

The Orbit–Lattice Interaction for Lanthanide Ions. II* Strain and Relaxation Time Predictions for Cubic Systems

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Abstract

An analysis of dynamic crystal field data for cubic systems is carried out in order to assess the possible usefulness of the superposition model in understanding the results of lattice strain and spin–lattice relaxation experiments. The data used in this work are the electron paramagnetic resonance (EPR) results for strained cubic crystals obtained by Buisson, Baker and their coworkers, and the spin–lattice relaxation results obtained by Buisson, Stapleton and their coworkers. A method of generalizing the superposition model to take into account long range electrostatic contributions without introducing additional unknown parameters is proposed, and shown to give consistent results. It is concluded that differences between bulk and local strains must be taken into account in any model of the dynamic crystal field, if it is to achieve success.

Introduction

In Part I of this series (Newman 1978)† a range of crystal field superposition model parameters for lanthanide ions were derived from electronic spectroscopic data. In spite of the problem of making proper allowance for local distortion effects, sufficient data now exist to show that the superposition model provides an adequate explanation of such data, at least to within about 20% accuracy. Nevertheless, this in itself does not provide evidence for the effectiveness of the superposition model in describing *dynamic* interactions between the 4f electrons and the crystal, although it does give us a *prima facie* reason for being optimistic in this respect.

In recent years a considerable amount of data has become available relating to the dynamic crystal field in cubic crystals, and some of this has recently been used to test the usefulness of the superposition model by Vial and Buisson (1975), North and Stapleton (1977*a*, 1977*b*) and Baker *et al.* (1977), as well as an alternative electrostatic model due to Buisson and Borg (1970). These papers came to rather definite conclusions about the inadequacy of the superposition model as a means of predicting values of the dynamic parameters, although the reasons for this apparent failure were unexplained. The aim of the present work is to give an overall reassessment of the results of comparing the theoretical predictions of the superposition model with experiment, to attempt to find reasons for its reported failure to describe dynamic parameters, and to discuss practical ways of improving it to provide a better interpretation of the experimental results.

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† Note the following erratum: the ratio R/R_0 should be replaced by R_0/R in equations (8), (9), (10) and (11) of Part I.

Formal Considerations

It has become customary (see e.g. Orbach and Blume 1962; Baker and van Ormondt 1974) to express the dynamic coupling between lattice vibrations and the open shell electrons of a paramagnetic ion as a coupling between strains in a continuous medium (representing the lattice) and corresponding changes in the crystal field parameters. Such a model is appropriate for the coupling to long wave (acoustic) phonons and to static (or slowly oscillating) applied stresses.

In this representation the dynamic, or orbit-lattice, Hamiltonian for lanthanide ions in sites of cubic symmetry may be written as

$$V_{\text{OL}} = \sum_{i,k,\beta} V(\Gamma_i, k) C(\Gamma_i, k, \beta) \varepsilon(\Gamma_i, \beta), \quad (1)$$

where $\varepsilon(\Gamma_i, \beta)$ are the 9 components of strain labelled according to the component β of the even parity irreducible representations Γ_i of the cubic group. The orbital angular momentum operators $C(\Gamma_i, k, \beta)$ are of order k and transform like the β th component of the representation Γ_i . There are 11 independent coupling parameters $V(\Gamma_i, k)$ in cubic symmetry, which are independent of the component label β .

We shall discuss more general aspects of orbit-lattice coupling in Part III of this series. Nevertheless, we shall find that it is important to keep in mind the limitations of equation (1). The main uncertainty is whether the local strains near a substituted ion are really equivalent to the bulk strain in the crystal. Cases are known where local behaviour is quite distinct from bulk behaviour. For example, it has recently been shown that Fe^{3+} ions substituted for Ti^{4+} in BaTiO_3 do not follow the motion of the Ti^{4+} ions in a ferroelectric transition (Siegel and Müller 1979).

Ivanenko and Malkin (1970) have calculated the local distortions and changes in the local elastic constants for lanthanide ions substituted into alkaline earth fluorides. Stedman and Newman (1971) questioned the accuracy of these local distortion results. Nevertheless, their qualitative conclusions regarding the behaviour of the local elastic constants seem likely to be correct. These showed Γ_3 strains to be relatively insensitive to the presence of a substituted ion, whereas Γ_5 strains can be considerably magnified for a tightly substituted ion. (In this coordination, Γ_3 strains do not involve radial displacements of the nearest neighbour fluorine ions.) In the case of the alkaline earth fluorides another complication arises from the fact (noted by Ivanenko and Malkin 1970) that the F^- ions do not necessarily move in accordance with the continuum strain.

Table 1 provides expressions for the 11 orbit-lattice coupling parameters of equation (1) in terms of the superposition model parameters \bar{A}_n and t_n , and also an alternative set of 5 parameters B_4 , B_6 , V_2 , V_4 and V_6 introduced by Buisson and Borg (1970). The Buisson and Borg model is electrostatic, so that its power law exponents are fixed at $t_2 = 3$, $t_4 = 5$ and $t_6 = 7$. On the other hand their model makes no assumptions about the dominance of nearest neighbour interactions, or even the validity of the point charge model, for it is based on the properties of a strained arbitrary charge distribution.

It will be noted that the Γ_5 expressions for eightfold coordination in Table 1 each contain two components, corresponding to the two distinct possible distortions of Γ_5 symmetry. The uniform strain model of the orbit-lattice interaction produces the relative weighting of the two components given in the table. Interpretations based on this weighting must, of course, be subject to considerable uncertainty.

Table 1. Orbit-lattice and static crystal field parameters at cubic sites

Parameters are expressed in terms of superposition model (SM) and Buisson and Borg (1970) parameters. This table is adapted from Table A2 of Baker and van Ormondt (1974), Table 1 of Baker *et al.* (1977) and Table 1 of North and Stapleton (1977), with some corrections

Parameter	SM (sixfold coordination)	SM (eightfold coordination)	Buisson and Borg (either coordination)
$V(\Gamma_1, 4)$	$-8\sqrt{\frac{1}{3}}t_4\bar{A}_4$	$\frac{6}{9}\sqrt{\frac{1}{3}}t_4\bar{A}_4$	$-\frac{8}{3}\sqrt{\frac{6}{7}}B_4$
$V(\Gamma_1, 6)$	$-16t_6\bar{A}_6$	$-\frac{10}{27}t_6\bar{A}_6$	$-\frac{4}{3}B_6$
$V(\Gamma_3, 2)$	$-4t_2\bar{A}_2$	$\frac{3}{3}\bar{A}_2$	$\frac{3}{2}V_2$
$V(\Gamma_3, 4)$	$8\sqrt{\frac{5}{3}}t_4\bar{A}_4$	$\frac{2}{5}\sqrt{\frac{5}{3}}\bar{A}_4$	$\frac{3}{4}V_4 + 8\sqrt{\frac{5}{3}}B_4$
$V(\Gamma_3, 6)$	$-16\sqrt{\frac{7}{2}}t_6\bar{A}_6$	$-\frac{2}{5}\sqrt{\frac{6}{14}}\bar{A}_6$	$\frac{3}{8}\sqrt{11}V_6 - \frac{2}{3}\sqrt{14}B_6$
$V(\Gamma_4, 4)$	$16\sqrt{\frac{3}{5}}\bar{A}_4$	$-\frac{1}{9}\sqrt{\frac{3}{5}}\bar{A}_4$	$32\sqrt{\frac{5}{21}}B_4$
$V(\Gamma_4, 6)$	$-16\sqrt{21}\bar{A}_6$	$-\frac{10}{27}\sqrt{21}\bar{A}_6$	$-\frac{6}{3}\sqrt{21}B_6$
$V(\Gamma_5, 2)$	$-8\bar{A}_2$	$-\frac{3}{9}(1-t_2)\bar{A}_2$	V_2
$V(\Gamma_5, 4)$	$16\sqrt{\frac{5}{3}}\bar{A}_4$	$\frac{6}{27}\sqrt{\frac{5}{3}}(1+\frac{2}{5}t_4)\bar{A}_4$	V_4
$V(\Gamma_5, 6a)$	$-4\sqrt{70}\bar{A}_6$	$\frac{6}{9}\sqrt{70}(1-\frac{1}{3}t_6)\bar{A}_6$	$-\frac{1}{3}\sqrt{70}B_6$
$V(\Gamma_5, 6b)$	$-6\sqrt{154}\bar{A}_6$	$\frac{6}{27}\sqrt{154}(1-\frac{1}{3}t_6)\bar{A}_6$	V_6
$A_4^0\langle r^4 \rangle$	$\frac{7}{2}\bar{A}_4$	$-\frac{2}{9}\bar{A}_4$	B_4
$A_6^0\langle r^6 \rangle$	$\frac{3}{4}\bar{A}_6$	$+\frac{1}{9}\bar{A}_6$	B_6

EPR Measurements on Stressed Cubic Crystals

A considerable amount of work has been carried out to determine the parameters in spin-lattice Hamiltonians by using electron paramagnetic resonance (EPR) results for strained crystals. This approach has the advantage that it avoids the problems associated with providing an adequate characterization of the phonon spectrum. Nevertheless, there remain several other aspects which require careful consideration when analysing experimental results.

Normally, insufficient results are obtained from stress measurements to enable us to determine all the parameters of the orbit-lattice Hamiltonian. The problems involved in carrying out such a determination are well exemplified by the extremely careful work of Baker and Currell (1976). They studied the EPR of $\text{Er}^{3+} : \text{MgO}$ and $\text{Dy}^{3+} : \text{CaF}_2$ under uniaxial stress, measuring a sufficient number of splittings to determine the spin-lattice parameters to (typically) 5%. However, the equations relating their measurements to the parameters $V(\Gamma_i, k)$ are so badly conditioned that their final results are quoted to an accuracy seldom better than 50% (see Table 2, second column).

The results of Baker and Currell (1976) are of particular relevance to our present discussion because they were employed by Baker *et al.* (1977) to test the superposition model. Their technique was first to determine the $V(\Gamma_i, k)$ from the experimental data and then to use least squares fitting to obtain the appropriate superposition model parameters. These were generally found to be considerably different from values that had been obtained from static crystal fields, leading Baker *et al.* to conclude that the superposition model is unreliable as a basis for predicting the orbit-lattice coupling parameters $V(\Gamma_i, k)$.

Table 2. Orbit-lattice coupling parameters for Er³⁺ : MgO

Experimental results and theoretical estimates of $V(\Gamma_i, k)$ are given. Units are 10^2 cm^{-1} ; the t_k are dimensionless

Parameter	BBV ^B	BBJ ^C	SM ^D	Parameter	BBV ^B	BBJ ^C	SM ^D
$V(\Gamma_3, 2)$	-132 (56)	-144	-96	\bar{A}_2	—	—	4
$V(\Gamma_3, 4)$	91 (30)	86.1	144.2	\bar{A}_4	1.271	1.262	1.271
$V(\Gamma_3, 6)$	-17 (10)	-43.5	-72.1	\bar{A}_6	0.221	0.225	0.221
$V(\Gamma_1)^A$	-15 (18)	96.4	2.1	t_2	—	—	6
$V(\Gamma_5, 2)$	-405 (240)	-96.0	-32	t_4	—	5	11.0
$V(\Gamma_5, 4)$	290 (200)	26.2	26.3	t_6	—	7	10.9
$V(\Gamma_5, 6a)$	210 (190)	-9.9	-7.4				
$V(\Gamma_5, 6b)$	-325 (300)	-29.0	-16.5				

^A Defined in terms of the parameters of Table 1 by $V(\Gamma_1) = V(\Gamma_1, 4) - 6.22 V(\Gamma_1, 6)$.

^B Baker *et al.* (1977) fit to experimental results; uncertainties in parentheses.

^C Borg *et al.* (1970), using the point charge model.

^D Superposition model results of the present work using crystal field parameters employed by Baker *et al.* (1977) for $k = 4$ and 6 and estimates derived from Part I for $k = 2$.

Table 3. Strain equations for parameters $V(\Gamma_3, 2)$ and $V(\Gamma_5, 2)$ in Er³⁺ : MgO and derived values

All quantities are in units of 10^2 cm^{-1} . Experimental uncertainty is of order 3–10%. Results are based on $k = 4$ and 6 intrinsic parameters and power law exponents used by Baker *et al.* (1977) and quoted in the text

Data label ^A	Equation	$V(\Gamma_i, 2)$
$A(\Gamma_3, e)^B$	$\left. \begin{array}{l} 2.93 \\ 240 \end{array} \right\} = 2.603 V(\Gamma_3, 2) + 908$	$\left\{ \begin{array}{l} -348 \\ -257 \end{array} \right.$
$M(\Gamma_3, A)$		
$M(\Gamma_3, C)$	$338 = 10.00 V(\Gamma_3, 2) + 2826$	-259
$M(\Gamma_3, D)$	$300 = 8.612 V(\Gamma_3, 2) + 2535$	-250
$A(\Gamma_5, 0)^B$	$\left. \begin{array}{l} 489 \\ 93 \end{array} \right\} = 13.96 V(\Gamma_3, 2) + 3983$	$\left\{ \begin{array}{l} -62.2 \\ -90.9 \end{array} \right.$
$M(\Gamma_5, C)$		
$M(\Gamma_5, A) + \frac{1}{2}M(\Gamma_3, B)$	$230 = -4.763 V(\Gamma_5, 2) - 203$	-73.0
$M(\Gamma_5, B) + \frac{1}{2}M(\Gamma_3, D)$	$1360 = -13.62 V(\Gamma_5, 2) - 55$	-80.6
	$565 = -18.94 V(\Gamma_5, 2) - 818$	
	$2360 = -40.33 V(\Gamma_5, 2) - 889$	

^A Baker and Currell (1976, Table 6) and Baker *et al.* (1977, Table 5) provide both the experimental data and coefficients used to derive the equations given. Equations for $M(\Gamma_3, B)$ and $M(\Gamma_3, E)$ have been omitted because data are of lower accuracy and linear relationships exist between equations for these cases and quoted Γ_3 data (see Baker *et al.* 1977). The expression for $M(\Gamma_3, D)$ corrects an error of sign in the coefficient of $C(\Gamma_3, 6)$ in Table 6 of Baker and Currell (1976).

^B Lower results of each pair are those obtained using relaxation data by Borg *et al.* (1970, Table 5).

In their analysis of the system Er³⁺ : MgO, Baker and Currell (1976) adopted the values 0.714 and 1.66 cm^{-1} for the Lea *et al.* (1962) parameters x and W that describe the static crystal field. These are equivalent to the superposition model parameters $\bar{A}_4 = 127.1 \text{ cm}^{-1}$ and $\bar{A}_6 = 22.1 \text{ cm}^{-1}$, whose ratio is $\bar{A}_4/\bar{A}_6 = 5.8$. However, an alternative estimate of this ratio, based on the garnet data quoted in Part I, is $75.9/21.1 = 3.6$. The significance of this difference is uncertain, firstly because the

metal-ligand distance in MgO is not known precisely, and secondly because there is very little information on the transferability of O^{2-} intrinsic parameters from one crystalline environment to another.

The weak link in the chain of argument given by Baker *et al.* (1977) lies in the initial conversion of the experimental data to orbit-lattice coupling parameters with the consequent loss of precision mentioned above. Alternative weighting of the data can shift the values obtained for the parameters $V(\Gamma_i, k)$ by considerably more than indicated by the uncertainties quoted by Baker and Currell (1976) (see Table 2). In addition, as mentioned by Baker and Currell (1976) and supported by the remarks above, there are doubts about the reliability of the available static parameters, especially for the system $Er^{3+} : MgO$, and so the equations relating the $V(\Gamma_i, k)$ to the experimental spin-Hamiltonian parameters are subject to considerable uncertainty. It is therefore very difficult to draw firm conclusions about the effectiveness of dynamic crystal field models by using this approach.

Our analysis of the data for $Er^{3+} : MgO$ is given in Tables 2 and 3. It can be seen from Table 2 that the worst discrepancies between theory and experiment occur for the $V(\Gamma_5, k)$, where the experimental results are an order of magnitude greater than the results of any conceivable calculation. In octahedral coordination the Γ_5 distortions do not involve radial motion of the nearest neighbour oxygen ions, so we would not expect a large correction to arise from the misfit of the substituted ion.

Rather than try an overall fit to uncertain data, it seems more appropriate to substitute estimated values of $k = 4$ and 6 superposition model parameters into the equations of Baker *et al.* (1977) to see whether reasonably consistent results can be obtained for the values of $V(\Gamma_3, 2)$ and $V(\Gamma_5, 2)$. The results of this calculation with the parameter values $\bar{A}_4 = 127.1 \text{ cm}^{-1}$ and $\bar{A}_6 = 22.1 \text{ cm}^{-1}$, together with the estimated power law exponents $t_4 = 10$ and $t_6 = 10$, are given in Table 3. The difficulties with the Γ_5 parameters are reflected in the considerable scatter of results and a derived value of $\bar{A}_2 = 1089 \text{ cm}^{-1}$, which is over twice the value expected according to the analysis of Part I. Nevertheless, the estimate of $V(\Gamma_5, 2)$ obtained using this approach is a factor of 5 down on the value obtained by Baker *et al.* (1977) by simply fitting the equations.

The $V(\Gamma_3, 2)$ results in Table 3 show much less scatter than those for $V(\Gamma_5, 2)$, although the experimental value of $A(\Gamma_3, \epsilon)$ obtained by Baker and Currell (1976) produces a noticeably different value. No reason is known for the large difference between the experimental results of Baker and Currell (1976) and Borg *et al.* (1970) for this parameter. Taking $V(\Gamma_3, 2) = -25400 \text{ cm}^{-1}$, we find

$$t_2 \bar{A}_2 = 6300 \text{ cm}^{-1},$$

which has the correct sign and gives, by comparison with the Γ_5 result, $t_2 = 5.8$. This is close to the value obtained in Part I for garnets, namely $t_2 = 5.6$. However, the excessively large value of \bar{A}_2 derived for this system suggests that it may not be possible to neglect long range electrostatic effects in the treatment of the dynamic crystal field for $k = 2$. We shall return to this problem in the next section.

Table 4 compares the superposition model predictions and the experimentally derived values (Baker *et al.* 1977) of $V(\Gamma_i, k)$ for the system $Dy^{3+} : CaF_2$. In this case the values of \bar{A}_4 and \bar{A}_6 used by Baker *et al.* are very similar to those derived in Part I, but as in the case of $Er^{3+} : MgO$ there are significant differences between the

two sets of dynamic parameters. We shall try to show that these differences are primarily due to the use of very poor conditioned equations to obtain the $V(\Gamma_i, k)$ in a situation where not all the uncertainties of the input data have been adequately allowed for.

Table 4. Orbit-lattice coupling parameters for $\text{Dy}^{3+} : \text{CaF}_2$

Superposition model (SM) predictions are compared with least squares fits to experimental data by Baker *et al.* (1977; BBV). Parameter units are 10^2 cm^{-1} ; the t_k are dimensionless

Parameter	BBV	SM	Parameter	BBV	SM
$V(\Gamma_3, 2)$	17(14)	43	\bar{A}_2		4
$V(\Gamma_3, 4)$	48(10)	30.3	\bar{A}_4	0.819	0.826
$V(\Gamma_3, 6)$	13(22)	-25.1	\bar{A}_6	0.234	0.236
$V(\Gamma_1)^A$	-31(17)	-51.5	t_2	—	5
$V(\Gamma_5, 2)$	0.8(4)	57.0	t_4	—	6.3
$V(\Gamma_5, 4)$	29(5)	89.0	t_6	—	10.1
$V(\Gamma_5, 6a)$	90(23)	-33.2			
$V(\Gamma_5, 6b)$	8(18)	-69.6			

^A Defined in terms of the parameters of Table 1 by

$$V(\Gamma_1) = V(\Gamma_1, 4) + 1.45V(\Gamma_1, 6).$$

Table 5. Strain equations for parameters $V(\Gamma_3, 2)$ and $V(\Gamma_5, 2)$ in $\text{Dy}^{3+} : \text{CaF}_2$ and derived values

All quantities are in units of 10^2 cm^{-1} . Experimental uncertainty is of order 3%

Data label	Equation ^A	$V(\Gamma_i, 2)$
$A(\Gamma_3, \epsilon)$	$-404 = -7.76 V(\Gamma_3, 2) - 55$	45.0
$M(\Gamma_3, A)$	$-407 = -7.845 V(\Gamma_3, 2) - 69$	43.1
$M(\Gamma_3, B)$	$-2490 = -26.53 V(\Gamma_3, 2) - 1248$	46.8
$M(\Gamma_3, 7)$	$-3180 = -54.93 V(\Gamma_3, 2) - 1019$	39.3
$A(\Gamma_5, 0)$	$385 = 10.19 V(\Gamma_5, 2) - 383$	75.4
$M(\Gamma_5, A) - \frac{1}{2}M(\Gamma_3, B)$	$1250 = -85.3 V(\Gamma_5, 2) + 7831$	77.2
$M(\Gamma_5, B) - \frac{1}{2}M(\Gamma_3, D)$	$-800 = 253.0 V(\Gamma_5, 2) - 11599$	42.7
$M(\Gamma_5, 7)$	$500 = -181.8 V(\Gamma_5, 2) + 11528$	60.7

^A See Baker and Currell (1976, Table 7) where both the experimental data and the coefficients used to derive these equations are given. The equation for $M(\Gamma_5, A) - \frac{1}{2}M(\Gamma_3, B)$ includes a correction to the coefficient of $V(\Gamma_5, 2)$ given by Baker and Currell. The result for $M(\Gamma_3, D)$ has been omitted as the quoted experimental uncertainty is 100%.

In producing the results given in Table 5, we have again adopted our alternative procedure of estimating the $V(\Gamma_i, 2)$ from values of the $V(\Gamma_i, k)$ for $k = 4$ and 6 , which are derived from the superposition model parameters of Part I. We see that very good consistency is obtained for $V(\Gamma_3, 2)$ although there is rather more scatter in the values of $V(\Gamma_5, 2)$. This could be due to the previously mentioned problems associated with determining the precise form of the local strain in Γ_5 symmetry. However, accepting the values as given we obtain (with an uncertainty of the order of 20%):

$$\bar{A}_2 = 408 \text{ cm}^{-1}, \quad t_2 = 5.5.$$

These results are in good agreement with those obtained from static parameters in Part I. Hence, the superposition model for static parameters is in good accord with the experimentally determined dynamic parameters for the system $\text{Dy}^{3+} : \text{CaF}_2$.

Buisson and Borg (1970) have pointed out that, *in a general electrostatic model*, certain linear relationships exist between the dynamic parameters for cubic sites which are independent of coordination. These are shown in the last column of Table 1, and reduce the 11 dynamic parameters to the 3 quantities V_2 , V_3 and V_4 if the 2 static cubic crystal field parameters which define B_4 and B_6 are already known. This parametrization is apparently stronger than the superposition model, which can involve as many as *four* extra parameters (t_2 , t_4 , t_6 and \bar{A}_2) if only the magnitudes of \bar{A}_4 and \bar{A}_6 are fixed by the static crystal field. However, the Buisson and Borg model has the disadvantage that it cannot be adapted to relate it to data derived from the static parameters of noncubic systems. Another problem is that it does not provide us with any *prima facie* expectations regarding the values of V_2 , V_3 and V_4 . In the discussions given above we have, in effect, reduced the unknown superposition model parameters to two by using values of t_4 and t_6 (in addition to \bar{A}_4 and \bar{A}_6) estimated from static crystal field data. Besides this, we have some qualitative expectations about possible values of \bar{A}_2 and t_2 derived from the study of the static parameters in noncubic systems. These features should make the superposition model much easier to test than the Buisson and Borg model.

An additional problem with the Buisson and Borg model occurs for the fluorites due to the fact that the negative ions do not necessarily follow the bulk strain. Baker *et al.* (1977) have shown in their Appendix that this problem can be overcome by introducing additional parameters, bringing the total number of dynamic parameters to seven.

It can easily be shown that the superposition model does not obey the Buisson and Borg constraints. For example, as shown in Table 1, their model predicts the fixed ratio $V(\Gamma_3, 2)/V(\Gamma_5, 2) = \frac{3}{2}$ for all cubic sites. In the superposition model this ratio is $\frac{1}{2}t_2$ for sixfold coordination and $3/(t_2 - 1)$ for eightfold coordination, which only equal $\frac{3}{2}$ when $t_2 = 3$ (its electrostatic value). The worst defect of the Buisson and Borg model is that it is based on the assumption of a purely electrostatic crystal field, which is well known to be incorrect. Hence, even if perfect fits to experimental data were obtained there would be no hope of interpreting the values of the parameters obtained in terms of *ab initio* calculations based on realistic charge distributions and including the important overlap and covalency contributions.

Baker and Fainstein (1975) have collected data for the dynamic spin-lattice Hamiltonian parameters of Tm^{2+} in three alkaline earth fluorites (see also Sabisky and Anderson 1970; Baker and van Ormondt 1974). Their results show an order of magnitude *increase* in these parameters as we go from the CaF_2 to the BaF_2 host crystal. This dependence on the host lattice is, of course, in the opposite sense to the change in magnitude of the static crystal field parameters, and thus also in the opposite sense to changes in the (dynamic) orbit-lattice coupling which would be obtained using any reasonable model. It follows that the observed behaviour of the spin-lattice parameters must be highly dependent on differences in amplitude of the local mode distortions and relatively little affected by changes in the magnitude of the orbit-lattice parameters. Hence, it is essential that any attempt to explain the absolute magnitudes of spin-Hamiltonian parameters should be based on the use of a reliable model of local strain effects.

A Generalized Superposition Model

The analysis of the quadrupolar field given in Part I suggests that it is sometimes useful to differentiate between the contact and electrostatic contributions to the $k = 2$ intrinsic parameters. Here we shall adopt the more rigorous approach of assuming that this separation should be made in the phenomenological parameters, so that electrostatic contributions can be from distant as well as near-neighbour ions.

In the case of the dynamic parameters a very simple way to proceed is to combine the superposition model and Buisson and Borg (1970) contributions to the $k = 2$ orbit-lattice parameters shown in Table 1, reinterpreting \bar{A}_2 as \bar{A}_2^c , the contact contribution. This procedure has the advantage that we can estimate the value of \bar{A}_2^c and possibly t_2^c using equation (12) of Part I. Even if t_2^c cannot be estimated reliably, we simply replace the original superposition model parameters (\bar{A}_2, t_2) by t_2^c and the Buisson and Borg (1970) parameter V_2 in our generalized model. This enables us to make a useful consistency test.

In the case of $\text{Er}^{3+} : \text{MgO}$, we have (averaging the results obtained in Table 3)

$$V(\Gamma_3, 2) = -25\,400 \text{ cm}^{-1} = -4t_2^c \bar{A}_2^c + \frac{3}{2}V_2,$$

$$V(\Gamma_5, 2) = -8\,700 \text{ cm}^{-1} = -8\bar{A}_2^c + V_2.$$

Using the value $\bar{A}_2^c = 235 \text{ cm}^{-1}$, derived from equation (12) of Part I and the parameters in the last column of Table 2, we find $V_2 = -6820 \text{ cm}^{-1}$ and $t_2^c = 10.5$. This sign of V_2 accords with a large contribution from the point charges on the O^{2-} ions. However, its magnitude can only be explained if we suppose that variable polarization is very important.

A similar approach for the system $\text{Dy}^{3+} : \text{CaF}_2$ gives

$$V(\Gamma_3, 2) = 4360 \text{ cm}^{-1} = \frac{3}{3} \bar{A}_2^c + \frac{3}{2} V_2,$$

$$V(\Gamma_5, 2) = 6400 \text{ cm}^{-1} = -\frac{3}{9}(1-t_2^c)\bar{A}_2^c + V_2.$$

It should be remembered, however, that the simple Buisson and Borg model of the electrostatic contributions, which gives the same V_2 in both equations, has doubtful validity in this case (Baker *et al.* 1977, Appendix). The value $\bar{A}_2^c = 254 \text{ cm}^{-1}$ obtained from equation (12) of Part I gives $V_2 = 1100 \text{ cm}^{-1}$ and $t_2^c = 6.9$. Both the sign and order of magnitude of V_2 are in accord with dominant contributions from the charges on the coordinated F^- ions (see Table 1). This might be expected in view of the small F^- dipolar polarizability.

It is interesting that the above results for t_2^c are very similar to empirical values of t_4 obtained in Part I for the corresponding ligands. This accords with our conceptual standpoint that similar mechanisms (i.e. overlap and covalency) provide the dominant contributions to both \bar{A}_2^c and \bar{A}_4 . The most important feature of this modified form of the superposition model is that no *additional free parameters are required*, for we can estimate \bar{A}_2^c reliably from the static parameters \bar{A}_4 and \bar{A}_6 .

We now consider the alternative possibility of using equation (12) of Part I to estimate values of t_2^c . This equation was based on the assumption that all three parameters \bar{A}_2^c , \bar{A}_4 and \bar{A}_6 are wholly due to overlap and covalency. Differentiating with respect to the lanthanide-ligand distance, we obtain

$$t_2^c \bar{A}_2^c = 3.64 t_4 \bar{A}_4 - 1.96 t_6 \bar{A}_6. \quad (2)$$

If, as is usually the case, $t_6 > t_4$ this equation gives $t_2^c < t_4$. For the two cases studied above we obtain

$$\text{Er}^{3+} : \text{MgO} \quad t_2^c = 10.0, \quad \text{Dy}^{3+} : \text{CaF}_2 \quad t_2^c = 5.6.$$

These are reasonably close to the values of t_2^c estimated above, but suggest that the assumption $t_4 = t_6$ for $\text{Er}^{3+} : \text{MgO}$ requires some modification.

Table 6. Input data and results of \bar{A}_2 derivation from spin-lattice relaxation data

Results are a summary by H. J. Stapleton (personal communication).
Units are cm^{-1} ; the t_k are dimensionless

Ion	\bar{A}_4	\bar{A}_6	t_4	t_6	$V(\Gamma_3, 2)$	\bar{A}_2
Dy^{3+}	49.7	5.2	8	12	-1672	2849
Er^{3+}	50.1	11.6	6	8	-9940	497
Yb^{3+}	41.4	8.8	8	12	-1817	151

Spin-Lattice Relaxation

In this section we discuss the spin-lattice relaxation results obtained for $\text{Yb}^{3+} : \text{Cs}_2\text{NaYCl}_6$ by North and Stapleton (1977a, 1977b) and for Er^{3+} and Dy^{3+} in the same host (H. J. Stapleton, personal communication). The lanthanide ions replace the Y^{3+} ions at cubic sites, the nearest neighbours being an octahedron of Cl^- ions. For each system it is possible to determine a single experimental quantity which is a function of the orbit-lattice coupling parameters alone, although the form of this function depends on a knowledge of the cubic crystal field parameters in the case of Er^{3+} and Dy^{3+} . (The reader is reminded of the remarks made in Part I to the effect that North and Stapleton (1977) incorrectly identified the intrinsic parameters, which invalidates their criticism based on permissible ratios of these parameters.)

In the case of Yb^{3+} the experimental results (North and Stapleton 1977a, 1977b) determine the dimensionless ratio

$$(27a_3^2 - 3a_5^2)/(5a_4^2 + 3a_6^2) = 7.91 \pm 2.53. \quad (3)$$

The spin-Hamiltonian parameters a_i may be expressed in terms of superposition model parameters as follows:

$$a_3 = \frac{40}{3 \cdot 0 \cdot 0 \cdot 3} \Delta^{-1} \left(-\frac{14 \cdot 3}{4} V(\Gamma_3, 2) + 26 t_4 \bar{A}_4 + 140 t_6 \bar{A}_6 \right), \quad (4)$$

$$a_5 = a_4 = \frac{16 \cdot 0}{1 \cdot 4 \cdot 3} \Delta^{-1} (13 \bar{A}_4 + 15 \bar{A}_6) = \frac{1}{3} \Delta, \quad (5)$$

where Δ is the $\Gamma_6 - \Gamma_8$ splitting of the ground multiplet. The North and Stapleton values of the intrinsic parameters are given in Table 6, which may be substituted into equation (12) of Part I to give $\bar{A}_2^c = 133 \text{ cm}^{-1}$.

Substituting equation (5) into (3), we obtain $|a_3| = 5.23 \pm 0.80$ so that, according to equation (4), we have the following constraint on the superposition model parameters,

$$-V(\Gamma_3, 2) + 0.728 t_4 \bar{A}_4 + 3.916 t_6 \bar{A}_6 = 2427 \pm 380 \text{ cm}^{-1}.$$

This is a useful result as we expect all the contributions on the left-hand side to be positive. As indicated in Part I, we expect power law exponents in the region $t_4 = 8$ and $t_6 = 12$ for Cl^- ions, giving

$$V(\Gamma_3, 2) = -1817 \pm 380 \text{ cm}^{-1},$$

which is the same sign but over an order of magnitude smaller than that found for $\text{Er}^{3+} : \text{MgO}$. Using the value of \bar{A}_2^c determined above and estimating $t_2^c = 7.5$, which is similar to the results found previously for O^{2-} and F^- ligands and in accord with equation (2), we have

$$V_2 = 1459 \text{ cm}^{-1}.$$

Unlike the strain cases discussed in the previous section this gives V_2 with the opposite sign to the nearest-neighbour Cl^- point charge contribution. However, in view of the more complicated crystal structure in this case, we cannot be certain of the expected sign of V_2 , especially as the highly polarizable Cs^+ ions are next-nearest neighbours.

An alternative approach, used by Stapleton and his coworkers, seeks to test the superposition model by separating the contributing factors in the expression $-4t_2 \bar{A}_2$ for $V(\Gamma_3, 2)$. This involves using the velocity of sound in the crystal, which is itself rather uncertain. North and Stapleton (1977*a*, 1977*b*) derive a value of the transverse velocity $v_t = 1.96 \times 10^5 \text{ cm s}^{-1}$ from their relaxation measurements, which is in reasonable accord with their reported direct measurement ($v_t = 3.01 \times 10^5 \text{ cm s}^{-1}$). Unfortunately, the analysis involves using the fifth power of v_t which is thus uncertain to at least a factor $(\frac{3}{2})^5 \approx 7.6$.

Stapleton (personal communication) has summarized the results obtained for the three ions Dy^{3+} , Er^{3+} and Yb^{3+} in $\text{Cs}_2 \text{NaYCl}_6$ (North 1977; Fish 1977) as shown in Table 6. The values of \bar{A}_4 and \bar{A}_6 , obtained from static data, show a disturbing irregularity as a function of ionic size. These values were used, along with the estimated values of t_4 and t_6 shown, to obtain the given values of $V(\Gamma_3, 2)$. The estimates of \bar{A}_2 given in the last column were based on the assumption $v_t = 2.0 \times 10^5 \text{ cm s}^{-1}$. Surprisingly, this leads to the derivation of very different values of t_2 and \bar{A}_2 for Dy^{3+} and Yb^{3+} , although similar values of $V(\Gamma_3, 2)$ were obtained. The very large value of $V(\Gamma_3, 2)$ obtained for Er^{3+} may be due to the use of different power laws in this case, but the author has insufficient data to test this hypothesis.

Given the many uncertainties in the formulation of the analysis summarized in Table 6, and the irregular values of the static crystal field parameters, it does not seem possible to draw firm conclusions from Stapleton's results.

Conclusions

A simple generalization of the superposition model which does not involve the introduction of further undetermined parameters has been proposed in order to provide a better description of the dynamic orbit-lattice coupling. This has been shown to give a reasonable explanation of strain results, although the spin-lattice relaxation data are, in our opinion, still not adequate to provide sufficiently stringent criteria for testing models. At the same time, it is clear from the experimental results that the generalized superposition model needs to be supplemented by a reliable theory of the relationship between bulk and local strains if it is to achieve real predictive power in the calculation of dynamic orbit-lattice coupling effects.

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Note added in proof

The work by G. E. Fish, M. H. North and H. J. Stapleton referred to in this paper is expected to appear shortly in *J. Chem. Phys.* under the title 'Tests of orbit-lattice interaction models using spin-lattice relaxation data of Er^{3+} , Dy^{3+} and Yb^{3+} in $\text{Cs}_2\text{NaYCl}_6$ '.

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