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First-principles calculation of the elastic stiffness tensor of aluminium nitride under high pressure

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Abstract. The first-principles method for calculating the elastic stiffness tensor of composite crystals has been given. Applying the present method to the wurtzite and rocksalt structures of AlN under normal and elevated pressure up to 25.8 GPa, we have determined the elastic stiffness tensor completely from first principles. The theoretical values for the wurtzite structure at normal pressure are in good agreement with the experimental ones given by Tsubouchi and Mikoshiba. The elastic stiffness constants have been evaluated from the total energies of the deformed static lattices. These energies have been calculated by using a calculation method based on the variational principle.

1. Introduction

Although the electronic and elastic properties of composite solids have been studied from first principles by a number of researchers [1, 2, 3, 4], no calculation of the elastic stiffness tensor of the solids has been reported up to now except for in the work on zincblende—GaAs and AlAs [5, 6]. The determination of this tensor on the basis of microscopic theory is a rather difficult problem for a structure having internal lattice parameters. When the crystal is deformed homogeneously, the internal electric field is induced according to the displacement of ions accompanying the deformation of the electron clouds, and this field urges the ions to move also. Thus this problem has to be solved self-consistently. The energy increment due to the deformation can be expressed as a sum of two parts: one is the energy dependent only on the external strain to which the classical elastic energy corresponds; the remaining part is the energy dependent on both the displacements of the ions in the unit cell and on the external strain. If we extract the first part, which we call the external strain energy, from the total energy of the deformed lattice, we can calculate the elastic stiffness tensor by considering several appropriate homogeneous deformations. In the present paper we shall show how to extract the external strain energy for a given homogeneous deformation on the basis of first-principles pseudopotential theory [7].

Aluminium nitride has a relatively high ionicity among the group of III–V semiconductors, crystallizes in the wurtzite structure and transforms to the rocksalt structure at about $P = 20$ GPa at room temperature [8]. This material has attracted much attention for possible applications as a dielectric substrate and acoustic wave resonator. Measurements of the elastic properties, such as the bulk modulus, longitudinal and transverse elastic wave velocities and Grüneisen constant [9, 10, 11, 12], have been performed under normal and high pressure. Owing to the difficulty in growing single crystal these data depend more or

less on the porosity of samples, so more precise estimates are required. Applying the surface acoustic wave method to thin films, Tsubouchi and Mikoshiba [13, 14] have determined the complete set of elastic stiffness, dielectric and piezoelectric constants.

Using the present method, we have calculated the elastic stiffness tensor for the wurtzite and rocksalt structures of aluminium nitride under high pressure.

2. Formalism and method

2.1.

We shall describe how the elastic stiffness tensor $c_{\alpha\gamma\beta\lambda}$ can be derived from the total energy calculation for solids.

We consider a strain-free dielectric having no spontaneous polarization. If the dielectric is subjected to a small homogeneous deformation characterized by the vector $w(\boldsymbol{x})$, the displacement of the k th ion at the position $\boldsymbol{q}(k)$ in the unit cell is written with the internal strain $d_\alpha(k)$ as

$$\tilde{d}_\alpha(k) = d_\alpha(k) + s_{\alpha\beta}q_\beta(k) \quad (1)$$

where $s_{\alpha\beta}$ is a component of the strain tensor \mathbf{s} defined by

$$s_{\alpha\beta} = \frac{1}{2} \left(\frac{\partial w_\beta}{\partial x_\alpha} + \frac{\partial w_\alpha}{\partial x_\beta} \right). \quad (2)$$

In equation (1) we use the convention that the sum is to be taken with respect to the repeated Cartesian indices, denoted by Greek letters. Hereafter we shall use this convention throughout. The increment of the total energy per cell due to the deformation is given up to the second order of $s_{\alpha\beta}$, $d_\alpha(k)$ and E the macroscopic electric field, formally as

$$\begin{aligned} \Delta E' = & \frac{1}{2} s_{\alpha\gamma} c'_{\alpha\gamma\beta\lambda} s_{\beta\lambda} + \sum_k d_\alpha(k) c''_{\alpha,\beta\lambda}(k) s_{\beta\lambda} + \frac{1}{2} \sum_{k,\ell} d_\alpha(k) c'''_{\alpha\beta}(k,\ell) d_\beta(\ell) \\ & - \sum_k d_\alpha(k) e'_{\alpha\beta}(k) E_\beta - \frac{1}{2} E_\alpha e'_{\alpha\beta} E_\beta - E_\alpha e_{\alpha,\beta\lambda} s_{\beta\lambda} \end{aligned} \quad (3)$$

where $e_{\alpha,\beta\lambda}$ are the components of the piezoelectric tensor. Other tensors appearing in equation (3) have similar meanings to $e_{\alpha,\beta\lambda}$. We do not, however, specify the other tensors precisely because we do not use them explicitly in the present discussion. When no macroscopic electric field is present the last three terms in equation (3) do not contribute to the energy increment. Since $\Delta E'$ is in the second order of $d_\alpha(k)$, for a given strain tensor $d_\alpha(k)$ is determined formally by the set of the linear equations derived from $\partial \Delta E' / \partial d_\alpha(k) = 0$. When the internal strains are eliminated, the energy increment becomes a function depending only on $s_{\alpha\beta}$, which may be written as

$$\Delta E = \frac{1}{2} s_{\alpha\gamma} c_{\alpha\gamma\beta\lambda}^E s_{\beta\lambda} \quad (4)$$

where $c_{\alpha\gamma\beta\lambda}^E$ is the stiffness tensor under constant electric field. Therefore if we obtain the minimum energy in the deformed lattice, varying the ion positions in the unit cell, but keeping $s_{\alpha\beta}$ constant, we can evaluate the elastic stiffness constants from equation (4). Hereafter we shall use $c_{\alpha\gamma\beta\lambda}$ as $c_{\alpha\gamma\beta\lambda}^E$ omitting the superscript E . In quantum mechanics, equation (4) is expressed with the use of the variation principle as

$$\begin{aligned} \Delta E = & \langle \Psi_{\mathbf{s}}(\boldsymbol{r}) | H | \Psi_{\mathbf{s}}(\boldsymbol{r}) \rangle - \langle \Psi(\boldsymbol{r}) | H | \Psi(\boldsymbol{r}) \rangle = \frac{1}{2} s_{\alpha\gamma} c_{\alpha\gamma\beta\lambda} s_{\beta\lambda} + \dots \\ \Psi_{\mathbf{s}}(\boldsymbol{r}) = & | \mathbf{1} + \mathbf{s} |^{-1/2} \Psi((\mathbf{1} + \mathbf{s})^{-1} \boldsymbol{r}) \end{aligned} \quad (5)$$

where $\Psi(r)$ denotes the ground state wave function of the undeformed structure and $\langle \Psi_s(r) | H | \Psi_s(r) \rangle$ should be optimized further with respect to the internal parameters when they are present in order to extinguish the excess forces acting on respective ions. On the basis of equation (4) we shall describe the method of the calculation of the elastic stiffness tensors for both the wurtzite (C_{6v}^4) and rocksalt (O_h^5) structure of AlN.

2.1.1. *Wurtzite structure.* In Voigt's notation the elastic stiffness tensor \mathbf{c} is expressed as

$$\mathbf{c} = \begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} \end{bmatrix} \quad (6)$$

with $c_{66} = \frac{1}{2}(c_{11} - c_{12})$. Let us introduce five types of homogeneous deformation $w_i(x)$, shown in table 1. For these deformations the energy increments ΔE derived from equation (4) are also shown in the same table. The table shows that if we obtain the values of ΔE_i ($i = 1, 2, \dots, 5$) we can determine $[c_{ij}]$ completely. With the help of table 1 the basic translation vectors of the deformed lattices $a_{\alpha i}$ can be derived readily from the basis vectors of the hexagonal lattice defined in the Cartesian coordinates as

$$\begin{aligned} a_1 &= \frac{1}{2}(\sqrt{3}a, a, 0) \\ a_2 &= \frac{1}{2}(-\sqrt{3}a, a, 0) \\ a_3 &= (0, 0, c) \end{aligned} \quad (7)$$

with a and c as the lattice constants. The results for the five deformations are shown in the same table. The sets of $a_{\alpha i}$ for the deformations 1 to 4 constitute monoclinic lattices and that for the fifth deformation constitutes a triclinic lattice.

Table 1. Wurtzite structure: the five deformations $w_i(x)$ with σ_i as a small constant used in the calculation of the elastic stiffness tensor \mathbf{c} and the corresponding energy increments ΔE_i . The basis vectors $a_{\alpha i}$ of the deformed lattice generated by the i th deformation $w_i(x)$ are given by $a_{\alpha i} = a_\alpha + v_{\alpha i}$. All the vectors are expressed in Cartesian coordinates.

i	w_i/σ_i	$\Delta E/\sigma_i^2$	v_{1i}/σ_i	v_{2i}/σ_i	v_{3i}/σ_i
1	$(x_1, 0, 0)$	$\frac{1}{2}c_{11}$	$\frac{1}{2}(\sqrt{3}a, 0, 0)$	$\frac{1}{2}(-\sqrt{3}a, 0, 0)$	$(0, 0, 0)$
2	$(x_1, -x_2, 0)$	$c_{11} - c_{12}$	$\frac{1}{2}(\sqrt{3}a, -a, 0)$	$\frac{1}{2}(-\sqrt{3}a, -a, 0)$	$(0, 0, 0)$
3	$(0, 0, x_3)$	$\frac{1}{2}c_{33}$	$(0, 0, 0)$	$(0, 0, 0)$	$(0, 0, c)$
4	$(x_1, 0, -x_3)$	$\frac{1}{2}(c_{11} + c_{33} - 2c_{13})$	$\frac{1}{2}(\sqrt{3}a, 0, 0)$	$\frac{1}{2}(-\sqrt{3}a, 0, 0)$	$(0, 0, -c)$
5	$(0, 0, x_2)$	$\frac{1}{2}c_{44}$	$\frac{1}{2}(0, 0, a)$	$\frac{1}{2}(0, 0, a)$	$(0, 0, 0)$

The problem remaining is that of how to search for the energy minimum configurations $d(k)$ effectively in the respective deformed lattices. The wurtzite structure consists of a stack of network structures of triangles constructed from Al and N ions along the c -axis, and the networks of the respective ions are the same forms when they are projected on the (001) plane (see figure 1).

The projected network of Al ions at $x_3 = \frac{1}{2}c$ is shifted from that at $x_3 = 0$ by $-\frac{2}{3}h$ with

$$h = \frac{1}{2}(a_{1i} - a_{2i}). \quad (8)$$

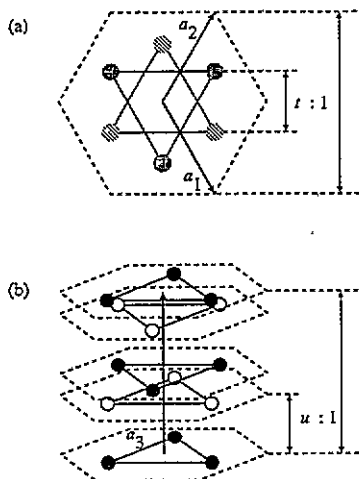


Figure 1. A pictorial representation of the internal parameters for the wurtzite structure. (a) Definition of t : the triangles of the same ions projected on the (001) plane. The figures are the same for Al and N ions. (b) Definition of u : the closed and open circles represent Al and N ions respectively.

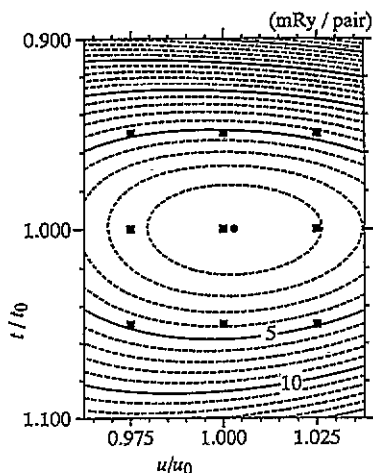


Figure 2. The equi-energy curves in the internal parameter space (u, t) in the wurtzite structure at $V/V_0 = 1.00$. (u_0, t_0) are the experimental values, equal to $(0.3821, \frac{1}{3})$. The solid square and circle represent, respectively, the calculated point and minimum energy point.

Since for the deformations w_i up to $i = 4$ with no internal strain the lattices are symmetric with respect to (a) the product of the exchange of Al and N ions and inversion about $(0, 0, \frac{1}{2}(1+u)c)$, (b) the reflection about the (x_1, x_3) plane and (c) the glide reflection about the (x_2, x_3) plane with translation vector $(0, 0, \frac{1}{2}c)$, we consider internal strain which preserves this symmetry. Therefore the non-equivalent ion positions in the unit cell for the respective lattices can be written generally as

$$\text{Al} \begin{cases} r(1) = \frac{1}{2}(a_{1i} + a_{2i}) + th \\ r(2) = \frac{1}{2}(a_{1i} + a_{2i}) - th + \frac{1}{2}a_{3i} \end{cases} \quad (9)$$

$$\text{N} \begin{cases} r(3) = \frac{1}{2}(a_{1i} + a_{2i}) + th + ua_{3i} \\ r(4) = \frac{1}{2}(a_{1i} + a_{2i}) - th + \left(u + \frac{1}{2}\right)a_{3i} \end{cases} \quad (10)$$

where the internal parameters u and t range over $0 < u < \frac{1}{2}$ and $0 < t < \frac{1}{2}$, respectively. Thus we get the minimum energy by scanning the internal parameter space (u, t) on the total energy for each structure. The search for the energy minimum becomes complicated for the fifth type of deformation. The set of basis vectors (a_{15}, a_{25}, a_{35}) constitutes a triclinic structure. In the structure, the oblique triangle networks of the respective ions stack along the x_3 -axis. For this type of deformation the symmetry of the lattice is lower than for the others, and consists of only (a) and (c). Considering internal strain which maintains this

symmetry, the ion positions are expressed as

$$\text{Al} \begin{cases} r(1) = \xi g + \eta h \\ r(2) = \xi g - \eta h + \frac{1}{2} a_{35} \end{cases} \quad (11)$$

$$\text{N} \begin{cases} r(3) = (2 - \xi)g + \eta h + \zeta a_{35} \\ r(4) = (2 - \xi)g - \eta h + \left(\zeta + \frac{1}{2} \right) a_{35} \end{cases} \quad (12)$$

with

$$g = \frac{1}{2}(a_{15} + a_{25}) \quad (13)$$

where ξ , η , ζ are the internal parameters to be varied in searching for the minimum energy.

2.1.2. Rocksalt structure. The elastic stiffness tensor is written in Voigt's notation as equation (6) with $c_{33} = c_{11}$, $c_{13} = c_{12}$ and $c_{66} = c_{44}$. In order to calculate the c_{ij} from equation (4), we introduce three types of deformation $w_i^c(x)$ given in table 2. From the energy increments ΔE_i shown in the table due to the respective deformations $w_i^c(x)$, the relations of c_{ij} and ΔE_i are evident. For the three types of $w_i^c(x)$ the original undeformed, i.e. rocksalt, structure is transformed respectively to the body-centred tetragonal, face-centred orthorhombic and body-centred orthorhombic structure. They have one, two and one pair of Al and N ions in the unit cell respectively. Considering the site symmetries of these structures, it is obvious that the energy minimum configurations in these structures are those with $r(\text{Al}) = \mathbf{0}$ and $r(\text{N}) = \frac{1}{2}(a_{1i} + a_{2i} + a_{3i})$ or *vice versa* with a_{ai} as the basis vectors of the respective structures.

2.2.

In the present theory the total energy of the system is calculated by using the first-principles pseudopotential method. Based on the density functional theory [15] within the local density approximation (LDA) [16] the total energy of a crystal measured from that of isolated ions and electrons is written, with pseudopotentials in Rydberg units, as [7]

$$\begin{aligned} E_{\text{total}} = & \sum_{k,n} \int \psi_{kn}^*(\mathbf{r})(-\nabla^2)\psi_{kn}(\mathbf{r}) d\mathbf{r} + \sum_{k,n,\mu,\ell} \int \psi_{kn}^*(\mathbf{r})U_{\ell}(\mathbf{r} - \mathbf{R}_{\mu})\hat{P}_{\ell}\psi_{kn}(\mathbf{r}) d\mathbf{r} \\ & + \frac{1}{2} \int \int \frac{2\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \frac{1}{2} \sum_{\substack{\mu,\lambda \\ \mu \neq \lambda}} \frac{2Z_{\mu}Z_{\lambda}}{|\mathbf{R}_{\mu} - \mathbf{R}_{\lambda}|} \\ & + \int \rho(\mathbf{r})\epsilon_{\text{xc}}(\rho(\mathbf{r})) d\mathbf{r}. \end{aligned} \quad (14)$$

$\psi_{kn}(\mathbf{r})$ is the wave function of the valence electrons of band index n and wave vector k . The indices k and n in the summations run through the occupied states. \hat{P}_{ℓ} is the projection operator on angular momentum ℓ , and U_{ℓ} is the angular-momentum-dependent pseudopotential. \mathbf{R} and Z are the position vector and the charge of ions respectively. ρ is the valence electron density, which has the form

$$\rho(\mathbf{r}) = \sum_{k,n} \psi_{kn}^*(\mathbf{r})\psi_{kn}(\mathbf{r}).$$

The last term is the exchange–correlation energy. The ground state wave functions are derived from the variational condition for E_{total} . The Bachelet–Hamann–Schlüter (BHS) potential [17] has been used for U_{ℓ} ; it is derived from an all-electron LDA calculation for an atom.

Table 2. Rocksalt structure: the three types of deformations $w_i^c(x)$ and the corresponding energy increments ΔE_i used in the calculation of the elastic stiffness tensor \mathbf{c} with σ_i^c as a small constant. The basis vectors $\mathbf{a}_{\alpha i}$ of the deformed lattice generated by the i th deformation $w_i^c(x)$ are given by $\mathbf{a}_{\alpha i} = \mathbf{a}_{\alpha} + \mathbf{v}_{\alpha i}$. All the vectors are expressed in Cartesian coordinates.

i	w_i^c/σ_i^c	$\Delta E/(\sigma_i^c)^2$	$\mathbf{v}_{1i}/\sigma_i^c$	$\mathbf{v}_{2i}/\sigma_i^c$	$\mathbf{v}_{3i}/\sigma_i^c$
1	$(x_1, 0, 0)$	$\frac{1}{2}c_{11}$	$\frac{1}{2}(0, 0, 0)$	$\frac{1}{2}(a, 0, 0)$	$\frac{1}{2}(a, 0, 0)$
2	$(x_1, -x_2, 0)$	$c_{11} - c_{12}$	$\frac{1}{2}(0, -a, 0)$	$\frac{1}{2}(a, 0, 0)$	$\frac{1}{2}(a, -a, 0)$
3	$(0, x_1, 0)$	$\frac{1}{2}c_{44}$	$\frac{1}{2}(0, 0, 0)$	$\frac{1}{2}(0, a, 0)$	$\frac{1}{2}(0, a, 0)$

For the local exchange–correlation energy we have used the form given by Perdew and Zunger [18], which is based on the numerical results of stochastic simulations of the uniform electron gas by Ceperley and Alder [19]. For sampling the k -points in the irreducible wedge of the Brillouin zone (IBZ) we adopt the special-point method [20, 21].

We take eight and ten points in the IBZ for the wurtzite and rocksalt undeformed structures, respectively. With this choice the electronic density and total energy are calculated accurately [21, 22] (The total energy differences have not changed within 10^{-4} Ryd/pair for sampling of 8 to 42 and 10 to 20 k -points, respectively, for the wurtzite and rocksalt structure.)

More special points are taken for the deformed lower-symmetry crystals which have larger volumes of the IBZ. We use sets of special points which have similar density in the BZ to that of the undeformed crystal. The cut-off value of the kinetic energy for the plane wave basis set is taken to be 34 Ryd which corresponds to the inclusion of about 950 plane waves in constructing the secular matrix. In practice we have used the symmetrized form in order to reduce the secular matrix when we could do so. In expanding the electronic density, effective potential and exchange–correlation energy in terms of the Fourier series of the reciprocal lattice vector \mathbf{G} , we have to take care of their convergence. From our analysis we have found that the calculated total energy depends greatly on the number of \mathbf{G} -vectors used.

In the present calculation we have taken into account about 3200 \mathbf{G} -vectors: We have confirmed that the total energy remains unchanged within 10^{-4} Ryd/pair for further inclusion of larger \mathbf{G} -vectors when the cut-off value for the plane wave basis set is taken to be 34 Ryd. When ΔE of a 10% strained lattice has 10^{-4} Ryd/pair error, the errors of the diagonal elements of the stiffness tensor are at most 2 GPa.

In computing the total energy for systems of varying size, the truncation of the basis set due to the kinetic energy cut-off introduces a discontinuity in the total energies whenever the number of plane waves used changes abruptly. To remedy this shortcoming we adopt the finite-basis correction method given by Francis and Payne [23]. This method improves the accuracy of the total energy differences without increasing the number of basis set elements. The method reduces computational effort, especially in our case where a lot of slightly different lattices should be considered.

3. Results for the wurtzite structure

3.1.

We have calculated the total energies of the wurtzite (i.e. strain-free) structure in the internal parameter space (u, t) at $V/V_0 = 1.00$ with $V_0 (= 12.56 \text{ cm}^3 \text{ mol}^{-1})$ [24] as the experimental equilibrium volume. Figure 2 shows the equi-energy map constructed from the nine values calculated by using the two-dimensional fitting method with third-order polynomials where the c/a ratio takes the experimental value (1.601) [24]. The energy minimum point is located at $(u, t) = (0.3832, 0.3333)$. These values are in good agreement with the experimental values $(u_0, t_0) = (0.3821, \frac{1}{3})$ [24]. The parameter t is fixed at $\frac{1}{3}$ in the ordinary wurtzite structure. From the results it has been confirmed that the experimentally observed values of u and t certainly realize the energy minimum configuration. The minimum energy obtained will be used in calculating ΔE_i .

3.2.

We have calculated the total energy for 9 to 11 and 27 sampling points respectively in the internal parameter space (u, t) and (ξ, η, ζ) in each deformed structure at $V/V_0 = 1.00$ where the deformation parameter σ_i defined in table 1 is taken to be -0.050 to 0.050 or -0.100 to 0.100 for the respective sampling points. We show, for example, the equi-energy maps for the structures generated from $w_2(x)$ and $w_4(x)$ in figure 4 and figure 3, respectively.

Here we point out that the relaxation of the ion position in the deformed structures is very important in calculating $[c_{ij}]$. Figure 5 shows the total energy versus σ_i curves for the relaxed and unrelaxed configurations in the deformed structures corresponding, respectively, to $w_1(x)$ and $w_3(x)$, where the unrelaxed values of (u, t) are taken to be the equilibrium ones of the ordinary wurtzite structure. The figures show that to use the unrelaxed configurations may produce significant errors in evaluating $[c_{ij}]$. Figure 6 shows the variations of (u, t) or (ξ, η, ζ) versus σ_i for $w_i(x)$, $i = 1$ to 5 . From the figure we can see that the internal parameters change appreciably from the equilibrium values of the ordinary wurtzite structure. It is interesting to observe the changes of the bond lengths and angles induced by the deformations for both the relaxed and unrelaxed configurations, which are shown in figure 8. The definitions of the bond lengths and angles are given in figure 7. Figure 8 shows that the unrelaxed structure leads to an appreciably different configuration under deformation in contrast to the relaxed one.

3.3.

Based on equation (4) with the results in 3.1 and 3.2, we have determined the values of c_{ij} at $V/V_0 = 1.00$: As shown in table 1, ΔE is proportional to square of the deformation parameter σ_i . From the coefficients of σ_i^2 estimated by least-squares fitting from data for five points, we have derived the values of c_{ij} . In table 3 we tabulated the theoretical values of c_{ij} together with experimental ones obtained by the surface acoustic wave method using thin films at room temperature. The theoretical values from the relaxed configurations are in good agreement with the experimental ones. The calculation from the unrelaxed configurations, however, gives rather higher values than the experiment for the diagonal elements of the tensor. This observation seems to be reasonable because a higher-energy, unrelaxed configuration must be more resistive, i.e. more stiff, against a small deformation than the relaxed one.

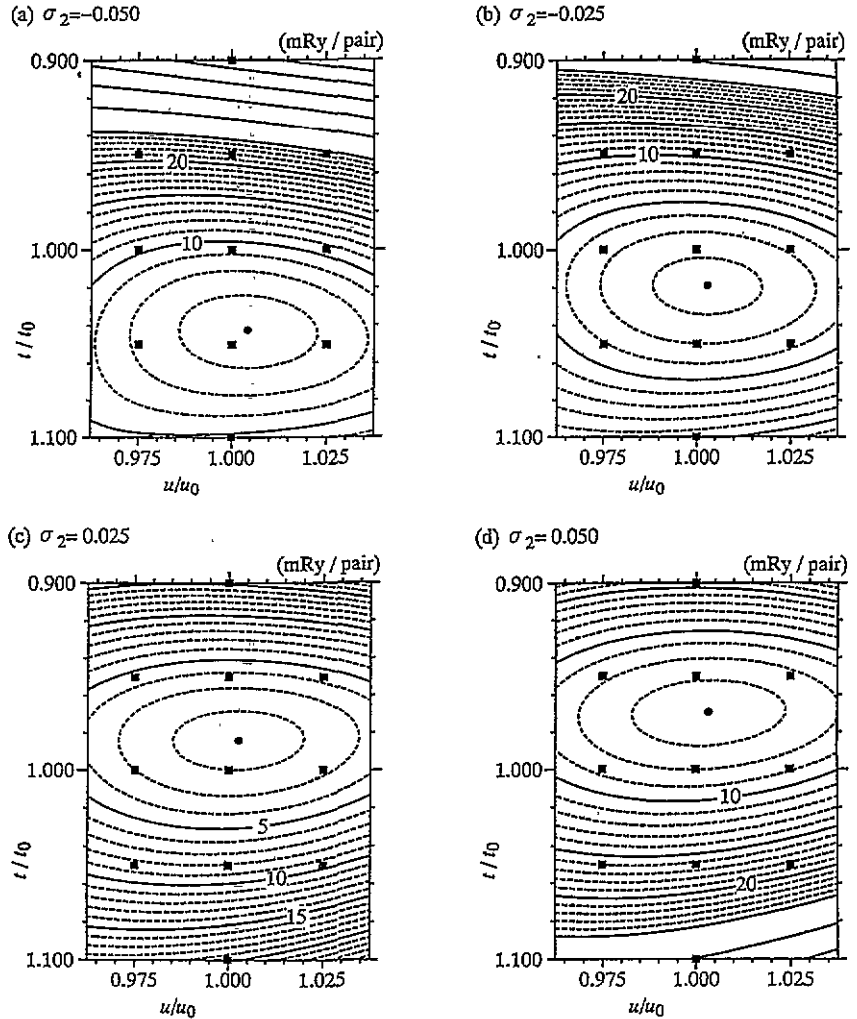


Figure 3. The equi-energy curves in the deformed lattice generated from the wurtzite lattice at $V/V_0 = 1.00$ by $w_4(x)$. (a) $\sigma_2 = -0.050$, (b) $\sigma_2 = -0.025$, (c) $\sigma_2 = 0.025$ and (d) $\sigma_2 = 0.050$. The notation is the same as in figure 2.

3.4.

At room temperature aluminium nitride transforms from the wurtzite structure to the rocksalt structure at about $P = 20$ GPa and for $V/V_0 = 0.93$. We have performed the calculation of $[c_{ij}]$ at $V/V_0 = 0.95$ and 0.90 where we have assumed the locations of the energy minima to be the same as they are for $V/V_0 = 1.00$. In calculating ΔE we added an isotropic and constant deformation $w_0(x) = \sigma_0(x_1, x_2, x_3)$ with $\sigma_0 = (V/V_0)^{1/3} - 1$ to the respective $w_i(x)$ in table 1 in order to reduce the cell volume to V . Figure 9 shows the total energy versus σ_i curves for $V/V_0 = 0.95$ and 0.90 together for $V/V_0 = 1.00$ where the energies are measured from the energy in the undeformed structure at $V/V_0 = 1.00$. In figure 9 (a) and (c) the asymmetry of the curves with respect to the origin results because the strains vary the volumes of the lattices. This effect vanishes for w_2 , w_4 and w_5 . The

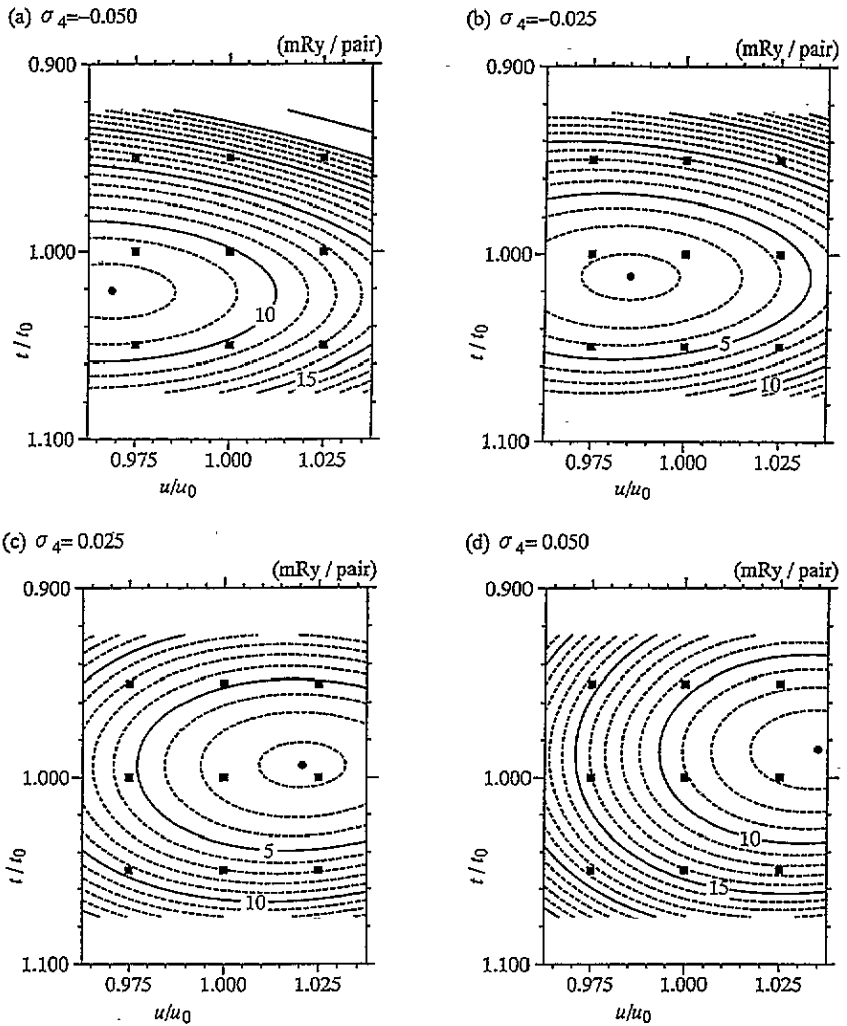


Figure 4. The equi-energy curves in the deformed lattice generated from the wurtzite lattice at $V/V_0 = 1.00$ by $w_2(\mathbf{x})$. (a) $\sigma_4 = -0.050$, (b) $\sigma_4 = -0.025$, (c) $\sigma_4 = 0.025$ and (d) $\sigma_4 = 0.050$. The notation is the same as in figure 2.

numerical results for $[c_{ij}]$ at $V/V_0 = 0.95$ and 0.90 are tabulated in table 3. From the table we can see that c_{11} and c_{33} increase but c_{44} and c_{66} decrease with increasing pressure under the transition pressure. Recently Ohta *et al* have measured elastic wave velocities under high pressure up to 4 GPa [25] and found that the longitudinal velocity increases with pressure and the transverse velocity decreases slightly with pressure. The observations agree qualitatively with the present theoretical prediction of the pressure dependence of c_{ij} , though the pressure dependences of $e_{\alpha,\beta\lambda}$ and the dielectric tensor under constant strain are necessary for detailed discussion. Unfortunately, at present we have no precise information about pressure dependence of $e_{\alpha,\beta\lambda}$ and the dielectric tensor under constant strain.

Taking a uniform deformation $w_0 = \sigma_0(x_1, x_2, x_3)$ in equation (4), the isothermal bulk

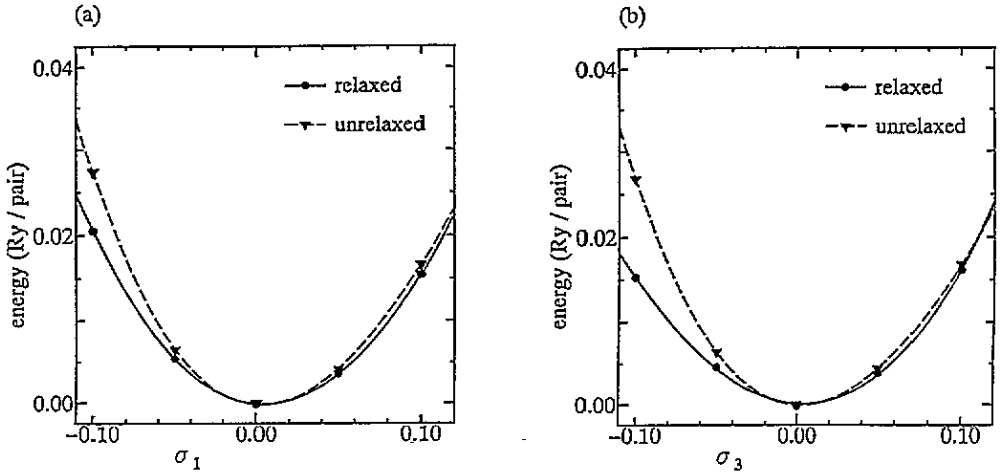


Figure 5. The total energy versus strain σ_i for the relaxed and unrelaxed configurations in the structure generated from the wurtzite structure at $V/V_0 = 1.00$ by $w_i(x)$. The energy is measured relatively from the wurtzite structure. (a) $w_1(x)$ and (b) $w_3(x)$.

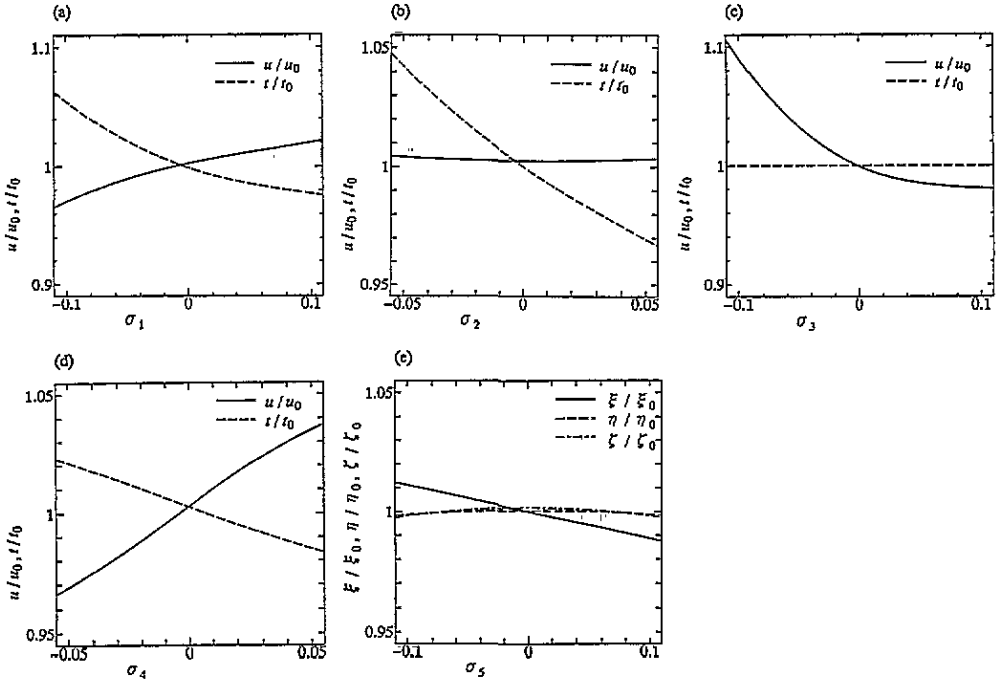


Figure 6. Variation of the internal parameters versus strain σ_i . u_0 and t_0 denote, respectively, the experimental values of the wurtzite structure at $V/V_0 = 1.00$. (a) For σ_1 , (b) for σ_2 , (c) for σ_3 , (d) for σ_4 and (e) for σ_5 .

modulus $B = -V(\partial P/\partial V)$ is written in terms of the elastic stiffness constants as

$$B = \frac{1}{9} \frac{\partial^2 \Delta E}{\partial \sigma_0^2} = \frac{1}{9} (2c_{11} + c_{33} + 2c_{12} + c_{14}). \quad (15)$$

On the other hand B can be calculated from the total energy versus volume curves with the

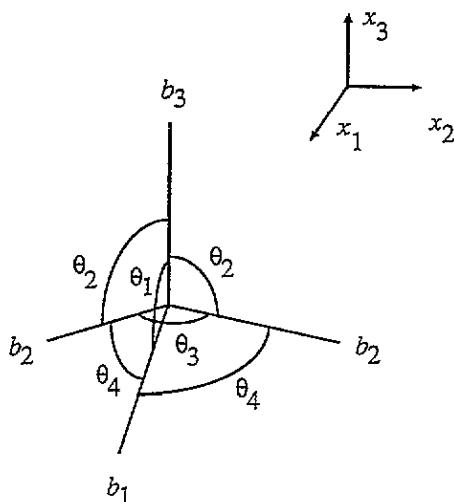


Figure 7. Definitions of the bond lengths b and angles θ for the deformed structures.

Table 3. The elastic stiffness constants c_{ij} (GPa) and the isothermal bulk modulus B (GPa) in the wurtzite structure. The parentheses denote the value for the unrelaxed configuration and square brackets denote the value of B derived from c_{ij} . The experimental values of c_{ij} are room temperature values given by Tsubouchi and Mikoshiba [13, 14]. $c_{66} = \frac{1}{2}(c_{11} - c_{12})$, $B = \frac{1}{9}(2c_{11} + c_{33} + 2c_{12} + 4c_{13})$.

	Theory			Experiment
	1.00	0.95	0.90	1.00
V/V_0	1.00	0.95	0.90	1.00
P (GPa)	0.0	12.4	25.8	0.0
c_{11}	380 (445)	421 (495)	447 (564)	345
c_{33}	382 (456)	391 (503)	421 (579)	395
c_{12}	114 (85)	176	192	125
c_{13}	127 (63)	150	146	120
c_{44}	109 (129)	104 (128)	114 (135)	118
c_{66}	133 (180)	123	127	110
B	207 [209]	236 [243]	261 [254]	[202]

help of $B = V(\partial^2 E / \partial V^2)$. To check the consistency of the present calculation we compare these values in table 3. The agreement is excellent. For the case of σ_3 we have confirmed that the volume variation of u is weak other than for large deformations (see figure 10).

4. Results for the rocksalt structure

The rocksalt structure is the high-pressure phase of aluminium nitride. In this phase the deformed structures, generated by the homogeneous deformations $w_i^c(\mathbf{x})$ defined in table 2, are themselves the relaxed configurations. We have carried out the total energy calculation for the deformed and undeformed structures at $V/V_0 = 0.819, 0.780$ and 0.750 . To reduce the volume from V_0 to V , we add an isotropic and constant deformation $w_0(\mathbf{x}) = \sigma_0(x_1, x_2, x_3)$ with $\sigma_0 = (V/V_0)^{1/3} - 1$ to each $w_i^c(\mathbf{x})$ defined in table 2. In figure 11 we show the total energy versus strain curves for w_1^c and w_3^c . In figure 11(a) the asymmetry of the curves with respect to the origin results because the strains vary the

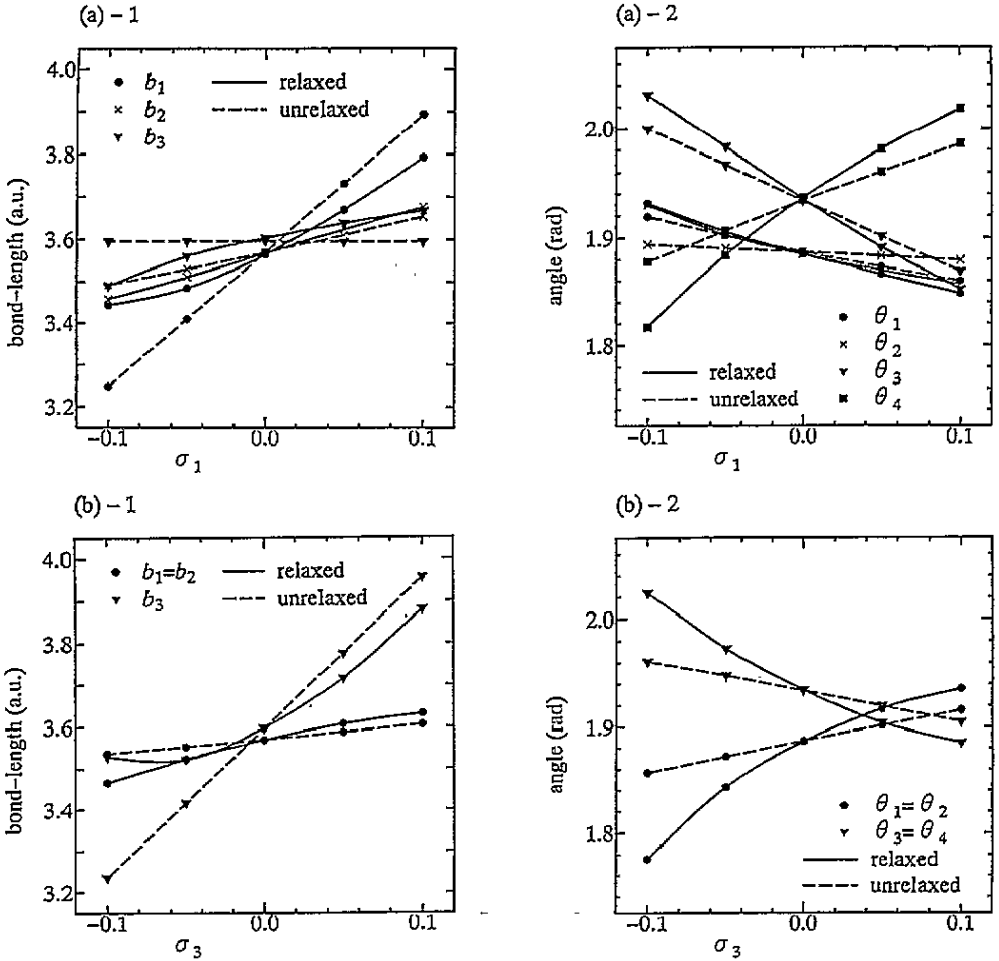


Figure 8. Variation of the bond lengths b and angles θ versus strain σ_i . (a) For σ_1 and (b) for σ_3 .

volumes of the lattices. This effect vanishes for w_3^c . From the curves we estimated the values of c_{11} and c_{44} by applying the least-squares fitting method to five sampling points. The constant c_{12} was estimated from the relation

$$B = \frac{1}{3}(c_{11} + 2c_{12}) \quad (16)$$

where the isothermal bulk modulus was calculated from the total energy versus volume curve of the undeformed rocksalt structure using the relation $B = V(\partial^2 E / \partial V^2)$. The numerical results are tabulated in table 4.

5. Conclusion

In the present paper we have developed a method for the complete determination of the elastic stiffness tensor of compound crystals from first principles. When a compound crystal is subjected to anisotropic homogeneous deformation, an internal electric field (the macroscopic plus Lorentz field) is produced and results in the appearance of induced electric

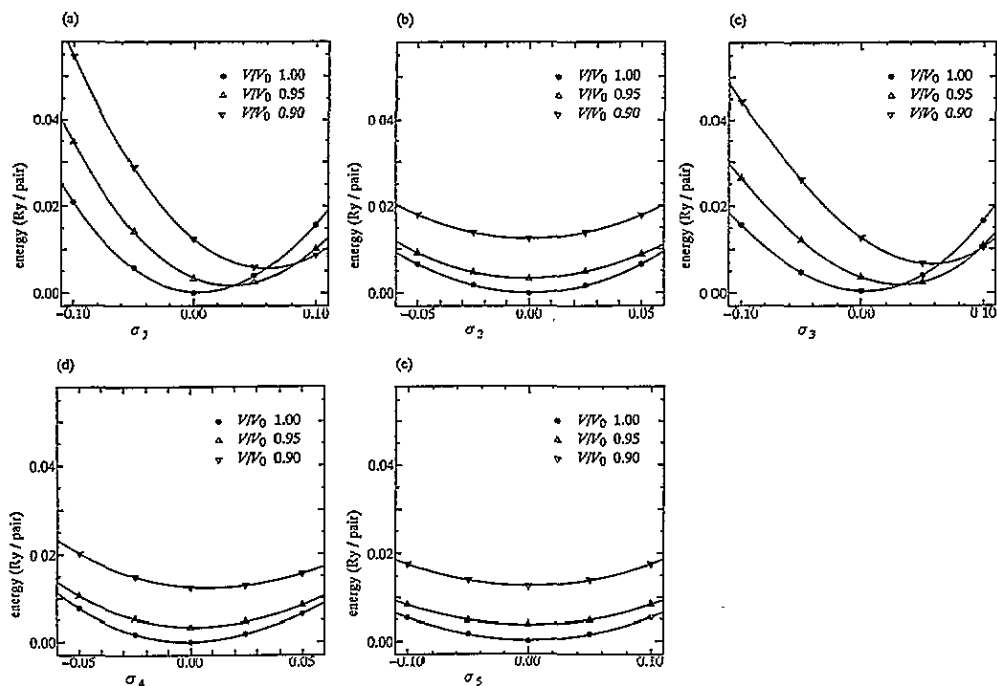


Figure 9. The total energy versus strain σ_i curves for the deformed structures generated from the wurtzite structure at $V/V_0 = 1.00$ by $w_i(x)$. The total energy is measured relatively from the undeformed structure at $V/V_0 = 1.00$. The starting relative volume for the anisotropic deformation $w_i(x)$ is expressed by V/V_0 . (a) For $w_1(x)$, (b) for $w_2(x)$, (c) for $w_3(x)$, (d) for $w_4(x)$ and (e) for $w_5(x)$.

Table 4. The elastic stiffness constants c_{ij} (GPa) and the isothermal bulk modulus B (GPa) in the rocksalt structure. Square brackets denote the value of c_{12} derived from c_{11} and B . $B = \frac{1}{3}(c_{11} + 2c_{12})$.

V/V_0	Theory		
	0.819	0.780	0.750
P (GPa)	-8.0	1.2	9.8
c_{11}	302	406	518
c_{12}	[110]	[106]	[84]
c_{44}	277	303	324
B	174	206	229

dipole moments. Therefore the ions rearrange their positions in the unit cell to reduce the system energy. The energy increase due to the effect is called the internal strain energy. Since the internal strain and electric field are mutually interrelated, it is very difficult to solve this problem self-consistently. However, we have shown that the internal strain energy can be removed from the theory if we find the configuration which gives the minimum total energy in the deformed lattice generated by a given external strain \mathbf{s} . In the present paper we call this the relaxed configuration in the deformed lattice. If the relaxed configuration is obtained, the energy increase due to the homogeneous deformation can be expressed in terms of the external strain only. Thus the problem reduces to the ordinary elastic theory.

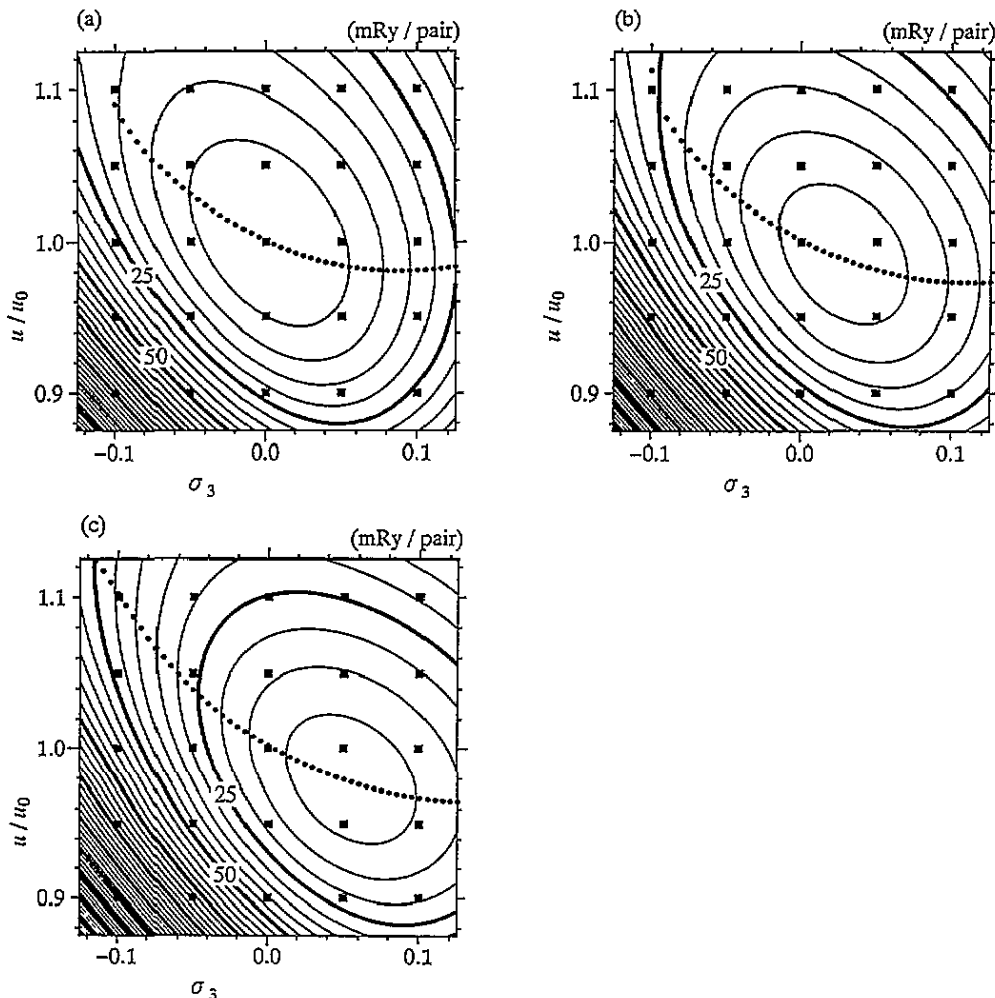


Figure 10. The curves for u versus σ_3 . The dotted curve denotes the energy minima at constant σ_3 . (a) $V/V_0 = 1.00$, (b) $V/V_0 = 0.95$ and (c) $V/V_0 = 0.90$.

The remaining problem is that of how to search for the relaxed configuration in the deformed lattice. By calculating the total energy for the possible configurations in the internal parameter space with the help of the first-principles pseudopotential method, we have determined the relaxed configuration. We have applied the present method to aluminium nitride. The theoretical values of the elastic stiffness constants are in agreement with the experimental ones within limits of 3–16%. The experimental values were derived from the measured data by using a non-linear fitting method in the space of eleven parameters. Therefore it is not necessarily clear at present whether the source of the difference is theoretical. As far as we are aware, this is the first attempt at a complete determination of the elastic stiffness tensor of a composite crystal which has internal lattice parameters to be optimized from first principles.

The present method differs from the method based on the stress theorem [5, 26]. To obtain reliable values of elastic constants, larger numbers of plane waves have to be used in the calculation based on the stress theorem than in the total energy calculation, because

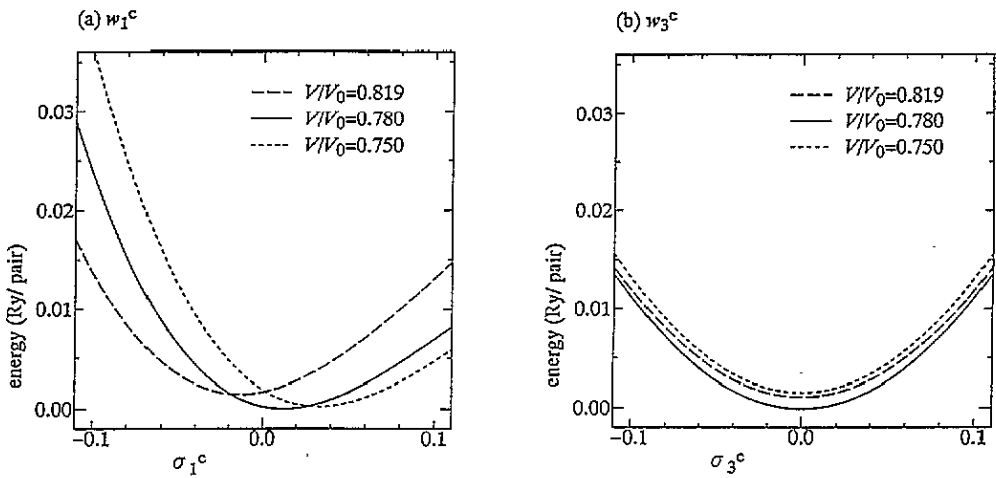


Figure 11. The total energy versus strain curves for the structures generated from the rocksalt structure at $V/V_0 = 1.00$ by $w_1^c(x)$ in the table 2. The letter V/V_0 denotes the relative volume at which the deformation $w_1^c(x)$ begins. The total energy is measured relatively from the undeformed structure at $V/V_0 = 0.7848$ which is the theoretical equilibrium volume of this phase. (a) For $w_1^c(x)$ and (b) for $w_3^c(x)$.

the former calculation in contrast to the latter one is not based on the variation principle. When treating a solid which contains row II elements, these numbers become significant. As was shown previously [27], the difference between the total energies of systems of nearly the same size can be accurately calculated for numbers of plane waves very much smaller than those required to ensure convergence of the absolute energies. A merit of the present method is the effective use of this fact. The present paper has demonstrated an efficient method for treating the case where internal displacements are present and has shown the results obtained by an actual application to AlN.

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