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Phonon Symmetries Determined from Space-Group Diagrams

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The representations of space groups describe the symmetry of crystal lattice vibrations. These representations are presented in a diagrammatic way easily understood by those familiar with *International Tables for Crystallography*. A few diagrams are considered in detail in an effort to bring out the salient points. The relevance of plane groups and Shubnikov groups is emphasized, though it is clear that these groups in themselves are not sufficient for a complete description of phonon symmetries. The diagrammatic description must be considered as complementary to the analytic approach, but unlike the latter it is not capable of a thorough description. A table is given for certain space groups which indicates to what extent the diagrams can be found useful, encompassing one-dimensional and a limited number of two-dimensional representations. Although higher dimensions involve too many problems and must be left to the analytic approach, the insight gained by drawing diagrams may prove beneficial.

Introduction

This paper introduces a diagrammatic description of the symmetries of lattice vibrations, building on the crystallographer's extensive knowledge and understanding of space-group diagrams. Whereas a space-group diagram represents the time-averaged crystal structure symmetry, the diagrams here developed represent the symmetries of the possible crystal lattice vibrations. For any one space group there are many symmetries for the lattice vibrations, and these are collectively called the space-group representations. These representations do not describe only the lattice vibrations, but describe any set of wave functions whose averages obey the space-group symmetry, such as the electronic wave functions. However, lattice vibrations will be used here as the basic example.

It has been customary to treat these representations algebraically, which is analogous to the algebraic description of space-group symmetry given for every group in Volume I of *International Tables for X-ray Crystallography* (1952). In these tables a geometrical description is given for most of the space groups, but eventually the complexity is such that the algebraic description alone is given. So it is with the space-group representations: a large number of the simpler representations can be adequately described geometrically, but a stage comes when the algebraic description alone must be used. At this stage, as with the study of space groups themselves, a thorough grasp of the scientific fundamentals has been obtained.

Phonons

A phonon is a quantum of lattice vibration, which is a wave travelling through the crystal. The wave is characterized by a wave vector $\mathbf{q}$ perpendicular to the planes of constant phase, related to the wavelength λ by $|\mathbf{q}|\lambda=2\pi$. The atoms in one Bravais lattice defined by the lattice translation vectors τ_j move with relative phases given by the factors

$$\exp(i\mathbf{q}\cdot\tau_j).$$

Furthermore, the phonon will belong to a space-group representation R, so that in order to describe the phonon both R and $\mathbf{q}$ must be given. In some cases this is sufficient to identify the phonon, but generally there will be more than one phonon of a given R and $\mathbf{q}$. This is analogous to the fact that in a crystal structure there may be more than one atom in a general or a special position. In the space-group diagrams only one general position is depicted; likewise in the representation diagrams only one general position is shown.

When there is more than one phonon corresponding to a certain R and $\mathbf{q}$, then each distinct phonon is said to belong to a different branch of the dispersion relation. The dispersion relation is the variation of phonon frequencies with $\mathbf{q}$, and as these are essentially continuous functions there are continuous branches for each occurrence of a representation. The wave vector $\mathbf{q}$ varies over the whole of the Brillouin zone, and a number of diagrams are required to describe the symmetries at the special points of the Brillouin zone, in contrast to the single diagram for space-group symmetry.

Phonon symmetry

A given space group has a certain set of symmetry operations. The symmetry operations which a given phonon can obey are contained in this set. Some of the space-group operations may be obeyed, while others may be disobeyed. For phonons of different representations different space-group operations will be obeyed or disobeyed, and in order to analyse the various possibilities we must first classify the space-group operations.

For a wave of a particular $\mathbf{q}$ the space-group operations can be classified into three types. First we must

construct a single plane of constant phase through the crystal, perpendicular to **q**, dividing the crystal into a region of advanced phase and a region of retarded phase.

Type 1

Symmetry elements of type 1 relate atoms all of which lie in the plane, and do not relate atoms in one region to atoms in the other region. Such elements will be rotation axes parallel to **q** and planes of symmetry containing **q**, where the symmetry planes are either mirror planes or glide planes with the glide translations perpendicular to **q**.

Type 2

The operation of a symmetry element of type 2 transforms any atom in the plane of constant phase into another parallel plane of constant phase related to the initial plane by a fixed phase difference. The action on all planes of constant phase is similar, changing the phase by a fixed amount. These elements will be screw axes parallel to **q** and glide planes containing **q** except those already classified as type 1. All these elements contain a fractional lattice translation, **d**, and the fixed phase difference between planes is **q** . **d** giving a change in the wave amplitude by a factor of exp (i**q** . **d**).

Type 3

All the remaining elements are of type 3, and relate atoms in one region to atoms in the other region. The atoms so related differ in phase by a factor which depends on their positions in the crystal, and therefore this phase factor is not constant. The symmetry elements will be all inversion centres and inversion axes, plus those axes, screw axes, mirror and glide planes not of types 1 and 2.

It must be emphasized that this classification is dependent on **q** as the relationship of the symmetry elements to the planes of constant phase is of fundamental importance. For a symmetry element to be obeyed by a phonon it must be of type 1, except in special circumstances to be described later. To illustrate this let us consider a phonon which obeys a diad axis. Through the crystal there will be a regular array of parallel diad axes relating one atom to an array of atoms lying in a plane perpendicular to the axial direction. All these atoms must move with the same phase for the symmetry to be obeyed, and thus they define a plane of constant phase. The wave vector must therefore be parallel to the diad axis direction, as stated as a condition for a symmetry axis to be of type 1. The conditions stated for mirror and glide planes to be of type 1 are similarly easily verified.

Elements of type 2 play a special role in that they can be 'partially satisfied' by the phonon. As an example let us take a screw diad axis along the crystal y axis. The array of parallel screw diads relates atoms in one plane perpendicular to the y axis to atoms in a parallel plane a distance $b/2$ away. For this symmetry to be obeyed the atoms in these two planes should move in phase. For reasons exactly similar to those governing the behaviour with respect to the true diad axis (type 1), the wave vector must be parallel to the symmetry axis, but this produces a change of $\frac{1}{2}qb$ in phase angle between the two planes considered above. Therefore the symmetry cannot strictly be obeyed because there is not the required zero phase difference. But there is a *constant* phase difference: so we widen the meaning of *obey* and state that a phonon obeys type 2 symmetry if the planes related by the fractional lattice translation **d** differ in phase angle by a constant **q** . **d** only. If on the other hand the wave vector is not parallel to the symmetry axis, then there can be no definite phase relation between these planes, and the operation is then defined as type 3.

There is no way in which type 3 symmetry can be obeyed, except for special values of **q** to be discussed later.

General q

A wave with a general wave vector may be defined as one where all the space-group symmetry operations are of type 3. There is therefore no symmetry which the phonon can obey, and so all the phonons of a particular **q** belong to the same space-group representation. The number of occurrences of this representation is equal to $3n$, where n is the number of atoms in the primitive unit cell. The structure can be thought of as n interpenetrating Bravais lattices. A single atom in one such lattice has three degrees of freedom of motion, but all the other atoms in the lattice must move

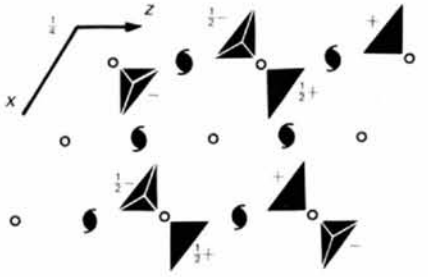


Fig. 1. The symmetry of the space group $P2_1/c$. The asymmetric unit is represented by a black tetrahedron, and the tetrahedron labelled + is viewed from an angle where only one face is visible.

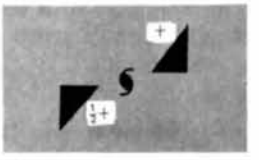


Fig. 2. The two asymmetric units of the space group $P2_1/c$ which are related by the screw diad, this being the only symmetry element of type 2 for a wave with wave vector **q** along the diad direction. The tetrahedron is now to be interpreted as a general displacement vector for any atom in a general position, in the course of such a wave.

in accordance with this atom but with phase angles of $\mathbf{q}\cdot\boldsymbol{\tau}_j$. The motion of the atoms in the other Bravais lattices is quite independent, giving a total of $3n$ degrees of freedom and $3n$ modes of vibration. This is a general result. For the case under consideration all these modes belong to the same representation, but for special cases of $\mathbf{q}$ the $3n$ modes are divided between the possible representations.

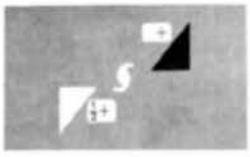


Fig. 3. The symmetry element of Fig. 2 now broken. The symmetry symbol now appears white, denoting antisymmetry, and the tetrahedron labelled $\frac{1}{2}+$ is also white, signifying that the vector it represents is the same as that in Fig. 2, except that its sign is reversed.

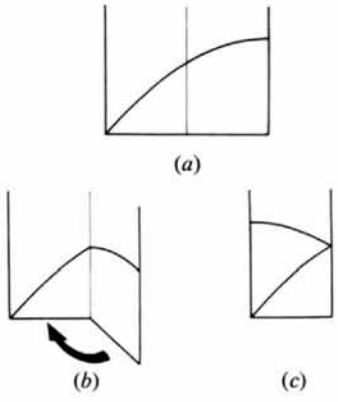


Fig. 4. (*a*) One branch of a dispersion diagram, showing a smooth variation over the Brillouin zone boundary which is at the middle. The left side corresponds (say) to the symmetric branch, *S*, and the right side to the antisymmetric branch, *A*. (*b*) Mapping the *A* branch into the left-hand part of the diagram. (*c*) The composite diagram, showing both the *S* and the *A* branches.

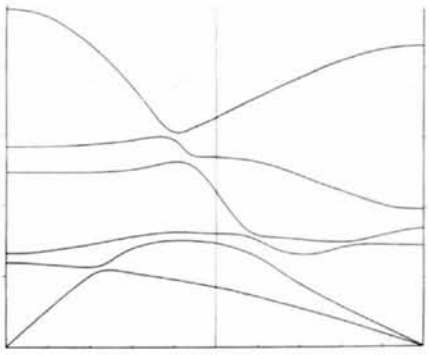


Fig. 5. The dispersion curves calculated for anthracene, with $\mathbf{q}$ along the screw diad axis. This is Fig. 2 of Pawley (1967) unfolded to correspond to Fig. 4 (*a*) above. Note that branches of the same representation never cross, though *S* and *A* branches cross after folding as in Fig. 4 (*c*).

q in a special direction

For special cases of $\mathbf{q}$ some of the space-group elements belong to type 1 or type 2. At this stage in our argument diagrams become very useful, so we will analyse the case of $\mathbf{q}$ along the screw diad of the space group $P2_1/c$. The symmetry elements and the general positions are combined in Fig. 1, where black tetrahedra are used to denote the general atomic positions. For the particular $\mathbf{q}$ there is no symmetry of type 1, the screw diads are of type 2 and the remainder are of type 3. Thus there are no operations of types 1 and 2 relating the atoms marked by + with those marked by −, which means that these atoms move independently in the wave, their amplitudes and phases being determined by the interatomic forces only. The atoms may therefore be divided into two unrelated sets, those marked with + and those marked with −. Because the sets are not related by possible phonon symmetry one set may be omitted from the diagram and we need consider only the other set, as in Fig. 2.

Whatever is said for one set can be said for the other. If the atoms of one set can move in accordance with the representation R_1 so can the atoms of the other set. If the representation R_2 is possible for one set it is also possible for the other, but it is impossible for the atoms of one set to move in accordance with R_1 while the others obey R_2 in the same mode of vibration. This can be understood by realising that it is not simply the atomic movements which must obey the symmetry, but also the interatomic forces. While the atoms of one set move in accordance with R_1, the interatomic forces alter in accordance with R_1 and so produce motions of the remaining atoms obeying R_1.

Fig. 1 is drawn with tetrahedra representing the general positions of the space group. Position is a vector property, as is displacement. Consequently the tetrahedra in this figure could represent any vector property, and in particular they can represent the displacement of the atoms in the general positions of the space group. In Fig. 1 the displacements clearly satisfy the space-group symmetry. Although there may be modes of vibration which satisfy the space-group symmetry this will not always be the case, and the diagrams must be modified to describe these other phonon symmetries.

Fig. 2 can now be interpreted as describing the motion in a mode where the screw diad is not broken (using 'not broken' in the sense already described for a type 2 operation). The alternative to retaining the symmetry is breaking it, and this is depicted in Fig. 3. The symmetry element which is broken is drawn white, whereas in Fig. 2 it was black. This broken symmetry element is now an element of antisymmetry and relates a white tetrahedron to a black one. The significance of the white tetrahedron is that the vector displacement that it would represent if it were black must be reversed in sign and therefore in direction. Either the symmetry or the antisymmetry must be obeyed; there is no other choice because a general displacement can

be expressed as a linear combination of a symmetric and an antisymmetric displacement. This will always be the case for symmetry operations of order two, and therefore for these cases the 'black and white' symmetry groups are appropriate.

There are thus two representations for this particular **q**, which can be called symmetric (S, Fig. 2) and antisymmetric (A, Fig. 3). Consider first the S mode. It is clear that there must be a phase difference of $\mathbf{q} \cdot \mathbf{b}/2$ ($\mathbf{d} = \mathbf{b}/2$) between the atom marked + and that marked $+\frac{1}{2}$ as the $\frac{1}{2}$ denotes the translation $\mathbf{b}/2$ of the screw diad. There is of course the same phase difference in the A mode along with the reversal of sign, though sign reversal is equivalent to a phase factor of π. In this sense we can argue that the S and A modes are similar, differing in the phase factor just mentioned: $\mathbf{q} \cdot \mathbf{b}/2 = qb/2$ for S and $\pi + qb/2 = (2\pi/b + q)b/2$ for A.

q on the zone boundary

We now use the fact that for each mode at **q** there is a degenerate mode at $-\mathbf{q}$; this is due to time reversal symmetry. Thus corresponding to $A(\mathbf{q})$ there is a mode $A(-\mathbf{q})$ whose phase factor of the previous paragraph is $(2\pi/b - q)b/2$, and therefore it is possible to find a value of **q** such that this phase factor is identical to that of $S(\mathbf{q})$. The condition is clearly $q = \pi/b$, but this is the special position on the boundary of the Brillouin zone. At this point the phonons belonging to the S branches become degenerate with those of the A branches. This is a common behaviour whenever there are symmetries of type 2: this phase factor caused by the glide or screw translations builds up to $\pi/2$ at the zone boundary, and if we plot the S branch up to the boundary and then continue the curve to larger **q** the branch becomes the A branch. This is shown schematically in Fig. 4 and as an example calculated dispersion curves for anthracene ($P2_1/c$) showing this behaviour are given in Fig. 5.

When there are no type 2 symmetries the behaviour at the zone boundary is different, and often it is possible to deduce what happens from diagrams. Unfortunately this aspect of the work cannot be complete, for at some very special points analysis becomes very difficult. This is often caused by the fact that our classification of the symmetry elements into three types breaks down in ways similar to that at $\mathbf{q} = 0$, as we shall see.

The Γ-point q = 0

The various points and directions in the Brillouin zones have been assigned letters from the Greek and Roman alphabets (Koster, 1957). Γ denotes the point $\mathbf{q} = 0$, where the phonons have infinite wavelength. In this case it is obvious that planes of constant phase do not exist as all atoms related to each other by any lattice translation move in phase. Our classification of symmetry elements becomes irrelevant, as all elements are of type 1. Therefore modes may exist which do not break elements such as inversion and inversion–rotation, whereas other modes exist which are antisymmetric with respect to these operations. The diagrams for the various modes are generally simple to draw as

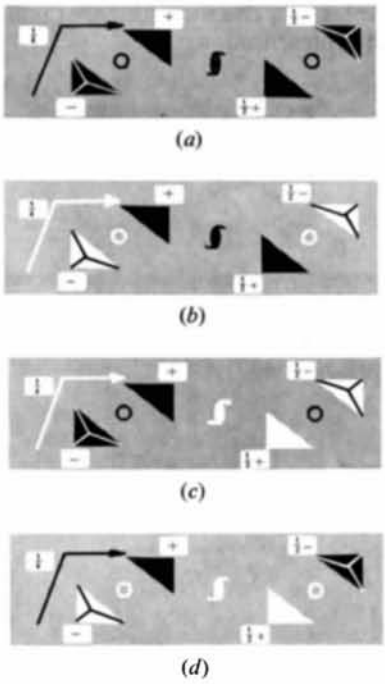


Fig. 6. The four representations for $P2_1/c$ at $\mathbf{q} = 0$, the Γ point. (*a*) Fully symmetric. (*b*) Screw diad symmetric. (*c*) Inversion centre symmetric. (*d*) Glide mirror symmetric.

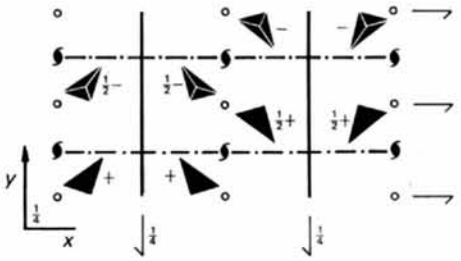


Fig. 7. Diagram for the space group *Pmnb*.

		2_z	J
M_z	2_y		
		M_x	2_z
E	M_y		

Fig. 8. Naming of the tetrahedra of Fig. 7 to correspond with the point-group symmetry operations.

in Fig. 6 for $P2_1/c$. Fig. 6(*a*) shows the fully symmetric mode, Fig. 6(*b*) is symmetric with respect to the screw diad 2_1, and Fig. 6(*c*) and (*d*) are symmetric with respect to the inversion centre J and glide mirror c respectively. Denoting the unit operation E we can compile Table 1 which is called the character table for the point group $2/m$ (Koster, 1957). An entry of 1 under an operation

Table 1. *Character table for the point group* $2/m$

		Operations				
		E	2_1	J	$C(m)$	Fig. 6
Modes	Γ_a	1	1	1	1	····(*a*)
	Γ_b	1	1	−1	−1	····(*b*)
	Γ_c	1	−1	1	−1	····(*c*)
	Γ_d	1	−1	−1	1	····(*d*)

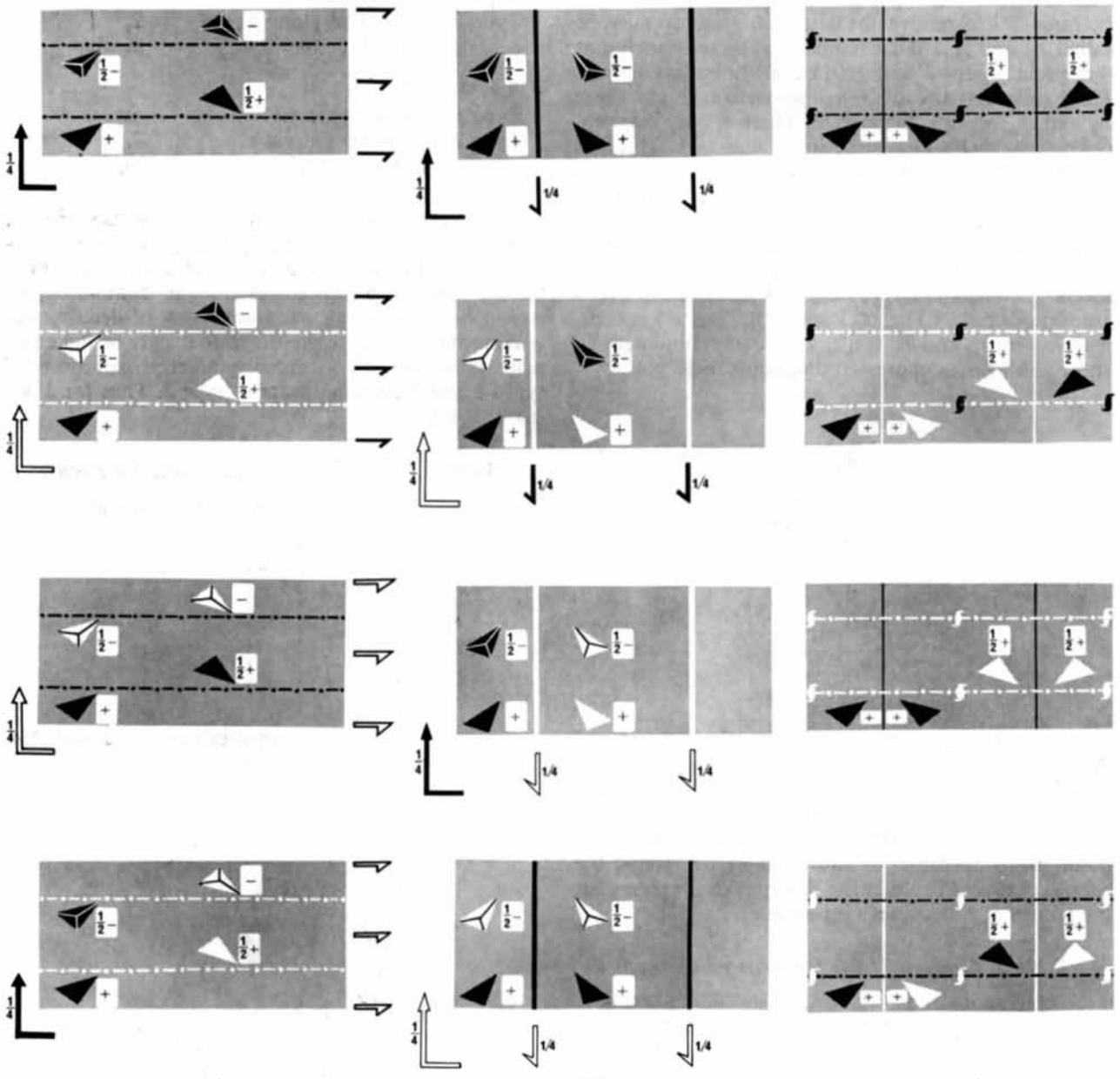


Fig. 9. The four representations for branches along each of the three orthorhombic directions.

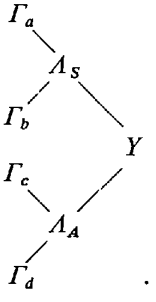
(*a*)	(*b*)	(*c*)
Σ_1	Δ_1	Λ_1
Σ_2	Δ_2	Λ_2
Σ_3	Δ_3	Λ_3
Σ_4	Δ_4	Λ_4

denotes that this operation is symmetric for the mode being described and -1 denotes an antisymmetric relationship. In this way point-group character tables are much used, especially in optical spectroscopy where the modes at the Γ point are studied.

Compatibility

The branches with **q** parallel to the y axis in our example $P2_1/c$ receive the letter Δ, so they may be called Δ_S and Δ_A. What happens to these branches at the special points Γ and Y (the zone boundary point)? The Y point has already been discussed, as this is where Δ_S and Δ_A become degenerate. There is only one representation at Y so no subscript is necessary. This fact can be deduced by observing that there are no type 3 symmetries which become operative at Y, though an example where this does happen will appear later.

It is easy to see from the diagrams what happens at Γ. The tetrahedra of Fig. 2 are reproduced (with rearrangement) in Fig. 6(*a*) and (*b*) while those of Fig. 3 are reproduced in Fig. 6(*c*) and (*d*). Thus Δ_S is compatible with Γ_a and Γ_b while Δ_A is compatible with Γ_c and Γ_d. All this is expressed diagrammatically:



Example: *Pmnb*

This space group was analysed as it is the symmetry of P_4S_3 in the lower phase (Leung, Waser, van Houten, Vos & Wiegers, 1957) and undergoes a plastic crystal phase transition. The space-group symmetry diagram is Fig. 7, where the eight tetrahedra correspond to the point-group operators as shown in Fig. 8. Using the character table (Table 2) the drawing of diagrams for the modes at Γ becomes very simple.

Table 2. *Character table for point group mmm*

		E	2_x	2_y	2_z	J	m_x	m_y	m_z
A_g	Γ_1	1	1	1	1	1	1	1	1
B_{1g}	Γ_2	1	1	−1	−1	1	1	−1	−1
B_{2g}	Γ_3	1	−1	1	−1	1	−1	1	−1
B_{3g}	Γ_4	1	−1	−1	1	1	−1	−1	1
A_u	Γ_5	1	1	1	1	−1	−1	−1	−1
B_{1u}	Γ_6	1	1	−1	−1	−1	−1	1	1
B_{2u}	Γ_7	1	−1	1	−1	−1	1	−1	1
B_{3u}	Γ_8	1	−1	−1	1	−1	1	1	−1

Now consider the three symmetry directions in turn.

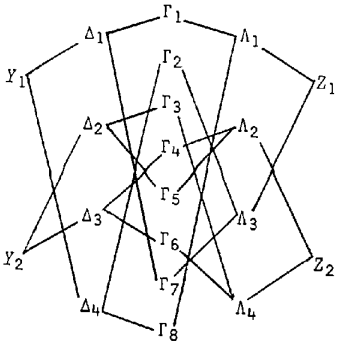
q direction	Corresponding operation of point group
Σ, **q** *along x axis*	
Type 1: glide plane *b*	m_z
Type 2: screw diad along *x*	2_x
diagonal glide *n*	m_y
Δ,**q** *along y axis*	
Type 1: mirror plane *m*	m_x
Type 2: screw diad along *y*	2_y
glide plane *b*	m_z
Λ,**q** *along z axis*	
Type 1: mirror plane *m*	m_x
Type 2: screw diad along *z*	2_z
diagonal glide *n*	m_y

Each direction yields a set of four diagrams, Fig. 9, in which the tetrahedra corresponding to type 3 operations do not appear. If Fig. 7 were drawn according to the eight representations Γ_i the compatibilities would be obvious; an alternative way of determining compatibilities is to write down that part of the character table relevant to those symmetry operations of types 1 and 2 omitting those of type 3. Thus for Σ we get Table 3.

Table 3. *Part of the character table for Pmnb*

	E	2_x	m_y	m_z	compatible with
Γ_1	1	1	1	1	Σ_1
Γ_2	1	1	−1	−1	Σ_2
Γ_3	1	−1	1	−1	Σ_3
Γ_4	1	−1	−1	1	Σ_4
Γ_5	1	1	−1	−1	Σ_2
Γ_6	1	1	1	1	Σ_1
Γ_7	1	−1	−1	1	Σ_4
Γ_8	1	−1	1	−1	Σ_3

Similarly we get the compatibilities for Δ and Λm, which are shown schematically:



On this diagram are shown the compatibilities at the zone boundary points $Y(\mathbf{q}=\pi/b)$ and $Z(\mathbf{q}=\pi/c)$, and to demonstrate how these have been determined let us examine the point X, $\mathbf{q}=\pi/a$ along the x axis. There are four tetrahedra to be considered, corresponding to

$E, 2_x, m_y, m_z$ of Fig. 8. Because there is a translation $\frac{1}{2}\mathbf{a}$ between the tetrahedra E & m_z and tetrahedra 2_x & m_y, a phase difference between these pairs builds up as $\mathbf{q}$ increases from Γ along all four branches. However, no phase difference can build up between E and m_z (or between 2_x and m_y) as these pairs are related by type 1 symmetry. As $\mathbf{q}$ varies along the Σ_1 branch E and m_z remain in phase just as they do in Σ_4. The phase difference between this pair and 2_x & m_y is zero at Γ and increases to $\pi/2$ at X, and continuing past X the phase difference increases further as the Σ_1 branch has now become the Σ_4 branch.

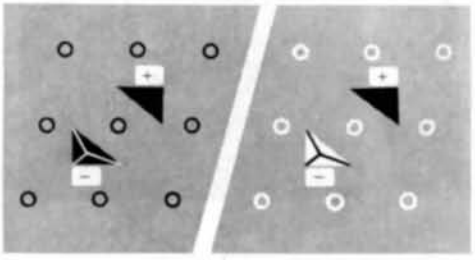


Fig. 10. The two representations for $P\bar{1}$ at the Γ point.

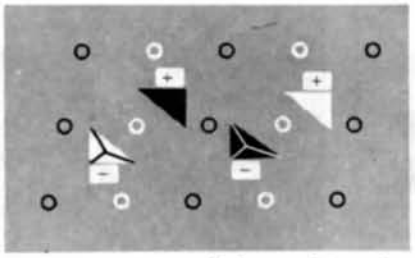


Fig. 11. A representation for $P\bar{1}$ for $\mathbf{q}$ midway between two reciprocal-lattice points.

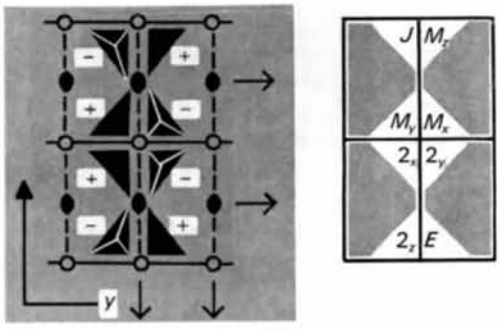


Fig. 12. The space group *Pccm* and the labelling of the tetrahedra.

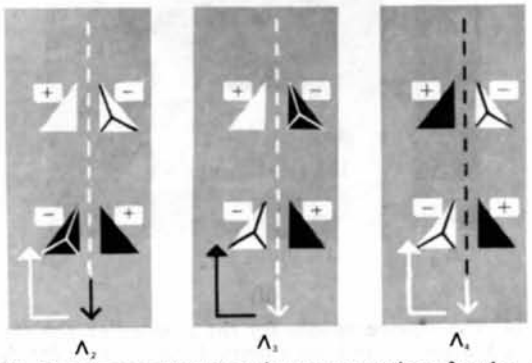
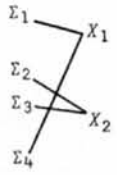


Fig. 13. The three antisymmetric representations for the Λ direction.

This behaviour is exactly similar to that of the Λ_S and Λ_A branches in the preceding monoclinic example, and therefore the Σ_1 and Σ_4 branches become degenerate at X. Similarly Σ_2 and Σ_3 become degenerate at X, shown schematically:



The degeneracies at Y and Z can be explained by a similar argument. It becomes increasingly difficult to explore the rest of the surface of the Brillouin zone with simple diagrams. One is tempted to draw diagrams with phase-factor labels on them, but this is verging on the algebraic method which we are trying to complement. However there are some more results which can emerge from our analysis.

Space group $P\bar{1}$

This is chosen for its simplicity. For a general $\mathbf{q}$ there are no operations of types 1 or 2 and so there is only one representation. At the Γ point of course there are the two representations of Fig. 10. Away from Γ the inversion is of type 3, but this fails to have its usual significance at the X point as shown by Fig. 11. The X point is on the Brillouin zone boundary half-way towards (100) with $\mathbf{q}$ parallel to the x^* axis, (we should throughout have used reciprocal axes when describing the direction of $\mathbf{q}$, but this is the first place where the distinction is necessary). At X there must clearly be two representations, X_S and X_A, where the antisymmetric mode is depicted in Fig. 11. As the space group is so simple it is obvious that half-way between any two reciprocal-lattice points the same separation into two representations will occur, though the pattern of inversion and anti-inversion operations will differ. These are the only places where there is more than one representation of $P\bar{1}$, and so $P\bar{1}$ is completely solved.

The inversion operation

In both $P\bar{1}$ and *Pmnb* space groups the centre of inversion J occurs, but different behaviour is noticed at the zone boundary. Why should this be so? Consider any of the directions Σ, Δ, Λ in *Pmnb*. In each case there is at least one operation of type 2, so that the phase difference between adjacent planes is (for Σ say) $\mathbf{q} \cdot \mathbf{a}$ but the phase difference between atoms related by the type 2 symmetry is $\frac{1}{2}\mathbf{q} \cdot \mathbf{a}$. At the zone boundary

$\mathbf{q} \cdot \mathbf{a} = \pi$ and we have antisymmetry associated with the translation $\mathbf{a}$, but the phase difference $\frac{1}{2}\mathbf{q} \cdot \mathbf{a} = \pi/2$ does not correspond to either a symmetry or an antisymmetry operation, in contrast to the $P\bar{1}$ example. Let us take a further example where there are some directions without any type 2 operations, where we expect behaviour similar to that in $P\bar{1}$.

Space group *Pccm*

The symmetry of this group is shown in Fig. 12. First let us dispose of the direction in which there are some type 2 symmetry elements.

Λ,$\mathbf{q}$ along z axis

Type 1: Diad relating E to 2_z
Type 2: Two glide planes
(a) relating E and m_x
(b) relating E and m_y.

There are four representations; the symmetric representation Λ_1 and the three shown in Fig. 13. Only E, 2_z, m_x and m_y appear in this figure. From arguments now familiar it is clear that Λ_1 and Λ_2 become degenerate at Z, likewise Λ_3 and Λ_4.

In the x and y directions there are no operations of type 2:

Λ,$\mathbf{q}$ along y axis

Type 1: Diad relating E and 2_y
Mirror plane relating E and m_z
Glide plane relating E and m_x.

There are four representations shown on the left sides of Fig. 14(a), (b), (c), (d), and these involve only E, 2_y, m_z and m_x. It is obvious from these figures that all the related positions lie in the same plane and no degeneracies can result at the point Y. In any mode of vibration belonging to one of these representations, the atoms denoted by J, 2_x, m_y and 2_z move always obeying the same symmetry but without any fixed phase relationship with E, 2_y, m_z and m_x. Therefore one set is omitted from the diagrams, consistent with previous practice.

Y,$\mathbf{q}$ along y axis, $|\mathbf{q}| = \pi/b$

At this point some symmetry previously of type 3 becomes operative between the two sets of four positions just mentioned, and the extra operations are those relating:

E with J, E with 2_x, E with m_y, E with 2_z.

The four possible symmetries at Y are shown in Fig. 14, juxtaposed with the figures for the Δ representations. One aspect of these diagrams is immediately obvious: the extra operations appear alternating along the y direction between true symmetry and antisymmetry. If these extra operations were replaced throughout one diagram by the reversed symmetry, in other words true symmetry for antisymmetry and vice versa, it is obvious that the symmetry group is unaltered. This has

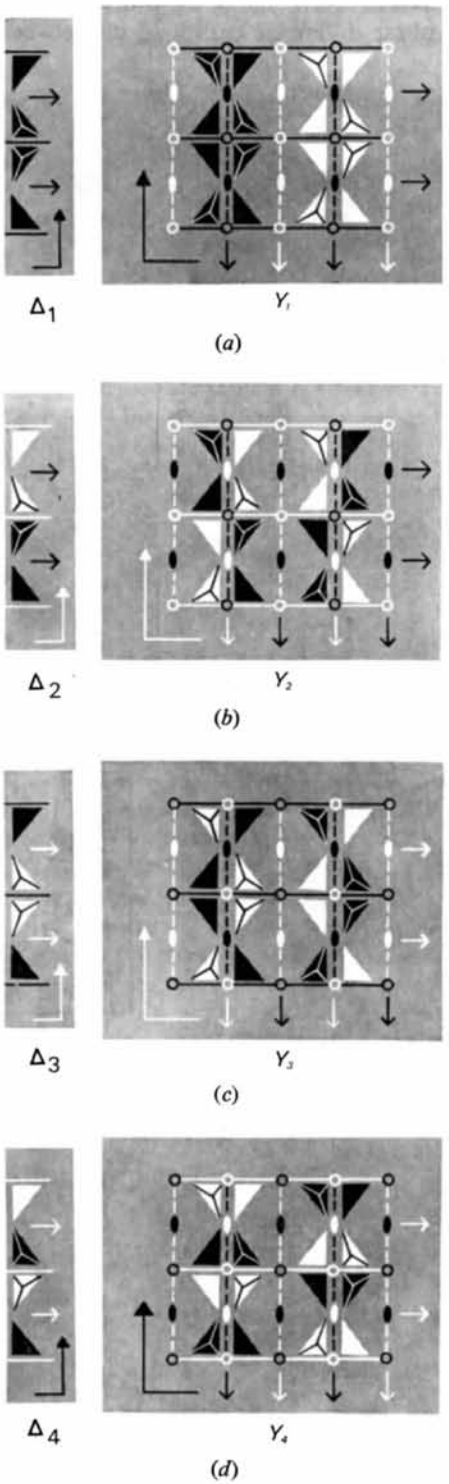


Fig. 14. The representations for the Δ direction (on the left of each diagram) and the Y point. (a) Δ_1 and Y_1, (b) Δ_2 and Y_2, (c) Δ_3 and Y_3, (d) Δ_4 and Y_4. As in Fig. 12 all tetrahedra pointing away from the observer are +, all others −.

been done for the Y_1 diagram, and is shown in Fig. 15 and is denoted Y_1'. The phase relationship between the sets $(E,2_y,m_z,m_x)$ and $(J,2_x,m_y,2_z)$ is now reversed, so that the atomic motions in the Y_1 and Y_1' modes are quite distinct, yet they are described by the same abstract symmetry group.

Throughout Fig. 14, E and m_y are moving in phase, giving Y_1, Y_2, Y_3 and Y_4. In Fig. 15 E and m_y are in antiphase giving Y_1', and a similar antiphase relationship occurs in modes Y_2', Y_3' and Y_4' not depicted.

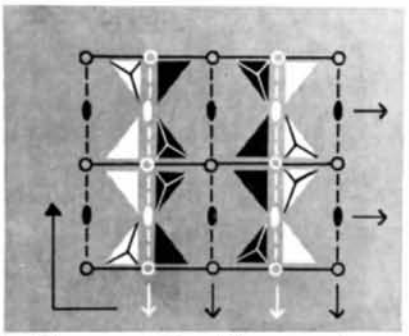


Fig. 15. The Y_1' representation. The symmetry operations of Y_1 which were of type 3 for Δ_1, Fig. 14 (*a*), are here replaced by antisymmetry operations and *vice versa*. The arrangement of symmetry elements is unchanged though half the tetrahedra have changed colour. Again the labelling + and − follows that of Fig. 12.

Σ and $X,\mathbf{q}$ along x axis

The situation in this direction is exactly similar to Δ and Y, owing to the special choice of space group.

Shubnikov groups

It should by now be very obvious that the symmetry groups concerned here are those known as Shubnikov groups, for which there is considerable literature (Belov, Neronova & Smirnova, 1957; Shubnikov & Belov, 1964).

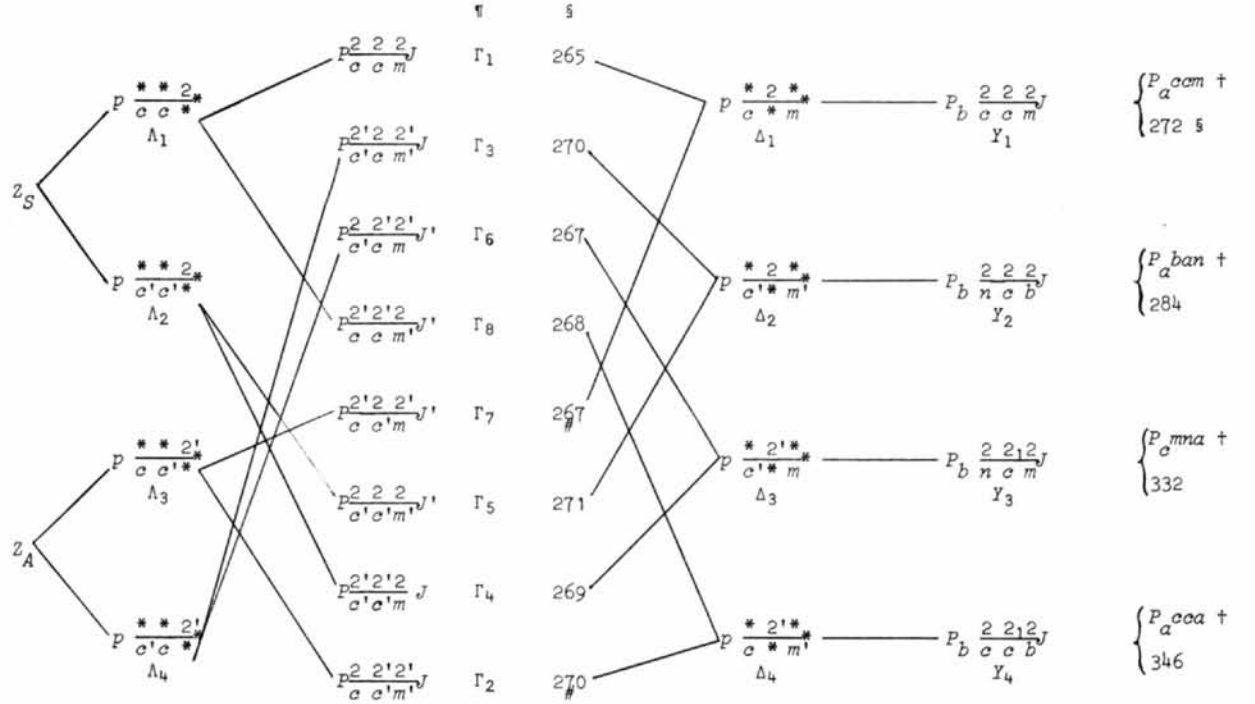
These references are not essential reading for understanding the present paper. The purpose of this paper is however to emphasize that these Shubnikov groups do have a use outside the usual field of magnetic crystal structures. The nomenclature for these groups can therefore be used in the description of certain modes of vibration. These groups have all been listed and named, the usual method of nomenclature is to write down the space-group symbol with the antisymmetry operations primed. For space group number 49, *Pccm*, there exist twelve Shubnikov groups

265	*Pccm*	269	*Pc'c'm*	273	P_ccm
266	*Pccm* 1′	270	*Pc'cm'*	274	P_Accm
267	*Pc'cm*	271	*Pc'c'm'*	275	P_Ccm
268	*Pccm'*	272	P_acm	276	P_Icm .

For the present illustrative purpose a fuller notation will be temporarily used in order to convey more of

Table 4. *Some compatibilities for the space group Pccm*

¶ See Table 3.
≠ x and y permuted.
§ Shubnikov group number.
† Reorientation required to achieve this standard symbol.



the space-group information, though it is not proposed that the accepted notation be altered.

A notation for the *Pccm* example

We need a symbol to work with which specifies each symmetry element of the space group, except of course the identity. We can use the full point-group nomenclature, $2/m\ 2/m\ 2/m$, adding the inversion centre J. Thus *Pccm* becomes

$$P\frac{2}{c}\frac{2}{c}\frac{2}{m}J\,.$$

This of course is the symmetry of the symmetric mode at $\mathbf{q}=0$, the Γ point, and corresponds to Shubnikov group 265 as listed in Table 4. The space group *Pccm* belongs to the same point group as *Pmnb*, and therefore the character table for *mmm* is here applicable. All the Γ modes are labelled in Table 4 in accordance with this character table (Table 2). Fig. 16 is the diagram for Γ_3, Shubnikov group 270, and its relation to the left-hand part of the diagram for Y_2 [Fig. 14(*b*)] is evident. The three entries below Γ_3 in Table 4 show similar relationships with earlier diagrams, Γ_6 with Fig. 14(*c*), Γ_8 with Fig. 14(*d*) and Γ_7 with Fig. 15.

Along the Δ and Λ directions the symbols for those elements of type 3 are replaced by an asterisk, whereupon the compatibilities at Γ are obvious. A small p is used for the lattice as the group is now a two-dimensional or plane group. This is equivalent to the method used in the *Pmnb* example, but now all the information of one line of the character table is contained in the symmetry symbol. Whereas the use of the character table is more appropriate for a computer procedure, the symbolic method is easier for the individual worker.

At the zone boundary point Y, the primitive orthorhombic cell becomes P_b, which denotes edge centring antisymmetrically along the y axis. The symmetry group becomes

$$P_b\frac{2(2,2_1)2}{(c,n)c(m,b)}J$$

where the elements missing in Δ reappear, but the other elements can take on one of two possibilities, the alternatives being bracketed together above. The appearance of the first within the brackets is compatible with an unprimed operation in Δ, whereas the second is compatible with the primed operation. These groups and their compatibilities are listed in Table 4.

All the groups at Y can be described as the direct product of the P_b lattice and a true symmetry group. This is demonstrated by Fig. 17 in which the true symmetry operations of Y_2 are drawn and accordingly only the black tetrahedra appear. This is the space group *Pncb*, a re-orientation of *Pban*, and so the group for Y_2 is P_bncb, a reorientation of P_aban (number 284). Clearly it is better for our purposes to use the non-standard orientation with the otherwise standard symbol P_bncb.

The 'black and white' nature of Shubnikov groups restricts their applicability to those cases where the phase relationships are 0 or π. Consequently at the Z point it is not possible to classify the symmetries as Shubnikov groups; instead the now familiar degeneracies occur. Let us call one mode Z_S, denoting the mode which is compatible with Λ_1 and hence compatible with the fully symmetric Γ_1. The other mode

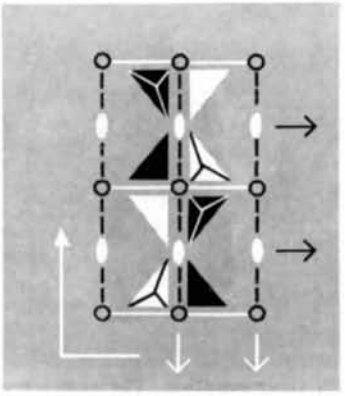


Fig. 16. Diagram for Γ_3, the Shubnikov group no. 270, derived from *Pccm*. The arrangement and colour of the tetrahedra are exactly the same as in the left side of Y_2, Fig. 14 (*b*), but as Γ_3 is for $\mathbf{q}=0$ there is no possibility of antisymmetric translational operations. Again the labelling + and − follows that of Fig. 12.

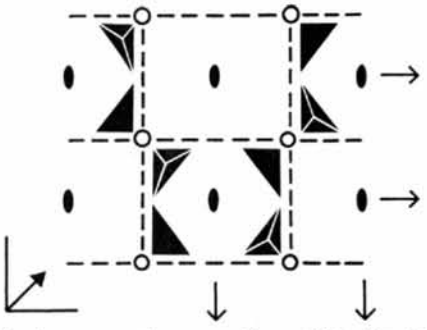


Fig. 17. The true symmetry operations of Y_2, Fig. 14 (*b*). Only the black tetrahedra appear here, and again these are labelled + and − as in Fig. 12. This is the space group *Pncb*.

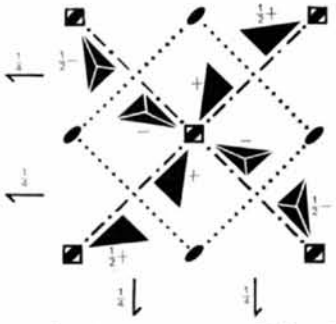


Fig. 18. Diagram for the space group $P\bar{4}2_1c$ viewed down the unique axis.

may be called Z_A without confusion, as in Table 4. The compatibilities are easily determined from Fig. 13 in the usual way. It should be remembered that in all cases such as this the modes Λ do not have the perfect plane-group symmetry, and thus the symbols used, *pcc*2, *pc′c′*2 *etc.*, are not plane-group symbols.

Primitive space groups from the point group *mmm*

With some practice it becomes fairly easy to write down the Shubnikov groups and compatibilities, though the task of doing this thoroughly is large. What now follows is an attempt at complete coverage for a small example: the sixteen primitive holosymmetric orthorhombic space groups at Γ, Σ, X, Δ, Y, Λ and Z. This is made feasible by setting up a large table (Table 5) for a particular group (*Pccm*) and relating this to a condensed table (Table 6) for the 16 space groups.

Table 5. *A summary of Table* 4 *with* Σ *and* X *included*

	Γ	Σ	X	Δ	Y	Λ	Z
1	*Pccm*	*p**cm*	$P_a ccm$	*pc**m*	$P_b ccm$	*pcc***	Z_S
2	*Pcc′m′*	*p**c′m′*	$P_a cna$	*pc**m′*	$P_b ccb$	*pcc′***	Z_A
3	*Pc′cm′*	*p**cm′*	$P_a cca$	*pc′**m′*	$P_b ncb$	*pc′c***	Z_A
4	*Pc′c′m*	*p**c′m*	$P_a cnm$	*pc′**m*	$P_b ncm$	*pc′c′***	Z_S
5	*Pc′c′m′*	As 2 above		As 3 above		As 4 above	
6	*Pc′cm*	As 1 above		As 4 above		As 3 above	
7	*Pcc′m*	As 4 above		As 1 above		As 2 above	
8	*Pccm′*	As 3 above		As 2 above		As 1 above	

The first column of Table 5 gives the Γ point symmetries listed in the order of the representations of Table 3. It is correct to write a similar column 1 for any of the space groups considered with primes in the same positions. For every such case the entries for lines 5, 6, 7 and 8 are the same as in Table 5, except for the entry under Γ. The entries under Σ, Δ and Λ have the first, second and third symbol respectively replaced by an asterisk; this is required in order to retain knowledge of the orientation of the axes. The arrangement of primes on these entries is the same as under Γ, and again this holds for all the space groups we are considering. Therefore these entries are so simple as to be considered redundant in Table 6. Consequently the useful entries for any space group are the sets of four entries under X, Y and Z. Only these appear in Table 6, and are sufficient for the compilation of a table such as Table 5 for any of the 16 space groups.

Concluding example, $P\bar{4}2_1c$

This example is chosen for a variety of reasons. It is the space group of adamantane below the plastic crystalline phase transition, which we are studying experimentally. The group theory has already been analysed (Luty, 1971) using the algebraic method, and it is clear from the results of these papers that errors in this method are easy to make and difficult to recognise. A

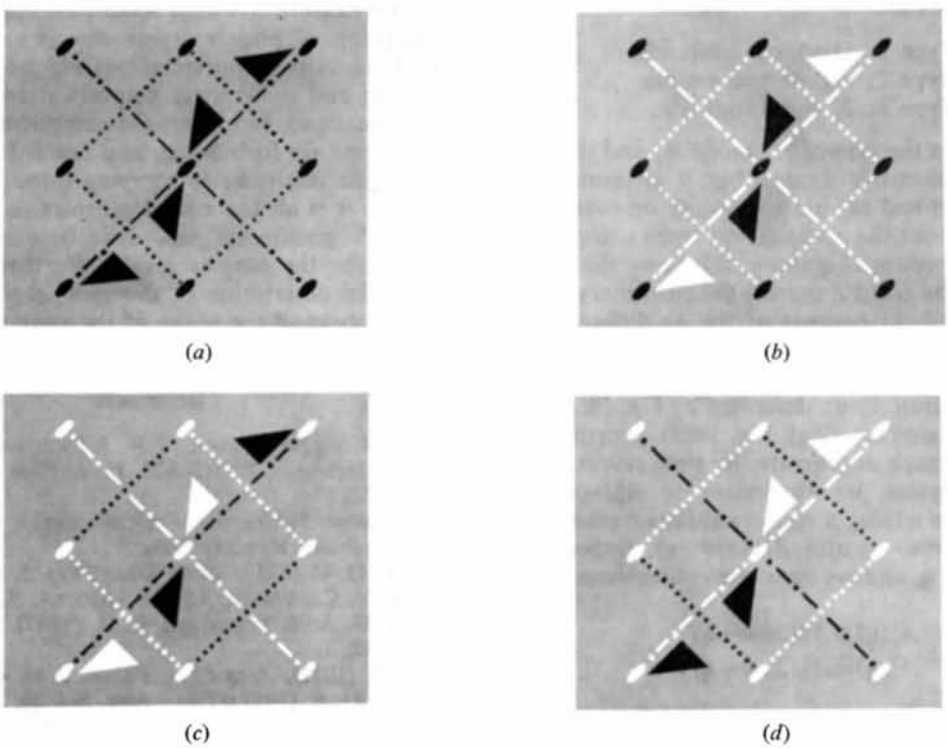


Fig. 19. The four representations of $P\bar{4}2_1c$ for **q** along the unique axis. (*a*) Λ_S, the fully symmetric mode. (*b*) Λ_A, antisymmetric with respect to all improper symmetry operations. (*c*) Λ_D, antisymmetric with respect to the diad operations. (*d*) Λ_D, degenerate with (*c*). The arrangement of symmetry operations is the same in (*c*) and (*d*), except that one is rotated through $\pi/2$. The labels $+$, $-$, $\frac{1}{2}+$ and $\frac{1}{2}-$ match those of Fig. 18.

Table 6. *Symmetries at X, Y, Z for primitive mmm space groups*

X	*Y*	*Z*	*X*	*Y*	*Z*	*X*	*Y*	*Z*	*X*	*Y*	*Z*
Pmmm			***Pnnn***			***Pccm***			***Pban***		
P_amaa	P_bmmm	P_cmmm	X_S	Y_S	Z_S	P_accm	P_bccm	Z_S	X_S	Y_S	P_cban
P_amaa	P_bmmb	P_cmcm	X_S	Y_A	Z_A	P_acna	P_bccb	Z_A	X_S	Y_A	P_cbnn
P_amma	P_bbmb	P_ccmm	X_A	Y_S	Z_A	P_acca	P_bncb	Z_A	X_A	Y_S	P_cnan
P_amam	P_bbmm	P_cccm	X_A	Y_A	Z_S	P_acnm	P_bncm	Z_S	X_A	Y_A	P_cnnn
Pmma			***Pnna***			***Pmna***			***Pcca***		
X_S	P_bmma	P_cmma	X_S	Y_S	Z_S	X_S	P_bmna	Z_S	X_S	P_bcca	Z_S
X_A	P_bmmn	P_cmca	X_S	Y_A	Z_A	X_S	P_bmnn	Z_S	X_A	P_bccn	Z_A
X_S	P_bbmn	P_ccma	X_A	Y_A	Z_A	X_A	P_bbnn	Z_A	X_S	P_bncn	Z_A
X_A	P_bbma	P_ccca	X_A	Y_S	Z_S	X_A	P_bbna	Z_A	X_A	P_bnca	Z_S
Pbam			***Pccn***			***Pbcm***			***Pnnm***		
X_S	Y_S	P_cbam	X_S	Y_S	Z_S	P_abcm	Y_S	Z_S	X_S	Y_S	Z_S
X_A	Y_A	P_cbnm	X_A	Y_S	Z_A	P_abna	Y_A	Z_S	X_A	Y_A	Z_A
X_A	Y_A	P_cnam	X_S	Y_A	Z_A	P_abca	Y_A	Z_A	X_A	Y_A	Z_A
X_S	Y_S	P_cnnm	X_A	Y_A	Z_S	P_abnm	Y_S	Z_A	X_S	Y_S	Z_S
Pmmn			***Pbcn***			***Pbca***			***Pmna***		
X_S	Y_S	P_cmmn	X_S	Y_S	Z_S	X_S	Y_S	Z_S	X_S	Y_S	Z_S
X_A	Y_S	P_cmcn	X_A	Y_A	Z_S	X_A	Y_A	Z_S	X_A	Y_A	Z_A
X_S	Y_A	P_ccmn	X_S	Y_S	Z_A	X_S	Y_A	Z_A	X_S	Y_A	Z_S
X_A	Y_A	P_cccn	X_A	Y_A	Z_A	X_A	Y_S	Z_A	X_A	Y_S	Z_A

final reason for the inclusion of this example is afforded by the following subtitle.

Degeneracies along Λ

Fig. 18 shows the space-group symmetry viewed down the z axis. For phonons with $\mathbf{q}$ along the z axis the group operations are

Type 1: Diad axis (also $\bar{4}^2$)
Type 2: c-glide and n-glide
Type 3: 2_1 and $\bar{4}$ (not $\bar{4}^2$).

Fig. 19 shows the symmetric mode Λ_S and the three possible antisymmetric modes, but it is immediately obvious that (*c*) and (*d*) are equivalent on rotation of either by $\pi/2$ about the z axis. These form a degenerate pair Λ_D for all values of $\mathbf{q}$ along Λ, leaving the symbol Λ_A for (*b*). At the point Z there is the customary degeneracy of Λ_S and Λ_A because of the $\frac{1}{2}c$ difference between the two pairs of positions. The same can be considered true for the Λ_D pair as follows. Let a mode have representation $\Lambda_D^1(\mathbf{q})$, described by Fig. 19(*c*), then the mode belonging to $\Lambda_D^2(\mathbf{q})$, Fig. 19(*d*), is orthogonal to the first although degenerate. By time-reversal symmetry these modes are equivalent to $\Lambda_D^1(-\mathbf{q})$ and $\Lambda_D^2(-\mathbf{q})$, and on adding a reciprocal-lattice translation these are $\Lambda_D^1(2\pi/\mathbf{c}-\mathbf{q})$ and $\Lambda_D^2(2\pi/\mathbf{c}-\mathbf{q})$, respectively. At Z, $\mathbf{q}=2\pi/\mathbf{c}-\mathbf{q}$, and we have the equivalences

$$\Lambda_D^1(\mathbf{q}) \equiv \Lambda_D^2(2\pi/\mathbf{c}-\mathbf{q})$$
$$\Lambda_D^2(\mathbf{q}) \equiv \Lambda_D^1(2\pi/\mathbf{c}-\mathbf{q}) .$$

This is the first example considered in this paper where a degenerate pair occurs for $\mathbf{q}$ other than at the zone boundary, and it clearly presents a problem for diagram interpretation. We have encountered double degeneracies already at special points of the Brillouin zone, and these often continue in the zone boundary. Unfortunately by this stage the limit of usefulness of the diagram description is reached and attempts to further it appear more and more similar to the analytic approach.

In conclusion it would seem that the diagrammatic description of phonon symmetry is very helpful for one-dimensional representations which are the majority of cases, and moderately helpful for two-dimensional representations. However, the complications of higher dimensions are forbidding, and one is forced to resort to analytic methods. In carrying through the analytic methods it is all too easy for errors to be made, and so the diagrammatic procedure becomes very useful in checking the simpler results. Furthermore, it gives a pictorial description of the symmetry of a phonon, which is beyond the scope of the analytic method.

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