

## Spin-Phonon and Lattice Contributions to the Ground-State Splitting of $\text{Gd}^{3+}$ and $\text{Eu}^{2+}$ in Scheelite Crystals

A. D. Gorlov

*Institute of Physics and Applied Mathematics, Ural Federal University named after the First President of Russia B. N. Yeltsin, pr. Lenina 51, Yekaterinburg, 620083 Russia*

*e-mail: Anatoliy.Gorlov@urfu.ru*

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**Abstract**—The EPR spectra of  $\text{Gd}^{3+}$  in  $\text{CaWO}_4$  single crystals have been studied at temperatures  $T = 1.8, 4.2,$  and  $114\text{--}300$  K, and the temperature dependence of the parameters  $b_n^m(T)$  of the spin Hamiltonian has been found. The behavior of  $b_2^0(T)$  has been analyzed. The spin-phonon and static lattice contributions  $b_2^0(F)$  and  $b_2^0(L)$  to  $b_2^0(T)$  have been revealed. For this purpose, the variation of  $b_2^0(L)$  has been calculated taking into account the thermal shifts of oxygen ions in  $\text{CaWO}_4$ . Similar analysis has been carried out for  $\text{CaWO}_4 : \text{Eu}^{2+}$  based on the EPR data of other authors (Bronstein, Voterra and Harvey, Kieft). It has been shown that at  $b_2^0(F) > 0$ , the variation of  $b_2^0(F)$  as a function of  $T$  for these impurity centers is described well by the Pfister model and a sign change of  $b_2^0(T)$  for  $\text{Eu}^{2+}$  is determined by thermal expansion of the lattice.

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Spectroscopic studies of crystals with the scheelite ( $\text{CaWO}_4$ ) structure with an impurity of rare-earth metals are stimulated by their wide use in practice [1–3]. The efficiency of devices based on these materials largely depends on the phonon spectrum, which affects both the relaxation characteristics and the positions of the impurity energy levels [4–7].

Numerous EPR studies of transition impurity ions in various crystals showed that the parameters  $b_n^m(T)$  of the spin Hamiltonian or the initial splitting constant depend significantly on temperature. These parameters that determine the ground-state splitting  $\Delta E$  of such centers depend on both the coordinates ( $R_i, \theta_i, \varphi_i$ ) of ligands surrounding the impurity and the thermal vibrations of the lattice sites of the crystal [4–11]. It is impossible to separate the contributions to  $\Delta E$  from the variations of the coordinates with increasing temperature and from the thermal vibrations of the lattice with the use of only EPR spectra. However, if one takes into account the temperature behavior of the parameters of the initial splitting, e.g.,  $b_n^0(L)$ , owing to changes in the coordinates of ligands (implicit effect), it proves possible to separate the contribution  $b_n^0(F)$  of the lattice vibrations (the phonon contribution or the explicit effect) [4] from the experimental  $b_n^0(T)$  values. Then, the difference between the experimental  $b_n^0(T)$

and calculated  $b_n^0(L)$  values at a given temperature should be attributed to the contribution  $b_n^0(F)$  of the lattice vibrations, i.e.,

$$b_n(F) = b_n^0(T) - b_n(L). \quad (1)$$

Hereinafter,  $b_n^0(F) = b_n(F)$  and  $b_n^0(L) = b_n(L)$ .

In this work, we separate these contributions to  $b_2^0$  for  $\text{Gd}^{3+}$  and  $\text{Eu}^{2+}$  in  $\text{CaWO}_4$  single crystals based on our EPR studies of  $\text{Gd}^{3+}$  in  $\text{CaWO}_4$ , the data of [12–15], and the results of X-ray structure analysis [16, 17].

It should be mentioned that the temperature dependence of  $b_n(L)$  is usually neglected in such studies [9–11]. In those works, where this contribution is taken into account, the estimates are carried out in the point-charge model with the use of the data on thermal expansion (compression) coefficients known in a limited temperature range (see references in [4–11]). We calculated  $b_n(L)$  in the superposition model [18], which has made a good showing. As will be shown below, our results clearly indicate the necessity of taking into account the variations of  $b_n(L)$  in the analysis of the temperature dependence of  $b_2^0$ , at least, in scheelite structures.

The dependence  $b_n^m(T)$  for  $\text{Gd}^{3+}$  and  $\text{Eu}^{2+}$  in  $\text{CaWO}_4$  was already partly studied in [12–15] but, in

**Table 1.** Parameters (in MHz) of the spin Hamiltonian of  $\text{Gd}^{3+}$  in  $\text{CaWO}_4$ 

Parameter	$T, \text{K}$						
	1.8	4.2	114(3)	153(3)	199(4)	240(4)	300(2)
$g_x = g_y$	1.992(1)	1.992(1)	1.9915(6)	1.9917(5)	1.9917(5)	1.9915(7)	1.9918(8)
$g_z$	1.992(1)	1.992(1)	1.9915(7)	1.9916(5)	1.9916(5)	1.9915(6)	1.9916(5)
$b_2^0$	-2757(1)	-2758(2)	-2739.7(4)	-2728.7(3)	-2716.7(3)	-2700.8(3)	-2679.6(3)
$b_4^0$	-71.9(5)	-71.7(5)	-71.4(3)	-70.9(3)	-70.2(3)	-69.4(3)	-68.4(3)
$b_4^4$	-437(4)	-438(4)	-434(2)	-432(2)	-429(2)	-425(2)	-420(2)
$P_2^0(\text{Gd}^{155})$	-59.49(1)	-59.5(4)	-59.2(4)	-59.0(4)	-58.8(4)	-58.5(5)	-58.3(5)
$P_2^0(\text{Gd}^{157})$	-63.36(1)	-63.3(4)	-62.7(4)	-62.6(4)	-62.5(4)	-62.3(5)	-62.2(5)

$b_6^0 = 0.6(8)$ ,  $b_6^4 = 13(11)$ ,  $b_6^6 = 0(2)$ ;  $A_x = A_y = 12.3(3)$ ,  $A_z = 12.4(3)$  and  $b_2^0(T)/P_2^0(T) = 46.2(3)$  for  $\text{Gd}^{155}$  and  $A_x = A_y = 16.2(3)$ ,  $A_z = 16.3(3)$  and  $b_2^0(T)/P_2^0(T) = 43.4(3)$  for  $\text{Gd}^{157}$  at all temperatures; the tabulated  $g_n$  values are used.

our opinion, the conclusions on the lattice and phonon contributions are incorrect. We analyzed the EPR data for  $\text{Eu}^{2+}$  in  $\text{CaWO}_4$  to determine the reason of a sign change of  $b_2^0(T)$  and to compare the parameters describing the temperature behavior of the initial splitting of two  $S$ -state rare-earth impurity ions in the same matrix. The obtained results can serve as reference data for testing the theoretical models of dynamic and static interactions near the impurity centers.

The  $\text{CaWO}_4 : \text{Gd}^{3+}$  crystals under investigation were grown by the Czochralski method with a 0.02 wt % impurity of  $\text{Gd}_2\text{O}_3$  (with the natural abundance of isotopes) in the mixture. The EPR spectra at various orientations of the external magnetic field  $\mathbf{H}$  and various temperatures were studied on a Bruker EMX plus X-band spectrometer. The EPR spectrum (the electron spin  $S = 7/2$ ) is a set of intense (allowed transitions with the spin projection change  $|\Delta M| = 1$ ) and weak (forbidden transition with  $|\Delta M| > 1$ ) signals. The positions of all transitions are described well by the spin Hamiltonian corresponding to the local symmetry  $D_{2d}$ ; i.e.,  $\text{Gd}^{3+}$  substitutes  $\text{Ca}^{2+}$  as was previously shown in [12, 13]. At all orientations of  $\mathbf{H}$ , we observed the hyperfine structure of the EPR signals associated with odd isotopes  $\text{Gd}^{155, 157}$  (nuclear spin  $I = 3/2$ ). The hyperfine structure is most clearly resolved in the spectra of forbidden electron-nuclear transitions (involving nuclear spin flips) owing to a low linewidth (0.4–1.0 G) even at  $T > 300$  K. Investigation of the hyperfine structure at various orientations of  $\mathbf{H}$  allowed finding the hyperfine ( $A_x = A_y, A_z$ ) and quadrupole ( $P_2^0$ ) interaction constants of odd isotopes. The technique of finding  $A_i$  and  $P_2^0$  is described in

[19]. The data obtained in the reference frame similar to that of [19] are given in Table 1. At close temperatures, they coincide with the results of [12, 13], except for the  $b_4^4$  values, which depend on the choice of the directions of the  $\mathbf{X}$  and  $\mathbf{Y}$  axes.

#### Temperature Dependence of $b_2^0$ for $\text{Gd}^{3+}$ and $\text{Eu}^{2+}$ in $\text{CaWO}_4$

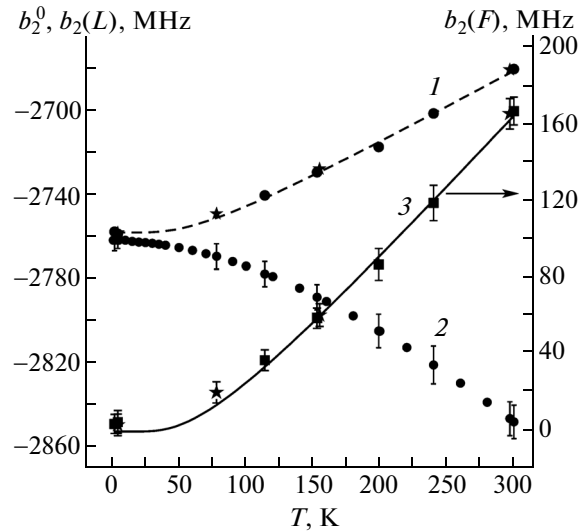
(1)  $\text{CaWO}_4 : \text{Gd}^{3+}$ . The experimental dependence  $b_2^0(T)$  for  $\text{Gd}^{3+}$  in  $\text{CaWO}_4$  is shown in Fig. 1, where the symbols at the curve  $I$  are the data of (circles) this work and (stars) [12, 13]. This parameter increases with increasing temperature, which is also exhibited by other crystals with the fluorite structure and the  $\text{Gd}^{3+}$  impurity [12, 13, 19, 20]. To find the ratio of two contributions to  $b_2^0(T)$  (see Eq. (1)) we calculated  $b_2(L)$  in the superposition model [18] taking into account the temperature variations of the coordinates of 8 oxygen ions nearest to the rare-earth impurity. To find  $b_2(L)$  we used the expression for  $b_2^0$  and the values of intrinsic parameters of  $\text{Gd}^{3+}$  quoted in [21]:

$$b_2(L) = \sum_i k_i(\theta) [b_{2p}(R_0/R_i)^3 + b_{2s}(R_0/R_i)^{10}]. \quad (2)$$

Here,  $b_{2p} = -1.289 \times 10^4$  MHz is the contribution of the point charge of  $\text{O}^{2-}$  at the distance  $R_0 = 2.34$  Å and  $b_{2s} = 6.892 \times 10^3$  MHz is the contribution of the overlap and covalence,  $k_i(\theta) = n/2(3\cos^2\theta_i - 1)$  are the coordination factors [18]. The ligands nearest to  $\text{Gd}^{3+}$  are separated into two quartets with equivalent contri-

butions to  $b_2^0$ , so that  $i = 1, 2$  and  $n = 4$ . We find their coordinates  $R$ ,  $\theta$  and  $\varphi$  in the  $\text{CaWO}_4$  lattice from the experimental results of [16, 17] using the functional dependences of the lattice parameters on  $T$  and the values of the coordinates  $x$ ,  $y$ , and  $z$  of the ligands. The distances  $\text{Gd}^{3+}-\text{O}^{2-}$  were calculated according to the formula  $R_i = R + (r_i - r_h)/2$  [22], where  $r_i$  and  $r_h$  are the ionic radii of the impurity and substituted ions from the Shannon tables [23]. The obtained values of  $b_2(L)$  are shown in Fig. 1 by dark circles 2. The errors in  $b_2(L)$  reflect the difference between the average values of the coordinates of  $\text{O}^{2-}$  (in the temperature range  $T = 5-300$  K) and the  $x, y, z$  values quoted in [17] for the specific temperatures. Since the obtained values of  $b_2(L)$  decrease and the values of  $b_2^0$  increase with an increase in temperature (Fig. 1), we can conclude that  $b_2(F) > 0$ .

Next, we consider the  $T$  dependence of the phonon-induced contribution  $b_2(F)$  to  $b_2^0$ , which we find from our experimental data according to Eq. (1). There are several theoretical models of the spin-phonon interaction affecting the positions of impurity energy levels in crystals: (i) the Huang model [5] assuming the dominant effect of optical phonons on  $\Delta E$  and, consequently, on  $b_2(F)$ ; (ii) the Shrivastava model [6], in which the leading contribution to  $\Delta E$  comes from acoustic phonons; and (iii) the Pfister model [7], which shows that the main role in the phonon-induced contribution is played by local optical vibrations of the impurity cluster. Each model assumes a specific temperature dependence of  $b_n(F)$ . Using the genfit procedure of the Mathcad package we



**Fig. 1.** (1) Dependence  $b_2^0(T)$  for  $\text{CaWO}_4 : \text{Gd}^{3+}$ , (2) the calculated  $b_2(L)$  values at different temperatures  $T$ , and (3) the dependence  $b_2(F)$  given by Eq. (3) with the parameters from Table 2. Squares on curve 3 are the values calculated according to Eq. (1). Circles and asterisks on curve 1 are the results obtained in this work and [12, 13], respectively.

find that the function that fits best this dependence is the one proposed in [7]:

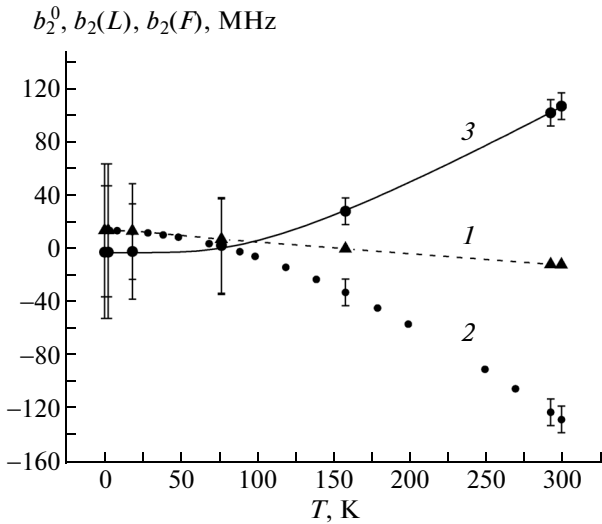
$$b_2(F) = b_2(0)[\coth(\hbar\omega/2kT) - 1], \quad (3)$$

where  $b_2(0)$  is the contribution of zero-point lattice vibrations,  $\omega$  is the frequency of the local vibrations of the cluster including the impurity and nearest ligands and  $k$  is the Boltzmann constant. In particular, curve 3 in Fig. 1 corresponds to Eq. (3) with the parameters  $b_2(0)$  and  $\omega$  for  $\text{Gd}^{3+}$  listed in Table 2. Squares at this

**Table 2.** Model parameters of the temperature dependences of  $b_2(F)$  and  $b_2^0$

Model	Parameter			
	$b_2^0(\text{RL}), \text{MHz}$	$b_2(0), \text{MHz}$	$\omega \times 10^{-13}, \text{rad/s}$	$\Theta_D, \text{K}$
$\text{Gd}^{3+}$				
Pfister [7]		73.6(78)	2.51(17)	
Pfister [7, 11]	-2789(3)	31.7(14)	2.36(12)	
Huang [5, 11]	-2757(3)	42.8(29)		455(19)
Shrivastava [6, 11]	-2757(3)	33.3(25)		250(12)
$\text{Eu}^{2+}$				
Pfister [7]		108.2(50)	4.28(11)	
Pfister [7, 11]	17.6(11)	-0.79(5)	0.23(2)	
Huang [5, 11]	16.7(10)	-0.72(5)		32(2)
Shrivastava [6, 11]	16.7(10)	-0.78(5)		23(2)

Errors in the parameters correspond to  $3\sigma$ .



**Fig. 2.** (1) Dependence  $b_2^0(T)$  for  $\text{CaWO}_4:\text{Eu}^{2+}$  according to the data of [14, 15], (2) calculated temperature dependence of  $b_2(L)$ , and (3) temperature dependence of  $b_2(F)$  calculated according to Eq. (1) (symbols) and Eq. (3) (solid curve) with the parameters taken from Table 2.

curve were found with the use of Eq. (1) (stars are the data of [12, 13]). The errors in  $b_2(F)$  shown in Fig. 1 take into account the uncertainty in finding  $b_2^0(T)$  and  $b_2(L)$  and the errors in the parameters in Table 2 correspond to the triple standard deviation, i.e.,  $3\sigma$ .

(2)  $\text{CaWO}_4:\text{Eu}^{2+}$ . The experimental dependence  $b_2^0(T)$  for  $\text{Eu}^{2+}$  in  $\text{CaWO}_4$  according to the data of [14, 15] (Fig. 2, symbols marked by 1) is almost linear, crossing the  $T$  axis. These results were analyzed in the same manner as for  $\text{Gd}^{3+}$  in  $\text{CaWO}_4$ .  $b_2(L)$  was calculated with the intrinsic parameters  $b_{2p} = -1.1548 \times 10^4$  MHz [24] at  $R_0 = 2.5$  Å and  $b_{2s} = 9.756 \times 10^3$  MHz; the latter was found in [25] at  $T = 1.8$  K.

The temperature dependence of  $b_2(L)$  is shown in Fig. 2, symbols marked by 2. This parameter decreases with an increase in temperature; in particular,  $b_2(L) > 0$  at  $T < 90$  K and changes its sign with an increase in  $T$ . Consequently,  $b_2(F) > 0$ . The sign change of  $b_2^0$  at  $T \sim 194$  K comes from the fact that at this temperature  $|b_2(L)| \sim b_2(F)$ . At  $T > 194$  K,  $b_2(F) < |b_2(L)|$  and their sum is negative, i.e.,  $b_2^0 < 0$ . Expression (3) with the parameters for  $\text{Eu}^{2+}$  given in Table 2 describes fairly well an increase in  $b_2(F)$  with increasing  $T$  (Fig. 2, curve 3). The errors in the parameters also correspond to  $3\sigma$ .

To estimate the influence of two contributions to the temperature dependence of  $b_2^0$  we find the ratio of  $\Delta b_2(L)$  (the difference between the values at  $T = 1.8$

and 300 K) to  $b_2(F)$  at  $T = 300$  K. The result is  $|\Delta b_2(L)/b_2(F)| \sim 0.5$  and  $\sim 1.2$  for  $\text{Gd}^{3+}$  and  $\text{Eu}^{2+}$ , respectively. This leads to a conclusion of the necessity of taking into account the temperature variation of  $b_2(L)$  in the analysis of  $b_2^0(T)$  for these impurity centers in  $\text{CaWO}_4$ . It should be also mentioned that in our previous work [25] we described the weak dependence  $b_2^0(T)$  for  $\text{Eu}^{2+}$  in  $\text{SrMoO}_4$  ( $\Delta b_2^0 \sim 10$  MHz in the temperature range  $T = 1.8\text{--}300$  K), which possibly also indicates mutual compensation of the spin–phonon and lattice contributions to  $b_2^0$ , i.e., the fact that  $|\Delta b_2(L)/b_2(F)| \sim 1$ .

We could not fit the dependence of  $b_2(F)$  on  $T$  by two other model functions [5, 6] for both  $\text{Gd}^{3+}$  and  $\text{Eu}^{2+}$  in  $\text{CaWO}_4$ . It turned out that the parameters of these functions depend crucially on the initial conditions, which makes their choice ambiguous. Only the inclusion of an additional parameter allows fitting the dependence of  $b_2(F)$  on  $T$ , but this parameter is lacking in the models [5, 6].

On the other hand, the experimental dependences  $b_2^0(T)$  for both  $\text{Gd}^{3+}$  and  $\text{Eu}^{2+}$  in  $\text{CaWO}_4$  can be fitted by any of the functions [5–7] taken in the form of Eqs. (2)–(4) of [11]. These expressions include the parameter  $b_n^0(\text{RL}) = \text{const}$  referred to as the hard-lattice contribution and the  $b_2(F)$  value in the models [5, 6] depends on the integral functions involving the Debye temperature  $\Theta_D$ . Fitting to all model functions resulted in the parameters given in Table 2. Curves 1 in Figs. 1 and 2 correspond to Eq. (2) of [11]. Clearly, in this approach, the entire temperature dependence  $b_2^0(T)$  is attributed to the spin–phonon contribution. In our opinion, this is the reason of different  $b_2(0)$ ,  $\omega$  and  $\Theta_D$  values for  $\text{Gd}^{3+}$  and  $\text{Eu}^{2+}$  in  $\text{CaWO}_4$ . Moreover, these parameters of two  $S$ -state rare-earth ions in the same crystal differ by an order of magnitude. This again indicates the necessity of taking into account the temperature variation of  $b_2(L)$ , whose role in the above description is played by  $b_2^0(\text{RL})$ .

The ratio of the spin–phonon contributions  $b_2(0)$  for  $\text{Gd}^{3+}$  and  $\text{Eu}^{2+}$  in  $\text{CaWO}_4$  in the model [7] is  $\sim 0.7$ . As was shown in the theoretical models of the works [4–7], the spin–phonon interaction results in the hybridization of the ground and excited states of the impurity ion leading to the temperature dependence of  $b_2(F)$ . If the excited state of  $\text{Eu}^{2+}$  lies below the excited state of  $\text{Gd}^{3+}$  in  $\text{CaWO}_4$ , this could explain the ratio of the spin–phonon contributions. On the other hand, a large amplitude of zero-point oscillations of the impurity cluster can also lead to a similar effect.

The temperature variations of the other parameters of the spin Hamiltonian ( $b_4^0$  and  $b_4^4$ , Table 1) resemble those previously observed in [13, 19, 20] for  $\text{Gd}^{3+}$  in isostructural crystals. We analyzed the temperature variations of these parameters only in the model [7] (Eq. (2) of [11] was used) to compare the  $\omega$  values, since, in our opinion, there are no adequate models for the calculation of the lattice contributions  $b_4(L)$ . The following results were obtained:  $b_4^0(\text{RL}) = -75.1$  MHz,  $\omega = 4.24 \times 10^{13}$  rad/s and  $b_4^4(\text{RL}) = -448.3$  MHz,  $\omega = 3.2 \times 10^{13}$  rad/s. As expected, the frequencies  $\omega$  differ from each other and from the values found for  $b_2^0(T)$ . These results indicate a noticeable contribution of the temperature variations of  $b_4^0(\text{RL})$  and  $b_4^4(\text{RL})$  to  $b_4^0(T)$  and  $b_4^4(T)$ , respectively, since the model [7] includes only one frequency of the local vibrations of the cluster that affects all parameters of the initial splitting. From this viewpoint, the results of [20], where only one frequency  $\omega$  was found for all dependences  $b_n^m(T)$ , seem surprising, since this is only possible under the condition  $b_n^m(\text{RL}) = \text{const}$  at all temperatures.

Thus, in this work, the dependences  $b_2^0(T)$  for  $\text{Gd}^{3+}$  and  $\text{Eu}^{2+}$  in  $\text{CaWO}_4$  were analyzed in the Huang [5], Shrivastava [6], and Pfister [7] models. The analysis showed that the model [7], in which local vibrations of the impurity cluster play the key role in the spin–phonon interaction, is most adequate. In this model, the spin–phonon contribution  $b_2^0(F) > 0$  was determined. The necessity of taking into account the temperature variation of the static-lattice contribution  $b_2^0(L)$ , especially for  $\text{Eu}^{2+}$  in  $\text{CaWO}_4$ , was established. It was found that the ratios of the changes of the lattice contribution in the temperature range  $T = 1.8\text{--}300$  K to the spin–phonon contribution at  $T = 300$  K are close to 0.5 and  $\sim 1.2$  for  $\text{Gd}^{3+}$  and  $\text{Eu}^{2+}$  in  $\text{CaWO}_4$ , respectively.

It was shown that the sign change of  $b_2^0(T)$  for  $\text{Eu}^{2+}$  in  $\text{CaWO}_4$  is caused by the sign change of the static-lattice contribution  $b_2^0(L)$  with an increase in the lattice constants with increasing temperature. At  $T > 194$  K  $b_2^0(L) < 0$  and  $|b_2^0(L)| > b_2^0(F)$ , which results in  $b_2^0 < 0$ .

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