

Rigid unit modes in crystal structures with octahedrally coordinated atoms

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ABSTRACT

The rigid unit mode analysis was initially developed to understand the phase transitions in aluminosilicate minerals containing corner-linked tetrahedra. Here the model is applied to a range of minerals with crystal structures that can be described as frameworks of linked octahedral and tetrahedral units, including garnet, sillimanite, titanite, and ellenbergerite. Consistent with a constraint analysis, there are no rigid unit modes in these minerals. Generalizing these results suggests that there will not be any easy ways to distort structures that have frameworks containing octahedral units. This result explains why polyhedral-tilting displacive phase transitions are not common in such minerals, whereas they occur in most aluminosilicate minerals containing only tetrahedral units. It also explains that it will be necessary for the tetrahedra and octahedra to distort when solid solutions are formed.

INTRODUCTION

Many insights into the behavior of aluminosilicate minerals containing linked SiO_4 and AlO_4 tetrahedra follow from the fact that the forces within the tetrahedra are much stronger than the forces that act between them. For example, it is much harder to distort a tetrahedron than to allow two tetrahedra linked at a common vertex to rotate against each other. This theory has been developed within the context of the rigid unit mode model (Dove et al. 1995; Hammonds et al. 1996; Dove 1997); the central point is that there may exist vibrational modes (or equivalently static deformations of the structure) in which all the tetrahedra can rotate without any having to distort. These vibrations, called rigid unit modes (RUMs), will have very low energy and can act as soft modes for displacive phase transitions. This approach has been applied to several aluminosilicates (Hammonds et al. 1996) and has been used to illuminate the behavior associated with phase transitions, and the ideas have been developed further to also explain phenomena such as negative thermal expansion (Pryde et al. 1996), zeolitic catalysis (Hammonds et al. 1997), and the low-energy excitations in glasses (Dove et al. 1997).

It is tempting to think that RUMs could also be found in systems with linked octahedral structural units. Indeed, the case of perovskite gives some credence to this hope, because it is both intuitive and confirmed by theory that the octahedral-tilting phase transitions in the perovskites arise from the existence of RUMs (Giddy et al. 1993). However, there is a simple analysis that can guide our

expectations. From a theory discussed by Maxwell (1864) in relation to the stability or flexibility of engineering structures, which has more recently been applied to the problem of the stiffness of glasses by Phillips (1979, 1981) and Thorpe and co-workers (Thorpe 1983; He and Thorpe 1985; Cai and Thorpe (1989), the number of zero-energy modes of deformation of a structure, N_f , is given by the difference between the total number of degrees of freedom of the constituent parts, F , and the number of constraints operating, C . For any rigid polyhedron, $F = 6$ per polyhedron. Where two polyhedra are linked at a common vertex, there are three constraints that require the position of the vertex of one polyhedron to be the same as the position of the vertex of the linked polyhedron. These three constraints are shared by the two polyhedra. For a material containing polyhedra with n vertices that are all linked to neighboring polyhedra at each corner, $C = 3n/2$ per polyhedron. If the polyhedra are all tetrahedra ($n = 4$), $N_f = F - C = 0$. On the other hand, if the polyhedra are octahedra ($n = 6$), $N_f = -3$ per polyhedron. The first result implies that crystals made from corner-linked tetrahedra are exactly on the borderline between being over-constrained (no RUMs) and under-constrained (i.e., floppy). But the second result suggests that that crystals made from corner-linked octahedra are well over-constrained. The observations and calculations of some RUMs in the cubic perovskite structure are clearly in contradiction of this simple theory and suggest some flaw in the reasoning. The flaw, as such, is the neglect of symmetry, which has the effect of making some of the constraints degenerate (i.e., no longer independent). This point has been explained in detail elsewhere (Giddy

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et al. 1993; Dove et al. 1996; Dove 1997), and we will return to it later. In all the silicates we have investigated, there are always some RUMs with wave vectors along special lines or on special planes in reciprocal space (Hammonds et al. 1996). In some systems such as zeolites (Hammonds et al. 1997), it has been shown that the standard Maxwell counting scheme can be severely violated. For materials containing edge-sharing octahedra we need to count the constraints slightly differently. For each edge there are five constraints operating that need to be shared between the two octahedra. Three of these come from the constraints forcing a pair of common vertices to have the same position, and the other two arise from the two shared edges having the same orientation. For materials containing face-sharing octahedra there are six constraints for each face, which again need to be shared by the two octahedra. How these constraints contribute to N_f depends on how many shared edges or faces there are.

As we have noted, the existence of RUMs in structures composed of frameworks of linked tetrahedra or octahedra implies a breakdown of the standard Maxwell constraint counting, and this arises from the symmetry making some of the constraints degenerate and hence redundant. To determine the number of RUMs in any material allowed by the existence of these degeneracies, we have cast the problem into the formalism of molecular lattice dynamics using our "split-atom method" (Giddy et al. 1993; Hammonds et al. 1994). In this approach, the only forces operating are those that mimic the forces required to distort the rigid units, and these are described using only a single force constant. This model will give a zero frequency for an RUM and a non-zero frequency for any other mode, the size of which depends directly on the distortions of the units caused by the vibrational motions. The dynamical matrix approach automatically takes account of the action of symmetry and has the advantage that it provides information about the wave vectors of the RUMs. In practice these calculations can be performed for special wave vectors only, following the approach of Hammonds et al. (1996), or calculations can be performed over a fine grid of wave vectors to yield a phonon density of states (Pryde et al. 1996).

RUM calculations are reported here for several minerals containing rigid octahedra, namely garnet, sillimanite, titanite, and ellenbergerite. The structures are drawn in Figure 1. Both garnet and titanite have a framework of corner-linked octahedra and tetrahedra. In these cases the number of constraints is straightforward to calculate. Sillimanite contains columns of edge-linked octahedra, and these columns are bridged by pairs of corner-linked tetrahedra. Each vertex of the octahedra, including those on the shared edges, are linked to tetrahedra. Ellenbergerite (Comodi and Zanazzi 1993a, 1993b) has a more complicated structure. The unit cell contains two types of octahedra, $2 \times \text{Oct}(1)$ and $6 \times \text{Oct}(2)$, and two types of tetrahedra, $2 \times \text{Tet}(1)$ and $6 \times \text{Tet}(2)$. The $\text{Oct}(1)$ octahedra form face-sharing columns along [001], and each vertex is also linked to a vertex of a $\text{Tet}(2)$ tetrahedron.

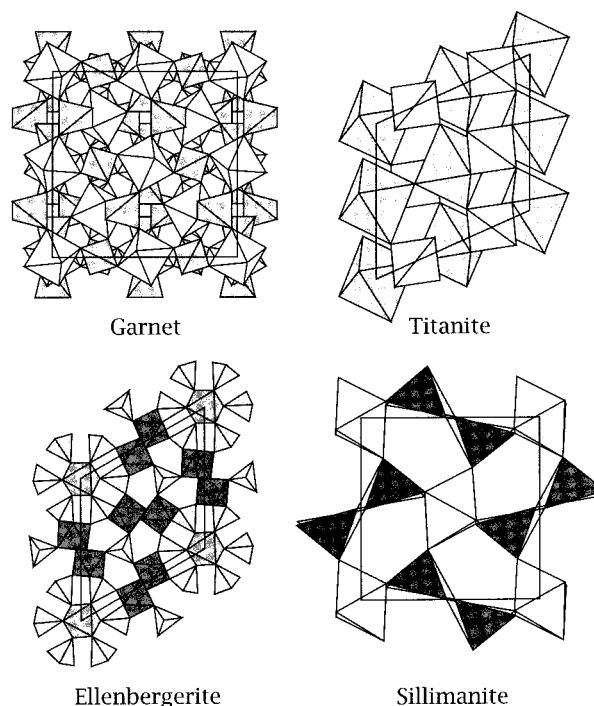


FIGURE 1. Crystal structures of garnet, titanite, sillimanite, and ellenbergerite, showing framework of linked octahedra and tetrahedra.

Each $\text{Oct}(2)$ octahedron is corner-linked to two other $\text{Oct}(2)$ octahedra, and one $\text{Tet}(1)$ and three $\text{Tet}(2)$ tetrahedra. Each $\text{Tet}(1)$ tetrahedron is linked to three $\text{Oct}(2)$ octahedra and has one non-bridging bond. Each $\text{Tet}(2)$ has one vertex linked to two $\text{Oct}(1)$ octahedra (linked to the point where these two octahedra share faces) and three $\text{Oct}(2)$ octahedra. Counting of constraints in this case requires a little more care.

For comparison we also cite results for ZrV_2O_7 (Pryde et al. 1996), perovskite (as discussed by Giddy et al. 1993), and quartz (as discussed by Hammonds et al. 1996). ZrV_2O_7 contains corner-linked ZrO_6 octahedra and VO_4 tetrahedra. Perovskite contains only corner-linked octahedra, and quartz contains only corner-linked tetrahedra. For the latter two materials we only consider the high-temperature phases.

For each of these systems we give the results from a standard Maxwell counting of N_f in Table 1. The quantity N_f/F gives a relative measure of the floppiness or stiffness of a structure. Large positive values of this indicate a greater degree of floppiness, and large negative values indicate a greater degree of stiffness. As mentioned above, for structures made from tetrahedra linked at each vertex $N_f/F = 0$. For structures made from tetrahedra only, but with some non-bridging bonds $N_f/F > 0$. On the other hand, the Maxwell counting applied to systems containing octahedra always gives $N_f/F < 0$, as we have outlined above.

TABLE 1. Enumeration of the numbers of degrees of freedom and constraints for our example materials

Mineral	Framework	Polyhedra	F	C	N_f/F
Perovskite	TiO ₃	[Oct]	6	9	-0.5
Garnet	Al ₂ Si ₃ O ₁₂	[Oct] ₈ [Tet] ₁₂	120	144	-0.2
Titanite	TiSiO ₅	[Oct] ₂ [Tet] ₂	24	30	-0.25
Sillimanite	Al ₂ SiO ₅	[Oct] ₄ [Tet] ₈	72	104	-0.444
Ellenbergerite	TiAl ₃ Si ₄ O ₁₉	[Oct] ₈ [Tet] ₈	96	120	-0.25
—	ZrV ₂ O ₇	[Oct] ₄ [Tet] ₈	72	84	-0.167
Silica	SiO ₂	[Tet] ₄	6	6	0
—	ZrW ₂ O ₈	[Oct] ₄ [Tet] ₈	72	72	0

Note: The second column gives the part of the chemical formula that comprises the crystal framework structure. The third column shows the types of polyhedra present and their relative amounts in the primitive unit cell, where [Oct] indicates an octahedron and [Tet] indicates a tetrahedron. The fourth and fifth columns give the numbers of degrees of freedom and constraints for the structure per unit cell. The sixth column gives a measure of the stiffness of the structure as given by the Maxwell counting scheme: the more negative this quantity, the stiffer the structure is predicted to be.

RESULTS

The computed densities of states are shown in Figure 2. For comparison, in perovskite there are RUMs for all wave vectors along the edges of the Brillouin zone, and in quartz there are lines of wave vectors containing RUMs as optic modes and a plane of RUMs as acoustic modes. The RUMs in the case of quartz are seen in the low-frequency parts of the density of states plot, where there is a significant enhancement of the density of states over the usual Debye ω^2 form at low frequencies. The example of quartz contrasts with all the others, where in the density of states plots follow the Debye form at low frequencies. We find that such plots give a good indication of the existence of RUMs in a system. The reader is referred to a similar comparison between the two negative thermal expansion materials ZrW₂O₈ and Zr(V,P)₂O₇ (Pryde et al. 1996), where the existence of RUMs in the tungstate is seen in a large density of states at low frequencies, whereas the absence of RUMs in the vanadate is seen by the standard Debye form of the density of states. In the case of perovskite, the density of states does not show the presence of a significant number of RUMs, but there is some excess over the Debye form at low frequencies. Although the RUMs in perovskite are well known, they actually are restricted to wave vectors along some special lines in reciprocal space, and there are far fewer RUMs than in the high-temperature phase of quartz. As a result, the density of states plot for perovskite looks more like the other materials containing octahedra than for quartz.

The results for each of the systems garnet, sillimanite, titanite, ellenbergerite, and ZrV₂O₇ (Pryde et al. 1996) are broadly the same, namely that there are no RUMs in any of these systems. We have checked the conclusion from the density of states plots by performing calculations for a wide range of specific wave vectors. This result leads to the generalization that except for special cases, such as cubic perovskite, materials with framework crystal structures containing linked octahedra will not have any RUMs, unlike framework structures containing linked tet-

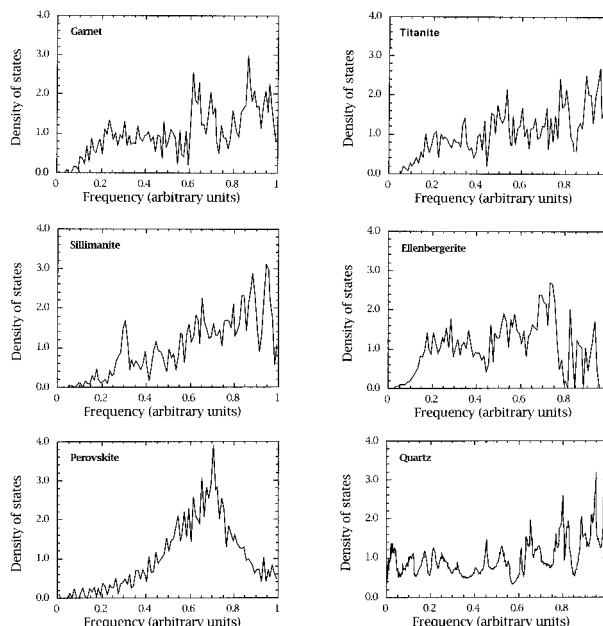


FIGURE 2. Computed phonon density of states for garnet, titanite, sillimanite, ellenbergerite, cubic perovskite, and hexagonal quartz obtained using our split-atom method as described in the text. The frequency scale is arbitrary since it is determined by the value of a single force constant whose value has been arbitrarily set to give a maximum frequency of 25 THz for quartz, but which has not been calibrated for any of the other structures.

rahedra only. We therefore need to ask what is so special about perovskite that allows it to have some RUMs, particularly when it can be seen from Table 1 that, in terms of the simple Maxwell counting scheme, it is actually the most highly constrained of the systems we have investigated. The answer in brief, as discussed in detail in Dove et al. (1996) and Dove (1997), is that the high symmetry of the cubic perovskite structure, in which the octahedra are oriented exactly in line with the crystal axes, allow many of the constraints to become degenerate. None of the other examples studied here have the same symmetric orientations of the octahedra, and so the prediction from the Maxwell counting scheme that these structures are over-constrained, and hence will have no RUMs, is confirmed by our direct calculations. The other special case is illustrated by ZrW₂O₈, which contains ZrO₆ octahedra and WO₄ tetrahedra, where the Maxwell counting scheme gives an exact balance between the numbers of constraints and degrees of freedom because one of the O vertices on the WO₄ tetrahedra is not linked to another unit (Pryde et al. 1996).

The general result that materials with frameworks containing linked octahedra only have RUMs in special cases actually provides several important implications into the behavior of these minerals. One insight that follows from our analysis is that we can now explain why polyhedra-tilting displacive phase transitions are uncommon in sys-

tems containing octahedra. Indeed the family of perovskites stands out as a special case in this respect, in contrast to the aluminosilicates with frameworks of linked tetrahedra, where these phase transitions are commonplace. The displacive phase transition in titanite (Meyer et al. 1996; Zhang et al. 1997) actually involves small displacements of the Ti cations rather than tilting of the polyhedra. Our results therefore mean that some caution needs to be applied before claiming the possible existence of displacive phase transitions in minerals with framework structures containing linked octahedra—phase transitions are more likely to arise from cation-ordering processes (Rauch et al. 1996). A second suggestion is that the formation of solid solutions in these systems will necessarily require distortions of the octahedra and tetrahedra—the crystal structures cannot accommodate the inclusion of cations with different sizes by simply allowing these polyhedra to rotate. Thus there will be a large energy cost associated with the formation of the solid solutions, and this may explain the origin of the excess enthalpies measured in the garnet solid solutions (Newton et al. 1977; Geiger et al. 1987).

In summary, our rigid unit mode analysis has suggested the general result that minerals with crystal structures built from frameworks containing octahedral units will have no easy modes of deformations except in special cases. This non-trivial result explains for the first time why polyhedral-tilting phase transitions are much less common in these materials than in aluminosilicates that contain only tetrahedra.

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