

# Ligand Ordering Parameters

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## *Abstract*

Lanthanide and actinide single-ligand crystal field parameters are shown to define similar spectrochemical series to the cubic parameter for 3d ions, providing direct evidence that the dominant electronic processes which cause crystal field splittings are the same for all open-shell ions. The contrast between the nephelauxetic series and the spectrochemical series and the existence of a strong empirical correlation between the former and ligand polarizability show that the nephelauxetic series cannot be determined by the admixture of ligand and open-shell wavefunctions as is often assumed. The influence of ligand polarizability on various spectroscopic parameters is then discussed.

## **Introduction**

It is well known (see e.g. Griffith 1961, p. 309) that the parameter  $Dq$ , which describes the cubic crystal field splitting in ions with 3d<sup>n</sup> open-shell configurations, can be used to define the *spectrochemical series*, in which the ligands are ordered by the magnitude of  $Dq$ . For inorganic complexes this may be expressed in the form:

$$\text{Free ion } (Dq = 0) < \text{I}^- < \text{Br}^- < \text{Cl}^- < \text{S}^{2-} < \text{F}^- < \text{O}^{2-}, \quad (1)$$

although the  $Dq$  value for  $\text{O}^{2-}$  ions shows some variability and is occasionally less than that for  $\text{F}^-$ .

Schäffer and Jørgensen (1958) have pointed out that it is possible to define another series, which they called the *nephelauxetic series*, by the amount the 3d<sup>n</sup> Racah parameters are reduced from their free-ion values when the ions are in crystals. These parameters are a measure of the potential energy of pairs of electrons in the 3d shell. The nephelauxetic series takes the form (ordered by the magnitude of the reductions):

$$\text{Free ion} < \text{F}^- < \text{O}^{2-} < \text{Cl}^- < \text{Br}^- < \text{I}^- \approx \text{S}^{2-} < \text{Se}^{2-} < \text{Te}^{2-}. \quad (2)$$

It differs from the spectrochemical series in two ways:

- (i) In terms of the magnitude of the effect, the ordering of the halides is *opposite* to that in the spectrochemical series in relation to the free ion.
- (ii)  $\text{O}^{2-}$  and  $\text{S}^{2-}$  are in different positions relative to the halide sequence.

The relative ordering of the halides in the two series is sometimes explained in terms of an 'ionicity versus covalency' model (see e.g. Johnston *et al.* 1966). If  $Dq$  is assumed to be predominantly electrostatic, the spectrochemical series may be

said to be ordered by *ionicity* ( $F^-$  being the most ionic). Then (i) above can be explained by assuming that the nephelauxetic series is ordered by the complementary quality *covalency* ( $F^-$  being the least covalent ion). However, the calculation of Sugano and Shulman (1963), and a considerable amount of subsequent work, has shown conclusively that the predominant contributions to  $Dq$  are due to overlap and covalency, where these terms have a relatively precise interpretation in the construction of electronic eigenstates from free-ion states. In the following we shall use the term 'covalency' in this sense; that is to say, it refers to the degree of admixture between open-shell states on a metal ion and those on neighbouring closed-shell anions. This type of covalency cannot be related simply to the more familiar concept used in discussions of covalent versus ionic bonding between atoms.

We must presume, therefore, that the spectrochemical series is ordered by overlap and covalency, which we shall refer to collectively as *contact interactions*. A simple demonstration of this proposition can be obtained by comparing the overlap integrals for several ligands at their usual distance from a given paramagnetic ion. Their relative magnitudes have the same ordering as  $Dq$ . This can easily be understood in terms of the formulation given by Sugano and Shulman (1963), which shows that the magnitude of these and similar integrals is the main factor in determining  $Dq$ .

If the spectrochemical series is determined by contact interactions, the nephelauxetic series must be determined by a different physical effect, because its ordering is quite distinct. The main aims of this paper are to:

- (1) demonstrate that both the spectrochemical and nephelauxetic series defined by the corresponding lanthanide and actinide ion parameters give the same ligand ordering as that defined by the iron-group ions;
- (2) show that there is considerable evidence that the nephelauxetic effect is related to ligand polarizability.

### Spectrochemical Series for Lanthanides and Actinides

Lanthanide and actinide ions only occasionally occur in even approximately cubic sites, so that we cannot use cubic crystal field parameters as a basis for ligand ordering. However, the superposition model (Newman 1971) allows us to extract 'intrinsic' crystal field parameters, which measure the strength of the metal-ligand interaction from experimental parameters by eliminating angle-dependence effects in sites of low symmetry. The determination of intrinsic parameters makes it possible to define spectrochemical series for both the lanthanides (with  $4f^n$  configurations) and actinides (with  $5f^n$  configurations).

From the collected data for lanthanide intrinsic parameters  $\bar{A}_4$  (see Table 1a), we obtain the series:

$$\begin{aligned} \text{Free ion } (\bar{A}_4 = 0) &< Cl^- < S^{2-} < O^{2-} \text{ (zircon structure crystals)} \\ &\lesssim O^{2-} \text{ (scheelites)} < F^- < O^{2-} \text{ (garnets)} < O^{2-} \text{ (oxides)}. \end{aligned} \quad (3)$$

Although the crystal field parameters are an order of magnitude smaller than those for  $3d^n$  ions, this is similar to the series (1) given in the Introduction, apart from an even more noticeable variation of the relative position of  $O^{2-}$  ligands in different crystals. Note, however, that the series obtained from  $\bar{A}_6$  would be slightly different.

Data for actinide crystal field parameters remain rather sparse, but we are able to determine the intrinsic parameters  $\bar{A}_4$  shown in Table 1b, which give the following ordering for  $U^{4+}$ :

$$\text{Free ion} < \text{Br}^- < \text{Cl}^- < \text{O}^{2-} (\text{zircon}) < \text{O}^{2-} (\text{oxides}). \quad (4)$$

**Table 1. Crystal field intrinsic parameters for lanthanides and actinides**

The  $\bar{A}$ -parameter values (in units of  $\text{cm}^{-1}$ ) are derived from experimental data, and errors are given in those cases where a reasonable basis for estimation exists

| Ion                                         | Ligand          | Host                            | $\bar{A}_2$    | $\bar{A}_4$  | $\bar{A}_6$ | Sources <sup>A</sup> |
|---------------------------------------------|-----------------|---------------------------------|----------------|--------------|-------------|----------------------|
| <i>(a) Trivalent lanthanide ions</i>        |                 |                                 |                |              |             |                      |
| $\text{Dy}^{3+}$                            | $\text{F}^-$    | $\text{CaF}_2$                  | —              | 78           | 23          | 1                    |
|                                             | $\text{Cl}^-$   | $\text{LaCl}_3$                 | 290            | 34           | 10          | 2                    |
|                                             | $\text{O}^{2-}$ | Garnets                         | —              | $91 \pm 4$   | $25 \pm 2$  | 3                    |
|                                             | $\text{O}^{2-}$ | $\text{CaWO}_4$                 | 407            | $63 \pm 5$   | 14          | 4                    |
| $\text{Er}^{3+}$                            | $\text{F}^-$    | $\text{LaF}_3$                  | —              | $60 \pm 5$   | $32 \pm 5$  | 5                    |
|                                             | $\text{Cl}^-$   | $\text{LaCl}_3$                 | 186            | 37           | 10          | 2                    |
|                                             | $\text{O}^{2-}$ | Garnets                         | $450 \pm 100$  | $77 \pm 4$   | $21 \pm 1$  | 3, 6                 |
|                                             | $\text{O}^{2-}$ | $\text{YVO}_4, \text{YPO}_4$    | $300 \pm 100$  | $50 \pm 5$   | $18 \pm 2$  | 7, 8                 |
|                                             | $\text{O}^{2-}$ | $\text{CaWO}_4$                 | 400            | $50 \pm 2$   | $17 \pm 3$  | 4                    |
| $\text{Eu}^{3+}$                            | $\text{Cl}^-$   | $\text{LaCl}_3$                 | $370 \pm 20$   | $35 \pm 2$   | $21 \pm 2$  | 2, 9                 |
|                                             | $\text{O}^{2-}$ | Garnets                         | —              | 60           | 31          | 3                    |
|                                             | $\text{O}^{2-}$ | $\text{YVO}_4$                  | —              | $50 \pm 10$  | $24 \pm 4$  | 7                    |
|                                             | $\text{O}^{2-}$ | $\text{LaAlO}_3$                | $1000 \pm 200$ | $63 \pm 2$   | $28 \pm 1$  | 9                    |
|                                             | $\text{O}^{2-}$ | $\text{La}_2\text{O}_3$         | $3750 \pm 500$ | $108 \pm 2$  | $14 \pm 1$  | 9                    |
|                                             | $\text{O}^{2-}$ | $\text{CaWO}_4$                 | 407            | $63 \pm 5$   | 14          | 4                    |
|                                             | $\text{O}^{2-}$ | $\text{La}_2\text{O}_2\text{S}$ | 1900           | $88 \pm 1$   | $19 \pm 1$  | 9, 10                |
|                                             | $\text{S}^{2-}$ | $\text{La}_2\text{O}_2\text{S}$ | 960            | $47 \pm 3$   | $4 \pm 1$   | 9, 10                |
| <i>(b) Actinide ion <math>U^{4+}</math></i> |                 |                                 |                |              |             |                      |
| $U^{4+}$                                    | $\text{Cl}^-$   | $\text{Cs}_2\text{UCl}_6$       |                | 258          |             | 11                   |
|                                             | $\text{Br}^-$   | $\text{Cs}_2\text{UBr}_6$       |                | 235          |             | 11                   |
|                                             | $\text{O}^{2-}$ | Zircon                          |                | $294 \pm 15$ |             | 12                   |
|                                             | $\text{O}^{2-}$ | $\text{UO}_2$                   |                | 1061         |             | 13                   |

<sup>A</sup> Sources of data are: 1, Stedman and Newman (1971b); 2, Curtis *et al.* (1969); 3, Newman and Stedman (1969); 4, Vishwamittar and Puri (1974); 5, Stedman and Newman (1971a); 6, Newman and Edgar (1976); 7, Newman and Stedman (1971); 8, Newman and Urban (1972); 9, Linares and Louat (1975); 10, Morosin and Newman (1973); 11, Johnston *et al.* (1966); 12, Mackey *et al.* (1975); 13, Rahman and Runciman (1966).

The similarity between the spectrochemical series for ions with  $3d^n$ ,  $4f^n$  and  $5f^n$  configurations should not surprise us, as *ab initio* calculations of crystal field splittings in  $4f^n$  ions (Ellis and Newman 1967, 1968; Anisimov and Dagys 1971; Málek 1971) show them to be predominantly due to the same type of process (i.e. contact interactions) as the  $3d^n$  splittings. Burns (1967) has calculated overlap integrals for  $\text{Tm}^{2+}$  with  $\text{F}^-$ ,  $\text{Cl}^-$  and  $\text{O}^{2-}$  which show the same ordering as the spectrochemical series. We conclude, therefore, that the spectrochemical series for all types of open-shell ions are essentially the same, and that the ordering of these series is determined (via the intrinsic crystal field parameters) by contact interactions, that is, by overlap and by covalency defined in terms of admixture of ligand and open-shell wavefunctions.

### Origin of Ligand Dependence of Electron–Electron Interaction in an Open Shell

Several authors (e.g. Johnston *et al.* 1966; Wensky and Moulton 1970) have pointed out that the Slater parameter shifts in lanthanide and actinide ions define nephelauxetic series similar to the series (2) for the iron-group ions in the Introduction. The table given by Griffith (1961, p. 310) shows that a similar ligand ordering is defined by the transition metal ions with  $4d^n$  and  $5d^n$  configurations.

The shifts of the fitted Slater parameters for lanthanide ions in crystals from their free-ion values are so small that the uncertainties in the fitting procedure may make the ligand ordering indeterminate. In such cases the ligand ordering can usually be determined from the ordering of the multiplet energies. For example, Table IV of Wensky and Moulton (1970) orders the magnitude of the shift from the free-ion value for  $\text{Pr}^{3+}$  as  $\text{Cl}^- > \text{Br}^-$ , while the energy levels in Table 1 of their paper as well as the work of Baumert *et al.* (1975) on  $\text{Nd}^{3+}$  show clearly that the proper ordering is  $\text{Br}^- > \text{Cl}^-$ .

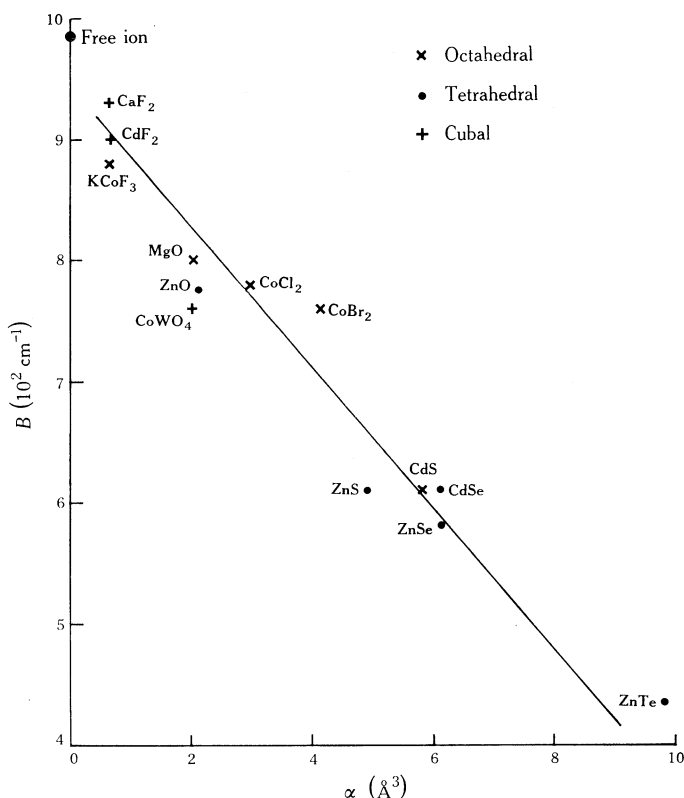
Weakliem (1962) noticed that the shifts in the Racah parameter  $B$  for  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  in several host crystals were closely correlated with ligand polarizabilities and explained this correlation in terms of the screening of the electron–electron interaction by the ligands. The empirical correlation was extended by Baranowski *et al.* (1967) to include some semiconducting host crystals, which produce considerably greater changes in  $B$ . Morrison *et al.* (1967) gave a classical formulation of this effect in which the paramagnetic ion is supposed to occupy a spherical hole in a uniform dielectric medium. This formulation gives an explicit relationship between the dielectric constant of the medium and the Slater parameter shifts but, unfortunately, the calculated shifts depend sensitively on the precise radius assumed for the spherical hole. Nevertheless, this very sensitively shows that it is the local environment which makes the dominant contribution and thus provides a theoretical basis for regarding the observed effect as being mainly due to the *ligand* polarizability, rather than the polarizability of the whole crystal.

An alternative explanation of the nephelauxetic effect has been given by Jørgensen (1962), who suggested that the decrease in the electron–electron interaction is primarily due to an increase in the size of the open-shell wavefunctions. Jørgensen associates this increased size with covalent bonding effects. Many attempts have been made to correlate the type of covalency parameters obtained in crystal field calculations with shifts in the Racah parameters (see e.g. Henrie 1974 and references therein), but no successful *ab initio* explanation of the nephelauxetic series has been, or can be, obtained in this way.

Jørgensen (1962, p. 59) has also referred to the possible importance of ‘central field covalency’ in expanding the open-shell electron distribution. He associates this with a reduction of the interaction of the open-shell electrons with the core charge due to ligand polarization effects. On the face of it, this process would explain the dependence of the Racah and Slater parameters on ligand polarizability. However, a *spherically symmetric* medium outside, and centred on, a paramagnetic ion does not contribute to the potential gradient in that ion. Hence no expansion of the electron distribution results at this level of approximation. Anisotropic effects would also give large contributions to the crystal field parameters.

As stated in the Introduction, the simple fact that the nephelauxetic and spectrochemical series are ordered very differently shows that the underlying mechanisms

which define the two series are distinct. The demonstrated relationship of overlap and covalency with the spectrochemical series is therefore evidence that these processes do not give the dominant contribution to the nephelauxetic effect. Further evidence for this has been given by Newman (1973), who calculated the overlap and covalency contributions to the Slater parameter shifts for  $\text{Pr}^{3+}$  in  $\text{PrCl}_3$ , and found them to be an order of magnitude smaller than the observed shifts.



**Fig. 1.** Values of the Racah parameter  $B$  for  $\text{Co}^{2+}$  plotted against ligand polarizability  $\alpha$ ; crystals with six-fold (octahedral), four-fold (tetrahedral) and eight-fold (cubal) coordination are indicated. The  $B$  values have been taken from Weakliem (1962), Baranowski *et al.* (1967), Lachowiecka *et al.* (1971) and Wray and Allen (1971).

Fig. 1 is an extended version of Weakliem's (1962) correlation diagram for  $\text{Co}^{2+}$  in various host crystals. This shows an effectively linear relationship between the ligand polarizabilities given by Tessman *et al.* (1953) and the shifts in the Racah parameter  $B$  (within the limits of experimental uncertainty). Some of the scatter in the figure is due to experimental uncertainty, but some may also be due to ligand-distance dependence.

The linear relationship shown in Fig. 1 may be expressed in terms of the formula

$$\Delta B = -K\alpha,$$

where  $\alpha$  is the ligand polarizability and the constant  $K$  is given by  $57 \text{ cm}^{-1} \text{\AA}^{-3}$ . A similar linear relationship is found for lanthanide and actinide ions. The  $F_2$  values

for  $\text{Pr}^{3+}$  collected by Wensky and Moulton (1970) and the  $\text{PrI}_3$  value determined by Clifton *et al.* (1971) allow us to establish the linear relation

$$\Delta F_2 = -K'\alpha,$$

where

$$K' = 4.3 \pm 0.3 \quad \text{cm}^{-1} \text{\AA}^{-3}.$$

$F_2$  values for  $\text{U}^{4+}$  have been obtained by Conway (1959), Johnston *et al.* (1966) and Mackey *et al.* (1975). These also give a good linear relationship for  $F_2$  with

$$K' = 6.8 \pm 0.5 \quad \text{cm}^{-1} \text{\AA}^{-3}.$$

We conclude, therefore, that there is overwhelming experimental evidence showing that the nephelauxetic effect\* is due to ligand polarizability, although the values of the proportionality constants obtained above have yet to be explained.

Spectroscopic measurements of ionic polarizabilities are of interest because they provide independent means of testing theories about the dielectric properties of crystals. In particular, the additivity of ionic polarizabilities assumed by Tessman *et al.* (1953) has been criticized (Van Vechten 1969) because it leads to a crystal-dependent  $\text{O}^{2-}$  polarizability. This makes it impossible to get an internal consistency check on the additivity rule as one can in the case of the alkali halides. It would therefore be of interest to see whether the predicted variation of  $\text{O}^{2-}$  polarizability is reflected in the Slater parameter shifts. Unfortunately, no sufficiently careful analyses of experimental data appear to exist which could be used to establish a definite scale of oxygen ligand polarizabilities. Some variability of the Racah parameters for different oxygen ligands certainly exists, however, and has been remarked upon for  $\text{Cr}^{3+}$  spectra by Wood *et al.* (1963).

A difficulty in interpreting the correlation between spectroscopic parameters and ligand polarizability arises from the fact that all spectroscopic parameters are functions of *ligand distance*. It follows that, in drawing diagrams such as Fig. 1, we shall get a scatter of points for a given ligand according to the metal–ligand distance in the material considered. There will be also a scatter of points depending on the *number of ligands*. The fact that the Racah parameter  $B$  varies only slightly with coordination number (as shown by Fig. 1) demonstrates that the ligand number and distance dependence of  $B$  tend to cancel.

In order to obtain a better understanding of the mechanisms relating ligand polarizability to the magnitude of the open-shell electron–electron interaction it is necessary to carry out experiments giving the distance dependence of  $B$  explicitly. Harada and Tsujikawa (1974) have used axial strain to determine changes of  $B$  in  $\text{Cs}_3\text{CoCl}_5$  (with  $\text{Cl}^-$  ligands) and  $\text{Cs}_3\text{CoBr}_5$  (with  $\text{Br}^-$  ligands). It is convenient to reinterpret their results in terms of power-law exponents  $n$  for the ligand-distance dependence  $R^{-n}$  of the *shift* in  $B$  from its free-ion value. Taking this free-ion value to be  $B_0 = 950 \text{ cm}^{-1}$  we obtain

$$n = 9.2 \pm 1.0 \quad \text{for } \text{Cl}^- \text{ ligands,}$$

$$n = 11.5 \pm 0.8 \quad \text{for } \text{Br}^- \text{ ligands.}$$

\* The term nephelauxetic (i.e. cloud expanding) is now seen to be rather unfortunate, as a reduced electron–electron repulsion could result in a *decrease* in the dimensions of the electron cloud.

We note that these results are based on the assumption by Harada and Tsujikawa of a power-law exponent  $n = 5$  for the cubic crystal field parameter in these systems. Writing this exponent as  $n_0$ , we can generalize the above results to

$$n = (1.84 \pm 0.20)n_0 \quad \text{for Cl}^- \text{ ligands,}$$

$$n = (2.30 \pm 0.16)n_0 \quad \text{for Br}^- \text{ ligands.}$$

It is also interesting to note that semiconducting materials lie on the same general correlation curve as ionic crystals in Fig. 1. This suggests that the concept of ionic (rather than bond) polarizability remains valid even for some semiconducting crystals.

It has been noted (Ballhausen 1962, p. 222) that the nephelauxetic series follows the same order as the electrochemical series which can, in turn, be related to the covalent bonding between atoms. In fact, if  $x$  is the electronegativity tabulated by Pauling (1960, p. 97), we can establish the following approximate relation for the polarizabilities  $\alpha$  (in  $\text{\AA}^3$ ):

$$\alpha = \{2.5/(x - 1.5)\}^2.$$

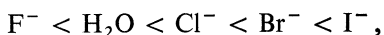
This might appear to show that the nephelauxetic series is related to covalency, which we have previously taken pains to disprove. However, such an argument would involve the confusion of the two types of covalency distinguished in the Introduction. The fact that the nephelauxetic series is correlated with the type of bonding between atoms is not directly related to the ligand–open-shell bonding between ions. Hence we reiterate that the shift in Slater (or Racah) parameters cannot be used to determine the admixture between ligand and open-shell wavefunctions, which is due to quite distinct processes.

### Other Spectroscopic Parameters which Correlate with Ligand Polarizability

Recent work (Newman and Urban 1972; Newman 1975*a*; Newman and Edgar 1976) has shown that the parameters  $b_m^n$  of the  $\text{Gd}^{3+}$  spin-Hamiltonian can be analysed into a linear combination of single-ligand contributions in the same way as the crystal field parameters (Newman 1971). Each contribution is represented by an axially symmetric single-ligand spin-Hamiltonian with parameters  $\bar{b}_m$ , which are referred to as ‘intrinsic spin-Hamiltonian parameters’ for the ligand in question.

It is found (Newman 1975*a*; Newman and Edgar 1976) that the  $\text{Gd}^{3+}$  parameter  $\bar{b}_4$  is subject to wide variations ( $-9 \times 10^{-4}$  to  $+19 \times 10^{-4} \text{ cm}^{-1}$ ), which do not correlate simply with the variations of the crystal field intrinsic parameters  $\bar{A}_4$  (and hence with the spectrochemical series). However, Newman (1975*b*) has shown that the observed  $\bar{b}_4$  values correlate well with ligand polarizability. A complicating aspect of this correlation, as well as of that between Slater parameters and polarizability (see e.g. Baumert *et al.* 1975), is the dependence of all spectroscopic parameters on ligand distance. Further studies of ligand-distance dependence effects are therefore an essential adjunct to obtaining a deeper understanding of ligand polarizability.

Peacock (1975) has shown that hypersensitive transition intensities in the lanthanides are also correlated with ligand polarizabilities, the relative ordering of ligands being given by



which has the same form as the nephelauxetic series (2). A theory of this interaction has been given by Mason *et al.* (1974), based on the electrostatic model of the crystal field. It is felt that the quantitative agreement with experiment obtained by these authors may be fortuitous, however, because certain important processes in lanthanide ions, such as outer shell screening, were not considered.

A fundamental question in understanding the relationship between ligand polarizability and spectroscopic parameters is whether or not the interaction is primarily electrostatic. This has always been assumed in previous calculations, but the success of the shell model of lattice vibrations shows that polarization induced by contact interactions plays an important role in ion-ion interactions. This type of process has yet to be considered as a possible mechanism contributing to ligand polarization by open-shell electrons.

## Conclusions

The conclusions from this work may be summarized as follows.

(1) Comparison of crystal field *intrinsic* parameters (obtained using the superposition model) has shown that identical spectrochemical series are defined by all transition metal ions. This is consistent with existing theoretical interpretations of crystal fields as always being mainly due to overlap and covalency.

(2) The nephelauxetic series, which is again similar for all transition metal ions, but quite distinct from the spectrochemical series, has been shown to be correlated with ligand polarizability and is thus not correlated with any expansion of the open-shell wavefunctions. This raises the possibility of using measured Slater parameters to test theories concerning the dielectric properties of insulating crystals.

(3) It has been shown that the nephelauxetic series is not related to covalency in the sense of an admixture of ligand and open-shell wavefunctions. Slater (or Racah) parameters cannot therefore be used to determine these admixtures, as has frequently been attempted in the literature (e.g. Henrie 1974).

(4) It is now known that three different spectroscopic parameters correlate with ligand polarizability, but existing quantitative theories of the mechanism, based on purely electrostatic effects, are suspect. It is necessary to carry out more detailed *ab initio* calculations of the effects of ligand polarizability allowing for 'contact' polarization (due to overlap and covalency) as well as polarization due to electrostatic fields.

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