Unique labelling schemes for local modes in lattices

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Abstract. Two procedures are described which together specify a unique point group labelling scheme for the irreducible components of local distortions in crystals. In the first procedure the group operators are factorised into a permutation part and a local (atomic) point group operation. The second depends on dividing the complete shells of atoms into subshells which are invariant under subgroups of the site (permutation) group.

1. Introduction

A wide range of experimental data is now becoming available on the effects of the dynamic crystal field interaction of paramagnetic ions in solids (Baker and Currell 1976, Fish *et al* 1980, Bates 1978, Schaack 1977). It is therefore appropriate to develop theories of the coupling between localised electron orbitals and lattice vibrations which have sufficient generality to be applied to a variety of phenomena. One necessity in carrying out this programme is the development of adequate group-theoretical descriptions of distortion modes of crystal complexes, as these form an intermediary in the coupling between the electronic orbitals in the paramagnetic ion and the lattice modes. The basic requirement of such descriptions is that irreducible representation labels should provide a complete and unique specification of every distortion mode in each site-symmetric shell of ions. Given this, it is possible to express the coupling in simple algebraic terms, so that diagrams of the local mode distortions and a full algebraic description of the local mode bases both become unnecessary. For example, this would enable us to obtain reductions in the number of orbit–lattice parameters following the method of Stedman and Minard (1981), without the need to compare diagrams of the local and lattice modes.

Analogous problems have been solved long ago in the theory of molecular vibrations (Wilson *et al* 1955, Flurry 1973). However, a rather different approach is necessary in the case of crystals because of the special convenience of retaining a Cartesian coordinate description of the normal modes rather than using the bond angle and bond length description commonly used for molecules. At the same time we shall find it especially appropriate to use the correlation theorem (Wilson *et al* 1955, p 121) when considering the labelling of the distortion modes of shells with many ions. A simplified proof of this theorem is given.

2. Factorisation

The first step in the classification of local modes is to distinguish the shells of atoms that transform into themselves under operations of the symmetry group G; i.e. the irreducible invariant atomic arrays. Our aim in this paper is to find a technique for labelling

the distortion modes of each shell using irreducible representation labels alone. It is easy to show that existing labelling schemes are inadequate in this respect. For example, the shell of eight atoms situated at the corners of a cube has the O_h representation:

$$A_{1g} + A_{2u} + E_g + E_u + T_{1g} + 2T_{1u} + 2T_{2g} + T_{2u}.$$

Apart from the T_{1u} and T_{2g} modes, this labelling is unique. However, the T_{2g} mode is particularly important in the coupling between this shell of atoms and the electronic states. We need to know, for example, *which* T_{2g} mode couples to a uniform strain and whether it is the same mode that is activated in a Jahn–Teller distortion.

The technique used in this paper is based on the factorisation concept. Each operator of the symmetry group G is broken down into two factors:

(i) a permutation of the ionic positions in the shell, defining G_P, and

(ii) a simultaneous rotation of the displacements of all ions, defining G_R.

Both G_P and G_R are isomorphic with G. Our labelling scheme is based on the reduction $G_R \otimes G_P \to G$. Flurry (1973) has used a related, but distinct, scheme to obtain symmetry-adapted distortions in molecules.

For example, in the case referred to above, the representation generated by the permutation of eight equivalent ions reduces to $A_{1g} + A_{2u} + T_{1u} + T_{2g}$. The direct

Table 1. Factorised labelling schemes for common coordinations.

Group	Coordination	Product representation	Expansion
O_h	6-fold	$T_{1u} \otimes A_{1g}$	T_{1u}
	(octahedral)	E_g	$T_{1u} + T_{2u}$
		T_{1u}	$T_{1g} + T_{2g} + E_g + A_{1g}$
	8-fold	$T_{1u} \otimes A_{1g}$	T_{1u}
		A_{2u}	T_{2g}
		T_{2g}	$T_{1u} + T_{2u} + E_u + A_{2u}$
		T_{1u}	$T_{1g} + T_{2g} + E_g + A_{1g}$
	12-fold	$T_{1u} \otimes A_{1g}$	T_{1u}
		E_g	$T_{1u} + T_{2u}$
		T_{2u}	$T_{1g} + T_{2g} + E_g + A_{2g}$
		T_{2g}	$T_{1u} + T_{2u} + E_u + A_{2u}$
		T_{1u}	$T_{1g} + T_{2g} + E_g + A_{1g}$
D_{3h}	3-fold	$A_2'' \otimes A_1'$	A_2''
		$E' \otimes A_1'$	E'
		$A_2'' \otimes E'$	E''
		$E' \otimes E'$	$E' + A_1' + A_2'$
	6-fold	$A_2'' \otimes A_1'$	A_2''
		$E' \otimes A_1'$	E'
		$A_2'' \otimes A_2''$	A_1'
		$E' \otimes A_2''$	E''
		$A_2'' \otimes E'$	E''
		$E' \otimes E'$	$E' + A_1' + A_2'$
		$A_2'' \otimes E''$	E'
		$E' \otimes E''$	$E'' + A_1'' + A_2''$

Note that it is necessary to use D_{3h} labelling, even if the combined system has C_{3h} symmetry, as $E \otimes E$ products give a repeated representation in C_{3h}.

product of these with the displacement representation T_{1u} contains the even representations (see table 1):

$$T_{1u} \otimes A_{2u} = T_{2g}$$

$$T_{1u} \otimes T_{1u} = T_{1g} + T_{2g} + E_g + A_{1g}.$$

Hence the labelling scheme based on $(O_h)_P$ and $(O_h)_R$ removes the ambiguity in the definition of the two T_{2g} states. It is also apparent which distortion mode couples to a uniform strain tensor, as this transforms as $T_{1u} \otimes T_{1u}$. Unfortunately, however, there is no simple rule to determine which allowed mode combination is involved in a Jahn–Teller distortion as this must depend on the magnitude of the coupling coefficients.

Table 1 gives the factorised labelling schemes for several coordinations of importance in the orbit–lattice coupling of lanthanide ions. However, the reduction of the permutation representation with respect to G_P does not always lead to a unique labelling. In such cases a higher level labelling scheme must be introduced, and this is discussed in the next section.

In tetrahedral symmetry (T_d) the displacement vector transforms as T_2. The permutations of four atoms at the vertices of a tetrahedron (see figure 1) transform as $A_1 + T_2$. Hence, in the case of tetrahedral coordination, the distortion modes are given by

$$T_2 \otimes A_1 = T_2$$

$$T_2 \otimes T_2 = T_1 + T_2 + E + A_1.$$

This provides unique labels for the repeated T_2 modes, which we write $(T_2 \otimes A_1)T_2$ and $(T_2 \otimes T_2)T_2$.

Symmetry coordinates, when required, can be obtained by reference to tables of coupling coefficients (e.g. Griffiths 1962). With the labelling shown in figure 1, the irreducible representation bases corresponding to T_d permutations of the four atom
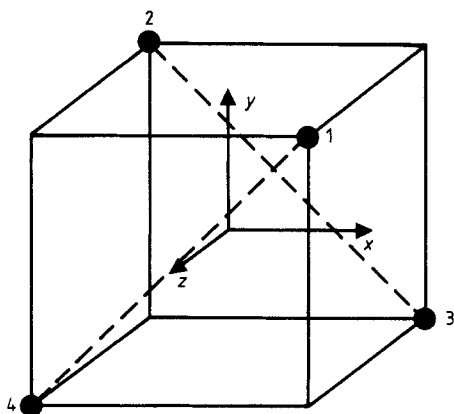

Figure 1. Tetrahedral coordination: labelling of ion positions in relation to common coordinates.

labels $\{i\}$ may be written:

$$A_1: \tfrac{1}{2}(\{1\}+\{2\}+\{3\}+\{4\})$$

$$T_2 x: \tfrac{1}{2}(\{1\}-\{2\}+\{3\}-\{4\})$$

$$T_2 y: \tfrac{1}{2}(\{1\}+\{2\}-\{3\}-\{4\})$$

$$T_2 z: \tfrac{1}{2}(\{1\}-\{2\}-\{3\}+\{4\}).$$

The product representations are obtained by attaching the appropriate combinations of the above labels as suffices to the T_2 displacements as determined by the coupling coefficients (Griffiths 1962, equations (2.7) and (2.23)):

$$\langle T_2 T_2 \alpha\beta | T_2 T_2 T_2 \gamma \rangle$$

$$= \sqrt{3} V \begin{pmatrix} T_2 & T_2 & T_2 \\ \alpha & \beta & \gamma \end{pmatrix} = -\frac{1}{\sqrt{2}} |\varepsilon_{\alpha\beta\gamma}| \qquad (\alpha, \beta, \gamma = x, y, z).$$

Hence the symmetry coordinates of the distortion mode $(T_2 \otimes T_2)T_2$ are given by

$$-\frac{1}{2\sqrt{2}} (y_1 - y_2 - y_3 + y_4 + z_1 + z_2 - z_3 - z_4)$$

$$-\frac{1}{2\sqrt{2}} (x_1 - x_2 - x_3 + x_4 + z_1 - z_2 + z_3 - z_4)$$

$$-\frac{1}{2\sqrt{2}} (x_1 + x_2 - x_3 - x_4 + y_1 - y_2 + y_3 - y_4)$$

in terms of a parallel set of unit vectors at each ion site. It can easily be verified that these symmetry coordinates correspond to the $(T_2 \otimes T_2)T_2$ uniform strain mode.

As the labelling scheme introduced in this section distinguishes between uniform strain modes and distinct modes of the same symmetry it is particularly well adapted to generalise the existing parametrisation scheme for orbit–lattice coupling. For example, in the case of eight-fold cubic coordination the standard eleven parameters (Newman 1980) can be retained, and an additional four parameters introduced to describe the electronic coupling with the $(T_{1u} \otimes A_{2u})T_{2g}$ mode. Superposition model expressions for these additional parameters will be reported in due course.

3. The correlation theorem

Wilson *et al* (1955) prove a remarkable theorem which provides an extended labelling scheme. A compact proof relevant to our application is given below.

Consider the basis generated by the permutation of a shell of n ions by the symmetry group G_P of order g. We suppose that it is possible to divide the n ions into n/m equivalent disjoint subshells of m ions, so that each subshell is symmetrical with respect to a particular subgroup H of order h in G_P. Each coset of H in G_P generates a distinct subshell of ions, so that $g/h = n/m$. Furthermore, we assume that it is possible to choose H such that the basis M generated by the permutations of m ions in each subset has a unique reduction with respect to H (i.e. no repeated irreducible representations). We can, of course, only be certain of this if H is Abelian.

We now focus attention on the basis generated by the action of all the operators in G_P on a given irreducible representation basis Γ_α of H of dimension γ_α contained in the basis M. Provided that each equivalent subset is described in the same way, this procedure generates a basis which transforms as Γ_α under *all* the n/m subgroups H of G_P and which has the dimension $n\gamma_\alpha/m$. It will not necessarily, however, generate an irreducible representation of G_P. The correlation theorem tells us how to determine its reduction. It states that $N_\alpha^{(\beta)}$, the number of times the irreducible representation $\Gamma^{(\beta)}$ of G_P appears in the basis generated by Γ_α, is equal to $N_\beta^{(\alpha)}$, the number of times the irreducible representation Γ_α of H appears in the representation $\Gamma^{(\beta)}$ of G_P.

The following proof of this result is simple and direct. The standard formula for $N_\alpha^{(\beta)}$ is

$$N_\alpha^{(\beta)} = \frac{1}{g} \sum_R \chi^{(\beta)}(R)^* \chi_\alpha(R)$$

where the sum is over all $R \in G_P$ and $\chi_\alpha(R)$ is the character of the $(n\gamma_\alpha/m)$-dimensional basis generated by Γ_α. We may write

$$\chi_\alpha(R) = \sum_i \chi_{i\alpha}(R)$$

where i labels the subbases transforming as Γ_α. Substituting into the first equation we obtain

$$N_\alpha^{(\beta)} = \frac{1}{g} \sum_i \sum_R \chi^{(\beta)}(R) \chi_{i\alpha}(R).$$

We now note that $\chi_{i\alpha}(R) = 0$ for $R \notin H_i$, where the suffix i is now used to label the subgroup corresponding to the subbasis i. The sum over R can thus be restricted to $R \in H_i$, and each of the g/h terms of the sum over i are equal. It follows that

$$N_\alpha^{(\beta)} = \frac{1}{g} \frac{g}{h} \sum_{R \in H_i} \chi^{(\beta)*}(R) \chi_{i\alpha}(R) = N_\beta^{(\alpha)}$$

independent of the choice of i. This completes the proof.

4. Local mode labelling in cubic symmetry

There are six distinct types of shell in O_h symmetry, which may be classified by the form of their typical position vectors relative to the centre of symmetry. If p, q and r are unequal integers, these vectors are

$(p\ 0\ 0)$:   6-atom shell (C_{4v})

$(p\ p\ p)$:   8-atom shell (C_{3v})

$(p\ p\ 0)$:   12-atom shell (C'_{2v})

$(p\ p\ q)$:   24-atom shell (C'_{1h})

$(p\ q\ 0)$:   24-atom shell (C_{1h})

$(p\ q\ r)$:   48-atom shell (none).

In each case we have given the 'defining' subgroup of O_h which leaves one of the atoms in the shell unchanged in position. Primes indicate that the C_2 axis, which defines $\sigma_h = iC_2$ (where i is the inversion operator) in 24-fold coordination, is *not* coincident with one of the C_4 axes of O_h.

The factorisation method has provided a unique labelling scheme for the first three cases, so we just note that the permutation representations in each of these three cases can be generated by the correlation theorem from the A_1 representations of their defining subgroups. The permutation representation for the 48-atom shell is just the regular representation of O_h. This contains repetitions of all irreducible representations of dimension 2 or 3. Several labelling schemes are possible, corresponding to different choices of subgroup in the correlation theorem. 48 atoms are never directly coordinated to a single paramagnetic ion, so our major interest in this case (see Bates 1978) is the possible ways in which the displacements in this shell can be coupled to displacements in shells with smaller numbers of atoms. It is possible to obtain unique reductions for each of the defining subgroups C_{4v}, C_{3v} and C'_{2v} of possible coordinated shells. These may easily be derived from the correlation diagrams in figure 2, and are given in full in table 2. It can be seen that, for a unique labelling, it is necessary that both C_{3v} and C_{4v} be reduced to an Abelian group. This is because the regular representation of O_h corresponds to regular representations of all its subgroups.
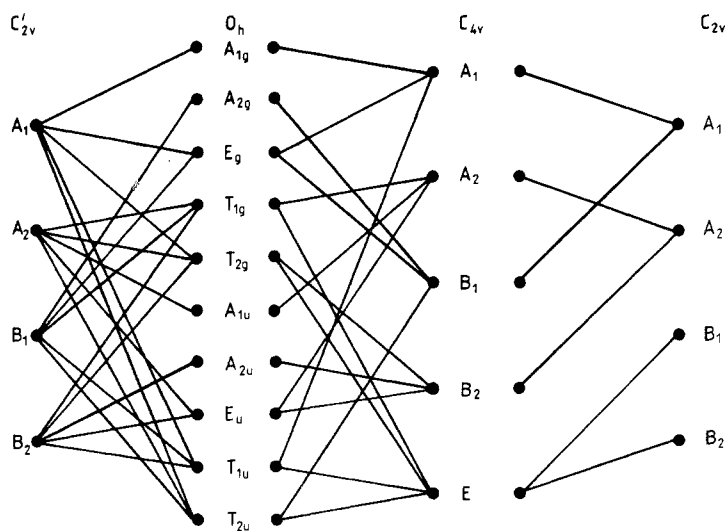

Figure 2. Correlation diagram for O_h subgroup labelling schemes.

Following the idea used by Bates (1978) we identify the subspace of the 48-atom shell representation which couples into the displacements of coordinated 6-fold, 8-fold and 12-fold shells as the subspace generated by the correlation theorem from the invariant representation of the appropriate subgroup. It follows that the appropriate subspaces are given in the top rows of each of the three sections of table 2. This group-theoretical procedure bypasses the need to use diagrams and the type of lengthy argumentation given by Bates (1978).

In the case of the C'_{1h} 24-atom shell we have two choices of labelling scheme corresponding to whether our interest is in coupling to 8-atom $(p = q)$ or 12-atom

Table 2. Mode labelling schemes for the O_h regular representation based on the correlation theorem.

6-fold reduction

C_{2v}	C_{4v}	O_h
A_1	A_1	$A_{1g}+E_g+T_{1u}$
A_1	B_1	$A_{2g}+E_g+T_{2u}$
A_2	A_2	$A_{1u}+E_u+T_{1g}$
A_2	B_2	$A_{2u}+E_u+T_{2g}$
B_1	E	$T_{1g}+T_{1u}+T_{2g}+T_{2u}$
B_2	E	$T_{1g}+T_{1u}+T_{2g}+T_{2u}$

8-fold reduction

σ_v	C_{3v}	O_h
A'	A_1	$A_{1g}+A_{2u}+T_{1u}+T_{2g}$
A'	E	$E_g+E_u+T_{1g}+T_{1u}+T_{2g}+T_{2u}$
A''	A_2	$A_{2g}+A_{1u}+T_{1g}+T_{2u}$
A''	E	$E_g+E_u+T_{1g}+T_{1u}+T_{2g}+T_{2u}$

12-fold reduction

C'_{2v}	O_h
A_1	$A_{1g}+E_g+T_{2g}+T_{1u}+T_{2u}$
A_2	$A_{1u}+E_u+T_{1g}+T_{2g}+T_{2u}$
B_1	$A_{2g}+E_g+T_{1g}+T_{1u}+T_{2u}$
B_2	$A_{2u}+E_u+T_{1g}+T_{2g}+T_{1u}$

($q = 0$) shells. Again, with the convention that the σ'_v plane does not contain a C_4 axis, we obtain the permutation representations:

$$C'_{2v}: A_1 + B_2$$

$$C_{3v}: A_1 + E.$$

Use of table 2 shows that both of these expressions are correlated to the O_h representation $A_{1g} + A_{2u} + E_g + E_u + T_{1g} + 2T_{2g} + 2T_{1u} + T_{2u}$. Note that the 8-atom and 12-atom distortions will each be coupled to a different subspace of this representation corresponding to their respective A_1 representations.

The C_{1h} 24-atom shell can be treated similarly, except that, in this case, we are interested in possible coupling to 6-atom ($q = 0$) or 12-atom ($p = q$) shells. With the same convention as above for C'_{2v} and the opposite convention for C_{2v} we obtain the subgroup representations

$$C'_{2v}: \qquad A_1 + B_1$$

$$(C_{2v})C_{4v}: (A_1)A_1 + (A_1)B_1 + (B_1)E$$

where the C_{2v} label is necessary to obtain a unique specification of the E representations. These subgroup representations are correlated to the O_h representation $A_{1g} + A_{2g} + 2E_g + T_{1g} + T_{2g} + 2T_{1u} + 2T_{2u}$.

5. Local mode labelling for LaCl₃ structure crystals

The C_{3h} La^{3+} site in $LaCl_3$ is surrounded by nine coordinated Cl^- ions, which comprise one 3-fold and one 6-fold shell. Each shell by itself has D_{3h} symmetry, so we have used this group to obtain the labelling scheme in table 1. In this case uniform strain corresponds to

$$(A_2'' + E') \otimes (A_2'' + E')$$
$$= (A_2'' \otimes A_2'')A_1' + (A_2'' \otimes E')E'' + (E' \otimes A_2'')E'$$
$$+ (E' \otimes E')E' + (E' \otimes E')A_1' + (E' \otimes E')A_2'.$$

Hence the following modes may be coupled to uniform strain:

3-fold: $(A_2'' \otimes E')E''$ $(E' \otimes E')E'$, A_1', A_2'.

6-fold: $(A_2'' \otimes A_2'')A_1'$ $(E' \otimes A_2'')E''$ $(A_2'' \otimes E')E''$ $(E' \otimes E')E'$, A_1', A_2'.

The question arises as to which combinations of 6-fold and 3-fold modes transform together under uniform strain. In order to answer this it is necessary to compare the phases of the 3-fold and 6-fold shell distortions. This can be achieved by the following process of *condensation*.

Pairs of ions in the 6-fold shell are brought into coincidence with those in the 3-fold shell by a continuous distortion process involving:

(a) a proper rigid rotation of the shell (about the z axis) and

(b) a contraction of certain distances.

The displacements of the pairs of coincident ions are then summed and renormalised and may vanish or be compared directly with those in the 3-fold shell. Comparing with the results of Stedman and Minard (1981) it becomes clear that modes of the same phase in the 3- and 6-fold shells are summed to produce the modes that couple to the uniform strain. The weighting used depends on the relative coordinates of the ions.

6. Discussion

We have described two methods which together enable us to specify unique group-theoretical labels for the irreducible distortion modes of atom shells in crystals. The first method is based on the introduction of a higher symmetry which decouples the permutation and coordinate rotation aspects of the group operations. The second is based on the correlation theorem which relates the symmetry properties of a complete shell to those of sets of equivalent subshells.

Unique labelling schemes are of importance in obtaining a unified picture of the various phenomena due to the orbit–lattice interaction. In particular, it has been possible to identify the modes which couple to uniform strain as these corresponding to the product representation of the vector bases of G_P and G_R. In the case of Jahn–Teller distortion where coupling of coordinated shells with more distant shells has to be considered, the correlation theorem provides a simple means of identification of the modes involved in the coupling.

Acknowledgments

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