

Analysis of Eu^{2+} Spin-Hamiltonian Parameters

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Abstract

The superposition model is used to determine single-ligand spin-Hamiltonian parameters for Eu^{2+} in a range of host crystals. The properties of these parameters are shown to be generally similar to those of the corresponding parameters for Gd^{3+} , although some striking differences occur in their relative magnitudes and distance dependence. Both the similarities and the differences confirm aspects of a previous interpretation of the spin-Hamiltonian parameters for $f^7 \text{ } ^8\text{S}_{7/2}$ ground states.

1. Introduction

There is now evidence, for a wide range of crystalline environments, that the Gd^{3+} ground state spin-Hamiltonian parameters may be analysed into superimposed axially symmetric single-ligand contributions (Newman and Urban 1975). It is therefore of some interest to see whether the spin-Hamiltonian parameters of other S-state ions can be analysed in the same way. Eu^{2+} is of particular interest because, although it has the same electronic structure as Gd^{3+} , its experimentally determined spin-Hamiltonian parameters are sometimes very different indeed (Kim and Moos 1967; Harvey and Kieft 1969).

In this paper we use the conventional notation b_n^m for observed spin-Hamiltonian parameters, and the special notation \bar{b}_n to represent the corresponding axially symmetric parameters (equivalent to b_n^0) for single-ligand contributions. This notation allows us to distinguish the \bar{b}_n from the axial components of the observed spin-Hamiltonian parameters and emphasizes the derivative nature of the \bar{b}_n . We refer to the \bar{b}_n as *intrinsic* parameters, as they are independent of the angular coordination of the ligands and are thus determined solely by the electronic processes of the interaction between the metal ion and a ligand. In this regard the variation of the parameters \bar{b}_n with distance is of particular interest as it is usually found to be quite different to the distance dependence of the corresponding crystal field parameters (Newman and Urban 1972). It is convenient to write this variation in the form

$$\bar{b}_n(R) = (R_0/R)^{t_n} \bar{b}_n(R_0)$$

so that it may be represented by the single parameter t_n in the region of a particular metal-ligand distance R_0 . Further details of the model and relevant tabulations are given by Newman and Urban (1975).

Stedman and Newman (1974, 1975) showed that the Eu^{2+} parameters for strained cubic sites in fluorite structure crystals could be understood in terms of the superposition model only if the parameters \bar{b}_2 were supposed to *increase* in magnitude

with increasing distance of the F^- ions (at least for the range of metal–ligand distances in these crystals). This is very odd behaviour, and in particular it contrasts with the behaviour of \bar{b}_2 for Gd^{3+} which is found to be nearly constant for small increases of ligand distance in a wide range of crystalline hosts (Newman and Urban 1975).

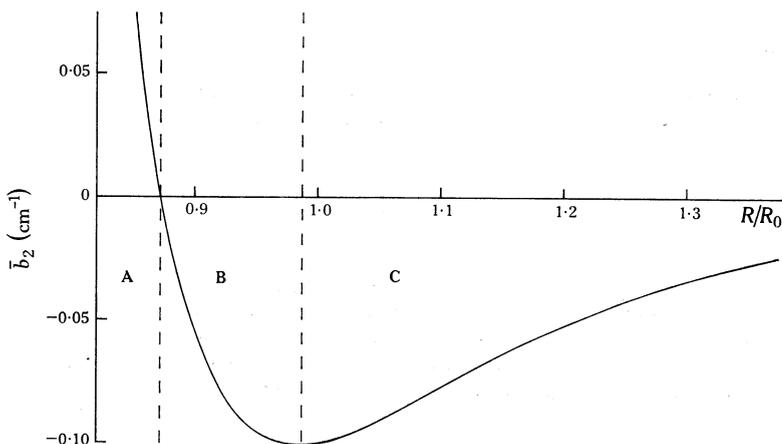


Fig. 1. Radial dependence of the intrinsic parameter \bar{b}_2 according to the model of Newman and Urban (1972). R_0 is the estimated ligand equilibrium distance for Gd^{3+} in the zircons. The equilibrium distances and the vertical scale may differ in other systems, although the form of the distance dependence is expected to be the same. Three regions are distinguished: (A) $\bar{b}_2 > 0$, $t_2 > 0$; (B) $\bar{b}_2 < 0$, $t_2 < 0$; (C) $\bar{b}_2 < 0$, $t_2 > 0$.

Nevertheless, both types of distance dependence are consistent with the distance variation of \bar{b}_2 proposed by Newman and Urban (1972) and shown in Fig. 1. The usual ligand equilibrium distance for Gd^{3+} corresponds to a point in region C near the minimum in this graph, while that for Eu^{2+} in fluorite structure crystals could be in region B. We examine this possibility in some detail in Section 2.

Another point requiring further investigation is the considerable variability of \bar{b}_4 for Gd^{3+} and its intriguing correlation with ligand polarizability (Newman 1975*b*). It is of interest to determine whether the Eu^{2+} parameter \bar{b}_4 shows a similar behaviour and to discover how sensitive this parameter is to the small differences in electronic structure between Eu^{2+} and Gd^{3+} .

2. Eu^{2+} in Cubic Sites

In order to carry out a detailed analysis of axial stress data for Eu^{2+} in CaF_2 , SrF_2 and BaF_2 it is necessary to have a reliable estimate of the local distortion of the crystal lattice near the substituted ion. This may be determined in several ways, each of which gives rather different results for the metal–ligand distances, as shown in Table 1. Edgar and Newman (1975) have shown that the calculation of local distortions by Ivanenko and Malkin (1969) leads to certain inconsistencies when applied to Gd^{3+} in the fluorites. Nevertheless, the Ivanenko and Malkin calculation of the ratio of local to bulk strains leads to consistent results. We have therefore interpolated their strain calculations for divalent ions to obtain an estimate of the power-law exponent of \bar{b}_4 as $t_4 = 10.6$, and the consequent estimates of local distortions are shown in the last row of Table 1.

The estimated value of the power-law exponent t_4 may be checked by comparing the value of $\bar{b}_4 = 14.4 \times 10^{-4} \text{ cm}^{-1}$ for Eu²⁺ in SrF₂ (with metal–ligand distance $R = 2.51 \text{ \AA}$) with the value $\bar{b}_4 (R = 2.87 \text{ \AA}) = 3.60 \times 10^{-4} \text{ cm}^{-1}$ for Eu²⁺ : KZnF₃ which can be derived from the results of Al'tshuler *et al.* (1974). This gives $t_4 = 10.3$, in close agreement with the value quoted above.

Table 1. Estimates of metal–ligand distances for Eu²⁺ in fluorite host crystals

Source of Estimate	Metal–ligand distance (Å)		
	CaF ₂	SrF ₂ ^A	BaF ₂
X-ray determination (undistorted host)	2.366	2.511	2.685
Hurren <i>et al.</i> (1969) (hydrostatic pressure)	2.450	(2.511)	2.580
Baberschke (1972) (ENDOR)	2.448	(2.511)	2.580
Ivanenko and Malkin (1969) (interpolated result)	2.377	2.481	2.553
Present work (using $t_4 = 10.6$)	2.460	(2.511)	2.568

^A Values in parentheses indicate that zero distortion has been assumed since the ionic radius of Eu²⁺ is similar to that of Sr²⁺; in fact, ionic distances in SrF₂ and EuF₂ differ by less than 0.01 Å (Wyckoff 1963). For this reason also the discrepancy of 0.03 Å shown in the result obtained by interpolation of the calculation of Ivanenko and Malkin (1969) is unrealistic.

We conclude from the estimates given in Table 1, and the above discussion of these estimates, that the Eu²⁺–F[–] distances in the fluorites are as follows:

$$\text{CaF}_2, 2.455 \pm 0.01 \text{ \AA}; \quad \text{SrF}_2, 2.511 \pm 0.002 \text{ \AA}; \quad \text{BaF}_2, 2.575 \pm 0.01 \text{ \AA}.$$

These values will now be used in the analysis of the puzzling variation of the intrinsic parameter \bar{b}_2 with distance mentioned in Section 1.

In Fig. 2 we plot the results for \bar{b}_2 obtained by Stedman and Newman (1974, 1975) and the same results with small corrections for local strain effects according to the theory of Ivanenko and Malkin (1969) as a test of self-consistency. In this graph the gradients are obtained using $\partial \bar{b}_2 / \partial R = -t_2 \bar{b}_2 / R$. The figure shows that fair consistency is obtained between the three negative gradients and the three \bar{b}_2 values when local strain effects are taken into account. The plotted results cannot be precisely accurate, however, as the three sets of data cannot be fitted to a smooth monotonic curve. Nevertheless, the small discrepancies can be removed by changes within the quoted errors in R , or possible errors in the \bar{b}_2 values and gradients of only $\sim 5\%$.

Hence, we have demonstrated the mutual consistency of the values of \bar{b}_2 and t_2 obtained by Stedman and Newman (1974, 1975) for Eu²⁺ in the host crystals CaF₂, SrF₂ and BaF₂ using the metal–ligand distances obtained from \bar{b}_4 variations. The six experimental results for \bar{b}_2 are all consistent with the hypothesis that its variation with distance corresponds to that in region B of Fig. 1. This raises the possibility that the experimental parameters b_n^m for Eu²⁺ can be quite different from those for Gd³⁺ in the same host crystal even if the ligand positions are identical for both substituted ions.

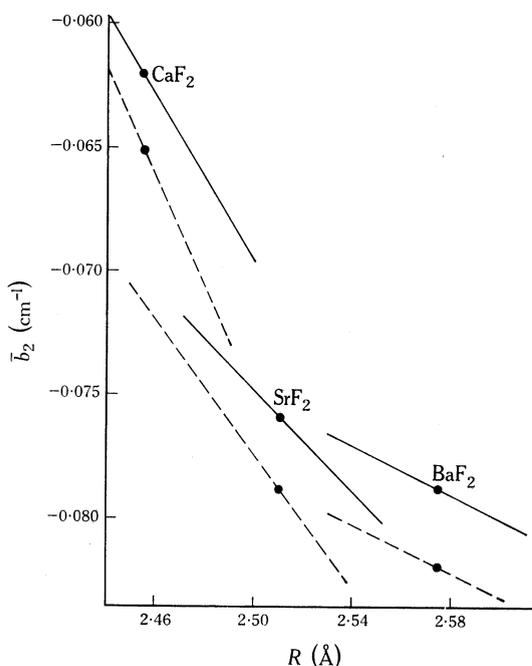


Fig. 2. Values of \bar{b}_2 and gradients for Eu^{2+} in cubic sites in the three indicated fluorite host crystals. The full lines plot the experimental results, while the dashed lines show the effects of correcting for local strain. The parameter R is the $\text{Eu}^{2+}-\text{F}^-$ distance derived from an analysis of the \bar{b}_4 variation (see text).

Table 2. Experimental spin-Hamiltonian parameters for Eu^{2+} and Gd^{3+} in dihalide hosts at room temperature

All the spin-Hamiltonian parameters are subject to an overall sign uncertainty as very low temperature experiments have apparently not been carried out. The angle α is that between the x axis (chosen to make $b_2^{-2} = 0$) and the crystallographic b axis; the principal axis (z) lies along the crystallographic a axis

Dihalide host, ion	Reference ^A	α (degrees)	Spin-Hamiltonian parameters (10^{-4} cm^{-1})						
			b_2^0	b_2^2	b_4^0	b_4^2	b_4^{-2}	b_4^4	b_4^{-4}
$\text{PbBr}_2, \text{Eu}^{2+}$	1	23.5	177(3)	-527(5)	5.6(9)	2(5)	-13(4)	26(6)	-24(3)
$\text{PbCl}_2, \text{Eu}^{2+}$	2	23.5(5)	107(1)	-527(2)	3.6(3)	1(2)	-6(2)	26(2)	-26(3)
Gd^{3+}	3	37(0.5)	99(2)	-437(2)	3.1(5)	13(2)	-0(10)	-12(10)	-39(10)
$\text{BaCl}_2, \text{Eu}^{2+}$	4	15	24	-450					
Gd^{3+}	5	39	90	-444					

^A References: 1, Willemsen and Hommels (1972); 2, Vreken and Volger (1965); 3, Beijerinck and Willemsen (1970); 4, Wever and den Hartog (1975); 5, Oosterhoff and den Hartog (1974).

3. Dihalide Hosts

Experimental results for dihalide hosts are collected in Table 2. These hosts do not show the large differences between the b_2^m values of Gd^{3+} and Eu^{2+} that have been found in LaCl_3 (Kim and Moos 1967) and CaWO_4 (Harvey and Kieft 1969). This suggests, at least for chlorine ligands, that the metal-ligand interaction processes are similar for both ions. This is consistent with the explanation of the difference between b_2^0 values for Eu^{2+} and Gd^{3+} in LaCl_3 given by Newman and Urban (1975), which is based on the sensitivity of this parameter to small changes in angular coordination in LaCl_3 .

Another noticeable feature of the results given in Table 2 is that the magnitude of b_4^0 for Eu^{2+} in PbBr_2 is considerably greater than that in PbCl_2 . This is in accordance with our finding for Gd^{3+} that $|\bar{b}_4(\text{Br}^-)| > |\bar{b}_4(\text{Cl}^-)|$ (Newman 1975a).

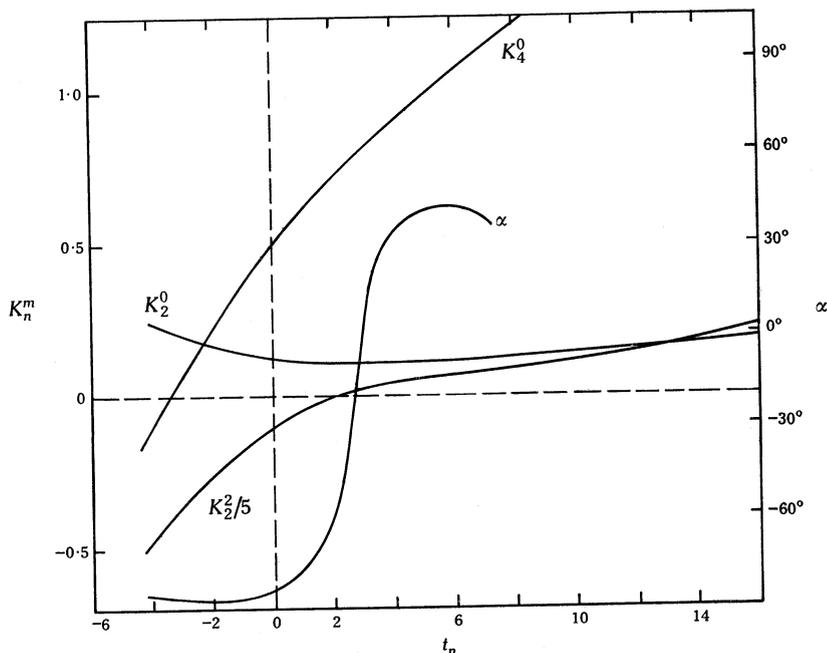


Fig. 3. Coordination factors K_n^m and local coordinate orientation α for Eu²⁺ ions in PbCl₂ plotted as a function of the power-law exponent t_n .

Table 3. Ligand positions in PbCl₂

The positions are given with respect to Pb at the origin and with axes aligned along the crystal axes. Distances are quoted relative to $R_0 = 3.000 \text{ \AA}$

R_0/R	θ (degrees)	ϕ (degrees)	R_0/R	θ (degrees) ^A	ϕ (degrees)
0.982	90.00	86.37	1.039	38.27	31.35
1.052	90.00	-35.01	0.978	42.50	253.64
0.975	90.00	194.17	0.827	51.78	140.22

^A In these three cases there is a second ion at $180^\circ - \theta$ with the same R , ϕ values.

In all cases, the sources quoted in Table 2 include a calculation of the $n = 2$ parameters based on the electrostatic field due to a point charge lattice sum. The results of these calculations agree fairly well with the experimental parameters b_2^0 and b_2^2 if (as was assumed) $b_2^0 > 0$ in all cases. Application of the superposition model is made difficult by the complicated structure of the dihalide crystals. Using the ionic positions in the crystal given by Wyckoff (1963), we have determined the coordination of the Cl⁻ ligands in PbCl₂ relative to the substituted ion. The results are shown in Table 3. The near-neighbour ligands cover a distance variation of $\pm 12\%$ about their median value, making the simple power-law approximation given in Section 1 of doubtful validity, especially in view of the local distortion to be expected in replacing Pb²⁺ by a lanthanide ion. Nevertheless, this approximation has been used to plot, as functions of t_n , values of the combined coordination factors $|K_2^2|$, K_2^0 and K_4^0 defined by

$$b_n^m = K_n^m(t_n) \bar{E}_n(R_0),$$

as well as the angle α (defined in Table 2). The resulting graphs are given in Fig. 3.

We expect, on the basis of previous work on Gd^{3+} , that $\bar{b}_2 \approx -0.1 \text{ cm}^{-1}$ and $\bar{b}_4 \approx -2 \times 10^{-4} \text{ cm}^{-1}$ for Cl^- ligands. Fig. 3 shows $K_2^0 > 0$ for all power-law exponents considered. This suggests that b_2^0 is negative for all systems, which is also consistent with the theoretical result $K_4^0 > 0$ combined with the negative sign of \bar{b}_4 for Cl^- which has been determined for Gd^{3+} (Newman 1975a). We are therefore led to the conclusion that *all* the parameters b_n^m in Table 2 should be changed in sign. Hence, if the signs of these parameters can be determined experimentally, we have a means of deciding the relative merit of the electrostatic and superposition models.

There are two alternative ways of deciding the most likely value of t_2 . We may compare the theoretical value of the ratio K_2^2/K_2^0 with b_2^2/b_2^0 , or compare the experimental and theoretical values of the angular deviation α between local field axes and the crystal axes. The first comparison (comparing Table 2 with Fig. 3) gives $t_2 \approx 0$ or $t_2 > 10$. The second comparison is complicated by the fact that α varies very rapidly with t_2 , in the range $1 < t_2 < 3$, but suggests that $t_2 \approx 2$. The deviation between these values could be due to many factors, as mentioned above. Nevertheless, we have reconfirmed our previous finding for Gd^{3+} (Newman and Urban 1972) that t_2 is very small and positive (except for the case of $\text{Eu}^{2+}-\text{F}^-$ discussed in Section 2). Taking $t_2 = 1 \pm 1$ we find (from b_2^0) that $\bar{b}_2 = -(915 \pm 100) \times 10^{-4} \text{ cm}^{-1}$ for Eu^{2+} in PbCl_2 . A similar calculation gives $\bar{b}_2(\text{Gd}^{3+} : \text{PbCl}_2) = -(740 \pm 100) \times 10^{-4} \text{ cm}^{-1}$.

Calculated values of the combined coordination factors $K_4^m(t_4)$ with $m \neq 0$ are much larger than can be fitted to reasonable values of t_4 and \bar{b}_4 . This suggests that there is a strong cancellation between contributions to the parameters b_4^m ($m \neq 0$), which is not reflected in our approximate calculation. We are therefore forced to estimate $\bar{b}_4(\text{Cl}^-)$ from b_4^0 alone. Assuming $t_4 = 12$, we obtain

$$\bar{b}_4(\text{Cl}^-) = b_4^0/0.74 = -4.9 \times 10^{-4} \text{ cm}^{-1}.$$

This is in good agreement with the value obtained using the results of Kim and Moos (1967) for $\text{Eu}^{2+} : \text{LaCl}_3$, namely

$$\bar{b}_4(\text{Cl}^-) = -4.2 \times 10^{-4} \text{ cm}^{-1}.$$

Independent estimates of this parameter are obtained in the next section.

4. Eu^{2+} in Alkali Halides

Most experimental results for the alkali halides refer to a site in which the Eu^{2+} ion replaces a cation and charge compensation is achieved by a neighbouring cation vacancy. This produces C_{2v} sites of the form shown in Fig. 4, which also defines the coordinate system and the angles which characterize the distortion from cubic symmetry. Experimental results are given in Table 4. In the distorted cubic site, the Eu^{2+} ligands are divided into three pairs, each giving a C_{2v} contribution to the observed parameters b_n^m . It is also possible that the cation vacancy may give a significant contribution to the $n = 2$ parameters. The superposition model (Newman and Urban 1975) thus gives the expression for these parameters as

$$b_n^m = K_n^m(\text{A}) \bar{b}_n(\text{A}) + K_n^m(\text{B}) \bar{b}_n(\text{B}) + K_n^m(\text{C}) \bar{b}_n(\text{C}) + K_n^m(\theta=90^\circ, \phi=0^\circ) \bar{b}_n(\text{O}),$$

where the symbol O denotes the vacancy. In this expression the \bar{b}_n values will depend

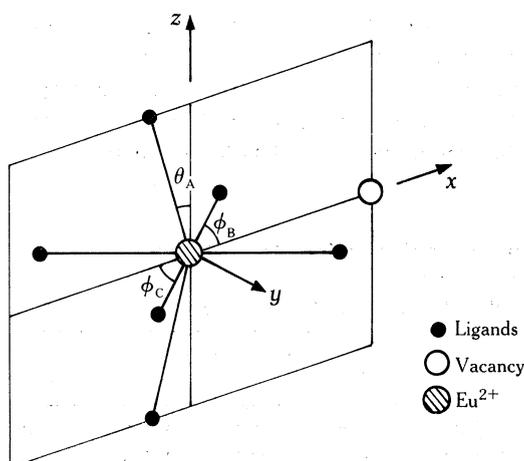


Fig. 4. Coordinate system and ligand coordination for Eu²⁺ substituted into C_{2v} sites in alkali halide crystals. The figure shows the xz σ_v plane containing two ligands with $\phi = 0^\circ$ at θ_A and $180^\circ - \theta_A$. The remaining four ligands are in the xy σ_v plane (with $\theta = 90^\circ$) in directions subtending approximately 45° with the x axis.

Table 4. Experimental spin-Hamiltonian parameters for Eu²⁺ in alkali halides at room temperature

Alkali halide	Reference ^A	Spin-Hamiltonian parameters (10^{-4} cm^{-1})						
		b_2^0	b_2^2	b_4^0	b_4^2	b_4^4	b_4^4/b_4^0	\bar{b}_4^B
NaCl	1	457.7	(-)74	-8.3	(-)14	44	-5.3	-2.4
	2	456	(-)74	-8.6	(+)6	51	-5.9	
NaBr	3	384.7	(-)18.3	-15.1	(+)55.6	72.6	-4.8	-4.2
KCl	4	341	(-)96	-5.0	(-)1.8	27	-5.4	
	5	343.5	-94.5	-5.0	-4.7	29.5	-5.9	-1.6
KBr	3	319.3	(-)81.9	-11.1	(+)8.8	49.7	-4.5	-3.0
	6	319.8	(-)84.9	-10.9	(+)5.6	50.7	-4.7	
RbCl	7	292.8	(-)134.4	-4.98	(+)6.6	11.3	-2.3	
	8	292.5	(-)134.4	-4.1	(+)4.4	21.7	-5.3	-1.2
RbBr	9	283.4	(-)117.9	-9.6	(+)11.2	44.8	-4.7	-2.7

^A References: 1, Aguilar *et al.* (1974); 2, Röhrig (1965); 3, Aguilar *et al.* (1975); 4, Pandey (1967); 5, Maevskii *et al.* (1975); 6, Maevskii and Kalabukhova (1973); 7, Pandey (1969); 8, Rubio *et al.* (1974); 9, Muñoz *et al.* (1975).

^B Results calculated from the formula (1) of Section 4.

on ligand distance and the K_n^m are determined by angular coordination. Values of the K_n^m as a function of distortion angle for each of the three pairs of ligands are given in Table 5.

Several conclusions can be drawn by comparing Tables 4 and 5. We first note that for any small distortion from cubic symmetry \bar{b}_4 is negative for both Cl⁻ and Br⁻ ligands. The experimental ratios b_4^4/b_4^0 are sufficiently close to -5 (except for one case) to suggest that only quite small distortions from cubic symmetry occur, and this confirms that the vacancy contribution to these parameters is not large. Near-cubic symmetry is also consistent with the small values of b_2^0 and b_2^2 compared with compensated sites in other crystals (Edgar and Newman 1975). In the case of small deviations from cubic symmetry it should be a fair approximation to calculate \bar{b}_4 using the mean value formula

$$\bar{b}_4 = \frac{1}{7}(b_4^0 - \frac{1}{5}b_4^4), \quad (1)$$

which gives the results shown in Table 4.

Comparison of data for the chlorides and bromides gives the large ratio $\bar{b}_4(\text{Br}^-)/\bar{b}_4(\text{Cl}^-) = 2.0 \pm 0.3$ for a given metal ion with considerably less variation than that of the intrinsic parameters themselves. These results agree qualitatively with the signs and relative magnitudes of \bar{b}_4 for Gd^{3+} in LaCl_3 and LaBr_3 . Uncertainties in the local coordination in the trihalides make more detailed comparisons unprofitable.

Table 5. Changes in coordination factors K_n^m in alkali halides due to deviations from cubic site symmetry

The angle ϕ_i can represent either the ϕ_B or ϕ_C shown in Fig. 4

Ionic arrangement in crystal	Distortion angle	Coordination factors K_n^m				
		$n, m = 2, 0$	2, 2	4, 0	4, 2	4, 4
Ligand pair in xz plane ($\phi = 180^\circ$)	$\theta_A = 0^\circ$	2.0000	0.0000	2.0000	0.0000	0.0000
	$\pm 2^\circ$	1.9964	0.0010	1.9970	0.0092	0.0000
	$\pm 10^\circ$	1.9096	0.0904	1.7064	0.8724	0.0080
	$\pm 20^\circ$	1.6490	0.3510	0.9500	3.0304	0.1198
Ligand pair in xy plane ($\theta = 90^\circ$)	$\phi_i - 45^\circ = 0^\circ$	-1.0000	0.0000	0.7500	0.0000	-8.7500
	$\pm 2^\circ$	-1.0000	∓ 0.02092	0.7500	± 0.3488	-8.6648
	$\pm 5^\circ$	-1.0000	∓ 0.5210	0.7500	± 0.8682	-8.2224
	$\pm 10^\circ$	-1.0000	∓ 1.0261	0.7500	± 1.7101	-6.7029
Positive ion vacancy		-0.5	1.5	-0.375	-2.5	4.375

Using the interionic distances given by Wyckoff (1963), we can use the \bar{b}_4 values quoted in Table 4 to estimate a value for t_4 . It should be emphasized, however, that the value $t_4 = 4 \pm 1$ obtained by this method is essentially a lower bound, as no allowance has been made for local distortion effects near the substituted Eu^{2+} ion.

It can be seen from Table 5 that *all* angular distortions from cubic symmetry as well as the cation vacancy give a net $K_2^0 < 0$. The positive experimental values of b_2^0 are therefore consistent with the usual result $\bar{b}_2 < 0$ for these systems, unless radial distortions dominate. However, the small power-law exponents found in most cases make this unlikely. If \bar{b}_2 has its usual magnitude, that is, $\bar{b}_2 \approx -0.15 \text{ cm}^{-1}$, we expect a mean value $K_2^0 \approx -0.2$ to give the observed parameters. As K_2^0 is rather insensitive to θ_A distortions, this may be mostly due to the cation vacancy. In either case we must postulate a $\phi_C + \phi_B$ change of about between $+1^\circ$ and $+5^\circ$ to produce the small observed values of b_2^0 . This is in accord with our intuitive expectation of $\phi_B > 45^\circ > \phi_C$. The complexity of the site makes it impossible to determine the value for \bar{b}_2 or to derive the local distortion from the experimental data.

5. Hosts with Oxygen Ligands

There are considerably less data available for Eu^{2+} with oxygen ligands than exist for Gd^{3+} . In this section we consider the Eu^{2+} spin-Hamiltonian parameters for alkaline earth oxide and CaWO_4 hosts. Overmeyer and Gambino (1964) have collected data for alkaline earth oxide hosts which show clearly that oxygen ligands can have either sign for \bar{b}_4 :

$$\bar{b}_4 (\text{cm}^{-1}) = -7.3 \times 10^{-4} (\text{CaO}), \quad 0.0 \times 10^{-4} (\text{SrO}), \quad 5.4 \times 10^{-4} (\text{BaO}).$$

This makes it clear that the \bar{b}_4 parameter for Eu^{2+} shows the same sign-changing

phenomenon that has already been noted for Gd³⁺ (Newman 1975*a*), the only difference being that Eu²⁺ shows a greater sensitivity than Gd³⁺ to changes in the oxide host lattice.

The data of Harvey and Kiefte (1969) combined with the structural considerations discussed by Newman (1975*a*) allow us to estimate

$$\bar{b}_4(\text{Eu}^{2+} : \text{CaWO}_4) = 13 \times 10^{-4} \text{ cm}^{-1}.$$

This large positive value suggests that the O²⁻ ions in this host have a similar electronic structure to F⁻ which, as we have seen, also has large positive \bar{b}_4 . This confirms the situation found for Gd³⁺ (Newman 1975*a*) where O²⁻ ions in garnets and scheelites gave positive values of \bar{b}_4 , in contrast to results for the same ligand in other hosts, where \bar{b}_4 can be negative. The analysis shows good internal consistency with that for Gd³⁺, as $\bar{b}_4(\text{Gd}^{3+}) = 9 \times 10^4 \text{ cm}^{-1}$ and

$$b_4^4/b_4^0(\text{Gd}^{3+}) = 6.16 \quad \text{while} \quad b_4^4/b_4^0(\text{Eu}^{2+}) = 6.32.$$

The main problem with the results of Harvey and Kiefte (1969) is that they give a very small value of b_2^0 for Eu²⁺, in contrast to the value for Gd³⁺ in the same host, namely $\bar{b}_2(\text{Gd}^{3+} : \text{CaWO}_4) = -894 \times 10^{-4} \text{ cm}^{-1}$ (Harvey and Kiefte 1971). As there is no evidence for small values of \bar{b}_2 in other systems it is natural to seek an explanation for this discrepancy in terms of differences in the local coordination. The crucial question is whether such a large difference in b_2^0 is consistent with the similar values of b_4^4/b_4^0 for the two systems noted above. In fact, distortions of all ligand positions by about 3° would be required to give cancelling contributions to b_2^0 , and these would produce 25% changes in the ratio b_4^4/b_4^0 .

We are therefore forced to look for explanations of the difference between b_2^0 for Eu²⁺ and Gd³⁺ in CaWO₄ in terms of a difference in the underlying processes causing a difference in the distance dependence of \bar{b}_2 in the two cases. The observed cancellation between competing contributions would require a large *negative* value of t_2 . This is in qualitative agreement with the negative values of t_2 determined for F⁻ ions (see Section 2) and again suggests that the electronic structure of O²⁻ ions in the scheelites is very similar to that of F⁻ ions. It has been suggested elsewhere (Newman 1975*b*) that this similarity is related to the *polarizability* of the ions, which varies considerably from one crystal to another for O²⁻ ions.

6. Discussion

The derivations of intrinsic parameters and their power-law exponents given in this paper have provided rather few direct tests of the validity of the superposition model for Eu²⁺ spin-Hamiltonian parameters. Nevertheless, we have shown that the overall picture for \bar{b}_2 and \bar{b}_4 values is very similar to that for Gd³⁺. In particular, we have found a similar ordering of the \bar{b}_4 parameter for halide ligands and an extreme variability of this parameter for O²⁻ ligands, covering both positive and negative values. This provides important supplementary evidence for the correlation between \bar{b}_4 and ligand polarizability that has been proposed elsewhere (Newman 1975*b*).

The main difference between Eu²⁺ and Gd³⁺ intrinsic parameters lies in the occurrence of large negative values of the power-law exponents t_2 describing the \bar{b}_2 variation. We have demonstrated the internal consistency of the data for F⁻ ions in this respect

(Section 2) and have shown that the data for the CaWO_4 host can only be explained on this assumption (Section 5). These results provide additional evidence that the variation of \bar{b}_2 with ligand distance takes the form shown in Fig. 1, as postulated by Newman and Urban (1972).

The aim of this type of analysis is to separate those features of the observed parameters which depend on crystal geometry from those which can give information about the electronic processes involved. This information is contained in the intrinsic parameters \bar{b}_n and their distance variation. It turns out that the parameters \bar{b}_n for $f^7 \text{ } ^8\text{S}_{7/2}$ ground states of Gd^{3+} and Eu^{2+} have some quite fascinating properties, which were not apparent in the experimental parameters b_n^m . This suggests that a proper *ab initio* calculation of the \bar{b}_n will hold some surprises, and will not just be a tedious exercise in adding together all possible contributions. It is hoped that the present work will help to stimulate interest in this problem.

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