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Mechanical treatment of structural phase transitions and related phenomena in crystals: a lattice dynamical study of pressure-induced structural transformations in perovskite-like ReO_3

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Abstract. The static interatomic forces that arise in a crystal owing to the change of external thermodynamic parameters are assumed to be responsible for lattice destabilization, and simple mechanical considerations that argue for this hypothesis are given. A model treatment of the simplest perovskite-like ReO_3 is performed, which provides the possibility to understand why this crystal loses its stability under hydrostatic compression, and becomes stable again when undergoing two successive structural phase transitions.

1. Introduction

In the recent work by Mirgorodsky *et al* (1990), the role of microscopic internal tensions in the mechanism of stress-induced structural instability of a lattice has been considered from the viewpoint of lattice dynamics. It has been pointed out that the pressure dependence of the eigenvalues of the dynamical matrix of a crystal, and hence their vanishing, could result just from the direct influence of those tensions on the second-order terms of the potential function (PF) of a stressed lattice, and therefore the pressure-induced loss of its stability could be described by a mechanical model of a crystal, without departing from the convenience of the harmonic approximation of the PF.

Although this hypothesis has been successfully employed for a preliminary investigation of the ferroelastic structural phase transition (SPT) in paratellurite TeO_2 (Mirgorodsky *et al* 1990), the nature of the lattice destabilization and its connection with soft-mode behaviour have been not elucidated there in detail.

In this paper we report the results of an application of ideas, presented previously (Mirgorodsky *et al* 1990), to a lattice dynamical study of the perovskite-like ReO_3 under compression, with particular emphasis on the computed pressure-induced soft-mode behaviour at some boundary points of the Brillouin zone, which causes two successive SPTs in this crystal.

It can be said that the predisposition of several classic ABO_3 perovskites to pressure-induced SPTs related to the condensation of the BO_6 unit rotatory phonons is well documented. Although no direct experiments have been made, this property could be revealed from the measured effect on the transition temperature of hydrostatic compression. This shows that, in all cases, when the transition is associated with a softening of zone

boundary modes in the initial cubic phase, the critical temperature increases with pressure (see Samara and Peercy 1981).

ReO₃ is the unique known case when the perovskite structure has an empty A position; it is the simplest one in this family. In contrast to the ABO₃ compounds, the pressure-induced SPTs in this crystal have been directly observed by various experimental methods (see below). However, no lattice dynamical treatments for this phenomenon have been conducted until now.

The present investigation had the following objectives:

(i) We wanted to visualize the mechanism of stress-induced instability in a simple mechanical system, and to reveal some steric criteria for soft-mode behaviour, which could gain a physical insight into the nature of SPTs in ReO₃.

(ii) We wished to explore whether internal tensions arising in the ReO₃ lattice as a linear response to external pressure could be primarily responsible for the structural instabilities.

(iii) We wished to understand how structural evolution such as that which is observed experimentally for ReO₃ at increasing pressure could arise from its cubic (*Pm3m*) phase.

In section 2 we discuss the mechanism of stress-induced destabilization of a linear triatomic system, which, we believe, can provide a key to the understanding of the behaviour of a compressed three-dimensional framework consisting of adjusted octahedra. In section 3 we examine the dynamical model of the ReO₃ lattice under pressure. Section 4 contains the discussion of the results, and some concluding remarks are given in section 5.

2. Examples

First, let us consider an isolated triatomic linear molecule, which consists of a central atom O linked along the *x* axis to two immobile (massive) neighbouring atoms B by equivalent perfect springs of stiffness K_x (figure 1). In the *y* direction atom O is held by an effective potential of stiffness K_y , which may originate, in particular, from three-body forces maintaining the B-O-B angle. (It is natural to assume that $K_x > K_y$.) In the initial stress-free state of the molecule, the frequencies of its stretching and bending normal vibrations are ω_0^x and ω_0^y respectively. The object of our interest is the atomic force constant V_{yy} , which specifies the equation of bending motion, and we shall concentrate on its behaviour in the molecule under stress.

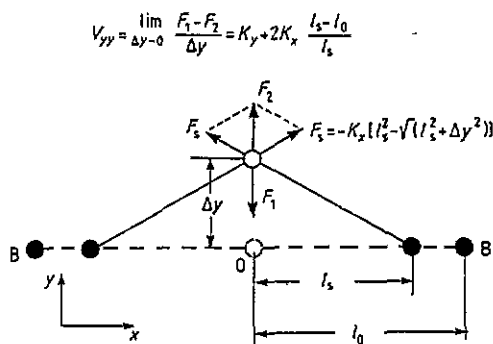


Figure 1. Forces that arise on the central atom of a linear stressed BO₂ molecule during its bending. The broken lines show the initial separation of atoms.

In the initial state the B-O bond length l is equal to l_0 , and $V_{yy} \equiv K_y$. If the molecule is contracted, i.e. $l = l_s < l_0$, forces

$$F_s = K_x(l_s - l_0) \quad (1)$$

would arise along both springs, and the effective restoring force F_y , which governs the motion of atom O along the y direction, would be simultaneously determined by harmonic force

$$F_1 = -K_y \Delta y \tag{2}$$

(Δy is atomic displacement) and by the y components of the two forces F_s (see figure 1). In accordance with definition

$$V_{yy} = -F_y / \Delta y \quad (\Delta y \rightarrow 0)$$

the following expression can be derived for the quantity under consideration:

$$V_{yy} = K_y + 2K_x(1 - l_0/l_s) \tag{3}$$

It determines the ω^y frequency of the strained molecule and decreases with the decrease of l_s . In particular, when length l_s reaches the critical magnitude

$$l_{crit} = l_0 / (1 + K_y/2K_x) \tag{4}$$

the V_{yy} value and, correspondingly, the ω^y frequency vanish, and the triatomic system becomes unstable against bending. If B-O bonds are shorter than l_{crit} , the B-O-B angle would seek to buckle, and the system would undergo the 'SPT'. Since only the O atom is involved in the normal vibrations, equation (4) can be rearranged as

$$(l_0 - l_{crit}) / l_{crit} = K_y / 2K_x = (\omega_0^y / \omega_0^x)^2 \tag{5}$$

Note that geometric and vibrational characteristics accessible for experimental measurements are directly interrelated in (5).

It is seen from figure 1 that the central question of the soft-mode concept, namely 'Where has the restoring harmonic force (F_1) gone?', is answered clearly. It is cancelled by the force (F_2) produced by interatomic tensions (F_s) originating from the contraction of the system and acting in a high-symmetry (equilibrium) configuration along the direction perpendicular to atomic displacements in the soft mode. In other words, the mechanism of destabilization of the B-O-B molecule under stress originates from a clearly mechanical effect: the O atom is exiled from its high-symmetry position by forces that in the equilibrium configuration act perpendicularly to the 'path of escape'.

It appears the above makes it possible to state some general ideas that can relate the softening of specific sorts of vibration of crystal lattices to the hydrostatic compression:

(i) The hydrostatic compression would soften rotatory vibration of a rigid polyatomic unit (molecule, complex ion, etc), if the latter occupies a special position in a lattice so that all its peripheral atoms lie on a symmetry element (rotation axis, reflection plane or inversion centre).

(ii) If the above unit contains a central atom in a special position, its out-of-special-position vibration would be softened by compression.

These statements emphasize steric aspects only and correspond to a rather speculative level of consideration; evidently, in a concrete structure much is specified by peculiarities of a lattice potential. Notwithstanding all this, instructive conclusions can be made even on such a level. As the simplest case, consider a linear one-dimensional BO lattice (chain) consisting of rigid BO₂ units linked by shared O atoms, thus forming flexible B-O-B bridges. Compression of this chain causes the total B-O-B bending stiffness to decrease. Eventually the chain becomes mechanically unstable with respect to antisynchronous

rotations of successive BO_2 units, and adopts a zig-zag configuration. We believe that this mechanism provides a key to the understanding of pressure-induced SPTs in crystals containing a framework (or layers) consisting of 'rigid' BO_6 octahedra, interconnected by shared O atoms forming linear B-O-B bridges.

In particular, the three-dimensional perovskite-like BO_3 lattice, which consists of adjusted BO_6 units and belongs to the $Pm3m$ space group (figure 2), may be regarded as being composed of three sets of mutually orthogonal linear BO chains having common atoms B. Since each chain is the source of a stress-induced structural instability, this lattice should possess a tendency to show SPTs until all three sets of chains are buckled simultaneously or in turn. In concrete perovskites (in oxides and fluorides) the effective stiffnesses of B-O-B angles (we mean that the O atom is oxygen or fluorine), as a rule, are very small. Therefore, the lowest-frequency modes in such lattices usually originate from those atomic motions which primarily change B-O-B angles or, equally, buckle BO chains. These are BO_6 unit rotations. Since they are sensitive to a contraction of the lattice (as could be seen from the above discussion), their softening and, even more, their vanishing, which gives rise to second-order SPTs, frequently occur in the perovskites as a result of a temperature decrease, or of the application of external pressure. It is typical that only two sets of the chains buckle first at some external influence; the third one stays linear for a while and can buckle later, if the influence increases (figures 2 and 3). The reason for such behaviour is beyond our simple considerations.

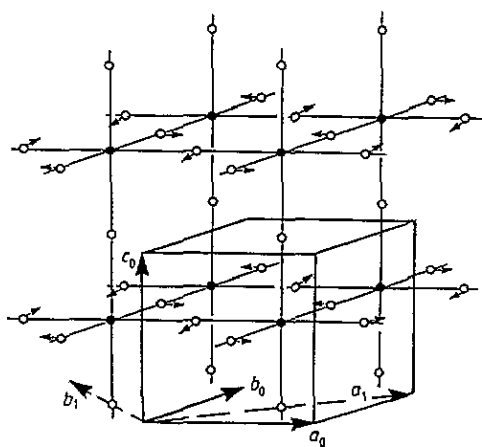


Figure 2. The simple cubic BO_3 lattice. The displacement pattern corresponds to the eigenvector of one M_3 phonon and provides the $Pm3m \rightarrow p4/mbm$ distortion. The translation vectors of the tetragonal structure are shown by broken lines.

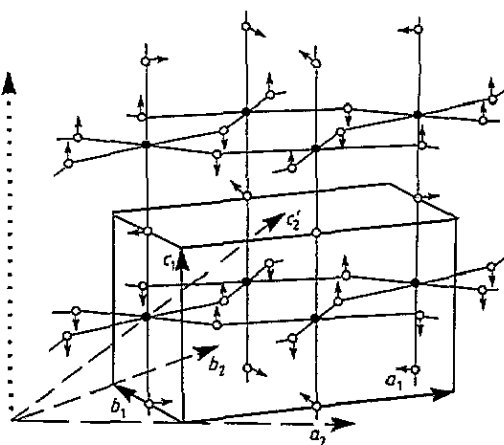


Figure 3. The $P4/mbm \rightarrow Immm$ transformation of the BO_3 lattice. The displacement pattern corresponds to the sum of the eigenvectors of two former M_3 phonons. The lattice will assume the cubic $Im3$ symmetry when all BO chains become equally buckled. The primitive cell of the orthorhombic structure is shown by dashed vectors; the dotted vector corresponds to the body-centred cell.

The lattice distortions that follow these SPTs are dictated by eigenvectors of the vanishing phonons at boundary points of the cubic Brillouin zone (BZ). These are the M points, if neighbouring octahedra along the tilt axis are tilted *in phase* about the axis (the M_3 representation), or the R point, if they are tilted *in antiphase* (the R_{25} representation) (see figure 4).

The speculativeness of the above considerations should lead us to the necessity to

test and to substantiate them by means of some experiments, and/or via a number of relevant quantitative lattice dynamical treatments; primarily, this concerns the perovskite-like structures. The ReO_3 lattice is the simplest one in the perovskite family, and seems to be the best candidate for such a treatment. Its behaviour under hydrostatic compression manifests the occurrence of pressure-induced SPTs, and there exists a great deal of experimental information about dynamical properties of ReO_3 , including frequencies of IR transmission spectra (Ishii *et al* 1976), elastic constants (Tsuda *et al* 1976, Pearsall and Coldren 1976), zone-boundary soft-mode behaviour (Axe *et al* 1985) and pressure-induced structural evolution (Jorgensen *et al* 1986).

3. The mechanical model of pressure-induced SPTs in the ReO_3 lattice

The SPT in ReO_3 was discovered by Razavi *et al* (1978) and since then has been investigated in a number of high-pressure experiments, the most recent and detailed of which is that of Jorgensen *et al* (1986). Thus, it was concluded that the structure of ReO_3 is cubic $Pm3m$ at ambient pressure ($P = 0$), tetragonal $P4/mbm$ between $P_1 = 5.0$ and $P_2 = 5.3$ kbar, and cubic $Im3$ at higher pressure. A pressure-induced softening of M_3 phonons in ReO_3 (ω_{M_3} equals 30 cm^{-1} at ambient pressure and vanishes at 5.15 kbar), observed by Axe *et al* (1985) through inelastic neutron scattering, has revealed the soft-mode mechanism of the structural transformation at $P = P_1$. This was claimed in the work by Jorgensen *et al* (1986) to be the second-order SPT with $Pm3m \rightarrow P4/mbm$ symmetry change arising via coordinated rotations of ReO_6 octahedra about one fourfold axis. The SPT at $P = P_2$ was specified in that paper as $P4/mbm \rightarrow Im3$, and was attributed to the first-order transition because of the lack of symmetry correlation.

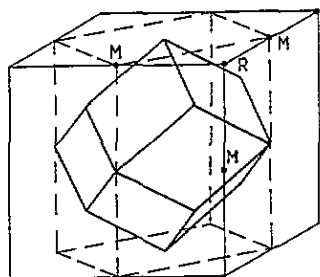


Figure 4. The cube \rightarrow tetragonal prism \rightarrow dodecahedron evolution of the first BZ corresponding to the $Pm3m \rightarrow P4/mbm \rightarrow Im3$ succession of SPTs in the ReO_3 lattice.

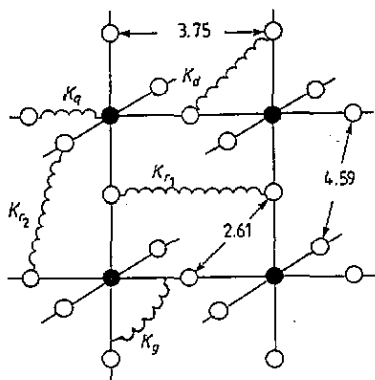


Figure 5. Fragment of the ReO_3 undistorted lattice. Internal coordinates involved in the GVFF are shown by springs, and corresponding interatomic distances are indicated (\AA).

A noticeable hint at the possibilities of SPTs in ReO_3 could be seen in the earlier lattice dynamical calculations by Ishii *et al* (1976), where a very simple general valence force field (GVFF) was used to describe elastic and vibrational properties of this crystal. Only three diagonal parameters related to the Re-O stretching (K_q), to the octahedron edge O-O stretching (K_d) and to the O-Re-O bending (K_g) were adopted there (see figure 5). Their magnitudes, 4.17, 0.05 and $0.23 \text{ mdyn \AA}^{-1}$, respectively, being uniquely

derived from three measured elastic constants, $C_{11} = 5.72 \times 10^{12}$, $C_{12} = 0.07 \times 10^{12}$ and $C_{44} = 0.68 \times 10^{12}$ dyn cm⁻², have provided quite satisfactory agreement between the vibrational frequencies found in the IR transmission (905 and 315 cm⁻¹) and the calculated ones (991, 354, 329 cm⁻¹). Among these the highest corresponds to the Re–O–Re stretching, while two others correspond to O–Re–O bendings. Since both M_3 and R_{25} phonon frequencies were obtained identical to zero in that work, the occurrence of zone-boundary instabilities in ReO₃ could be suspected.

It is remarkable that the measured elastic and vibrational properties of ReO₃ give us a fortunate opportunity to realize some sort of the '*experimentum crucis*' concerning the validity of formula (5), and thereby to estimate the plausibility of our basic idea. Really, the linear Re–O–Re bridge can be regarded as an analogue of the triatomic system in figure 1 (the huge mass of rhenium makes it practically immobile). Thus the left-hand side of formula (5) actually describes the relative change of linear dimensions of the ReO₃ lattice at the moment of Re–O–Re buckling at $P = P_1$, and this formula may be reduced to view $kP_1 = (\omega_0^y/\omega_0^x)^2$. Here k is the linear compressibility of ReO₃, whose experimental magnitude is about 1.74×10^{-4} kbar⁻¹ (Pearsall and Coldren 1976, Tsuda *et al* 1976, Schirber and Morosin 1979, Batlogg *et al* 1984). By assigning experimental frequencies of 905 and 30 cm⁻¹ to ω_0^x and ω_0^y values respectively, we derive from the above equation the 6.3 kbar magnitude for pressure P_1 , which can be regarded as quite reasonable, taking into account the oversimplified manner of its estimation.

In our study of the ReO₃ lattice dynamics we have focused *exclusively* on the pressure-induced behaviour of ReO₆ rotation modes belonging to M and R points of the BZ of the initial *Pm3m* structure. The force field derived by Ishii *et al* (1976) was essentially intra-octahedral and therefore could not provide non-vanishing frequencies of those modes. To improve it, we have added, as a first step, the potential of the shortest inter-octahedral contacts r_1 (see figure 5), described by springs of stiffness K_{r_1} , which correspond to oxygen atoms, separated by one translation of 3.7504 Å (structural data from Jorgensen *et al* (1986) were used throughout this work). This led to non-zero frequencies of M_3 and R_{25} phonons, but kept them equal in value ($\omega_{M_3} = \omega_{R_{25}}$).

The dynamical effect of lattice compression was simulated in our work through two-body tensions f_q , which were computed as a linear response to the appearance of external stress, and automatically were included as components of atomic force constants (see Mirgorodsky *et al* 1990). Thus it has been established that the hydrostatic compression provided an equal decrease of $\omega_{R_{25}}$ and ω_{M_3} values, i.e. they should vanish simultaneously at a certain pressure $P > 0$. Since this was not the case for ReO₃, the problem to make $\omega_{R_{25}} > \omega_{M_3}$ arose at the first step of our calculations. If two adjusted ReO₆ octahedra are regarded as a unit Re₂O₁₁, the M_3 phonon may be visualized as its rotation as a whole around the fourfold axis, whereas the R_{25} phonon corresponds to its torsion. Thus the condition $\omega_{R_{25}} > \omega_{M_3}$ could be maintained by a certain inter-octahedral potential counteracting this torsion; therefore one more force constant K_{r_2} was added to the PF of ReO₃. This described the stiffness of the next (after r_1) oxygen–oxygen contacts r_2 with length 4.593 Å (figure 5).

So, the GVFF of ReO₃, used in our work, contained five parameters: three intra-octahedral force constants estimated by Ishii *et al* (1976) were complemented by the inter-octahedral ones, $K_{r_1} = 0.0018$ and $K_{r_2} = 0.0003$ mdyn Å⁻¹. The magnitudes of the latter were adopted to reproduce the ω_{M_3} frequency at ambient pressure, and to give some reasonable estimate of $\omega_{R_{25}}$. All these parameters were kept fixed during our further calculations, and pressure-induced evolution of M_3 and R_{25} phonons was due to two factors only:

- (i) increase of internal tensions f_q , which altered atomic force constants; and
- (ii) changes of the lattice geometry.

Strictly speaking, to explore the mode behaviour as a function of increasing pressure, the lattice energetics must be considered explicitly, and the quantities of interest must be evaluated for a lattice geometry and for internal tensions that provide a minimum of the interatomic energy for a given pressure. The possibilities of such an approach within the framework of the GVFF will be analysed in our following paper devoted to the model investigation of the 'compressibility collapse' in ReO_3 .

In the present paper we have followed a less consistent method, used previously (Mirgorodsky *et al* 1990), in which we regarded lattice geometry and external pressure as independent factors that determine the internal tensions via the fulfilment of equilibrium conditions. In this way we could attempt to study separately the influence of those factors on the mode variation, and hence to visualize their roles in the destabilization mechanism.

The results of the calculations are collected in table 1. Case A represents M_3 and R_{25} phonon frequencies for $P = 0$. Only one structural parameter ($a_0 = b_0 = c_0$) is free for the $Pm\bar{3}m$ lattice. Therefore the sole tension of Re–O bonds (labelled below as f_q) sufficed to satisfy equilibrium conditions in this phase for $P > 0$. For $f_q = 0.0082$ mdyn corresponding to pressure $P_1^{\text{calc}} = 5.84$ kbar, the ω_{M_3} frequency vanished, while $\omega_{R_{25}}$ was 9.3 cm^{-1} (case B). This meant the loss of lattice stability against the distortion described as any combination of three M_3 phonons. In accordance with the data presented by Jorgensen *et al* (1986), we have described this distortion through coordinated rotations of rigid ReO_6 octahedra around $[001]$ axes, i.e. through the eigenvector of the M_3 phonon at point $(\pi/a_0, \pi/a_0, 0)$ (figure 2). Owing to this distortion, the lattice would transform from cubic $Pm\bar{3}m$ structure to tetragonal $P4/m\bar{b}m$ with doubling of the unit cell in the xy plane ($a_1 \simeq \sqrt{2}a_0$, $c_1 \simeq c_0$). Its cube-like first BZ becomes a tetragonal prism. As a consequence, the M point $(\pi/a_0, \pi/a_0, 0)$ shifts to the Γ point $(0, 0, 0)$, two other M points merge together at corner $(\pi/a_1, \pi/a_1, \pi/c_1)$, and the R point assumes the $(0, 0, \pi/c_1)$ position (see figure 4).

To fulfil the equilibrium conditions in this new phase, three internal tensions were considered, namely, f_{q_1} for Re–O bonds lying in the xy plane, f_{q_2} for Re–O bonds along the z axis, and f_{r_1} for those r_1 inter-octahedral contacts whose length was shortened owing to the $Pm\bar{3}m \rightarrow P4/m\bar{b}m$ deformation. The behaviours of former M_3 and R_{25} phonons in the tetragonal phase of ReO_3 are shown as cases C, D, E and F of table 1. The first three of them correspond to a fanciful situation, when pressure $P = P_1^{\text{calc}}$ remains constant, while the lattice is being progressively distorted via rotations of ReO_6 octahedra; column F demonstrates a net effect of pressure increase.

As follows from case C, the tetragonal distortion, itself, stabilizes the lattice kinematically — even a slight tilt of ReO_6 octahedra for angle $\alpha \simeq 0.5^\circ$ around $[001]$ axes provides a noticeable increase of the just-vanished phonon frequency at the Γ point, and to a certain extent ($\Delta\omega^2 = 36 \text{ cm}^{-2}$) hardens one of the low-frequency vibrations at point $(0, 0, \pi/c_1)$. Both these most strain-sensitive modes correspond to ReO_6 rotation vibrations around $[001]$ axes (R_z).

The distortion-induced stabilization of the tetragonal lattice against degenerate rotations R_x and R_y at the $(\pi/a_1, \pi/a_1, \pi/c_1)$ point also took place (cases D and E), but was much slower. Even for case E corresponding to the experimental lattice geometry just before the second SPT, which destroys the $P4/m\bar{b}m$ symmetry, the kinematical hardening of former M_3 phonons at point $(\pi/a_1, \pi/a_1, \pi/c_1)$ was only about 4.5 cm^{-1} ($P = P_1^{\text{calc}}$, $f_{q_1} = 0.0078$, $f_{q_2} = 0.0082$, $f_{r_1} = 0.00083$ mdyn). Note that internal tensions in the buckled chains are less than those in the linear ones ($f_{q_1} < f_{q_2}$). This confirms the opinion of Jorgensen *et al*

Table 1. The calculated dependence of R₂₅ and M₃ phonon frequencies ω (cm⁻¹) on pressure P (kbar) and on ReO₆ rotation angles α and β (degrees).

BZ point	Cubic Pm3m (a ₀ = b ₀ = c ₀)			Tetragonal P4/m3m (a ₁ = b ₁ ≅ √2a ₀ , c ₁ ≅ c ₀)						Orthorhombic Immm (a ₂ ≅ b ₂ ≅ c ₂ ≅ 2a ₀)			Cubic Im3 (a ₃ = b ₃ = c ₃ ≅ 2a ₀)			
	Case A	Case B	BZ point	Case C	Case D	Case E	Case F	Case G	Case H	Case I	Case G	Case H	Case I	Case G	Case H	Case I
π (1/2, 1/2, 1/2)	P = 0 α = 0 β = 0	P = P ₁ ^{calc} = 5.84 α = 0 β = 0	π (0, 0, 1/2)	P = 5.84 α ≅ 0.5 β = 0	P = 5.84 α = 1 β = 0	P = 5.84 α = 3 β = 0	P = P ₂ ^{calc} = 6.1 α = 3 β = 0	P = 6.1 α = 3 β ≅ 0.5	P = 6.1 α = 3 β = 2.5	P = 7.3 α = 6.65 β = 6.65	P = 6.1 α = 3 β ≅ 0.5	P = 6.1 α = 3 β = 2.5	P = 7.3 α = 6.65 β = 6.65	P = 6.1 α = 3 β ≅ 0.5	P = 6.1 α = 3 β = 2.5	P = 7.3 α = 6.65 β = 6.65
π (1/2, 1/2, 0)	31.9 31.9 31.9	9.3 9.3 9.3	π (0, 0, 1/2)	9.3 9.3 11.0	9.3 9.3 18.0	9.3 9.3 51.0	7.7 7.7 51.0	9.6 9.6 52.0	51.7 51.7 61.0	56.0 56.0 58.0	9.6 9.6 52.0	51.7 51.7 61.0	56.0 56.0 58.0	9.6 9.6 52.0	51.7 51.7 61.0	56.0 56.0 58.0
π (1/2, 0, 1/2)	30.5	0	(0, 0, 0)	6.1	15.0	50.7	50.0	51.0	84.0	85.0	51.0	84.0	85.0	51.0	84.0	85.0
π (1/2, 0, 1/2)	30.5	0	π (1/2, 1/2, 1/2)	0.5	1.5	4.5	0	4.6	32.0	34.0	4.6	32.0	34.0	4.6	32.0	34.0
π (0, 1/2, 1/2)	30.5	0	π (1/2, 1/2, 1/2)	0.5	1.5	4.5	0	4.8	35.0	34.0	4.8	35.0	34.0	4.8	35.0	34.0

al (1986) concerning the relaxation effect arising in ReO_3 after the $Pm3m \rightarrow P4/mbm$ distortion.

Case F shows that a small pressure increase of 260 bar ($P = P_2^{\text{calc}} = 6.10$ kbar, $f_{q_1} = 0.0083$, $f_{q_2} = 0.0088$, $f_{r_1} = 0.00088$ mdyn) cancels the effect of kinematical stabilization of the $P4/mbm$ phase, and the pair of lowest-frequency modes at the $(\pi/a_1, \pi/a_1, \pi/c_1)$ point vanishes, making the lattice unstable again. The relevant phonon condensation should reduce the symmetry of the crystallographic class from tetragonal D_{4h} to orthorhombic D_{2h} . This corresponds to results obtained by Glazer (1975), according to which any in-phase tilt of the octahedra about an axis lying in the xy plane transforms the $P4/mbm$ (D_{4h}^5) perovskite structure into $Immm$ (D_{2h}^{25}) (figure 3). In the $Immm$ phase ReO_3 has a body-centred lattice with a double (relative to the $P4/mbm$ structure) primitive unit-cell volume, and its first BZ is a slightly distorted dodecahedron (figure 4). It is noteworthy that ReO_3 enters this phase in having two just-vanished phonons at the Γ point and a couple of zone-boundary phonons at point $(0, 0, \pi/c_1)$, which have manifested steady softening during pressure variation from zero up to P_2^{calc} (31.9 and 7.7 cm^{-1} respectively). On the other hand, we have revealed that it was the structural distortion that kinematically stabilized the lattice in the tetragonal phase, and hence we might anticipate that the orthorhombic phase would be stabilized similarly. To establish whether or not this was the case, we have made a series of calculations to study the mode behaviour during structural deformations produced by equal antisynchronous rotations of ReO_6 octahedra through angles β around twofold axes in the xy plane. This corresponded to the change of atomic coordinates in the primitive cell, derived from the sum of two 'freezing-in' phonon eigenvectors (see figure 3).

Cases G and H show quite definitively that orthorhombic distortion of ReO_3 at P_2^{calc} provides a steep increase of frequencies of former soft phonons. This led us to the conclusion that the $Immm$ modification of ReO_3 had no further tendency to pressure-induced destabilization related to ReO_6 octahedron rotations, and that a further increase of pressure had to be accompanied by 'normal' continuous structural evolution of the lattice, owing to which it should stabilize in approaching asymptotically the cubic $Im3$ symmetry (see below). Case I represents the results of calculations performed for $P = 7.30$ kbar with the $Im3$ lattice geometry found for this pressure by Jorgensen *et al* (1986). These demonstrate that the joint effect of the lattice distortion increase and of the corresponding internal tension variations provides stabilization of the lattice.

4. Discussion

Let us consider the computational results. These show that the present mechanical model of ReO_3 simulates the appearance of two pressure-induced instabilities in this crystal related to the sequential vanishing of M_3 phonons at different P_1^{calc} and P_2^{calc} pressures whose magnitudes are in reasonable agreement with experimental data. It is significant that no fitting was used to describe such mode behaviours, and it can be said that the destabilization agent, i.e. the bond tension effect, is present in our study as a model-independent mechanical property of the lattice.

In our case the consistency of these bond tensions with the GVFF of ReO_3 can be checked by comparison of their magnitudes, derived in this work from equilibrium conditions for the lattice under increasing pressure, and those calculated just from Hooke's law as

$$f = -K \Delta l. \quad (6)$$

Here K is the stiffness of a bond whose length change Δl is produced by pressure P . Thus, in estimating the variation of Re-O bonds at pressure $P \leq P_1$ as $\Delta l = l_0 k P$, we obtain

$f_q(P_1) = K_q l_0 k P_1 = 0.0080$ mdyn, which is practically equal to the magnitude mentioned above for case B.

It can be seen from table 1 that the evolution of the tetragonal phase in the pressure range P_1^{calc} to P_2^{calc} results from competition between the two factors indicated above: (i) the internal tension increase, which destabilizes the lattice against the buckling of linear Re–O–Re chains passing along the [001] direction, i.e. against coordinated tilts of ReO_6 octahedra about an axis lying in the xy plane; and (ii) the progressive lattice distortion (specified by angle α of octahedron rotation around [001]), which makes the lattice more stable.

While the role of factor (i) rises linearly with pressure, the α angle–pressure dependence is non-linear so that $d\alpha/dP \rightarrow \infty$ at $P = P_1$, as follows from the data of Jorgensen *et al* (1986). Therefore, factor (ii) would dominate just above P_1 and, hence, keep the lattice stable during a certain pressure increase until factor (i) begins to prevail, owing to which the lattice eventually loses its stability at pressure P_2 .

According to the present work, the stress-induced symmetry evolution of ReO_3 is $Pm3m \rightarrow P4/mbm \rightarrow Immm \rightarrow Im3$, which corresponds to the succession of second-order SPTs, whereas Jorgensen *et al* (1986) have described it as $Pm3m \rightarrow P4/mbm \rightarrow Im3$, where the last symmetry change implied the first-order SPT. Let us discuss this divergence in more detail by appealing to the paper by Glazer (1975).

Coordinated rotations of ReO_6 octahedra around three cubic axes through equal angles must transform the initial cubic $Pm3m$ structure into the cubic $Im3$ irrespectively of how these rotations are performed, simultaneously or one after another. Let, at first, ReO_6 octahedra in the $Pm3m$ lattice be tilted around [001] axes by angle α , and the symmetry of the space group be lowered to $P4/mbm$. If, then, ReO_6 octahedra undergo equal rotations around both [100] and [010] axes through angle $\beta < \alpha$, the lattice assumes $Immm$ symmetry, and the difference between α and β angles would provide a measure of the deviation of the orthorhombic $Immm$ structure from cubic $Im3$.

Evidently, if angle β continues to increase, the lattice will reach the cubic $Im3$ symmetry when β becomes equal to α . The geometric considerations by Glazer (1975) and the results of our present work suggest that the ReO_3 lattice may be converted continuously from the tetragonal $P4/mbm$ into the cubic $Im3$ structure necessarily via the intermediate $Immm$ phase, which was not revealed in the work by Jorgensen *et al* (1986), where this transformation has been specified as discontinuous.

It appears that the divergence in results could be understood within the framework of the following scenario. Owing to the condensation of one M_3 phonon at $P = P_1$, ReO_6 octahedra begin to turn around [001] axes by angle α , and Re–O chains in the xy plane buckle, whereas ones along the rotation axis stay undistorted. According to Jorgensen *et al* (1986), angle α varies with pressure as $\alpha \sim (P - P_2)^n$, $n = 0.322$. Correspondingly, derivative $d\alpha/dP$ is very large just above P_1 but quickly decreases at higher pressure.

At $P = P_2$ linear Re–O chains along the [001] direction lose their stiffness against buckling, and at pressure $P > P_2$ the ReO_6 octahedra begin to tilt through angle β around the former [100] and [010] directions with the same pressure dependence for angle β as that for angle α . As a result, the lattice assumes the $Immm$ symmetry, and stays orthorhombic until α and β angles become equal. At the moment $P = P_2$ angle α is about 3.6° , while β is zero, but $d\beta/dP \gg d\alpha/dP$; therefore angle β very quickly ‘overtakes’ angle α , and these quantities practically coincide at a small increase of compression. In particular, at pressure $P_2 + 2$ kbar, which corresponds to 7.3 kbar in the work of Jorgensen *et al* (1986), the $\alpha - \beta$ difference is about 0.2° , and the distinction between the actual symmetry and the $Im3$ one is so slight that it could be easily missed.

It is well known (see e.g. Glazer 1975, Scott 1976) that many diffraction studies of perovskite structures near SPTs have suffered from such difficulties, which accounted for a number of incorrect works. In this connection, it should be emphasized that the data presented by Jorgensen *et al* (1986) lead to a volume compressibility of ReO_3 in the $Pm3m$ phase of about $10.4 \times 10^{-4} \text{ kbar}^{-1}$, which is twice as much as that found independently by different groups (Pearsall and Coldren 1976, Tsuda *et al* 1976, Schirber and Morosin 1979, Batlogg *et al* 1984).

Thus, we venture the opinion that above P_2 the ReO_3 lattice is orthorhombic $Immm$ on a microscopic level, but, at increasing compression, it asymptotically evolves to cubic $Im3$ symmetry. In particular, for the pressures used in the diffraction experiments (7.3 kbar and more), it does not differ from the $Im3$ structure within experimental uncertainty. We believe that this can reconcile the contradiction under discussion.

Special attention should be paid to the mechanism of lattice stabilization after the SPTs. Within the framework of our model it originates from a purely kinematic effect. In particular, the post-transition hardening of the rotatory soft mode whose vanishing is responsible for the SPT at $P = P_1$ could be explained as follows. In the highest-symmetry phase its frequency is determined by weak inter-octahedral springs without any contribution from the much stronger intra-octahedral ones. When the lattice is distorted via the M_3 phonon condensation, this restriction fails, and both intra- and inter-octahedral forces would govern this mode jointly. In so far as the contribution of the former forces increases with the lattice distortion, some sort of kinematical self-stabilization mechanism arises.

It is highly likely that ReO_3 is not a unique case when such a mechanism occurs. In particular, according to Scott (1983), this is a purely steric effect that stiffens the rotatory vibration of PO_4 tetrahedra in the monoclinic phase of $\text{LaP}_5\text{O}_{14}$ just after the $D_{2h}^{16} \rightarrow C_{2h}^5$ ferroelastic SPT, triggered by its softening in the high-symmetry phase. We can point out also that it is clearly seen from a number of dynamical models of quartz (e.g. Barron *et al* 1976, McMillan and Hess 1990) that a similar effect provides the increase from zero up to $\approx 200 \text{ cm}^{-1}$ of the frequency of the rotatory vibration of SiO_4 units (soft mode) in the quartz lattice, when the latter undergoes evolution on cooling from T_c to room temperature. A detailed lattice dynamical treatment of this evolution including the modelling of the pressure-induced $\beta \rightarrow \alpha$ SPT in quartz will be discussed elsewhere (Mirgorodsky 1993).

One more source of post-transition lattice stabilization can be suggested. This has essentially anharmonic nature and originates from the sharp shortening of certain interatomic bonds (or contacts) in a just-distorted crystal, owing to which actual stiffnesses of these bonds necessarily would increase, and therefore the lattice would restore its stability. In particular, such an anharmonic effect was found to be predominant in the stabilization mechanisms of paratellurite TeO_2 in the ferroelastic phase (Mirgorodsky and Grigor'eva 1992), and of La_2CuO_4 just after the $D_{4h}^{17} \rightarrow D_{2h}^{18}$ SPT (Mirgorodsky *et al* 1993). The lack of relevant experimental information for ReO_3 does not give us the possibility to discuss it in this present paper.

5. Concluding remarks

The above results seem to be quite promising in that they demonstrate that the simplest dynamical model of a crystal, dealing with the interatomic springs and their tensions, suffices to explain why a high-symmetry lattice under compression loses its stability and, correspondingly, undergoes a spontaneous deformation owing to which it becomes stable again.

Since the presence of internal tensions in a lattice is a fundamental intrinsic property of a crystal (see e.g. Nielsen and Martin 1985), those must be involved in a lattice dynamical treatment irrespectively of their source. Note that in our model the tensions could be simply derived with the help of equation (6) for a given set of internal strains Δl . The latter may have their origin in a change of temperature, and thus the mechanism of temperature-induced SPTs can be examined. In this case the notion of temperature-induced internal tensions would be adopted.

It appears, generally, that the model enables one to take into account the influence on the PF of the some external action, if the corresponding microscopic strain pattern is known, and thereby to consider its effect on the dynamical properties of the lattice. In particular, in the case when this effect dominates in the mechanism of the external-action-induced destabilization of a crystal, the model can provide a simple tool to study it. We believe that such cases are not so rare.

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