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The Determination of Rigid-Unit Modes as Potential Soft Modes for Displacive Phase Transitions in Framework Crystal Structures

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Abstract

This paper describes a computational method for the determination of all possible phonon modes in framework crystal structures that leave the fundamental structural units (tetrahedra and octahedra) undistorted. Such rigid-unit modes (RUMs) are prime candidates as soft modes for displacive phase transitions, such as in the perovskite structure, and this computational method can be used to rationalize the phase transitions in any framework structure. The method has been programmed for general use. The RUM approach is illustrated by consideration of the perovskite, quartz and cristobalite structures.

1. The concept of rigid-unit modes

Many silicate crystal structures are composed of SiO_4 tetrahedra that are linked to other tetrahedra by corner-sharing oxygen atoms to give a semi-infinite framework connectivity. Quartz is one well known example of what we call a *framework structure*. Such framework structures are not confined to silicates: $AlPO_4$ and As_2O_5 are examples of nonsilicate framework structures. Many framework structures are found to undergo displacive phase transitions (Carpenter, 1988; Salje, 1988). In some respects this might seem to be counter-intuitive, because Si–O bonds are strong and the tetrahedra are difficult to distort. However, such phase transitions can occur without any significant distortions of the SiO_4 tetrahedra. Quartz is a good example of this (Megaw, 1973; Grimm & Dorner, 1975; Boysen, Dorner, Frey & Grimm, 1980; Berge, Baccheimer, Dolino, Vallade & Zeyen, 1985; Vallade, Berge & Dolino, 1992). The high-temperature (β) phase of quartz (Fig. 1*a*) has hexagonal symmetry and the low-temperature (α) phase (Fig. 1*b*) has trigonal symmetry. In the quartz structure, the SiO_4 tetrahedra are connected as linked spirals and at the phase transition the spirals are distorted by rotations and displacements of the tetrahedra. Megaw (1973) has discussed the structures

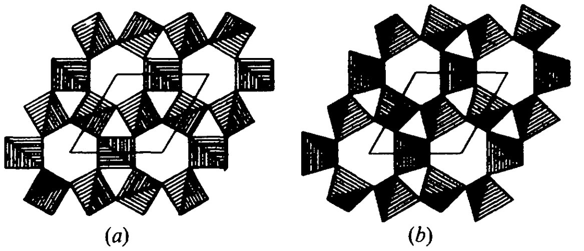

Fig. 1. (*a*) Projection of the hexagonal phase of quartz down [001], in which the SiO_4 tetrahedra are shown as shaded units. (*b*) Projection of the trigonal phase of quartz down [001].

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of other silicate crystals from this perspective and Glazer (1972) has extended this analysis to the different phase transitions in perovskites in which the BO_6 octahedra rotate without distortion.

The displacive phase transition in quartz is driven by a normal soft optic phonon, which has recently been measured by inelastic neutron scattering (Dolino, Berge, Vallade & Moussa, 1992). This phonon is an example of a normal mode that is able to propagate without distortions of the tetrahedra. We are prompted to ask whether such vibrational modes, which involve distortions of the basic structure framework but which do not distort the SiO_4 tetrahedra, are more common? Such modes can be called *rigid-unit modes* (RUMs). Boysen *et al.* (1980) were the first to consider the issue of rigid-unit modes and they deduced the existence of one RUM at a zone-boundary wave vector in quartz. Berge *et al.* (1985) and Vallade *et al.* (1992) have extended this analysis and have shown that a number of different types of RUM exist in the β phase of quartz. These include a RUM at $\mathbf{k} = 0$, which acts as the soft mode for the α–β transition, and a whole branch of RUMs along the Σ direction, $[\xi, 0, 0]$, in reciprocal space, which is responsible for the incommensurate phase transition. Berge *et al.* (1985) and Vallade *et al.* (1992) have been able to account for many of the features of the incommensurate phase transition by the existence of these rigid-unit modes. This basic picture has been confirmed by molecular-dynamics simulations (Tautz, Heine, Dove & Chen, 1992). It would seem reasonable to expect that RUMs might exist in a large number of framework structures and their existence would provide the basic explanation for the existence of the displacive phase transitions observed in such structures.

In this paper, we tackle the basic question of how we can predict the occurrence of RUMs in any given framework structure. Vallade (Berge *et al.*, 1985; Vallade *et al.*, 1992) appears to have been the first person to pursue this question in a systematic way for quartz, by testing all the special points, symmetry lines and planes of symmetry in reciprocal space for the existence of RUMs. Although this enumeration of the RUMs in quartz was obtained by hand [the details of the method are outlined in Vallade *et al.* (1992)], most framework structures are more complex than quartz and hand calculations are generally impractical. The purpose of this paper is to present a pragmatic method for the determination of the complete set of RUMs in any framework structure. We note that we mostly have in mind cases where adjacent units share a single oxygen atom, but the ideas can also be applied to cases where adjacent units (usually octahedra) share two oxygen atoms along a common edge. A similar question has been tackled for glasses, where the corresponding modes are called *floppy modes* (Döhler, Dandoloff & Bilz, 1980; Thorpe, 1983; He & Thorpe, 1985; Cai & Thorpe, 1989). There are some differences, however, between the work on glasses and the present case. In particular, we are interested only in systems that are built as frameworks of rigid units, whereas the work on glasses is more generally applied to any system with rigid connectivity. Furthermore, we are now interested in the wave-vector dependence, which is not an issue in glasses. We will also see below that the work on glasses cannot be applied to crystalline materials as it predicts that there are no rigid-unit modes in crystalline silicates, contrary to our findings. We explain this apparent contradiction in § 2.

Before we describe the practical method we have developed for the enumeration of the set of RUMs for any framework structure, we outline some points of principles that highlight the essence of the problem (§ 2). We then describe a computational method and illustrate the main features using a two-dimensional analogue of the perovskite structure (§ 3). We conclude by describing the application of the method to three examples, perovskite, quartz and cristobalite (§ 4). Some of the implications of the RUM model — which are more numerous than one might have expected — have been described elsewhere (Dove, Giddy & Heine, 1992*a*,*b*) and the application of the RUM model to the phase transition in quartz has been described in detail by Berge *et al.* (1985) and Tautz *et al.* (1992). A detailed application of the RUM model to a number of systems that are of interest will be described elsewhere (Giddy, Dove, Hammonds, Winkler & Heine, 1993).

2. Framework rigidity and the issue of flexibility

At first glance, it is by no means obvious that RUMs will be geometrically allowed in a silicate structure. From a qualitative viewpoint, it is easy to conceive of topological structures that are floppy (*i.e.* that have zero-frequency vibrational modes), such as a two-dimensional set of four rods joined into a square (Fig. 2*a*). In this example, the structure is unstable against a shear of the square. On the other hand, it is also

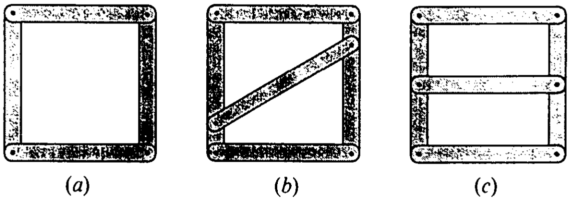
(*a*) (*b*) (*c*)

Fig. 2. (*a*) Four rods hinged at the corners, forming a structure that is easily sheared. (*b*) The same four rods cross braced with a fifth rod, giving rise to a stiff structure. (*c*) The original four rods braced with a fifth rod constrained to be parallel to two of the other rods. This structure can now be sheared.

easy to conceive of structures that are cross braced and hence rigid, such as the square of rods with a fifth rod connected across the diagonal (Fig. 2*b*). Indeed, there is a theorem that has been used extensively in the study of the dynamics of glasses (Döhler *et al.*, 1980; Thorpe, 1983; He & Thorpe, 1985; Cai & Thorpe, 1989), which simply states that any structure with F degrees of freedom and C independent constraints will only be floppy if $F > C$. This is simple to illustrate in our example of connected rods. The four rods in Fig. 2(*a*) each have three degrees of freedom (two translations and one rotation), giving $F = 12$. There are two constraint equations governing the connections at each joint, giving $C = 8$. Thus there are 4 $(12-8)$ remaining degrees of freedom. Two of these are the uniform translations of the whole structure, one is the rotation of the whole structure and the fourth is the shear of the structure. Addition of the cross brace in Fig. 2(*b*) gives $F = 15$ and $C = 12$. We are left with only the uniform translations and rotation and the shear mode is no longer allowed. For a crystal structure with no constraints on the position or orientation of the crystal, this criterion is generalized to the condition that $F > C + 6$. In our terminology, this means that a three-dimensional structure will only support $(F - C - 6)$ RUMs if $F > C + 6$. We note that a rigid body has six degrees of freedom (three translational and three rotational). For a tetrahedron connected to four other tetrahedra, each of the oxygens at the corners has three constraints on its position (it needs to be at the same position as the same atom in the connected tetrahedron). These three constraints are shared by the two tetrahedra. Adding all the constraints leads to a total of six per tetrahedron, so that the number of constraints is the same as the number of degrees of freedom. Thus, according to the criterion, framework silicates are a marginal case, with a fine balance between the number of degrees of freedom and the number of constraints.

In many cases, however, it turns out that the number of *independent* constraints is actually slightly lower. This case is illustrated in Fig. 2(*c*), where the cross brace is now parallel to two of the rods. As before, $F = 15$. However, in this case the number of independent constraints is actually lower than the number we calculated for the structure in Fig. 2(*b*). If we consider now the fifth rod, we see that if we constrain one end of the cross-brace rod to be correctly joined to one of the rods that forms the square and we simply constrain its orientation to be parallel to the top rod, we have actually added only three independent constraints rather than four. So we have gained an additional degree of freedom,which can be identified with the same shear of the structure that is found in the structure shown in Fig. 2(*a*). This illustrates the fact that in framework structures some of the constraints are not independent, thus allowing the existence of some RUMs but usually not many compared with the total number of normal modes in the crystal. Thus we may expect that the RUMs will often be restricted to a small finite set of wave vectors, for example along the high-symmetry lines in reciprocal space, or in zones. This will be found for the examples given below. However, this is not a general statement; we have found cases in which there are one or more RUMs for all wave vectors (Giddy *et al.*, 1993).

We noted in § 1 that the analysis previously applied to glasses (Döhler *et al.*, 1980; Thorpe, 1983; He & Thorpe, 1985; Cai & Thorpe, 1989) predicts that for silicates the number of rigid-unit modes is zero (Döhler *et al.*, 1980). The apparent contradiction between this result and the results we present below has been outlined in the preceding paragraph - symmetry allows for some of the constraints to become degenerate. This point is not an issue in the study of glasses. In cases where the RUMs are restricted to lines of planes of wave vectors in reciprocal space, the number of rigid-unit modes is almost zero when compared to the total number of normal modes. However, in those cases where there is one or more RUM for each wave vector, the total number of RUMs will amount to a few percent of the total number of normal modes. In these cases, the result for glasses fails spectacularly.

Simply counting constraints and degrees of freedom, however, only gets us part of the way to the goal of being able to deduce the existence of RUMs in any framework structure. Aside from the fact that it is difficult to deduce the number of independent constraints, such an analysis does not tell us the wave vectors of such modes. For this reason, we have developed an alternative approach, which we now outline.

3. Computational method: the molecular approach and the split-atom method

3.1. *The basic idea*

We call our method the *molecular approach*, the essence of which is to treat the problem of determining the set of RUMs as a problem in molecular lattice dynamics. In our application, we treat each rigid unit as an independent rigid entity, or 'molecule'. The atoms that are shared by two rigid units are treated as two distinct particles, or 'atoms' (one per molecule) with a separation of zero. These are given the name *split atoms*. The system is then subject to two constraints, namely that the rigid units are unable to distort and that the pairs of split atoms cannot move apart. The rigid-molecule constraint is treated as a strict constraint, but we treat the zero-separation constraint for the split atoms as a slack constraint by inventing an interaction potential operating between two split atoms, $\varphi(d)$, that is harmonic with respect to the split-atom separation distance d:

$$\varphi(d) = (1/2)Kd^2. \tag{1}$$

The force constant K would have infinite value for a strict constraint. Clearly, if a phonon is calculated to have zero frequency (*i.e.* zero potential energy) in this model, it implies that the split atoms do not separate in this mode and it is a RUM.

We have implemented this approach by modifying the standard molecular-lattice-dynamics program *CRASH*, written by Pawley (1972). The principal modification is the inclusion of the slack constraint potential (1). No other potentials are used in the modified program. We have given the modified program the name *CRUSH*. It was the relatively easy nature of the task of modifying the *CRASH* program that motivated the pragmatic choice of the molecular approach.

The model of split atoms interacting *via* the potential (1) is not as unphysical as it appears at first sight. In reality, of course, the shared oxygen atoms cannot split into two: what happens instead for a phonon that is not a RUM is that the units have to distort. Thus, the force constant K is to be interpreted as an average force constant for all types of distortion of the units, giving some measure of the stiffness of the units. If the magnitude of K is chosen as some average force constant for the different types of distortion, then we expect our procedure to give at least a qualitative picture of the phonon spectrum.

3.2. *Example*: *two-dimensional perovskite*

A simple example will serve to illustrate our molecular approach. Consider the two-dimensional projection of the perovskite structure (Fig. 3). The basic units are the O_6 octahedra, and we can neglect the A and B cations. We allow only the x and y translations of the units and the rotations of the octahedra about the z axis; we label these dynamic variables as u, v and θ, respectively. For simplicity, the molecular mass has been set as unity (in arbitrary units). The unit-cell length is denoted a; the bond lengths are therefore equal to $a/2$. The Hamiltonian for this model is given by

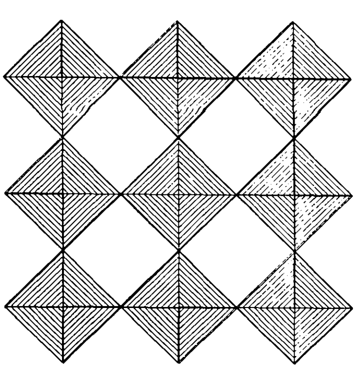

Fig. 3. The ideal two-dimensional perovskite structure, with one rigid unit per unit cell. The rigid units, shown as squares in this projection, are shaded.

$$\begin{aligned}\mathscr{H} = {} & (1/2)\sum_{m,n}(\dot{u}_{m,n}^2 + \dot{v}_{m,n}^2 + a^2\dot{\theta}_{m,n}^2)\\ & + (K/2)\sum_{m,n}[(u_{m,n} - u_{m+1,n})^2 + (u_{m,n} - u_{m,n+1})^2\\ & + (v_{m,n} - v_{m+1,n})^2 + (v_{m,n} - v_{m,n+1})^2\\ & + a^2(\theta_{m,n} + \theta_{m+1,n})^2 + a^2(\theta_{m,n} + \theta_{m,n+1})^2\\ & + 2a(u_{m,n} - u_{m,n+1})(\theta_{m,n} + \theta_{m,n+1})\\ & + 2a(v_{m,n} - v_{m+1,n})(\theta_{m,n} + \theta_{m+1,n})],\end{aligned} \tag{2}$$

where m, n identifies the position of the rigid unit in the two-dimensional square lattice. The vibrational frequencies $\omega(\mathbf{k})$ for this system for any wave vector $\mathbf{k} = \xi\mathbf{a}^* + \zeta\mathbf{b}^*$ can be calculated from the dynamical matrix, $\mathbf{D}(\mathbf{k})$, in the usual manner:

$$\omega^2(\mathbf{k})\begin{bmatrix} u(\mathbf{k}) \\ v(\mathbf{k}) \\ \theta(\mathbf{k}) \end{bmatrix} = \mathbf{D}(\mathbf{k})\cdot\begin{bmatrix} u(\mathbf{k}) \\ v(\mathbf{k}) \\ \theta(\mathbf{k}) \end{bmatrix}, \tag{3}$$

where the dynamical matrix has the form

$$\mathbf{D}(\mathbf{k}) = \begin{bmatrix} 4K(1-\alpha) & 0 & \beta K \\ 0 & 4K(1-\alpha) & -\gamma K \\ -\beta K & \gamma K & Ka^2(1+\alpha) \end{bmatrix} \tag{4a}$$

$$\alpha = (\cos 2\pi\xi + \cos 2\pi\zeta)/2 \tag{4b}$$

$$\beta = ia\sin 2\pi\zeta \tag{4c}$$

$$\gamma = ia\sin 2\pi\xi \tag{4d}$$

and $u(\mathbf{k})$ *etc.* are the spatial Fourier transforms of the real-space variables u *etc.* The normal-mode frequencies can be obtained from the diagonalization of $\mathbf{D}(\mathbf{k})$.

Apart from the trivial acoustic-mode solution at $\mathbf{k} = 0$ ($\alpha = 1, \beta = \gamma = 0$), the only solution with $\omega = 0$ is a single mode at $\mathbf{k} = (0.5, 0.5)$, when $\alpha = -1, \beta = \gamma = 0$. The eigenvector of this mode involves only the rotation θ. A set of calculated dispersion curves for this model is shown in Fig. 4. Note that, owing to the coupling between the rotational and translational variables (the off-diagonal components of the dynamical matrix), the transverse acoustic mode at the zone centre changes to a purely rotational mode at the zone boundary. The anticrossing that leads to this change is evident in Fig. 4.

3.3. *Practical implementation*

The perovskite example has illustrated both the molecular method for the enumeration of the set of RUMs and the application of the *CRUSH* program. We found that *CRUSH* will give unambiguous results for relatively small values of K (of the order of 5000 kJ mol^{-1} Å^{-2}). Rounding errors in *CRUSH* typically give RUM frequencies with maximum values of ~0.01 THz, compared with typical frequencies of >5 THz for all other modes. Thus the RUMs can easily be identified in the program output. The program was modified to use isotropic inertia tensors for all rigid units, with the tensor axes lying parallel to the Cartesian axes used in the program. This is a good approximation because the units are always nearly exact tetrahedra or octahedra and it makes the interpretation of the eigenvectors given in the output much easier. *CRUSH* can handle more than one unit in the structure and also more than one type of unit.

We have interfaced *CRUSH* with the group-theory program of Warren & Worlton (1974) to enable us to assign a symmetry to each RUM. The fact that all the RUMs have zero frequency means that their calculated eigenvectors will generally be mixed, even over modes of different symmetry. However, by projecting the symmetry eigenvectors back onto the calculated RUM eigenvectors we can easily unmix and assign unique symmetries to the different RUMs. We have also interfaced *CRUSH* with the structure-drawing program *STRUPLO* (Fischer, 1985) in order to give a graphical representation of the $\mathbf{k}=0$ RUM distortions.*

3.4. *Comparison with alternative approach*

We should compare this approach with a possible alternative method, namely one which treats the molecular constraint as a slack constraint and the constraint that keeps the positions of the shared atoms identical as a strict constraint. This approach could be carried out using a conventional lattice-dynamics program, with strong intramolecular interactions (*e.g.* Si–O bonds and O–Si–O bond angles) and no intermolecular interactions, and indeed we have used this approach for some calculations (Dove *et al.*, 1992*b*). This approach, however, has three drawbacks in comparison with the method we have used. The first drawback is that the calculated eigenvectors are not given in terms of rotations or translations of individual rigid units, so that a separate sorting of external and internal modes would be necessary. The second drawback is that a good potential model would have to be invented that would be applicable to different types of rigid units (tetrahedral or octahedral, and different with respect to the central cations). Moreover, before a calculation can be performed, it would be desirable to perform a preliminary structure-relaxation calculation. This is not trivial if RUMs are present, as the structure can relax with a modulation given by the set of eigenvectors of the RUMs with no cost in energy. Imposition of symmetry can help in most cases but will not help if there is a RUM that does not break the symmetry. These problems do not occur with our approach. The third drawback, which is the least serious of the three, is that unless the system contains only tetrahedral rigid units with sharing of all atoms (assuming that the atoms at the centers of the rigid units are not included), the number of calculated modes will be higher than with our method, producing more unwanted output.

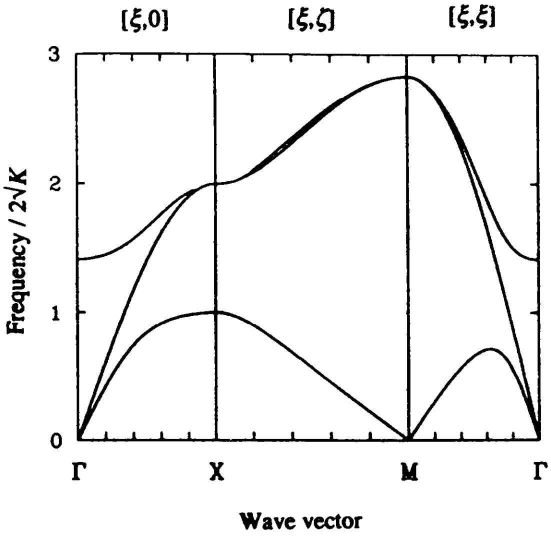

Fig. 4. Calculated dispersion curves for the two-dimensional perovskite along the three symmetry directions.

3.5. *Some practical points*

It is often found that the symmetry of a given crystal structure does not constrain the tetrahedra to have the ideal shape. In many of our applications, we use both idealized geometries as well as the actual structures with slightly distorted tetrahedra. We have found that in some cases the use of distorted tetrahedra means that the calculated RUM frequency is no longer zero but has a small value, so we try to use idealized structures whenever possible. For complex structures that contain only tetrahedra of the same kind, we generate the idealized structures using a lattice-energy minimization program that incorporates only harmonic potentials for the shortest Si–O and O–O bonds.

We have also demonstrated the existence of a simple rule, that in some cases *different rigid-unit modes do not commute*. By this, we mean that, after a structure has been distorted by one RUM eigenvector, many of the other RUMs no longer have calculated frequencies of zero. This effect is seen experimentally in quartz: an *M*-point mode of the α phase is observed

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* The suite of programs we have developed is written in standard Fortran. The programs are run on a VAX computer under VMS, but we believe that they can be compiled and run on any standard computer. The source codes and sample data files are available by electronic mail from MARTIN@MINP.ESC.CAM.AC.UK.

Table 1. *Rigid-unit modes in the cubic and tetragonal phases of perovskite*

Wave vector	Rigid-unit modes in the cubic phase	Rigid-unit modes in the tetragonal phase
(0, 0, 0)	(Three acoustic)	(Three acoustic)
(0.5, 0.5, ζ)	One rotational (z)	
(0.5, ζ, 0.5)	One rotational (y)	One rotational (y)
(ζ, 0.5, 0.5)	One rotational (x)	One rotational (x)
(0.5, 0.5, 0.5)	Three rotational	Two rotational
(0.5, 0.5, 0)	One rotational (z)	
(0.5, 0.0, 0.5)	One rotational (y)	One rotational (y)
(0.0, 0.5, 0.5)	One rotational (x)	One rotational (x)

to soften on approaching the transition (Boysen *et al.*, 1980). In the β phase this mode is a RUM, but in the α phase, which can be described as the β phase modulated by a single RUM at $\mathbf{k} = 0$, it gains a finite frequency proportional to the square of the amplitude of the distortion. This rule will be illustrated in some of our examples in § 4.

4. Sample results

4.1. *Cubic and tetragonal perovskite*

The results of the *CRUSH* analysis for the cubic perovskite structure are given in Table 1. The triply degenerate rotational RUM at $\mathbf{k} = (0.5, 0.5, 0.5)$ is the mode that is observed to soften in the antiferroelectric phase transition in $SrTiO_3$ [see Bruce & Cowley (1981) for a review of this phase transition]. In addition, one rotational RUM is allowed along each of the edges of the Brillouin zone. The existence of this mode has been observed by inelastic neutron scattering (Stirling, 1972). It was found that the whole branch softens on approaching the phase transition until the mode at $\mathbf{k} = (0.5, 0.5, 0.5)$ reached zero frequency first (the branch along the edge has a slight dispersion, with the minimum at this wave vector). The fact that a number of RUMs exist whilst only one specific mode softens illustrates one limitation of the RUM description of phase transitions, namely that we are not in a position to explain why any one particular RUM is observed to soften first in preference to another possible RUM.

The analysis presented above was carried out on the ideal undistorted paraphase. What happens when we perform a RUM analysis on the structure of a distorted phase? In Fig. 5, we show a distorted version of the two-dimensional projection of the perovskite structure that was shown in Fig. 3. It turns out that in this case there are no rotational RUMs at any wave vector. The reason for this is clear from a close look at the distorted structure. If the units are to rotate without changing their size, the unit cell needs to shrink. This coupling to strain becomes of higher order in the high-symmetry case shown in Fig. 3. Thus, in order to preserve the existence of the rotational RUM, we would need to include strain as a dynamical variable in the model. However, the three-dimensional structure with the antiferroelectric distortion at $\mathbf{k} = (0.5, 0.5, 0.5)$ still has some rotational RUMs, which are also described in Table 1. These modes correspond to rotations of the octahedra out of the planes and can themselves generate additional phase transitions as found in a number of other perovskites (Glazer, 1972).

We have included perovskite in our examples because it provides a clear illustration of the basic principles. However, it is known that the octahedra in many perovskites are not actually very rigid; in the case of $SrTiO_3$ there is a soft optic phonon at $\mathbf{k} = 0$ that involves a ferroelectric distortion of the octahedra. However, the tetrahedra in silicates are much more rigid and our analysis is applicable in these cases. We believe that this is also true for tetrahedra containing other cations, such as aluminium and phosphorus. In this respect, we note that the force constants for $AlPO_4$ berlinite deduced from measurements of phonon dispersion curves do not differ substantially from those for SiO_2 (Bethke, Eckold & Hahn, 1992).

4.2. *Hexagonal and trigonal quartz*

We have used *CRUSH* to confirm that our model gives results that are fully consistent with the analysis of Berge *et al.* (1985) and Vallade *et al.* (1992) for the hexagonal β phase of quartz. We have extended the analysis to include all the zone-boundary points and the complete set of results is given in Table 2. It should be noted that there are RUMs at all special points in the Brillouin zone and along many of the high-symmetry lines. There is also one band of RUMs in a plane in reciprocal space, which correspond to acoustic modes in the long-wavelength limit. The optic RUM at Γ gives the distortion associated with the α–β phase transition and one of the branches of RUMs along Σ is the branch that is responsible for the incommensurate phase transition (the other branch is an acoustic branch).

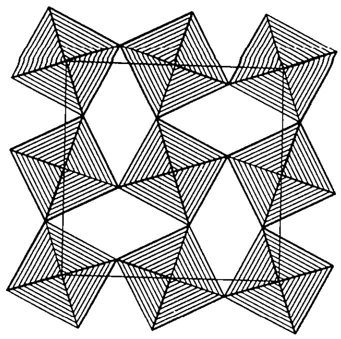

Fig. 5. The distorted two-dimensional perovskite structure, with two octahedra per primitive unit cell.

Table 2. *Rigid-unit modes in the hexagonal and trigonal phases of quartz*

Wave vector	Rigid-unit modes in the hexagonal phase*	Remaining in the trigonal phase
0, 0, 0	$\Gamma_2(+^2\Gamma_3, \Gamma_5$ acoustic)	(Three acoustic)
0, 0, ξ	$\Delta_2, \Delta_4, \Delta_6$	
$\xi, \xi, 0$	Λ_2	Yes
$\xi, 0, 0$	$2\Sigma_2$	
0, 0, 1/2	$^2A_2, A_5$	1
1/3, 1/3, 1/2	H_2	Yes
1/3, 1/3, 0	K_2	Yes
1/2, 0, 1/2	L_1	Yes
1/2, 0, 0	$2M_2$	1
$\xi, \xi, 1/2$	Q_2	Yes
1/2, 0, ξ	U_1	Yes
$\xi, \zeta, 1/2$	1	Yes
$\xi, \zeta, 0$	1	Yes

* The letters represent the wave vector, the subscripts give the mode symmetry and the superscripts denote the degeneracy of the mode.

Table 3. *Rigid-unit modes in the cubic and tetragonal phases of cristobalite*

Wave vector	Rigid unit modes in the cubic phase*	Remaining in the tetragonal phase
0, 0, 0	$^3\Gamma_5^-(+^3\Gamma_{10}^-$ acoustic)	1(+three acoustic)
$\xi, \xi, 0$	Σ_2	Yes
$\xi, 0, 0$	$^2\Delta_3$	
ξ, ξ, ξ	$^2\Lambda_3, \Lambda_2$	
1/2, 1/2, 1/2	$L_2, {}^2L_4$	
$\xi, 1, \xi$	S_2	
1, 0, 0	$^2X_4$	
ξ, ξ, ζ	1	

* The letters represent the wave vector, the subscripts give the mode symmetry and the superscripts denote the degeneracy of the mode.

In Table 2, we also list the RUMs found in the trigonal phase. We note that, whilst some of the RUMs remain in the trigonal phase, a number can no longer be classed as rigid-unit modes. Among these are the M-point RUM that was studied in some detail by Boysen *et al.* (1980). This illustrates the rule of the non-commutation of rigid-unit modes.

4.3. *Cubic and tetragonal cristobalite*

The results of a *CRUSH* analysis of the cubic β phase of cristobalite ($Fd\bar{3}m$) are presented in Table 3. We note that in this case there are RUMs for wave vectors in the [1, 1, 0] zone as well as at special points and along symmetry directions. The X_4 RUM is the mode that gives the distortion associated with the α–β phase transition at 503 K (Hatch & Ghose, 1990; Schmahl, Swainson, Dove & Graeme-Barber, 1992). The existence of these planes of RUMs has been demonstrated by diffuse electron scattering (Hua, Welberry, Withers & Thompson, 1988). These authors were able to correlate their results with calculations of the RUM eigenvector at one special wave vector.

We have also determined the set of RUMs for the low-temperature tetragonal phase ($P4_12_12$) and these are also listed in Table 3. Very few RUMs remain in the tetragonal phase, which again illustrates the rule of the non-commutation of rigid-unit modes. This prediction has been verified by inelastic neutron scattering (Swainson & Dove, 1993).

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