and Eq. 5 we can obtain $W$ for the other ions. In particular, for Er$^{3+}$ we obtain $W_{Er} = 1.3(4)$ K, where the error bar includes 20% of experimental errors and 10% from the uncertainty of $\delta$. We see that, within the error bars, the values $W_{Er}$ and $W_{Dy}$ agree. Using again $W_{Dy}$ we determined $W_{Yb} = 7(2)$ K. The Yb$^{3+}$ energy levels are also shown in Fig. 5. Once the set of $(x,y)$ and $W$ parameters are known for a given R, their corresponding CFPs $B_{in}^n$ are calculated (see Table I).

Assuming that the $\langle \rho^n(R) \rangle$ values are, within 10%, of their values in insulators, 28 the actual CFPs $A_{in}^n$ can be estimated

$$A_{4}^n \simeq -33(10)K/a_0^4$$
$$A_{6}^n \simeq 4(1)K/a_0^6$$
$$A_{8}^n \simeq 44(15)K/a_0^8 \quad \quad (7)$$

where $a_0$ is the Bohr radius. The main sources of error are the experimental $\Delta_1$ and theoretical $\delta$ uncertainties.

For Nd$^{3+}$ the $(x,y)$ values that account for the measured anisotropic $g$-values of the quadrupole ground state are given in Table I. These values correspond to a point in the Er$^{3+}$ $(x,y)$ space (filled circle in Fig. 4), which is different than that for the other R$^{3+}$ ions. This suggests that the large Nd$^{3+}$ ionic radius, as compared with those of the other R$^{3+}$ and the intermediate valence of the Ce ions, probably causes a large local crystal distortion close to the Nd$^{3+}$ site. Additional experimental information, involving the excited CF levels, would be needed to determine $W_{Nd}$ in this compound. Therefore, the complete set of actual CFPs $A_{in}^n$ for Nd$^{3+}$ cannot be given. Nevertheless, the $(x,y)$ values for Nd$^{3+}$ are compatible with $W_{Nd} < 0$. In Fig. 5 we present the Nd$^{3+}$ energy levels using arbitrarily $W_{Nd} = -5$ K (see caption of Fig. 5).

The CF splittings of the $J$-multiplet determine $M(H,T)$

$$M(H,T) = \frac{\sum_{i=1}^{2J+1} m_i(H)e^{-E_i(H)/k_B T}}{\sum_{i=1}^{2J+1} e^{-E_i(H)/k_B T}} \quad \quad (8)$$

where $m_i(H)$ and $E_i(H)$ are the magnetization and energy eigenvalue of each eigenstate of the Hamiltonian (Eq. 2) computed at a finite $H$ using Eq. 8 and the CFPs $B_{in}^n$ given in Table I. The dashed curves in Fig. 2 show the calculated magnetization, $M(H,2$ K)$$ and $M(H,12$ K)$$, for two concentrations of Dy$^{3+}$, Er$^{3+}$ and Yb$^{3+}$ as compared to the experimental data. In all cases the sample holder diamagnetism was previously determined and subtracted from the total magnetization. Also, the paramagnetic contribution of the undoped CeFe$_4$P$_{12}$ host lattice was measured and subtracted. At low-$T$ ($2$ K $\leq T \leq 12$ K) that magnetization is less than 10% of the samples doped with Er $(x = 0.0017)$ and Dy $(x = 0.0034)$ and $\sim 30\%$ of the one doped with Yb $(x = 0.0023)$. 

FIG. 5: (color online) CF energy levels for the studied R$^{3+}$ ions in CeFe$_4$P$_{12}$. For Nd$^{3+}$ we used arbitrarily $W_{Nd} = -5$ K. Thus, if the actual $W_{Nd}$ value is known the Nd$^{3+}$ energy levels should be scaled by $-W_{Nd}/5$ K. The high of the dotted line boxes indicate the uncertainty of the energy levels.
CONCLUSIONS

The filled skutterudite CeFe₃P₁₂ compound is a small gap (≈ 1500 K) semiconductor. Hence, the R³⁺ spin-lattice relaxation via an exchange interaction with ce is inhibited (Korringa process), since the ce must be promoted via exponential activation. This is verified by the absence of a linear T-term in our low-T ΔH data (see Fig. 1). Similarly, a g-shift (Knight shift) is not expected. Therefore, the shift of the g-value of the Kramers ground-doublet relative to that in O₆ symmetry (y = 0) is due to the B⁵(₆)₆(₆)₆-term in Hₖ. For O₆ symmetry the Kramers doublet g-values are unique (independent of the CFs) and the exchange coupling in a metallic host is simple obtained from the g-shift of the resonance. Our calculation showed that the presence of the new term results always in an isotropic g-value and a negative g-shift for the doublet ground states for J = 7/2 and 15/2. For impurities in metallic hosts with T₅ symmetry, when studied by ESR, a negative g-shift results in a complication to evaluate the sign and magnitude of the exchange interaction between the R³⁺ localized magnetic moment and the ce.

In summary, in this work we measured the ESR for Dy⁴⁺, Er⁴⁺ and Yb⁴⁺ ions doped into the filled skutterudite CeFe₃P₁₂ with T₅₈ structure. We obtained the three CFs B₉ⁿ, determined the CF ground state, explained the unexpected Er⁴⁺ g-value, and found the CF overall splitting for the J₅⁺ ground state multiplet. With the obtained CFs we could fit the low-T M(H,T) of the crystals used in the ESR experiments. Moreover, our working assumption that the actual CFs A₉ⁿ are about the same for Dy⁴⁺, Er⁴⁺ and Yb⁴⁺ in this compound turned out to be very plausible. A similar work could be carried out on undoped compounds such as LnFe₃P₁₂, for Ln = Nd, Gd, Dy, etc., all Kramers ions with magnetic ground multiplet. Besides, this work and our preliminary ESR data in the doped unfilled skutterudites CoSb₃ put in evidence the importance of the extra B⁵(₆)₆(₆)₆-term in Hₖ for compounds with T₅₈ symmetry. In addition, we emphasized the extra caution we need to have when ESR is used to determine the exchange parameter in metallic compounds with T and T₅₈ symmetry.

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