PHYSICAL REVIEW B VOLUME 48, NUMBER 18 1 NOVEMBER 1993-II

Lattice dynamics and prediction of pressure-induced incommensurate instability of a β-Si_3N_4 lattice within a simple mechanical model

A. P. Mirgorodsky*
Institute for Silicate Chemistry, Russian Academy of Sciences, Odoevskogo Street 24, corpus 2,
Saint Petersburg 199155, Russia

M. I. Baraton and P. Quintard
Laboratory of Ceramic Materials, LMCTS, Faculty of Sciences, 123 Avenue Albert Thomas, F-87060 Limoges, France

(Received 10 May 1993)

The dynamical properties of β-Si_3N_4 (C_{6h}^2) have been investigated within the framework of a simple phenomenological model, based on a short-range pair potential. In developing the model, we have discussed some structural peculiarities of the lattice, which argue for the possibility of its pressure-induced destabilization, caused by interatomic bond tensions arising as a response to external influence. Thus, the nature of the instability can be attributed to a purely mechanical effect whose description does not require any *ad hoc* model parameters. The simulation of the hydrostatically compressed lattice has demonstrated the vanishing of a low-frequency mode inside the Brillouin zone ($k=0,0,0.36$) at a pressure of 72 kbar, thus predicting a second-order phase transition to a structure with incommensurate modulation along the z direction. Since the destabilization of β-Si_3N_4 has never been observed, in contrast to the α (C_{3v}^4) $\Longrightarrow$ β (C_{6h}^2) conversion, this theoretical result has been considered in detail, including aspects of its reliability and of the possibility of the β-α structural transformation proceeding via an intermediate incommensurate phase.

I. INTRODUCTION

Various computational methods originating from lattice-dynamical theory are presently available, ranging from the simplest ones, based on two-body interatomic potentials, to the most elaborate which use *ab initio* electronic-structure and energy calculations. Their application to materials science and to fundamental solid-state problems is of special interest when direct experimental studies of the substance under consideration are not possible. Silicon nitride, Si_3N_4, is a particular example of such a material. Although it is of tremendous engineering importance, little is known in detail about its dynamical properties. This is primarily due to the unavailability of Si_3N_4 in the form of single crystals required for measurement. Up to now, the experimental information is limited by IR and Raman spectra of polycrystalline specimens,[1,2] and by compressibility coefficients, derived from powder diffraction studies at high pressure.[3]

Unlike a number of computational works devoted to the electronic properties of Si_3N_4 (Refs. 4,5), to our knowledge no lattice-dynamical-model investigations of this material have been performed, except for a recent work of Wendel and Goddard[6] that dealt with a number of fundamental physical characteristics. Among their results compared with measured values were compressibility coefficients and optically (IR- and Raman-) active phonon frequencies. The former beautifully reproduced the experimental magnitudes, whereas the latter provided a reasonable agreement with observed bands of high-frequency (stretching) vibrations, and approximately corresponded to the lower frequency part of the spectrum.

The main objective of the present paper is beyond the scope of problems covered in the above work. We wished to investigate the mechanical stability of the β-Si_3N_4 lattice at high pressure. Our interest in this topic was stimulated by some preliminary considerations (see below), mainly qualitative, predicting a pressure-induced softening of some low-frequency modes of this lattice, which eventually could lead to a structural phase transition. Therefore, we wanted to check this hypothesis numerically. To reveal the physical essence of the matter, we chose an extreme simplification of the interatomic potential model, thus presenting an approach diametrically opposed to that of Ref. 6.

The description of the β-Si_3N_4 structure, given in Sec. II, can be regarded as a starting point for our basic concept which is briefly outlined in Sec. III. Details of the model are considered in Sec. IV, while results and discussion are given in Sec. V. Section VI contains concluding remarks.

II. STRUCTURE

In contrast to the great variety of silicon oxide and silicon carbide crystalline structures, the Si_3N_4 silicon nitride family consists of two members only, α and β phases. Both are stable at ambient conditions. The higher symmetry β phase has a hexagonal lattice (space groups $C_{6h}^2, N176$) with a primitive cell containing two Si_3N_4 formula units ($a=7.606$ Å, $c=2.909$ Å). The lower symmetry α phase is trigonal ($C_{3v}^4, N159$) and has a primitive cell nearly twice as large ($a=7.746$ Å, $c=5.619$ Å) with twice as many atoms.[3] Both structures consist of SiN_4 tetrahedra forming three-dimensional networks with each N corner common to three tetrahedra. As concerns NSi_3 polyhedra, these have pyramidlike form in the α phase, whereas the β phase can be regarded as being built of planar $N2Si_3$ and nearly planar $N1Si_3$ triangles with each Si corner common to four triangles which are oriented perpendicular to the direction (001) or along it (Fig. 1).

All atoms in β-Si_3N_4 are located in mirror planes, the threefold rotation axis passing through each nitrogen N2. As a specific structural unit of the β-Si_3N_4 lattice, the sequence of SiN_4 tetrahedra repeated by translation along z can be considered. The tetrahedra are oriented such that the longest edges coincide with vector c, thus forming a linear chain of nitrogen atoms. Six equivalent sequences pass through the primitive cell. Three of these, having common N2 atoms, compose a trihedral whatnotlike column in which shelves are planar $N2Si_3$ groups. It has the C_{3h} point symmetry. Thus, through each cell two such columns pass, being interrelated by diad and hexad screw axes. In totality, they compose the β-Si_3N_4 lattice as a honeycomblike structure with empty tunnels along those axes (see Fig. 1).

The α structure is more difficult to visualize.[3,7] Here we emphasize that all NSi_3 triangles are warped in this lattice, and there are two sorts of sequences consisting of nonequivalent tetrahedra which are twisted with respect to one another by about 60°–70° around z. Accordingly, the above-mentioned nitrogen chains are buckled, which doubles the translation vector c. The local short-range atomic structure of α-Si_3N_4 is very much like the β phase with only slightly broader bond-length and bond-angle distribution.[8]

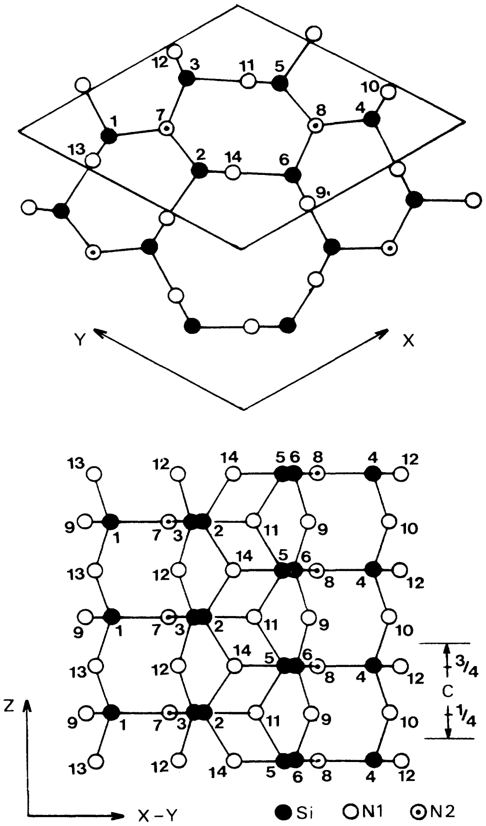

FIG. 1. Projections of the β-Si_3N_4 structure. The numbering of atoms corresponds to the contents of the primitive cell shown at the top.

As to the polymorphism, the $\alpha \Longrightarrow \beta$ conversion ($C_{3v} \Longrightarrow C_{6h}$) takes place with rising temperature. This effect was discussed in a number of works (see e.g., Refs. 9 and 10, and references therein), but, to the best of our knowledge, there have been no studies aimed at understanding the transition mechanism on the microscopic level.

III. CONCEPT AND METHOD

In the language of lattice dynamics, the basic idea[11] of the present model's approach to the pressure-induced lattice destabilization is that interatomic forces arising in the crystal as a response to its compression would alter the atomic force-constant matrix and soften certain vibrational modes of the lattice; eventually one of them could vanish because the lattice would cease to be mechanically stable.

It has been pointed out in Ref. 11 that the alteration of atomic force constants would necessarily arise even if the lattice is considered as a "balls and perfect springs" static system whose potential function is truncated at the second-order terms (the harmonic approximation). Actually, let the above-mentioned springs be specified by their lengths q and by Hooke's coefficients (stiffnesses) K, and let the lattice be under external isotropic pressure P. This means that all springs are stressed and hence, produce interatomic forces (bond tensions) which we label F. The physical and methodological self-consistency of the model implies that the next two conditions are satisfied (matrix contraction is used in formulas given below):

(i) there is no net force acting on any atom,

$$B_x F = 0 \; ; \tag{1}$$

(ii) external pressure P is balanced by internal tensions F,

$$B_u F = -P \tag{2}$$

(matrices B_x and B_u are determined by lattice geometry).

The internal energy variation ΔV, caused by the change of lattice geometry, can be written on the basis of interatomic length changes, so-called q coordinates,

$$\Delta V = F \Delta q + \tfrac{1}{2} \Delta q K \Delta q \; , \tag{3}$$

or on the basis of Cartesian atomic displacements x,

$$\Delta V = \tfrac{1}{2} x V_{xx} x + \cdots \; , \tag{4}$$

where V_{xx} is the atomic force-constant matrix. The Δq and x quantities are interrelated via the Taylor series,

$$\Delta q = B_x x + \tfrac{1}{2} x B_{xx} x + \cdots \; . \tag{5}$$

The substitution of (5) in (3) provides condition (1), reflecting the vanishing of the linear term in (4), and gives the following exact expression for the matrix V_{xx}:

$$V_{xx}=B_x K B_x + B_{xx} F \ . \tag{6}$$

This represents in a general view the well-known result of the lattice-dynamical theory:[12] A short-range potential, whatever its form, contributes to the V_{xx} two components, a radial (longitudinal) one which is described by the first term in the right-hand side of (6), and a tangential (transverse) one corresponding to the second term. We wish to emphasize that the pressure dependence of the V_{xx} value is essential in an internally consistent mechanical model of a crystal, since a tangential part of V_{xx}, in fact, is formed by forces F depending upon the external pressure via Eq. (2). Note that this conclusion was obtained taking no account of the anharmonic part of the potential function [i.e., higher than second-order terms in (4)]. Therefore, the pressure-induced behavior of phonon modes can be analyzed within such a model without departing from the convenience of the standard harmonic approximation in the lattice dynamics.

Recall now, that in the equation of atomic vibrations, the tangential part of the V_{xx} value specifies forces which act perpendicularly to lines connecting the interacting atoms. The effect of these forces on frequencies depends upon the sign of the tensions F. More detailed consideration[13] allows one to make the following statements: if a lattice contains some symmetrical fragments occupying special positions, for example, straight chains, linear bridges B-A-B, or planar "starlike" AB_n units consisting of a central atom A and n bonds (rays) A-B, the compression of these fragments, i.e., the appearance of negative bond tensions F, should soften bending vibrations of the above-mentioned chains or of B-A-B bridges, as well as out-of-plane vibrations of the AB_n units. Eventually, any of these vibrational modes can vanish and the corresponding structural fragments can buckle (warp) in lowering the symmetry of the lattice, i.e., in inducing a structural phase transition.

To apply the above ideas to the β-Si_3N_4 lattice, some correlation between its structure and vibrational spectrum is desirable to begin with. First, let us recall that the experience of the qualitative analysis of vibrations of ionic-covalent frameworklike lattices[14] teaches us that it is reasonable to specify high-frequency modes of their spectra as motions of relatively light atoms in local potential wells, produced by more massive nearest neighbors. In particular, the motion of symmetric and antisymmetric vibrations of T-O-T bridges was found to be quite adequate in describing stretching vibrations in the spectra of oxide frameworks containing twofold coordinated oxygen atoms.[15]

In the case of the silicon nitride framework, it appears that the NSi_3 triangles can be chosen for this goal (see Ref. 16). The primitive cell of β-Si_3N_4 consists of eight such units. Among those, two are strictly planar ($N2Si_3$), and the remaining six are nearly planar (the altitude of the $N1Si_3$ pyramid is about 0.04 Å only). Thus, in-plane motions of nitrogen atoms in NSi_3 triangles, classified as Si-N stretching vibrations, should complete the highest frequency region of the spectra, while their out-of-plane displacements should be associated with certain vibrations in the low-frequency part.

According to the statements made above, the softening of the latter vibrations may be expected under hydrostatic compression. In other words, they can be considered as a source of pressure-induced instability of the β-Si_3N_4 lattice due to the vanishing of one of them. Whether this effect can be a trigger for the destructive $\beta \Longrightarrow \alpha$ phase transition seems to be an intriguing question implying that the β lattice is a prototype for the α structure. In this connection, the following structural peculiarities of the α phase are of increasing interest:

(i) The lattice has double c spacing with respect to that of the β phase.

(ii) All NSi_3 fragments are essentially buckled.

(iii) The sequences of SiN_4 tetrahedra are crooked.

Consequently, in starting this work, we were spurred on by the questions:

(i) Whether, among low-frequency vibrational modes of β-Si_3N_4 at the $(0,0,\pi/c)$ boundary point of the Brillouin zone, there exists one manifesting the pressure-induced softening.

(ii) Whether its eigenvector could reflect the local displacement pattern specifying the actual difference between the high- and the low-symmetry phases of Si_3N_4. At the same time we realized that no phonon condensation by itself could literally be responsible for the $\beta \Longrightarrow \alpha$ conversion: a discontinuity of the structural transformation was evident [see Figs. 3(a)–3(b) in Ref. 3]. The lack of symmetry correlation between the two phases also testifies to the first-order character of the transition.

IV. MODEL

The design of the present dynamical model of β-Si_3N_4 was based on our previous experience related to the Si_2N_2O lattice.[16] Initially, the radial part of the potential function was described by the internal force field of SiN_4 tetrahedra consisting of Si-N bonds and N-N edge stretching force constants, and the N-Si-N bending ones. Further, in adapting this model for β-Si_3N_4 we have reduced it to a pairwise force field including additional intertetrahedral Si-Si interactions. The absence of external pressure corresponds to vanishing interatomic tensions F, i.e., to the zero tangential part of the V_{xx} matrix. The force field of the stress-free β-Si_3N_4 lattice contains six two-body stiffness parameters K, whose magnitudes are presented in Table I. They were derived from a fitting procedure in which the known dynamical properties of β-Si_3N_4 at ambient pressure were involved.

The external pressure was introduced in our computational scheme through the tangential part of the atomic force constants V_{xx}. Strictly speaking, the compression should alter all quantities in expression (6). In our case, to keep maximum physical transparency when considering the lattice under stress, and, correspondingly, in trying to operate with a minimum of variable parameters, we have concentrated exclusively on internal tensions F. Actually, on the one hand, the values of K were kept constant "by definition" (perfect springs); on the other hand,

TABLE I. Geometric characteristics and forces field parameters of β-Si_3N_4: interatomic distances (Å), stiffnesses K (mdyn/Å) and tensions F (mdyn).

Atoms involved	Distance	Stiffness K	Tensions (F) for $P=72$ kbar
SiN_4-tetrahedron bonds			
Si-N2	1.705	4.00	−0.068
Si-N1	1.739	3.50	−0.072
Si-N1	1.752	3.30	−0.065
SiN_4-tetrahedron edges			
N1-N1,N2	2.78−2.83	0.30	−0.016
N1-N1	2.909	0.09	−0.0015
Intertetrahedron contacts			
Si-Si	2.90−3.05	0.25	0

it was experimentally established[3] that β-Si_3N_4 did not undergo a noticeable structural distortion (an internal relaxation) at high pressure, which permitted us to keep the lattice geometry (i.e., matrices B_x, B_{xx}, and B_u) unchanged.

Hence, in our calculations, the pressure-induced increase of tensions F was the sole factor destabilizing the lattice. Their magnitudes, derived from Eqs. (4) and (5) for different P, have been automatically included in the computational scheme as components of the atomic force constants V_{xx} in compliance with (6). Thus, no new *ad hoc* parameters were introduced in our lattice-dynamical model of the stressed crystal.

V. RESULTS AND DISCUSSION

In the first step, we dealt with optically active vibrations and compressibility of stress-free β-Si_3N_4. In this way, the set of force constants K was evaluated, a model analysis of IR- and Raman-scattering spectra was performed, the mechanism of compressibility was analyzed, and the elastic constant matrix was estimated. In the second step, our attention was focused on the pressure-induced behavior of low-frequency dispersion curves along the (00ξ) direction (the Δ direction) including the $A(0,0,\pi/c)$ point.

The symmetry species distribution of zone-center normal coordinates of β-Si_3N_4 is

$$\Gamma=4\Gamma_1^+(A_g)+3\Gamma_1^-(A_u)+3\Gamma_2^+(B_g)+4\Gamma_2^-(B_u)+2\Gamma_3^+(E_{1g})+5\Gamma_4^+(E_{2g})+5\Gamma_3^-(E_{1u})+2\Gamma_4^-(E_{2u}) .$$

In representations A_g, B_u, E_{1u}, and E_{2g}, atoms may move in the x-y plane only, whereas in representations A_u, B_g, E_{2u}, and E_{1g}, atomic displacements are restricted by the z direction. In the IR spectra 6 bands $(2A_u+4E_{1u})$ may be found and 11 bands $(4Ag+2E_{1g}+5E_{2g})$ in the Raman spectra. As mentioned above, the stretching Si-N modes can be specified as in-plane vibrations of nitrogen atoms in NSi_3 planar triangles. There are two vibrations per triangle. Consequently, the total spectrum should contain 16 stretching vibrations, distributed as follows:

$$1A_g(R)+1E_{1g}(R)+2E_{2g}(R)+1A_u(IR)+2E_{1u}(IR)+1B_g(\text{inactive})+1B_u(\text{inactive})+E_{2u}(\text{inactive})$$

Thus, three bands complete the high-frequency region in the IR spectrum, and four in the Raman scattering. In both cases, the highest band must originate from the motions of N2 nitrogens in the x-y plane ($1E_{2g}$ or $1E_{1u}$), since Si-N2 bonds are considerably shorter (and thus more stiff) than the rest (Table I).

All calculated zone-center frequencies are presented in Table II along with measured ones. There is no drastic divergence between our model and the experimental data concerning positions of Raman-active modes except in the range 700–900 cm^{-1}, which is essentially empty in the present calculations (we believe, the observed bands in that region mean the presence of α-Si_3N_4 in a specimen). More dramatic are the discrepancies in the low-frequency part of the IR spectrum. This could signify a shortcoming of our model (which certainly was oversimplified), if the absence of IR bands below 300 cm^{-1} had been proved in practice. Besides, the known experimental data did not substantiate this condition (no measurement below 200 cm^{-1}).

Two principal differences between our theoretical zone-center spectrum and that in Ref. 6 deserve to be noted here:

(i) While frequencies of IR-active modes below 600 cm^{-1}, perhaps, are underestimated in our work, it is highly likely that those in Ref. 6 are essentially overestimated.

(ii) In contrast to the result presented in Table II, the high-frequency part ($\nu > 600$ cm^{-1}) of the A_g representation which should contain one Si-N stretching mode, is empty in Ref. 6. The latter seems to us rather mysterious, since we have no hint of this effect within our considerations.

The calculated elastic constant magnitudes are (in GPa) as follows:

$$c_{11}=315,\ c_{12}=239,\ c_{13}=222,\ c_{33}=332\ ,$$

$$c_{44}=40, \text{ and } c_{66}=38\ .$$

These lead to the compressibility coefficients (10^{-13} Pa^{-1}),

$$K_a=12.9,\quad K_c=12.9,\quad \text{and } K_v=38.7,$$

while the measured ones are 12.9, 12.6, and 39.0, respectively.[3] Our analysis of these values confirms a point of

TABLE II. Experimental and calculated frequencies of long-wave vibrational modes of β-Si_3N_4 (cm^{-1}).

Raman active				IR active			Optically inactive		
Expt.[a]	Calculated			Expt.[a]	Calculated		Calculated		
	A_g	E_{1g}	E_{2g}		A_u	E_{1u}	B_g	B_u	E_{2u}
			85						
144	137	130							
186							185	170	196
210			269		250				
229	280					274	268		
				380					
				447		419			
451			510					490	
619	613			580				600	
732									
865									
928		958		910	950				
939	981		975						
				985		982	982	981	974
1047			1050	1040		1049			

[a] Data taken from Ref. 1.

view[3] that the high hardness of the silicon nitride lattice must be mainly attributed to a steric factor. The mutual arrangement of the SiN_4 tetrahedra is such that their cooperative reorientation is not possible under lattice compression which, necessarily, would lead to a distortion of tetrahedra, thus giving rise to great restoring forces. This explains the huge difference between the compressibility of β-Si_3N_4 and that of α-quartz, 39 and 274 (10^{-13} Pa^{-1}), respectively. Although SiO_4 tetrahedra are essentially harder than the SiN_4 one, their internal potential is practically not involved in the mechanism of compression of α-quartz, which is mainly determined by tetrahedron rotations, and, hence, by weak inter-tetrahedral forces,[17] unlike the case of Si_3N_4.

Before considering phonon branches along the Δ direction, note that the corresponding point symmetry of vibrational space inside the Brillouin zone (BZ) is C_6, and the mode distribution

$$\Delta=7\ {}^{(1)}\Delta_1+7\ {}^{(1)}\Delta_2+7\ {}^{(2)}\Delta_3+7\ {}^{(2)}\Delta_4$$

(dimensionalities of symmetry species are shown in brackets) with the following $\Gamma \Longrightarrow \Delta$ compatibility relations:

$$A_g+A_u \Longrightarrow \Delta_1\ ,\quad B_g+B_u \Longrightarrow \Delta_2\ ,\quad E_{1g}+E_{1u} \Longrightarrow \Delta_3\ ,$$

and

$$E_{2g}+E_{2u} \Longrightarrow \Delta_4\ .$$

Upon reaching the $A(0,0,\pi/c)$ point, all dispersion curves must merge in pairs in doubling their dimensionalities:

$${}^{(1)}\Delta_1+{}^{(1)}\Delta_2 \Longrightarrow {}^{(2)}A_1\ ,\quad {}^{(2)}\Delta_3+{}^{(2)}\Delta_4 \Longrightarrow {}^{(4)}A_2\ ,$$

thus demonstrating time inversion symmetry. So, the A point contains one two-dimensional and one four-dimensional irreducible representation:

$$A=7\ {}^{(2)}A_1+7\ {}^{(4)}A_2\ .$$

We shall restrict our current interest to the low-frequency part of the spectrum in paying major attention to modes originating from the out-of-plane motions of nitrogen atoms in silicon-nitrogen triangles.

Corresponding long-wave vibrations of N2 nitrogens belong to A_u and B_g species (z displacements), and have theoretical frequencies 250 and 185 cm^{-1} (for stress-free crystal), respectively. Six modes in question relating to N1 nitrogens (x-y displacements) belong to A_g, B_u, E_{1u}, and E_{2g} representations (280, 170, 274, and 85 cm^{-1}). Consequently, vibrations from Δ_1 and Δ_2 dispersion curves (except the Γ point) include atomic motions which simultaneously warp all the triangles, whereas those from Δ_3 and Δ_4 curves must keep the $N2Si_3$ ones planar. Thus, the former should be of primary interest to us.

The low-frequency curves of representations Δ_1 and Δ_2 are presented in Fig. 2. When the isotropic compression of the lattice was introduced in our model, all frequencies in this region dropped, but those corresponding to the out-of-plane vibrations of NSi_3 triangles were affected considerably. Eventually, the Δ_2^1 curve coming from the lowest long-wave B_u mode touched the abscissa axis at the point $(0,0,0.36)2\pi/c$ (see Fig. 2) for $P_c=72$ kbar (corresponding magnitudes of tensions F are given Table I), that corresponds to a phase transition to an incommensurate (IC) structure. No other vanishing mode for this pressure was found.

Obviously, the main point of the discussion must concern the reliability and physical meaning of this result. Consequently, three points should be considered:

(i) The mechanism of the lattice destabilization.

(ii) The reliability of the above P_c magnitude estimate.

(iii) The possibility to relate the predicted IC instability to the $\beta \Longrightarrow \alpha$ transformation of Si_3N_4.

They can be answered as follows:

(i) Within the framework of the present approach,[11,13] the mechanism of lattice destabilization is dictated just by the laws of mechanics, and originates from interatom-

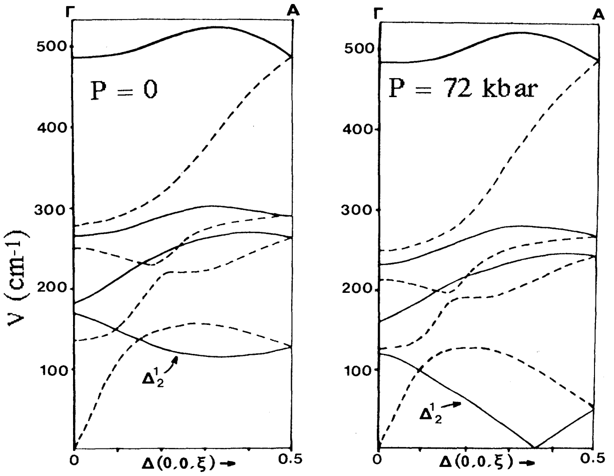

FIG. 2. The Δ_1 (broken curves) and Δ_2 (solid curves) dispersion branches for different pressure $P(\nu < 500\ \mathrm{cm}^{-1})$.

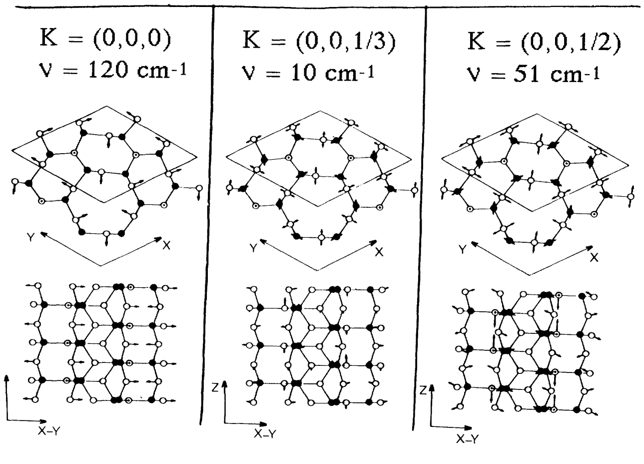

FIG. 3. Frequencies and eigenvectors of Δ_1^1 modes corresponding to different wave vectors k for a pressure of 72 kbar.

ic repulsive forces arising as a response to lattice compression. In our model, these forces are interpreted as bond (perfect spring) tensions. The physical meaningfulness of these values seems to be evident. However, during compression of real crystal, the bond-tension effect *destabilizing* the lattice must be necessarily accompanied by the bond-stiffness increase (arising as a result of interatomic separation decrease), which would augment the mode frequencies, thus *stabilizing* the structure. Whether or not the stability limit of the lattice can be reached eventually depends upon which of the above factors predominates. Taking into account the exceptional hardness of the crystal under consideration and a very small pressure dependence of the interatomic separation in its lattice[3] (this was confirmed by our additional calculations using the scheme proposed in Ref. 18), we venture the opinion that the predicted effect of the pressure-induced destabilization of the β-Si_3N_4, by itself, seems to be credible.

(ii) Within our model, the P_c magnitude depends upon the position of the lowest Δ_2^1 dispersion branch which currently cannot be experimentally checked. In this connection, certain misgivings can be caused by the above-mentioned discrepancy between calculated and measured frequencies of polar modes. If the region below 380 cm^{-1} is empty in the IR spectrum, our force field model must be modified to move some modes upward. In turn, this could provide an augmentation of the Δ_2^1 branch. In the light of such a possibility, the P_c magnitude, derived from present calculations, may be expected to be underestimated.

(iii) According to above results, the β-Si_3N_4 lattice can be destabilized by hydrostatic compression via the vanishing of a soft mode belonging to the Δ_2^1 dispersion branch at point $k_c = (0,0,0.36)2\pi/c$. A condensation of this mode would lead to an IC modulation of the lattice and to the lowering of its point symmetry to the C_3 class. As a rule, IC phases are not stable and, owing to the variation of thermodynamic conditions, evolve to *in-lock* normal structures. To visualize displacement patterns corresponding to different modes from the Δ_2^1 branch, we present in Fig. 3 three eigenvectors, calculated at points $\Gamma, (0,0,1/3)2\pi/c$, and A for pressure P_c. The second of them, being obtained in the vicinity of k_c, can be regarded as the shape of the vanishing mode. The lattice distortion originating from its condensation would contain, in principle, some features intrinsic to the α-Si_3N_4 lattice; all NSi_3 triangles begin to buckle, and the SiN_4 tetrahedron sequences have a tendency to crook. However, within any phenomenological model, it is dangerous to extrapolate a further development of this distortion, since the interatomic potential of the lattice is expected to be strongly affected by the redistribution of the nitrogen lone-pair electron density that would arise when NSi_3 groups assume pyramidlike configurations. In particular, this should prevent a diminution of the N2-N2 separation, ordered by the mode condensation, and, perhaps, could be responsible for the breaking of Si-N bonds. Note that both these effects are necessary for the $\beta \Longrightarrow \alpha$ phase transformation to occur. In our opinion, the above considerations make it possible to hypothesize that the α phase can be obtained from the β phase via an intermediate IC state:

$$\beta(C_{6h}) \Longrightarrow \mathrm{IC}(C_3) \Longrightarrow \alpha(C_{3v}) .$$

VI. CONCLUSION

The present lattice-dynamical model of β-Si_3N_4 realistically describes its elastic and long-wave vibrational properties at ambient conditions and provides some physical insight into their origins. In simulating the lattice under hydrostatic compression, this model predicts the pressure-induced vanishing of a mode within the BZ, that corresponds to a second-order phase transition in an IC structure belonging to the C_3 crystallographic class. It is significant that no fitting was used to obtain this result. Moreover, it can be said that the appearance of a destabilizing agent in a stressed crystal, i.e., of interatomic bond tensions, is a model-independent mechanical property of the lattice.

The model cannot tell us how the predicted IC structure of Si_3N_4 will develop at further compression, but the analysis of the above results does not contradict a hypothesis that the *in-lock* point of its evolution can correspond to the α phase.

We hope that the present work can stimulate new investigations of this material; in particular, detailed experimental studies of its properties near the $\alpha \Longrightarrow \beta$ conversion temperature, and structural measurements at high pressures.

Besides, it is well known that, very frequently, a predisposition of a lattice to instability is dictated just by structural factors because a series of isostructural crystals can possess a tendency to undergo similar phase transitions. In this spirit, adopted throughout this paper, β-Si_3N_4 should correspond to such a case. In this connection we want to recall that this material belongs to the family of phenacitelike structures, some of which can provide possibilities for single-crystal experiments.

ACKNOWLEDGMENTS

The main results of this paper were obtained while one of the authors (A.P.M.) was at the Faculty of Sciences of the University of Limoges. It is a pleasure for him to express appreciation for the hospitality of Professor Bernard Frit in his laboratory (LMCTS). The authors are extremely grateful to Dr. Mikhail B. Smirnov for a series of illuminating discussions, and especially for making available his crystal-mechanics code CRYME and to Dr. Vyacheslav P. Smirnov for help in some aspects of the work. The Laboratory of Ceramic Materials and Surface Treatments is "Unité Associée No. 320 au CNRS."

---

*To whom correspondence should be addressed.

[1] N. Wada, S. A. Solin, J. Wong, and S. Prochazka, J. Non-Cryst. Solids **43**, 7 (1981).

[2] J. P. Luongo, J. Electrochem. Soc. **130**, 1560 (1983).

[3] L. Cartz and J. D. Jorgensen, J. Appl. Phys. **52**, 236 (1981).

[4] S. Y. Ren and W. Y. Ching, Phys. Rev. B **23**, 5656 (1981); X. N. Xu and W. Y. Ching, Physica B **150**, 32 (1988).

[5] A. Y. Liu and M. L. Cohen, Phys. Rev. B **41**, 10 727 (1990).

[6] J. A. Wendel and W. A. Goddard III, J. Chem. Phys. **97**, 5048 (1992).

[7] H. M. Jennings, J. O. Edwards, and M. H. Richman, Inorg. Chim. Acta **20**, 167 (1976).

[8] K. Kato, Z. Inoue, K. Kijima, T. Yamane, and J. Kawada, J. Am. Ceram. Soc. **58**, 10 (1975).

[9] W. P. Clancy, Microscope **22**, 279 (1974); D. R. Messier, F. L. Riley, and R. J. Brook, J. Mater. Sci. **13**, 1199 (1978).

[10] P. Sajgalik, J. Eur. Ceram. Soc. **8**, 21 (1991); J. Mater. Sci. **26**, 6083 (1991).

[11] A. P. Mirgorodsky, M. B. Smirnov, and L. Z. Grigor'eva, Solid State Commun. **73**, 153 (1990).

[12] W. Cochran, Crit. Rev. Solid State Sci. **2**, 1 (1971).

[13] A. P. Mirgorodsky and M. B. Smirnov, J. Phys. Condens. Matter (to be published).

[14] A. N. Lazarev, A. P. Mirgorodsky, and I. S. Ignat'ev, *Vibrational Spectra of Complex Oxides* (Russian) (Nauka, Leningrad, 1975).

[15] A. N. Lazarev, *Vibrational Spectra and Structure of Silicates* (Consultants Bureau, New York, 1972).

[16] A. P. Mirgorodsky, M. I. Baraton, and P. Quintard, J. Phys. Condens. Matter **1**, 10 053 (1989).

[17] A. N. Lazarev and A. P. Mirgorodsky, Phys. Chem. Miner. **18**, 231 (1991).

[18] M. B. Smirnov and A. P. Mirgorodsky, Solid State Commun. **70**, 915 (1989).