

The Orbit-Lattice Interaction for Lanthanide Ions. I Determination of Empirical Parameters

D. J. Newman

Department of Solid State Physics, Research School of Physical Sciences,
Australian National University, P.O. Box 4, Canberra, A.C.T. 2600.

Abstract

The coupling between lattice vibrations and electrons in the partly filled shells of paramagnetic ions is normally presumed to take place via a localized complex consisting of the paramagnetic ion surrounded by its ligands. In such cases the number of parameters is reduced significantly by the use of the superposition model. This model, with some related approximations, has been employed to determine coupling parameters for fluorine, chlorine and oxygen ligands using both experimental and theoretical results.

Introduction

Many physical processes occur as a result of the coupling between lattice displacements and the electrons in partly filled shells of paramagnetic ions, yet little progress has been made in constructing realistic Hamiltonians for this coupling. It is usual to break the coupling mechanism into two aspects, which can then be treated as separate problems:

- (i) The excitation of local modes in an ionic complex, consisting of the paramagnetic ion and a single shell of surrounding ligands, by the lattice vibrations.
- (ii) The coupling between the local modes of the complex and the electrons in the partly filled shell of the paramagnetic ion due to modulation of the crystal field.

This model omits long-range electrostatic coupling effects which may, however, be added in separately. Both aspects of the problem have been discussed extensively in the literature (see e.g. Orbach and Stapleton 1972), where it is made clear that (ii) is the main stumbling block in obtaining reliable quantitative orbit-lattice Hamiltonians.

The assumption made in omitting long-range interactions between the lattice vibrations and the electrons in the paramagnetic ions is already incorporated in the superposition model of the crystal field (Newman 1971). It is only necessary to introduce the further assumption that each ligand acts *independently* on the open-shell electrons to use this model in the treatment of problem (ii) above. A formulation of this approach has been given by Curtis *et al.* (1969). In the next section we consider a modified formulation, closely related to the application of the superposition model in static crystal field theory.

Superposition Model of Dynamic Crystal Field

According to the superposition model, the static crystal field can be expressed as a sum of axially symmetric contributions from the individual ligands. In particular, each crystal field parameter can be written (in Stevens's normalization) as

$$B_n^m = A_n^m \langle r^n \rangle = \sum_i K_n^m(\theta_i \phi_i) \bar{A}_n(R_i), \quad (1)$$

where the sum is over the ligands at $R_i = (R_i \theta_i \phi_i)$ and the $\bar{A}_n(R_i)$ are intrinsic parameters describing the axially symmetric crystal field due to a ligand at distance R_i . The 'coordination factors' $K_n^m(\theta_i \phi_i)$ are functions of the ligand angular positions determined using the transformation properties of spherical harmonics. They are normalized so that $K_n^0(0,0) = 1$. A list of these functions for a restricted set of n, m values has been given by Newman and Urban (1975, p. 816).

In most practical applications of equation (1) there will be several ligands at the same distance R_v from the central paramagnetic ion, so the summation can be rearranged as

$$B_n^m = \sum_v \bar{K}_n^m(v) \bar{A}_n(R_v), \quad (2)$$

where

$$\bar{K}_n^m(v) = \sum_{j \in v} K_n^m(\theta_j \phi_j)$$

are the 'combined coordination factors' for the set of equidistant ligands at R_v labelled v .

Dynamic crystal field parameters are defined as the differentials $\partial B_n^m / \partial \epsilon_r$, where the ϵ_r represent normal mode displacements in the paramagnetic complex. Using equation (1) we obtain

$$\frac{\partial B_n^m}{\partial \epsilon_r} = \sum_i \frac{\partial R_i}{\partial \epsilon_r} K_n^m(\theta_i \phi_i) \frac{\partial \bar{A}_n}{\partial R_i} + \sum_i \left(\frac{\partial \theta_i}{\partial \epsilon_r} \frac{\partial K_n^m(i)}{\partial \theta_i} + \frac{\partial \phi_i}{\partial \epsilon_r} \frac{\partial K_n^m(i)}{\partial \phi_i} \right) \bar{A}_n. \quad (3)$$

It is thus appropriate to define two sets of 'dynamic coordination factors',

$$\gamma_n^m(\theta_i \phi_i \Gamma) = \frac{\partial R_i}{\partial \epsilon_r} K_n^m(\theta_i \phi_i), \quad \beta_n^m(\theta_i \phi_i \Gamma) = \frac{\partial \theta_i}{\partial \epsilon_r} \frac{\partial K_n^m(i)}{\partial \theta_i} + \frac{\partial \phi_i}{\partial \epsilon_r} \frac{\partial K_n^m(i)}{\partial \phi_i},$$

so that

$$\frac{\partial B_n^m}{\partial \epsilon_r} = \sum_i \{ \gamma_n^m(i, \Gamma) \bar{A}_n'(i) + \beta_n^m(i, \Gamma) \bar{A}_n(i) \}. \quad (4)$$

This expression may also be simplified if the ligands are separated into equidistant sets (at R_v) as:

$$\frac{\partial B_n^m}{\partial \epsilon_r} = \sum_v \{ \bar{\gamma}_n^m(v, \Gamma) \bar{A}_n'(v) + \bar{\beta}_n^m(v, \Gamma) \bar{A}_n(v) \}, \quad (5)$$

where

$$\bar{\gamma}_n^m(v, \Gamma) = \sum_{j \in v} \gamma_n^m(\theta_j \phi_j \Gamma), \quad \bar{\beta}_n^m(v, \Gamma) = \sum_{j \in v} \beta_n^m(\theta_j \phi_j \Gamma).$$

In the above expressions we have treated the differential \bar{A}_n' as a distinct parameter. However, it is usual to assume that the function $\bar{A}_n(R)$ can be expressed as a power law in R , at least over a limited range of R . We may therefore write

$$\bar{A}_n'(R) = -t_n \bar{A}_n(R)/R,$$

where R is the ligand distance. This also allows us to relate the different $\bar{A}_n(v)$. Hence we may regard the quantities \bar{A}_n and t_n as giving a complete description of the dynamic crystal field.

Most work on dynamic coupling to date has used the point-charge approximation for the ligands, in which these parameters take the following values for a single electronic charge (in atomic units):

$$\bar{A}_2 = \frac{\langle r^2 \rangle}{2R^3}, \quad \bar{A}_4 = \frac{\langle r^4 \rangle}{8R^5}, \quad \bar{A}_6 = \frac{\langle r^6 \rangle}{16R^7}, \quad (6)$$

giving $t_n = 2n + 1$. It is now generally accepted that this approximation is quite unrealistic, even for the lanthanides, and the determination of the \bar{A}_n and t_n is a far more complex problem (Newman 1971).

Expressions for the dynamic coordination factors in a variety of paramagnetic complexes will be given in a forthcoming publication. The aim of the present work is to show that reliable values of the parameters \bar{A}_n and t_n for the lanthanides can now be obtained. Several procedures are available which can provide this information:

- (a) Static (or quasi-static) strain experiments on systems with high site symmetry.
- (b) Comparison of crystal field parameters in several different, but isomorphic, systems.
- (c) Analysis of static crystal field parameters for sites with at least two ligand distances.
- (d) *Ab initio* calculations and related models.

All three of the experimental procedures are faced with the problem that, in the case of substituted ions, there will be some differences between bulk and local properties of the crystal. Careful analysis is required to eliminate the uncertainties arising from such effects. Strain experiments on crystals containing substituted paramagnetic ions are particularly difficult to interpret, since local elastic constants may change as well as the ionic positions at equilibrium.

Given that reliable values of \bar{A}_n and t_n can be obtained using one or more of the procedures (a)–(d) above, it is unnecessary to regard any of the parameters in the orbit-lattice Hamiltonian as indeterminate in interpreting spin-lattice relaxation data. This makes it possible to use such data as a test of the superposition model. Unfortunately, previous tests of this nature have been rather inconclusive owing to confusion in the interpretation of symbols (North and Stapleton 1977) or to the use of a completely different symbolism (Baker and van Ormondt 1974).

F[−] Ligands

A considerable amount of experimental data has been collected for lanthanide ions in cubic sites in fluorite structure crystals. Such data are particularly appropriate for the method (b) described in the previous section, as it is relatively simple to calculate local distortions or to use indirect experimental means such as ENDOR to estimate them. An example of this approach is the work by Anderson *et al.* (1975), who find power-law exponents for Tm^{2+} in CaF_2 , SrF_2 and BaF_2 of the order $t_4 = 10.5 \pm 0.5$ and $t_6 = 11.5 \pm 1.5$. These results should be more accurate than

a previous analysis by Stedman and Newman (1971), who obtained a mean value for divalent ions of $t_4 = t_6 = 5.7 \pm 0.9$, due to an underestimate of the static local distortion around a substituted ion in these crystals. The static strain experiments of Axe and Burns (1966) also underestimate local distortion effects, and give the power-law exponents $t_4 = t_6 = 6.8 \pm 0.3$.

This section is devoted to a re-examination of the data for lanthanide ions in the fluorites in order to be able to obtain more reliable estimates of t_4 and t_6 . We first address ourselves to the question of whether $t_4 = t_6$ for lanthanide ions substituted in fluorite structure crystals, as this can be decided without reference to the actual lanthanide–ligand distances involved. It is also independent of the superposition model, since in cubic symmetry the crystal field parameters themselves are a function of the lanthanide–ligand distance R alone, so there is no need to relate measured parameters to intrinsic parameters in order to eliminate angular variation effects. We can therefore write

$$\frac{t_6}{t_4} = \frac{\log(A_6 \langle r^6 \rangle_{R_1} / A_6 \langle r^6 \rangle_{R_2})}{\log(A_4 \langle r^4 \rangle_{R_1} / A_4 \langle r^4 \rangle_{R_2})}. \quad (7)$$

Table 1. Intrinsic parameters for lanthanide ions in fluorite structure crystals

Ion	Ionic radius ^A (Å)	Intrinsic parameters \bar{A}_n (cm ⁻¹)			Exp. data source ^B
		CaF ₂ \bar{A}_4, \bar{A}_6	SrF ₂ \bar{A}_4, \bar{A}_6	BaF ₂ \bar{A}_4, \bar{A}_6	
Gd ³⁺	0.938	86.8, 27.8	77.1, 23.3	69.4, 17.5	1
Tb ³⁺	0.923	84.2, 27.0	80.6, 24.9	74.8, 22.6	2
Dy ³⁺	0.908	82.6, 23.6	77.9, 21.3	73.9, 19.0	3
Er ³⁺	0.881	78.8, 21.8	71.7, 19.3	66.9, 17.1	4
Yb ³⁺	0.858	68.5, 19.4			5
Ho ²⁺	—	94.8, 16.4	80.0, 13.6	67.5, 11.7	6
Dy ²⁺	—	75.5, 17.7	67.2, 15.8	59.5, 13.8	7
Tm ²⁺	—	60.8, 15.6	53.0, 12.8	44.6, 10.6	8

^A Taken from the CRC Handbook (1975–6).

^B Sources: 1, O'Hare *et al.* (1969); 2, Davydova *et al.* (1976); 3, Al'tshuler *et al.* (1970); 4, Aizenberg *et al.* (1971); 5, Kiro and Low (1970); 6, Weakliem and Kiss (1967); 7, Kiss (1965); 8, Hayes and Smith (1971).

A collection of experimental data for lanthanide ions in the three hosts CaF₂, SrF₂ and BaF₂ has yielded the intrinsic parameters listed in Table 1. However, the derivation of Dy²⁺ parameters implicitly assumes that $t_4 = t_6$, so we cannot derive any information from equation (7). The results for the remaining systems may be summarized as:

$$t_6/t_4 = 1.7 \pm 0.3 \quad \text{for trivalent ions;}$$

$$t_6/t_4 = 1.1 \pm 0.2 \quad \text{for divalent ions.}$$

Edgar and Newman (1975) used strain data for the Gd³⁺ spin-Hamiltonian to estimate ligand distances for Gd³⁺ substituted into cubic sites in fluorite structure crystals. Their results have recently been confirmed using ENDOR by Baker and Christidis (1977). From the data given in Table 1 and with the assumption that the Gd³⁺ ligand distances are at least approximately valid for other trivalent ions, we

obtain the following power-law exponents:

- (a) for Gd^{3+} , $t_4 = 10.7 \pm 1.3$, $t_6 = 21.6 \pm 4$;
 (b) for Tb^{3+} , Dy^{3+} and Er^{3+} , $t_4 = 6.3 \pm 1.4$, $t_6 = 10.1 \pm 1.1$.

The striking differences between Gd^{3+} and the other trivalent ions are probably due to the different nature of the crystal field in this ion (Newman 1970; Judd 1977).

Fig. 1 plots experimental \bar{A}_4 parameters for Tb^{3+} , Dy^{3+} and Er^{3+} , the straight line fits being drawn with the same gradient (corresponding to $t_4 = 6.3$) for all three ions. This graph allows us to derive an approximate formula for all the \bar{A}_4 parameters, namely

$$\bar{A}_4(R) = \bar{A}_4(R/R_0)^{6.3}, \quad (8)$$

where \bar{A}_4 may be chosen arbitrarily, provided R_0 is specified. For

$$\begin{aligned} \bar{A}_4 = 75.9 \text{ cm}^{-1} \quad \text{we obtain} \quad R_0 &= 2.373 \text{ \AA} \quad \text{for } \text{Er}^{3+}, \\ &= 2.401 \text{ \AA} \quad \text{for } \text{Dy}^{3+}, \\ &= 2.410 \text{ \AA} \quad \text{for } \text{Tb}^{3+}. \end{aligned}$$

The differences between R_0 are very close to the differences in ionic radii of the ions. This suggests that equation (8) may be used as a general extrapolation formula giving $\bar{A}_4(R)$ for any trivalent lanthanide ion with a fluorine ligand. The corresponding graph for $\bar{A}_6(R)$ (Fig. 2) gives

$$\bar{A}_6(R) = \bar{A}_6(R/R_0)^{10.1}, \quad (9)$$

where

$$\begin{aligned} \bar{A}_6 = 20.3 \text{ cm}^{-1} \quad \text{and} \quad R_0 &= 2.376 \text{ \AA} \quad \text{for } \text{Er}^{3+}, \\ &= 2.401 \text{ \AA} \quad \text{for } \text{Dy}^{3+}, \\ &= 2.438 \text{ \AA} \quad \text{for } \text{Tb}^{3+}. \end{aligned}$$

Figs 1 and 2 also serve to confirm the relative ligand distances in the substituted fluorites determined by Edgar and Newman (1975), as all three sets of data for a given value of $\log R$ in both graphs lie in a 'best fit' position for their value of $\log R$ in relation to the fitted lines. This criterion could have been used to determine the relative ligand distances in SrF_2 and BaF_2 , assuming zero distortion in the case of CaF_2 . In this case the Tb^{3+} value of R_0 is greater than would be suggested by differences in ionic radii.

Porcher and Caro (1976) have determined crystal field parameters for Eu^{3+} substituted for Y^{3+} in C_{4v} sites in KY_3F_{10} , providing an alternative source of information on F^- intrinsic parameters. Observed parameters and calculated coordination factors for each of the two groups of F^- ions are given in Table 2.

The observed $n = 4$ and $n = 6$ parameters can be understood using the superposition model if we accept the values

$$\begin{aligned} \bar{A}_4 &= 78.4 \pm 2 \text{ cm}^{-1}, & t_4 &= 16.6; \\ \bar{A}_6 &= 19.7 \pm 2 \text{ cm}^{-1}, & t_6 &= 9.1; \end{aligned}$$

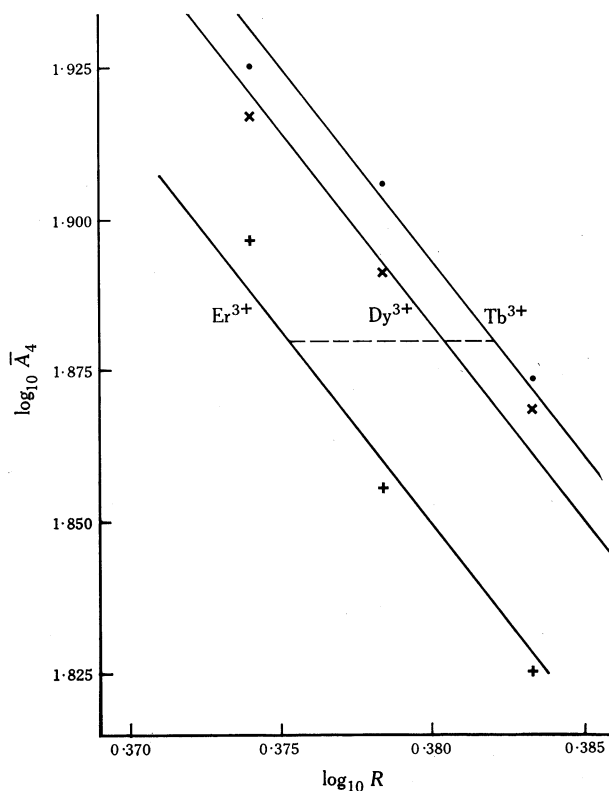


Fig. 1. Plots of $\log \bar{A}_4$ (\bar{A}_4 in cm^{-1}) against $\log R$ (R in \AA) for Er^{3+} , Dy^{3+} and Tb^{3+} ions in fluorite hosts. Fitted lines with $t_4 = 6.3$ are shown, giving equation (8) in the text. The horizontal dashed line corresponds to $\bar{A}_4 = 75.9 \text{ cm}^{-1}$.

Table 2. Superposition model analysis data for $\text{Eu}^{3+} : \text{KY}_3\text{F}_{10}$

n, m values	Observed parameters ^A	Calculated coordination factors ^B	
	$A_n^m \langle r^n \rangle$ (cm^{-1})	$K_n^m(1)$	$K_n^m(2)$
2, 0	-276 ± 8	0.016	0.112
4, 0	-170 ± 3	-1.564	-1.612
4, 4	360 ± 24	-7.715	7.347
6, 0	24.6 ± 2	0.870	0.751
6, 4	164 ± 14	-18.72	18.99

^A Obtained by Porcher and Caro (1976) and here expressed in Stevens's normalization.

^B The four ions included in $K_n^m(1)$ have positions $\mathbf{R}_1 = (R_1, \theta_1, \phi_1 + 90^\circ)$ where $R_1 = 2.33 \text{ \AA}$, $\theta_1 = 54.57^\circ$, $\phi_1 = 45^\circ$ and r is an integer; similarly, \mathbf{R}_2 is given by $R_2 = 2.19 \text{ \AA}$, $\theta_2 = -53.60^\circ$ and $\phi_2 = 0$.

for F^- ligands at a distance of 2.19 \AA from Eu^{3+} . The values of t_4 and t_6 are of a similar order of magnitude to the values determined for cubic systems, although t_4 is greater than t_6 , probably due to local distortion effects. The superposition model cannot explain the observed sign of $A_2^0 \langle r^2 \rangle$, given the X-ray determination of ionic positions and the usual condition $\bar{A}_2 > 0$, again suggesting the importance of local distortion effects in this system.

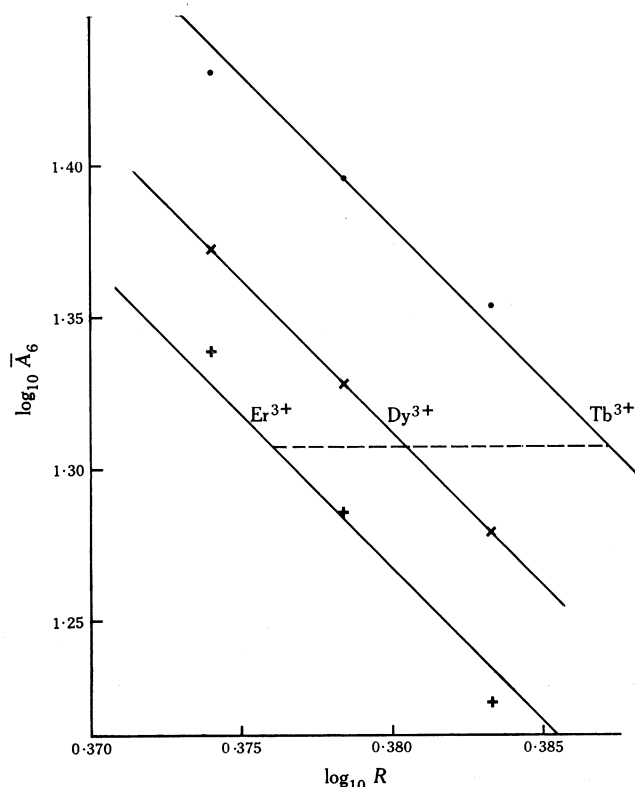


Fig. 2. Plots of $\log\{\bar{A}_6 \text{ (cm}^{-1})\}$ against $\log\{R \text{ (Å)}\}$ for Er^{3+} , Dy^{3+} and Tb^{3+} in fluorite hosts. Fitted lines with $t_6 = 10.1$ are shown, giving equation (9) in the text. The horizontal dashed line corresponds to $\bar{A}_6 = 20.3 \text{ cm}^{-1}$.

To summarize, we have found the power-law exponent t_6 to be greater than had been suggested prior to the work of Anderson *et al.* (1975). The cubic-site results for the ratios t_6/t_4 , which are independent of both the superposition model and local distortion effects, show t_4 to be significantly smaller than t_6 for the trivalent lanthanides. Formulae have been derived for the intrinsic parameters \bar{A}_4 and \bar{A}_6 of Dy^{3+} , Er^{3+} and Tb^{3+} which can be extrapolated for other trivalent lanthanides. Similar formulae can be written down for the divalent lanthanides using the values of t_4 and t_6 obtained by Anderson *et al.* and the intrinsic parameters quoted in Table 1.

Cl^- Ligands

Cheng and Dorain (1976) have recently determined the cubic crystal field parameters for Pr^{3+} ions in octahedrally coordinated sites with Cl^- ligands in single crystals of $\text{Cs}_2\text{NaPrCl}_6$. The intrinsic parameters for this system can thus be determined as

$$\bar{A}_4 = 82.4 \text{ cm}^{-1}, \quad \bar{A}_6 = 52.8 \text{ cm}^{-1},$$

which are considerably larger than experimental results give for $\text{Pr}^{3+}:\text{LaCl}_3$ (Margolis 1961). They are also rather different from the parameters determined by Dunlap and Shenoy (1975) for $\text{Cs}_2\text{NaPrCl}_6$, namely $\bar{A}_4 = 137 \text{ cm}^{-1}$ and $\bar{A}_6 = 56 \text{ cm}^{-1}$.

Assuming the Na-Cl distance in $\text{Cs}_2\text{NaPrCl}_6$ to be the same as in NaCl we may use X-ray data (Morss *et al.* 1970) to determine the $\text{Pr}^{3+}\text{-Cl}^-$ distance as 2.673 \AA , compared with 2.953 \AA in LaCl_3 . Using intrinsic parameters determined from experimental data for $\text{Pr}^{3+}:\text{LaCl}_3$ (Curtis *et al.* 1969), $\bar{A}_4 = 38.8 \text{ cm}^{-1}$ and $\bar{A}_6 = 15.8 \text{ cm}^{-1}$, in conjunction with the results of Cheng and Dorain (1976), we derive the power-law exponents

$$t_4 = 7.9, \quad t_6 = 12.1.$$

Although slightly larger, these have a remarkably similar ratio to that already determined for F^- ligands in fluorite crystals. They may also be compared with the results of the *ab initio* calculation by Curtis *et al.* (1969) which gives

$$t_4 = 9.6, \quad t_6 = 10.6.$$

This represents an unusually good agreement between theory and experiment for these parameters.

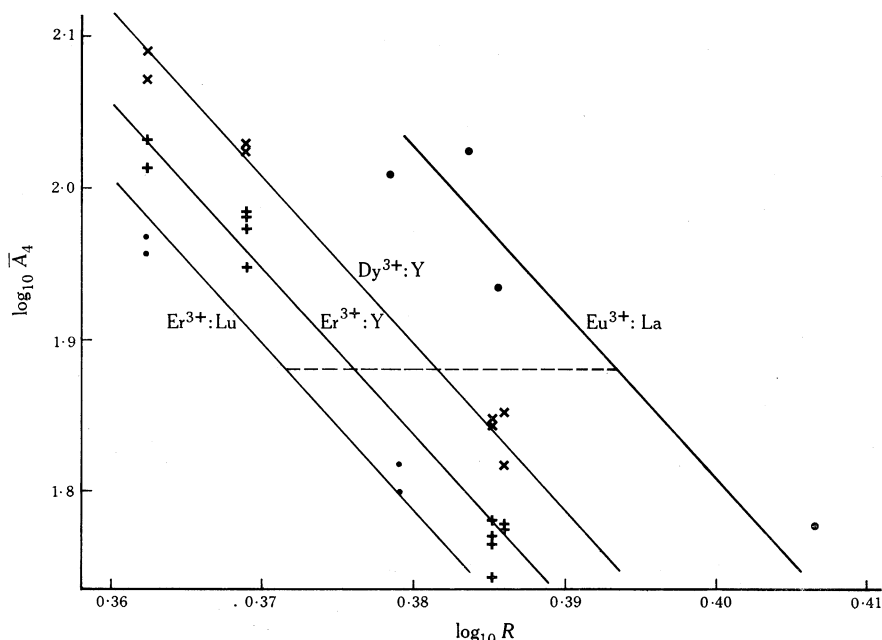


Fig. 3. Plots of $\log\{\bar{A}_4 (\text{cm}^{-1})\}$ against $\log\{R (\text{\AA})\}$ for various lanthanide ions with oxygen ligands. Fitted lines corresponding to $t_4 = 11.0$ are shown, giving equation (10) in the text. The horizontal dashed line corresponds to $\bar{A}_4 = 75.9 \text{ cm}^{-1}$.

O^{2-} Ligands

Values of the intrinsic parameters \bar{A}_4 and \bar{A}_6 for several trivalent lanthanides in garnet host crystals have been determined by Newman and Stedman (1969). A plot of the results for \bar{A}_4 in $\text{Er}^{3+}:\text{YGaG}$, ErGaG and ErAlG gives remarkable consistency, as is shown in Fig. 3, where $t_4 = 11.0$. In this figure lines of the same gradient have also been fitted to \bar{A}_4 values for Dy^{3+} in garnet hosts, $\text{Er}^{3+}:\text{LuGaG}$ and Eu^{3+} in a variety of host crystals (Linares and Louat 1975). As Linares and

Louat showed, there is not very good consistency between \bar{A}_4 values for Eu^{3+} in the host $\text{La}_2\text{O}_2\text{S}$ and its values in LaAlO_3 and La_2O_3 , and hence the points for this ion in Fig. 3 show considerable scatter. This is to be expected for O^{2-} ligands, which show variable ionicity (Newman 1977). Nevertheless, the differences between the fitted lines for Dy^{3+} and Er^{3+} can be understood in terms of differing ionic radii, following our explanation of the relative \bar{A}_4 and \bar{A}_6 values in the fluorites. The general formula takes the form

$$\bar{A}_4(R) = \bar{A}_4(R/R_0)^{11.0}, \quad (10)$$

where

$$\begin{aligned} \bar{A}_4 = 75.9 \text{ cm}^{-1} \quad \text{and} \quad R_0 = 2.377 \text{ \AA} \quad \text{for} \quad \text{Er}^{3+} \text{ replacing } \text{Y}^{3+}, \\ = 2.352 \text{ \AA} \quad \text{for} \quad \text{Er}^{3+} \text{ replacing } \text{Lu}^{3+}, \\ = 2.407 \text{ \AA} \quad \text{for} \quad \text{Dy}^{3+} \text{ replacing } \text{Y}^{3+}, \\ = 2.456 \text{ \AA} \quad \text{for} \quad \text{Eu}^{3+} \text{ in } \text{La}_2\text{O}_2\text{S}, \\ = 2.494 \text{ \AA} \quad \text{for} \quad \text{Eu}^{3+} \text{ in } \text{La}_2\text{O}_3 \text{ and } \text{LaAlO}_3. \end{aligned}$$

As is shown in Fig. 4, the fitted \bar{A}_6 values obtained by Newman and Stedman (1969) have considerably greater scatter than the fitted \bar{A}_4 values. Nevertheless, there is still good consistency between the values obtained for Er^{3+} and Dy^{3+} in the gallium and aluminium garnets. It is not possible to distinguish between \bar{A}_6 values for Er^{3+} in LuGaG and the other garnets. With these reservations in mind, the following approximate general formula for garnet hosts may be derived:

$$\bar{A}_6(R) = \bar{A}_6(R/R_0)^{10.9}, \quad (11)$$

where

$$\begin{aligned} \bar{A}_6 = 21.2 \text{ cm}^{-1} \quad \text{and} \quad R_0 = 2.377 \text{ \AA} \quad \text{for} \quad \text{Er}^{3+}, \\ = 2.450 \text{ \AA} \quad \text{for} \quad \text{Dy}^{3+}. \end{aligned}$$

The \bar{A}_6 values for Eu^{3+} in various hosts obtained by Linares and Louat (1975) do not show any systematic relationship to the garnet values. It is worth remarking, however, that these authors obtain consistent fits to experimental data using a value of t_6 close to 11. This value can therefore be taken as universally valid for O^{2-} , although there is apparently no universally valid value of \bar{A}_6 .

It is interesting to compare the above results with those obtained by Vishwamittar and Puri (1974a) for $\text{Er}^{3+}:\text{YVO}_4$. Their derived intrinsic parameters are $\bar{A}_4 = 51 \text{ cm}^{-1}$, $\bar{A}_6 = 27 \text{ cm}^{-1}$, while equations (10) and (11) give $\bar{A}_4 = 93.2 \text{ cm}^{-1}$, $\bar{A}_6 = 26.3 \text{ cm}^{-1}$. All the results for zircon structure crystals show such relatively low values for \bar{A}_4 , which may be interpreted as the effect of covalent bonding (e.g. in the VO_4 complex) removing much of the effective charge of the oxygen ion. It is therefore necessary to be very careful in using equation (10) to obtain values of \bar{A}_4 .

Intrinsic parameters have also been determined for trivalent ions in a variety of scheelite hosts (Vishwamittar and Puri 1974b). For example, $\text{Er}^{3+}:\text{CaWO}_4$ (with $R = 2.466 \text{ \AA}$) gives the experimental values $\bar{A}_4 = 51 \text{ cm}^{-1}$, $\bar{A}_6 = 17 \text{ cm}^{-1}$. Equations (10) and (11) give, for this value of R , $\bar{A}_4 = 50.6 \text{ cm}^{-1}$, $\bar{A}_6 = 15.0 \text{ cm}^{-1}$, which is excellent agreement in view of the many uncertainties involved in deriving these parameters from data in substituted ions. This suggests that covalent bonding effects are not important in these systems.

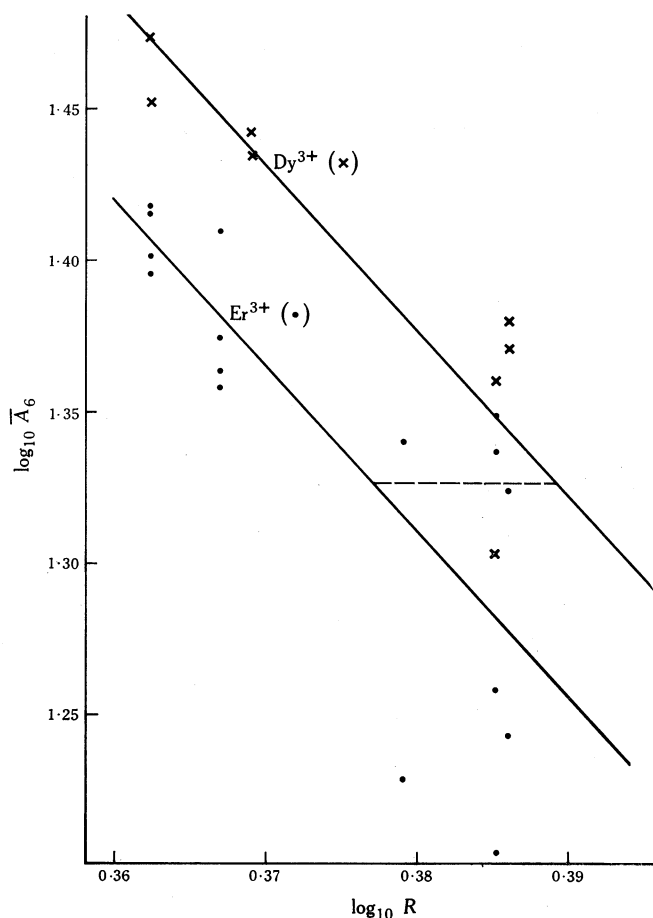


Fig. 4. Plots of $\log\{\bar{A}_6 \text{ (cm}^{-1})\}$ against $\log\{R \text{ (Å)}\}$ for Er^{3+} and Dy^{3+} substituted for Y^{3+} and Lu^{3+} in garnets with oxygen ligands. Fitted lines corresponding to $t_6 = 10.9$ are shown, giving equation (11) in the text. The horizontal dashed line corresponds to $\bar{A}_6 = 21.2 \text{ cm}^{-1}$.

Analysis of $n = 2$ Parameters

Relatively little work has been carried out to determine the intrinsic parameters \bar{A}_2 and power-law exponents t_2 from experimental values of the $A_2^m\langle r^2 \rangle$ because of the additional uncertainties involved in this procedure for $n = 2$. These uncertainties are:

- (i) The $A_2^m\langle r^2 \rangle$ include significant electrostatic contributions from distant ions, so the usual 'ligand only' form of the superposition model may not be appropriate.
- (ii) There are generally fewer parameters $A_2^m\langle r^2 \rangle$ than there are for higher n values, so that self-consistency checks are difficult to obtain.

Any useful estimates of the \bar{A}_2 and t_2 must therefore be based on an attempt to separate the intrinsic parameters into their electrostatic parts \bar{A}_n^e and their 'contact' parts \bar{A}_n^c arising from overlap, covalency, charge penetration and exchange. The contact interactions arise mainly from one-electron matrix elements between the

lanthanide f shell and the outer s^2p^6 configuration of the ligand, and thus do not perturb the $m_l = 2$ and $m_l = 3$ f-electrons, so we may write the orbital energies $E(m_l=2) = E(m_l=3) = 0$. This gives the following relation between the \bar{A}_n^e (Curtis *et al.* 1969):

$$\bar{A}_2^e = \frac{40}{143}(13\bar{A}_4^e - 7\bar{A}_6^e) = 3.64\bar{A}_4^e - 1.96\bar{A}_6^e. \quad (12)$$

Using the energy zero defined above we may write the f-electron orbital energy ratio $E(m_l=1)/E(m_l=0) = \lambda$. The intrinsic parameter ratios can then be expressed in the form

$$\frac{\bar{A}_2^e}{\bar{A}_6^e} = \beta = \frac{40}{13} \left(\frac{2+3\lambda}{2-3\lambda} \right), \quad \frac{\bar{A}_4^e}{\bar{A}_6^e} = \frac{12}{13} \left(\frac{3+\lambda}{2-3\lambda} \right) = \gamma \text{ (say)}, \quad (13)$$

where the symbol β was introduced by Newman and Price (1975). It was pointed out in that paper that it is a very good approximation to write $\bar{A}_6^e = \bar{A}_6$ (that is, $\bar{A}_6^e = 0$) so that \bar{A}_2^e can be readily derived from experimentally determined values of \bar{A}_6 if β can be assumed to be constant. The above equations show that this is equivalent to assuming λ to be constant. It should be also noted that equations (13) generalize equations (11) of Linares and Louat (1975) which correspond to the case $\lambda = 0$.

If $\bar{A}_4^e = 0$, equation (12) can be used to determine \bar{A}_2^e from the experimentally determined values of \bar{A}_4 and \bar{A}_6 quoted in the previous sections. A better approximation should be obtained, however, if the formulae of equations (6) are used to determine the ratio \bar{A}_4^e/\bar{A}_2^e . Introducing the usual screening factors $1-\sigma_n$ we have

$$\frac{\bar{A}_4^e}{\bar{A}_2^e} = \frac{1}{4} \frac{\langle r^4 \rangle}{\langle r^2 \rangle} \frac{1}{R^2} \frac{1-\sigma_4}{1-\sigma_2} = \mu \text{ (say)}, \quad (14)$$

where calculations give $\langle r^4 \rangle / \langle r^2 \rangle \approx 2.0$ a.u. (e.g. Coulthard 1973). Unfortunately, the screening factors are not very well determined. Using the estimated ratio $(1-\sigma_4)/(1-\sigma_2) = (1-0.0)/(1-0.8) = 5$ (Newman and Price 1975), we obtain

$$\mu = 0.70/R^2,$$

where R is measured in ångströms. A little manipulation then gives

$$\begin{aligned} \bar{A}_2 &= \bar{A}_2^e + \bar{A}_2^c = \bar{A}_2^e + \beta \bar{A}_6 \\ &= \mu^{-1}(\bar{A}_4 - \gamma \bar{A}_6) + \beta \bar{A}_6, \end{aligned} \quad (15)$$

where

$$\gamma = (\beta + 1.96)/3.64.$$

Use of the formula (15) requires the determination of β . This was found by Newman and Price (1975) to be approximately 5.4, giving $\lambda = 0.18$ and $\gamma = 2.0$. Experimentally determined ratios \bar{A}_4/\bar{A}_6 in excess of this value may be taken to indicate a significant electrostatic contribution to \bar{A}_4 . Values less than this, such as the ratio $\bar{A}_4/\bar{A}_6 = 1.89$ obtained from the data of Vishwamittar and Puri (1974a) quoted previously, suggest that $\gamma = 2.0$ may be an overestimate. If we assume \bar{A}_2^e to have the R dependence given by equations (6), an estimate of t_2 can be obtained from

equation (15) as follows,

$$t_2 = \{3\mu^{-1}(\bar{A}_4 - \gamma\bar{A}_6) + \beta\bar{A}_6 t_6\} / \bar{A}_2, \quad (16)$$

where \bar{A}_2 is to be calculated using equation (15).

Determination of $n = 2$ Parameters

The above equations will now be used to estimate values of \bar{A}_2 and t_2 from experimental data for $n = 4$ and $n = 6$ parameters. These estimates will be compared with more direct attempts to estimate these parameters from experimental values of the $A_2^m\langle r^2 \rangle$ and the results of *ab initio* calculations. Our previous results for trivalent lanthanides with F^- ligands (taking Er^{3+} with $R = 2.373 \text{ \AA}$) give

$$\bar{A}_2 = 386 \text{ cm}^{-1} \quad (\text{with } \bar{A}_2^c = 110 \text{ cm}^{-1}), \quad t_2 = 5.0.$$

This is consistent with the experimental result obtained for $Yb^{3+}:\text{CaF}_2$ by Baker and van Ormondt (1974) using uniaxial strain, namely $\bar{A}_2 = 410 \text{ cm}^{-1}$. It is also reasonably consistent with the result obtained by Newman (1973) for interstitial F^- ions in CaF_2 , $\bar{A}_2 = 409 \text{ cm}^{-1}$, although this ion is more distant and that analysis ignored local distortion effects.

Baker and van Ormondt (1974) studied the effect of uniaxial stress on Tm^{2+} substituted into CaF_2 , SrF_2 and BaF_2 and obtained values for \bar{A}_2 of 534, 526 and 450 cm^{-1} respectively for these hosts. These values are far from being in accord with those obtained from the model derived in the previous section which are, respectively, 323, 295 and 259 cm^{-1} . This discrepancy suggests that there may be factors which invalidate the use of the present model parameters for divalent ions, such as a reduced screening of the electrostatic contribution \bar{A}_2^c .

Taking $\sigma_2 = 0.8$ and $\sigma_4 = 0$ (which is consistent with the choice of the ratio $(1 - \sigma_2)/(1 - \sigma_4)$ given above) the calculation of Newman and Curtis (1969) for the $Pr^{3+}-F^-$ system at $R = 2.492 \text{ \AA}$ gives $\beta = 4.2$ and

$$\bar{A}_2 = 309 \text{ cm}^{-1} \quad (\text{with } \bar{A}_2^c = 85 \text{ cm}^{-1}), \quad t_2 = 3.2,$$

in reasonable accord with the values for trivalent ions determined from experimental data. A problem with making comparisons of this type is the absence of any calculation of the screening of the charge penetration contributions. The calculation of Newman and Curtis shows that equation (12) underestimates the (negative) charge penetration contributions to \bar{A}_2^c by about 50%. This provides a reasonable, if accidental, estimate of the screening of these contributions. Adjusting the results of the Newman and Curtis calculation to include this effect gives

$$\bar{A}_2 = 369 \text{ cm}^{-1} \quad (\text{with } \bar{A}_2^c = 145 \text{ cm}^{-1}), \quad t_2 = 4.2.$$

A similar procedure carried out for the $Pr^{3+}-Cl^-$ system with a spacing of $R = 2.953 \text{ \AA}$ gives $\bar{A}_2 = 175 \text{ cm}^{-1}$ ($\bar{A}_2^c = 85 \text{ cm}^{-1}$), in close agreement with the value (188 cm^{-1}) of this parameter determined for the $Pr^{3+}-I^-$ system by Newman *et al.* (1971). Unfortunately the parameters obtained for Cl^- ligands by Cheng and Dorain (1976) do not give reasonable results using the above formulae because we have $\bar{A}_4/\bar{A}_6 < 2$. This indicates that when the ligand becomes very close to the lanthanide ion, we must expect a reduction to occur in the parameter λ , with

consequent changes in β and γ . Taking the extreme value $\lambda = 0$ we obtain, for $R = 2.673 \text{ \AA}$, $\bar{A}_2 = 261 \text{ cm}^{-1}$, and comparison with the previous result gives the *very approximate* result $t_2 = 4.0$.

North and Stapleton (1977) have recently tested the superposition model for orbit-lattice coupling in $\text{Yb}^{3+}:\text{Cs}_2\text{NaYCl}_6$ using measured spin-lattice relaxation rates. Unfortunately, their parameters denoted \bar{A}_k are not the same as the \bar{A}_k defined by the present author in previous work and employed in this paper. Writing the North and Stapleton parameters as \bar{A}'_k , the relationships are

$$\bar{A}'_2 = 2\bar{A}_2, \quad \bar{A}'_4 = 8\bar{A}_4, \quad \bar{A}'_6 = 16\bar{A}_6.$$

In terms of *their* parameters, the empirical relation given by equation (5) of North and Stapleton (1977) should read

$$\bar{A}'_2 \geq \bar{A}'_4 \geq \bar{A}'_6.$$

Because of this confusion in the definition of the \bar{A}_k , the contradiction that North and Stapleton claim to have found between their results and this inequality is, in fact, incorrect. Parameters derived from the static crystal field are

$$\bar{A}'_4 = 331.4 \text{ cm}^{-1}, \quad \bar{A}'_6 = 140.8 \text{ cm}^{-1},$$

while their experiment gives

$$560 \text{ cm}^{-1} \leq t_2 \bar{A}'_2 \leq 1250 \text{ cm}^{-1}.$$

If t_2 is estimated to take its electrostatic value ($= 3$), then *both* the above inequalities are satisfied for $331 \text{ cm}^{-1} \leq \bar{A}'_2 \leq 417 \text{ cm}^{-1}$, showing the superposition model to be consistent with the spin-lattice relaxation measurements in this case.

The garnet results may be interpreted using the formulae (15) and (16) to give (for Er^{3+})

$$\bar{A}_2 = 371 \text{ cm}^{-1} \quad (\bar{A}_2^s = 122 \text{ cm}^{-1}), \quad t_2 = 5.6.$$

This is rather different from the result obtained by Newman and Edgar (1976) by direct application of the superposition model to data for the $n = 2$ parameters. For Er^{3+} it was found that $\bar{A}_2 = 451 \text{ cm}^{-1}$ and $t_2 = 2.5$. However, these results are understandable considering the assumptions made by Newman and Edgar concerning the magnitude of local distortion, and the fact that no account was taken of long-range contributions to the electrostatic field.

The parameters for $\text{Er}^{3+}:\text{CaWO}_4$ ($R = 2.466 \text{ \AA}$) analysed by Vishwamittar and Puri (1974*b*) give (on the assumption $t_2 = 5$) $\bar{A}_2 = 388 \text{ cm}^{-1}$. This result is not very sensitive to the choice of t_2 , the uncertainty being less than the differences between different sets of experimental results. Again assuming $t_2 = 5$, the result for $R = 2.377 \text{ \AA}$ (comparable with the garnet result quoted above) is $\bar{A}_2 = 466 \text{ cm}^{-1}$. This extrapolation ignores local distortion effects. Given the various uncertainties, a realistic assessment for Er^{3+} with ionic oxygen ligands at about 2.4 \AA is thus

$$\bar{A}_2 = 425 \pm 50 \text{ cm}^{-1}, \quad t_2 = 4 \pm 2.$$

As a final example we consider the system $\text{Eu}^{3+}:\text{LaAlO}_3$, for which details of the superposition model analysis have been given by Linares and Louat (1975).

Their results were $\bar{A}_2 = 834 \text{ cm}^{-1}$, $\bar{A}_4 = 63.4 \text{ cm}^{-1}$, $\bar{A}_6 = 28.3 \text{ cm}^{-1}$, $t_2 = 6$, $t_4 = 12$ and $t_6 = 11$ at $R = 2.55 \text{ \AA}$ with an error estimate of the order of 20% on \bar{A}_2 . Equations (15) and (16) give a rather different estimate of \bar{A}_2 , namely

$$\bar{A}_2 = 216 \text{ cm}^{-1} \quad (\bar{A}_2^e = 63), \quad \text{with} \quad t_2 = 8.7,$$

showing this system to be much less ionic than the garnets. Comparison of the calculated value of $\bar{A}_4^e = \gamma \bar{A}_6$ with equations (6) suggests an effective electronic charge of the order -0.8 . It should be noted that the ionicity of oxygen ions will not be determined by differences to their bonding with the lanthanide ion, but rather by their bonding with other ions in the crystal (in this case Al^{3+}).

Summary and Conclusions

We have investigated the determination of orbit-lattice coupling parameters for lanthanide ions with fluorine, chlorine or oxygen ligands in insulating crystals using the superposition model and various related assumptions. Apart from certain hosts, such as the zircon structure crystals, where the oxygen atoms form part of a tightly bound covalent cluster, the superposition model describes the static and strain parameters well. It should therefore also be suitable to describe dynamic effects if the values of the parameters \bar{A}_n and t_n are known. These parameters have been evaluated for $n = 4$ and 6 for a variety of systems and new general formulae (equations 8–11) have been derived for fluorine and oxygen ligands. The results also show fluorine and chlorine to have similar power-law dependences, and the intrinsic parameters \bar{A}_4 and \bar{A}_6 to be very similar in magnitude for fluorine and oxygen ligands.

Greater difficulties are involved in determining values of \bar{A}_2 and t_2 directly from experimental data, so a rather different approach has been employed which is based on a model of the crystal field as a sum of contact and point-charge electrostatic contributions. This model gives consistent results, but their accuracy is relatively uncertain in the absence of adequate experimental comparisons.

Acknowledgment

The author is grateful to Dr D. C. Price for a critical reading of the manuscript.

References

- Aizenberg, I. B., Malkin, B. Z., and Stolov, A. L. (1971). *Sov. Phys. Solid State* **13**, 2155.
- Al'tshuler, N. S., Eremin, M. V., Luks, R. K., and Stolov, A. L. (1970). *Sov. Phys. Solid State* **11**, 2921.
- Anderson, C. H., Call, P., Stott, J., and Hayes, W. (1975). *Phys. Rev. B* **11**, 3305.
- Axe, J. D., and Burns, G. (1966). *Phys. Rev.* **152**, 331.
- Baker, J. M., and Christidis, T. (1977). *J. Phys. C* **10**, 1059.
- Baker, J. M., and van Ormondt, D. (1974). *J. Phys. C* **7**, 2060.
- Cheng, C., and Dorain, P. B. (1976). *J. Chem. Phys.* **65**, 785.
- Coulthard, M. A. (1973). *J. Phys. B* **6**, 2224.
- CRC Handbook (1975–6). 'Handbook of Chemistry and Physics', 56th edn (Ed. R. C. Weast) (Chemical Rubber Co.: Cleveland, Ohio).
- Curtis, M. M., Newman, D. J., and Stedman, G. E. (1969). *J. Chem. Phys.* **50**, 1077.
- Davydova, M. P., Stolov, A. L., and Shcherbakov, V. D. (1976). *Sov. Phys. Solid State* **18**, 1656.
- Dunlap, B. D., and Shenoy, G. K. (1975). *Phys. Rev. B* **12**, 2716.
- Edgar, A., and Newman, D. J. (1975). *J. Phys. C* **8**, 4023.

- Hayes, W., and Smith, P. H. S. (1971). *J. Phys. C* **4**, 840.
- Judd, B. R. (1977). *Phys. Rev. Lett.* **39**, 242.
- Kiro, D., and Low, W. (1970). In 'Magnetic Resonance' (Eds C. K. Coogan, F. S. Ham, S. N. Stuart, J. R. Pilbrow and G. V. N. Wilson) (Plenum: New York).
- Kiss, Z. J. (1965). *Phys. Rev.* **137**, A1749.
- Linares, C., and Louat, A. (1975). *J. Phys. (Paris)* **36**, 717.
- Margolis, J. S. (1961). *J. Chem. Phys.* **35**, 1367.
- Morss, L. R., Siegal, M., Stenger, L., and Edelstein, N. (1970). *Inorg. Chem.* **9**, 1771.
- Newman, D. J. (1970). *Chem. Phys. Lett.* **6**, 288.
- Newman, D. J. (1971). *Adv. Phys.* **20**, 197.
- Newman, D. J. (1973). *J. Phys. C* **6**, L271.
- Newman, D. J. (1977). *Aust. J. Phys.* **30**, 315.
- Newman, D. J., Bishton, S. S., Curtis, M. M., and Taylor, C. D. (1971). *J. Phys. C* **4**, 3234.
- Newman, D. J., and Curtis, M. M. (1969). *Chem. Phys. Lett.* **3**, 158.
- Newman, D. J., and Edgar, A. (1976). *J. Phys. C* **9**, 103.
- Newman, D. J., and Price, D. C. (1975). *J. Phys. C* **8**, 2985.
- Newman, D. J., and Stedman, G. E. (1969). *J. Chem. Phys.* **51**, 3013.
- Newman, D. J., and Urban, W. (1975). *Adv. Phys.* **24**, 793.
- North, M. H., and Stapleton, H. J. (1977). *J. Chem. Phys.* **66**, 4133.
- O'Hare, J. M., Detrio, J. A., and Donlan, V. L. (1969). *J. Chem. Phys.* **51**, 3937.
- Orbach, R., and Stapleton, H. J. (1972). In 'Electron Paramagnetic Resonance', Ch. 2 (Ed. S. Geschwind) (Plenum: New York).
- Porcher, P., and Caro, P. (1976). *J. Chem. Phys.* **65**, 89.
- Stedman, G. E., and Newman, D. J. (1971). *J. Phys. Chem. Solids* **32**, 2001.
- Vishwamittar and Puri, S. P. (1974a). *Phys. Rev. B* **9**, 4673.
- Vishwamittar and Puri, S. P. (1974b). *J. Chem. Phys.* **61**, 3720.
- Weakliem, H. A., and Kiss, Z. J. (1967). *Phys. Rev.* **157**, 277.

Manuscript received 5 September 1977

