

## Crystal Field Effects in S-state Ions due to Exchange Polarization

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

It is shown that the matrix elements of the tensor operators describing a new type of crystal field can be calculated using the properties of the spin  $\leftrightarrow$  quasi-spin transformation. The relationship of this field to electron correlation in open shells is clarified, and its contribution to the ground state splittings of S-state ions is discussed.

### Introduction

There is considerable interest in obtaining an understanding of the physical processes underlying the observed splitting of the S ground state of ions with half-filled shells, such as  $\text{Gd}^{3+}$ . An important aspect of these splittings is that significant contributions arise from processes which give small (i.e. unobservable) contributions to the crystal field splittings in other open shell ions. In particular, Wybourne (1965, 1966) pointed out that large contributions to the S-state splittings arise from the relativistic crystal field. A more recent analysis (Newman and Urban 1972) has made it clear that other processes must also make important contributions to these splittings.

Schwiesow and Crosswhite (1969) suggested that the large deviations of the excited state levels of  $\text{Gd}^{3+}$  from fitted crystal field parameters could be explained in terms of an effective 'charge conjugation invariant' form of the crystal field. This makes nonzero contributions to diagonal matrix elements of the type

$$\langle f^7 {}^6L M_L M_S | V | f^7 {}^6L M'_L M'_S \rangle$$

(where  $L$  represents an arbitrary total orbital angular momentum), for which the crystal field contribution is identically zero. Newman (1970) pointed out that a crystal field of the type postulated by Schwiesow and Crosswhite could arise as a result of there being a difference between the radial forms of the spin-up and spin-down electronic wavefunctions. Freeman and Watson (1961) have obtained a Hartree-Fock solution for  $\text{Gd}^{3+}$  showing a considerable spin dependence of the radial wavefunctions in this ion due to exchange polarization.

The purpose of the present work is to give a formal treatment of this new type of crystal field (which we shall call the *exchange crystal field*), relating it explicitly to the 'classical' crystal field and giving a prescription for the evaluation of its matrix elements. At the same time we shall establish the validity of the intuitive diagrammatic representation of  $\text{Gd}^{3+}$  matrix elements given by Newman (1970) and find a relationship between the exchange crystal field and the correlation crystal field discussed in that paper.

### Spin $\leftrightarrow$ Quasi-spin Transformation

Judd (1967a) introduced the concept of 'complementary' states related by the interchange of spin and quasi-spin quantum numbers. This transformation can be expressed simply as a transformation of the annihilation and creation operators for electrons in a given  $nl$  shell  $a_{m_1 m_s}, a_{m_1 m_s}^\dagger$  as

$$a_{m-}^\dagger \leftrightarrow (-1)^{l-m} a_{-m-}, \quad (1)$$

the spin-up operators remaining unchanged. It is easily checked that the commutation relations are preserved by this transformation. The spin operators

$$\left. \begin{aligned} S_+ &= \sum_m a_{m+}^\dagger a_{m-}, & S_- &= \sum_m a_{m-}^\dagger a_{m+}, \\ S_z &= \frac{1}{2} \sum_m (a_{m+}^\dagger a_{m+} - a_{m-}^\dagger a_{m-}) \end{aligned} \right\} \quad (2a)$$

become quasi-spin operators (Flowers and Szpikowski 1964)

$$\left. \begin{aligned} Q_+ &= \sum_m (-1)^{l-m} a_{m+}^\dagger a_{-m-}^\dagger, & Q_- &= \sum_m (-1)^{l-m} a_{-m-} a_{m+}, \\ Q_z &= \frac{1}{2} \sum_m (a_{m+}^\dagger a_{m+} + a_{m-}^\dagger a_{m-} - 1), \end{aligned} \right\} \quad (2b)$$

where the sums are over the orbital states within a given  $nl$  shell.

Judd (1967b) has noted that hole-particle conjugation of the spin-down electrons (as represented by equation 1) corresponds to a simple interchange of the representations of  $U_7$  which span the spin-down states of the lanthanide  $f^N$  shell. In the standard notation this transformation interchanges the number of ones and zeros in the representation  $[1 \dots 1 \ 0 \dots 0]$ . We now see that the equivalence of this transformation to equation (1) proves it to be equivalent to the spin  $\leftrightarrow$  quasi-spin transformation relating equations (2a) and (2b). Hence the results obtained by Judd (1967b) are relevant to the present discussion. In particular, this formulation shows that the spin  $\leftrightarrow$  quasi-spin transformation gives a complete mapping of the states with an even number of electrons in the  $nl$  shell onto the states with an odd number of electrons in the same shell. The vacuum state  $|f^0\rangle$  transforms as

$$|f^0\rangle \rightarrow |f^7 \ ^8S M_S = -\frac{7}{2}\rangle.$$

This validates the use of Feynman diagrams by Newman (1970), in which

$$|f^7 \ ^8S M_S = -\frac{7}{2}\rangle$$

replaces the vacuum state. Hence, every Feynman diagram defined in the usual way with respect to the vacuum state has a new and well-determined significance after the spin  $\leftrightarrow$  quasi-spin transformation.

### Transformation of the Crystal Field

The crystal field is a one-particle spin-independent potential of the form

$$\hat{V} = \sum_{m_1 m_2 \mu} a_{m_1 \mu}^\dagger a_{m_2 \mu} \langle m_1 | V | m_2 \rangle,$$

where  $V$  may be expressed in terms of the unit tensor operators  $U_q^{(k)}$  as

$$V = \sum_{q, \text{ even } k} \beta_q^k U_q^{(k)}.$$

The spin  $\leftrightarrow$  quasi-spin transformation gives

$$\begin{aligned} \hat{V} &\rightarrow \hat{V}_T = \sum_{m_1 m_2} (a_{m_1+}^\dagger a_{m_2+} + a_{-m_1-}^\dagger a_{-m_2-}^\dagger) \langle m_1 | V | m_2 \rangle \\ &= \sum_{m_1 m_2} (a_{m_1+}^\dagger a_{m_2+} - a_{m_1-}^\dagger a_{m_2-}^\dagger) \langle m_1 | V | m_2 \rangle + \beta_0^0, \end{aligned} \quad (3)$$

where we have used the relation  $\langle -m_1 | V | -m_2 \rangle = \langle m_2 | V | m_1 \rangle$ . Hence,  $V_T$  represents the difference in the crystal field experienced by electrons with spin-up and spin-down. It is not invariant under rotations in spin space, as it depends on the arbitrary choice of the spin quantization axis for the state corresponding to the vacuum state.

We note that an alternative way of writing  $\hat{V}_T$  is

$$\hat{V}_T = \sum_{m_1 m_2 \mu} a_{m_1 \mu}^\dagger a_{m_2 \mu} \langle m_1 \mu | \sigma_z V | m_2 \mu \rangle + \beta_0^0. \quad (4)$$

Dropping the additive constant and transforming to an arbitrary axis of quantization, we can generalize the operator expression  $\sigma_z V$  to

$$V_T = (4/7\hbar^2) \sum_i \mathbf{s}_i \cdot \mathbf{S} V_i,$$

where  $\mathbf{S}$  represents the total spin operator for the many-electron state. This is just the spin-dependent operator proposed by Newman (1970) to account for the observations of Schwiesow and Crosswhite (1969). It may also be written in the more symmetric form

$$V_T = (2/7\hbar^2) \sum_{i,j} \mathbf{s}_i \cdot \mathbf{s}_j (V_i + V_j), \quad (5)$$

which suggests that we refer to  $V_T$  as the *exchange crystal field*.

The main aim of this work, however, is to find a procedure for evaluating the many-electron matrix elements of  $V_T$  so that it can be employed in fitting experimental data. Let the transform of the unit tensor operator  $U_q^{(k)}$  be  $X_q^{(k)}$ , so that

$$V \rightarrow V_T = \sum_{kq} \beta_q^k X_q^{(k)}.$$

Using the fact that matrix elements are invariant under the spin  $\leftrightarrow$  quasi-spin transformation, we may evaluate the matrix elements of  $X_q^{(k)}$  between  $f^7$  states which are diagonal in total spin  $S' (= Q)$  as follows.

$$\begin{aligned} &\langle f^7 \tau^{(2Q+1)} L M_L, Q' = S, M'_S = M_Q | X_q^{(k)} | f^7 \tau^{(2Q+1)} L' M'_L, Q' = S, M'_S = M_Q \rangle \\ &= \langle f^N \tau Q M_Q^{(2S+1)} L M_L, M_S = 0 | U_q^{(k)} | f^N \tau Q M_Q^{(2S+1)} L' M'_L, M_S = 0 \rangle, \end{aligned} \quad (6)$$

where  $N$  is even and the common label  $\tau$  indicates that the remaining quantum numbers for all states are identical.

According to the Wigner-Eckart theorem, the right-hand side of equation (6) may be written as

$$(-1)^{L-M_L} \begin{pmatrix} L & k & L' \\ -M_L & q & M'_L \end{pmatrix} (f^N \tau Q M_Q^{(2S+1)L} \parallel U^{(k)} \parallel f^N \tau Q M_Q^{(2S+1)L}).$$

It follows that the matrix elements of  $X_q^{(k)}$  which are diagonal in  $S'$  may be determined using

$$\begin{aligned} \langle f^7 \tau^{(2S'+1)L} M_L, Q'=S, M'_S | X_q^{(k)} | f^7 \tau^{(2S'+1)L'} M'_L, Q'=S, M'_S \rangle \\ = (-1)^{L-M_L} \begin{pmatrix} L & k & L' \\ -M_L & q & M'_L \end{pmatrix} M'_S \\ \times (f^N \tau, Q=S', {}^{(2S+1)}L \parallel U^{(k)} \parallel f^N \tau, Q=S', {}^{(2S+1)}L). \end{aligned} \quad (7)$$

There are also matrix elements of  $X^{(k)}$  between  $f^7$  states of different total spin  $S'$  with the same value of  $M'_S$ . Following the same procedure as above we find that these can be evaluated using the relation

$$\begin{aligned} \langle f^7 \tau^{(2Q+1)L} M_L, Q'=S, M'_S=M_Q | X_q^{(k)} | f^7 \tau^{(2Q+3)L'} M'_L, Q'=S, M'_S=M_Q \rangle \\ = (-1)^{L-M_L} \begin{pmatrix} L & k & L' \\ -M_L & q & M'_L \end{pmatrix} \\ \times (f^N \tau Q M_Q^{(2S+1)L} \parallel U^{(k)} \parallel f^N \tau, Q+1, M_Q^{(2S+1)L'}), \end{aligned} \quad (8)$$

where, again, the reduced matrix elements of  $U^{(k)}$  have been tabulated by Nielson and Koster (1963).

Racah (1943, equation 67) gives the relation which enables us to remove the  $M'_S (=M_Q)$  dependence of the reduced matrix element. In terms of quasi-spin formalism this may be written

$$\begin{aligned} (f^N \tau Q M_Q^{(2S+1)L} \parallel U^{(k)} \parallel f^N \tau, Q+1, M_Q^{(2S+1)L'}) \\ = \left( \frac{(Q+M_Q+1)(Q-M_Q)}{2Q+1} \right)^{\frac{1}{2}} \\ \times (f^N \tau Q, M_Q=-Q, {}^{(2S+1)}L \parallel U^{(k)} \parallel f^N \tau, Q+1, M_Q=-Q, {}^{(2S+1)}L'). \end{aligned} \quad (9)$$

If this equation is used it becomes unnecessary to look up separate reduced matrix elements for each value of  $M'_S (=M_Q)$ .

An attempt to use second-order perturbation theory to calculate the spin dependence of the  $4f$  radial wavefunctions for  $\text{Gd}^{3+}$ , and hence  $V_T$ , gave an effect that was an order of magnitude too large. This failure is presumably due to the fact that higher order contributions, due to the spin polarization of closed shells, are also important. Nevertheless, the result makes it unlikely that  $V_T$  is negligible for  $\text{Gd}^{3+}$ .

### Transformation of the Correlation Crystal Field

The correlation crystal field is a general two-particle spin-independent effective potential

$$\hat{U} = \frac{1}{2} \sum_{m_i \mu_i} a_{m_2 \mu_2}^\dagger a_{m_1 \mu_1}^\dagger a_{m_3 \mu_3} a_{m_4 \mu_4} \langle m_1 m_2 | U | m_3 m_4 \rangle, \quad (10)$$

which includes anisotropic components due to the effect of the crystalline environment on the electron-electron interaction, but which is normally taken to exclude the large isotropic Coulomb interaction ( $U = e^2/r_{12}$ ). In tensor operator form it may be written

$$U = \sum_{k_1 k_2} A_{q_1 q_2}^{k_1 k_2} T_{q_1}^{(k_1)}(\mathbf{r}_1) T_{q_2}^{(k_2)}(\mathbf{r}_2), \quad (11)$$

where  $k_1 + k_2$  is restricted to even values (Bishton and Newman 1970). A consideration of possible mechanisms (Newman *et al.* 1971) suggests that terms with even  $k_1$  and  $k_2$  dominate, so we shall neglect the odd- $k$  terms in the following.

In order to investigate the effect of the spin  $\leftrightarrow$  quasi-spin transformation on  $\hat{U}$ , it is convenient to separate it into four components depending on the spin suffixes of the operators:

$$\hat{U} = \sum_{\mu_1 \mu_2} \hat{U}(\mu_1 \mu_2). \quad (12)$$

Transforming the operator products in equation (10) according to the spin  $\leftrightarrow$  quasi-spin transformation (1), we find that

$$\begin{aligned} \hat{U} \rightarrow \hat{U}' &= \hat{U}(++) + \hat{U}(--) - \hat{U}(+-) - \hat{U}(-+) \\ &+ \frac{1}{2} \sum_{m_1 m_2} (\langle m_1 m_2 | U | m_1 m_2 \rangle - \langle m_1 m_2 | U | m_2 m_1 \rangle) \\ &+ \sum_{m m_1 m_2} a_{m_1 +}^\dagger a_{m_2 +} \langle m_1 m | U | m m_2 \rangle. \end{aligned} \quad (13)$$

The matrix elements of  $\hat{U}$  with respect to given states of  $f^N$  will be equal to the matrix elements of  $\hat{U}'$  with respect to the complementary states. Judd (1967*b*) has discussed some consequences of this relation in the special case where  $\hat{U}$  represents the Coulomb interaction. We are more concerned here with relationships between the anisotropic parts of  $\hat{U}$ .

The last term of equation (13) has the form of the exchange crystal field described in the previous section. Hence the correlation crystal field in the  $f^2$  configuration gives a contribution in the sextet states of the  $f^7$  configuration which can be represented as an exchange crystal field, quite apart from any processes which contribute directly to this potential. This means that a parameterization of the type suggested by Schwiesow and Crosswhite (1969), which neglects explicit consideration of the correlation crystal field, will nevertheless include some contributions from this source.

The components  $\hat{U}(++)$  and  $\hat{U}(--)$  give zero contribution to the sextet states of  $f^7$ . Hence equation (13) shows that the contribution of the correlation crystal field to the energy of these states is equal and opposite to that in the  $f^2$  states with the same  $L$  values, apart from the extra term already discussed.

## Conclusions

It has been shown that the spin  $\leftrightarrow$  quasi-spin transformation allows us to adapt tables of matrix elements for the unit tensor operators  $U_q^{(k)}$  so that they can be used to calculate matrix elements of the tensor operators  $X_q^{(k)}$  which describe the exchange crystal field. This new type of field has been demonstrated to be equivalent to the spin-dependent field proposed by Newman (1970). The existence of an effective correlation contribution to the exchange crystal field for  $f^7$  systems has also been noted.

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## References

- Bishton, S. S., and Newman, D. J. (1970). *J. Phys. C* **3**, 1753.  
Flowers, B. H., and Szpikowski, S. (1964). *Proc. Phys. Soc. London* **84**, 673.  
Freeman, A. J., and Watson, R. E. (1961). *Phys. Rev. Lett.* **6**, 277, 388.  
Judd, B. R. (1967a). 'Second Quantization and Optical Spectroscopy' (Johns Hopkins Univ. Press).  
Judd, B. R. (1967b). *Phys. Rev.* **162**, 28.  
Newman, D. J. (1970). *Chem. Phys. Lett.* **6**, 288.  
Newman, D. J., Bishton, S. S., Curtis, M. M., and Taylor, C. D. (1971). *J. Phys. C* **4**, 3234.  
Newman, D. J., and Urban, W. (1972). *J. Phys. C* **5**, 3101.  
Nielson, C. W., and Koster, G. F. (1963). 'Spectroscopic Coefficients for the  $p^n$ ,  $d^n$  and  $f^n$  Configurations' (M.I.T. Press).  
Racah, G. (1943). *Phys. Rev.* **63**, 367.  
Schwiesow, R. L., and Crosswhite, H. M. (1969). *J. Opt. Soc. Am.* **59**, 592.  
Wybourne, B. G. (1965). *J. Chem. Phys.* **43**, 4506.  
Wybourne, B. G. (1966). *Phys. Rev.* **148**, 317.

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