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The Relation of Inner Compressibilities to the Pressure Dependence of Atomic Position Parameters in Simple Crystal Structures

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Abstract

The application of hydrostatic pressure to crystals in which some atoms occupy sites with polar point-group symmetry causes the position coordinates of these atoms to change. This phenomenon is here related to *inner compressibility tensors*. These arise naturally in the theory of inner elasticity, where they are linear combinations of the macroscopic linear compressibilities weighted by components of the *internal strain tensors*, and they indicate the ease with which the separation between pairs of sublattices may change under pressure. The form of the inner compressibility tensors is presented for eleven simple crystal structures involving up to four atoms in the basis. Finally, the inner compressibilities and constraining equations for components of the internal strain are obtained from the pressure dependence of the structure of the elements As, Sb, Bi, Se, Te and I.

Introduction

A recent study of the effect of stress on the structure factors of crystals in which some atoms occupy sites lacking inversion symmetry was principally devoted to uniaxial stress in twenty simple crystal structures (Cousins, 1983, hereafter referred to as C). It was shown that the key quantities determining the crystal response are the inner compliance tensors: products of internal strain tensors and the macroscopic elastic compliance tensor.

In this paper the effect of hydrostatic pressure on the structure factors of simple crystals is examined. The key quantities in this case prove to be linear

combinations of components of the inner compliance tensors and these are termed inner compressibilities by analogy with the definition of bulk compressibility.

The structures affected are those in which the point symmetry of at least one set of equivalent atoms belongs to one of the ten polar point groups: 1, *m*, 2, *2mm*, 4, *4mm*, 3, *3m*, 6 and *6mm*. This is because the coordinates of such atoms are not totally fixed: eight of the point groups have one degree of freedom, *m* has two and 1 has three. The value of a free parameter in the unstressed crystal will generally change when the crystal is subject to hydrostatic pressure. In a study of the structure of arsenic under pressure Morosin & Schirber (1972) remark that the variation of *u* with *p* is not given by elastic constants. In the strict sense of macroscopic elastic constants this is true, but when attention is paid to the interactions between sublattices, as in inner elasticity theory (Cousins, 1978), it is found that du/dp is given by the quantities that are here designated inner compressibilities. This is shown in § 1 and formal results are presented for eleven of the structures treated in C.

Two strategies for determining the inner compressibility are discussed in § 2 and the independent components for six elements are presented in § 3. In § 4 the connection between the inner compressibility, the internal strain and the macroscopic linear compressibilities is made explicit for the six elements treated in the previous section.

1. Inner compressibility and the pressure derivatives of atomic position coordinates

If a crystal consists of *n* atoms per lattice point sited at positions \mathbf{x}^α ($\alpha = 1, 2, \dots, n$) and having form factors $f_\alpha(\theta, \lambda)$, the square of the structure factor takes

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the form

$$|F(\mathbf{H})|^2 = \sum_{\alpha=1}^n \{f_{\alpha}(\theta, \lambda)\}^2 + 2 \sum_{\pi=1}^{n(n-1)/2} g_{\pi}(\theta, \lambda) \cos \chi_{\mathbf{H}}^{\pi}, \quad (1)$$

where π is one of the $n(n-1)/2$ interlattice indices defined by $\pi = \alpha + (\beta - \alpha - 1)(2n - \beta + \alpha)/2$ with $\beta > \alpha$, $g_{\pi}(\theta, \lambda) \equiv f_{\alpha}(\theta, \lambda)f_{\beta}(\theta, \lambda)$ and

$$\chi_{\mathbf{H}}^{\pi} = 2\pi\mathbf{H} \cdot (\Delta\mathbf{x})^{\pi} = 2\pi\mathbf{H} \cdot (\mathbf{x}^{\beta} - \mathbf{x}^{\alpha}). \quad (2)$$

Note that where π is a factor in an expression it has its usual meaning of 3.14159

The pressure derivative of (1) can be approached in two different ways. Firstly, the line developed in C may be followed in which case the phase $\chi_{\mathbf{H}}^{\pi}$ is augmented by $\psi_{\mathbf{H}}^{\pi}$ under the application of a general stress σ . The new phase is given by

$$\chi_{\mathbf{H}}^{\pi} = \chi_{\mathbf{H}}^{\pi} + \psi_{\mathbf{H}}^{\pi}, \quad (3)$$

where

$$\psi_{\mathbf{H}}^{\pi} = 2\pi H_i A_{ij}^{\pi} S_{JK} \sigma_K. \quad (4)$$

In (4) A^{π} is an internal strain tensor, S is the elastic compliance tensor and summation over repeated subscripts is assumed. For hydrostatic pressure $\sigma_K = -p\delta_K$, where $\delta_K = 1$ if $K = 1, 2$ or 3 and is zero otherwise. It is possible to remove compensating length factors from \mathbf{H} and A^{π} by introducing $\mathbf{h} \equiv a\mathbf{H}$ and $\bar{A}_{ij}^{\pi} \equiv (1/a)A_{ij}^{\pi}$, whereupon (4) becomes

$$\psi_{\mathbf{H}}^{\pi} = -2\pi p h_i \bar{A}_{ij}^{\pi} S_{JK} \delta_K. \quad (5)$$

In C the product $\bar{A}_{ij}^{\pi} S_{JK}$ was written Σ_{iK}^{π} and was termed the inner compliance. Equation (5) indicates that it is possible to go a step further and to define inner compressibilities through

$$K_i^{\pi} \equiv \Sigma_{iK}^{\pi} \delta_K = \Sigma_{i1}^{\pi} + \Sigma_{i2}^{\pi} + \Sigma_{i3}^{\pi} \quad (6)$$

and to write (5) as

$$\psi_{\mathbf{H}}^{\pi} = -2\pi p h_i K_i^{\pi} \quad (7)$$

for the pressure-induced increment to the phase.

The second approach is to recognize that (3) is the Taylor expansion of $\chi_{\mathbf{H}}^{\pi}$ to two terms, so that $\psi_{\mathbf{H}}^{\pi} = p(d\chi_{\mathbf{H}}^{\pi}/dp)_0$. Now $\chi_{\mathbf{H}}^{\pi}$ is not a function of the absolute cell parameters but only of the atomic position coordinates. Thus if compensating length factors are again used (2) becomes

$$\chi_{\mathbf{H}}^{\pi} = 2\pi h_i (\Delta\mathbf{x})_i^{\pi} / a \quad (8)$$

so that

$$\frac{d\chi_{\mathbf{H}}^{\pi}}{dp} = 2\pi h_i \frac{d}{dp} \left(\frac{(\Delta\mathbf{x})_i^{\pi}}{a} \right) \quad (9)$$

and thus

$$\psi_{\mathbf{H}}^{\pi} = 2\pi p h_i \left[\frac{d}{dp} \left(\frac{(\Delta\mathbf{x})_i^{\pi}}{a} \right) \right]_0. \quad (10)$$

From the comparison of (7) and (10) it can be seen that

$$K_i^{\pi} = -\frac{d}{dp} \left[\left(\frac{(\Delta\mathbf{x})_i^{\pi}}{a} \right) \right]_0. \quad (11)$$

This is the central result that was to be established.

Certain points need to be made clear. Firstly, $(\Delta\mathbf{x})_i^{\pi}$ represents a Cartesian component of $(\Delta\mathbf{x})^{\pi}$ and h_i a Cartesian component of the reduced reflection vector. This is necessary because the tensors involved in the description of elasticity are all Cartesian. Secondly, the crystal structures to be discussed relate to rhombohedral, hexagonal, orthorhombic and tetragonal cells so that the choice of a needs careful consideration. For orthorhombic, tetragonal and hexagonal systems it is the length of the cell edge in the Ox_1 direction, i.e. $a = |\mathbf{a}_1|$. In the rhombohedral cell all edges have the same length $a_R = |\mathbf{a}_1|$ and the angle between edges is the same, α . The value of a is then βa_R where $\beta^2 = 2(1 - \cos \alpha)/3$.

Table 1 displays the form of the inner compressibility tensor for the eleven structures under discussion. On the right of the table are the derivatives of the atomic position coordinates, modified by certain axial ratios that arise when Cartesian coordinates are involved, that correspond to the single independent component of inner compressibility belonging to each structure (except for iodine where two independent components occur). The allocation of coordinates in each structure can be found in Table 2 in C.

The significance of the signs and magnitudes of the K_i^{π} can be understood by considering the significance of the atomic position parameters. The observed values of the latter indicate positions in the unit cell where a specific atom finds a local minimum in the interaction potential due to all other atoms. If hydrostatic pressure causes such local minima to shift relative to one another then the associated inner compressibilities will be non-zero and will have signs corresponding to the directions of the shifts of minima in accordance with (11). If (6) is expanded fully it can be seen that inner compressibilities are linear combinations of the macroscopic linear compressibilities k_i weighted by components of the internal strain. Thus

$$K_i^{\pi} = \bar{A}_{i1}^{\pi} k_1 + \bar{A}_{i2}^{\pi} k_2 + \bar{A}_{i3}^{\pi} k_3. \quad (12)$$

From previous experience we expect the \bar{A}_{ij}^{π} components to be no larger than about 0.3 and hence anticipate that the K_i^{π} will be no larger than the largest of the linear compressibilities.

2. Determination of the inner compressibility

There are two methods that can be used: a simple one suitable for the structures discussed here and a general one applicable to any structure.

Table 1. Form of the inner compressibility tensors and the equivalent pressure derivative of the atomic coordinates

Structure	π	Symmetry	Form	Equivalent expression for the non-zero component†
α -Uranium	1	$m2m$	$[0, K_2, 0]^*$	$2\beta(dw/dp)$
Arsenic	1	$3m$	$[0, 0, K_3]^*$	$2\delta(dw/dp)$
Samarium	1	$3m$	$\equiv -2K^2$	
Cadmium chloride	2	$3m$	$[0, 0, K_3^2]$	$-\delta(dw/dp)$
	3	$3m$	$\equiv -K^2$	
Cadmium iodide	1	$3m$	$\equiv -2K^2$	
	2	$3m$	$[0, 0, K_3^2]$	$-\gamma(dw/dp)$
	3	$3m$	$\equiv -K^2$	
Selenium	1	$m\perp(a_1 + a_2)$	$K_2^2[\sqrt{3}/2, -1/2, 0]$	$\sqrt{3}(du/dp)$
	2	$m\perp a_1$	$[0, K_2^2, 0]$	
	3	$m\perp a_2$	$K_2^2[\sqrt{3}/2, 1/2, 0]$	
Wurtzite	1	$\bar{6}m2$	$\equiv 0$	
Nickel arsenide	2	$3m$	$[0, 0, K_3^2]$	$\gamma(dw/dp)$
	3	$\bar{6}m2$	$\equiv 0$	
	4	$3m$	$\equiv K^2$	
	5	$3m$	$\equiv K^2$	
	6	$3m$	$\equiv K^2$	
Lead oxide ($G \equiv mm2$)	1	$4mm$	$\equiv -2K^2$	
	2	G	$[0, 0, K_3^2]$	$-\gamma(dw/dp)$
β -Neptunium ($G = 2\parallel Ox_3$)	3	$4m2$	$\equiv 0$	
	4	G	$\equiv -K^2$	
	5	G	$\equiv K^2$	
	6	G	$\equiv -K^2$	
Iodine/gallium	1	$m\perp Ox_1$	$\equiv K^4 - K^2$	
	2	$m2m$	$[0, K_2^2, 0]$	$-2\beta(dw/dp)$
	3	$m\perp Ox_1$	$\equiv -(K^4 + K^2)$	
	4	$mm2$	$[0, 0, K_3^4]$	$2\gamma(dw/dp)$
	5	$mm2$	$\equiv -K^4$	
	6	$m2m$	$\equiv -K^2$	

* Where the sole interlattice index is 1 it may be omitted without ambiguity.

† β and γ denote the zero-pressure ratios b/a and c/a in orthorhombic, tetragonal or hexagonal structures. $\delta^2 = (1 + 2 \cos \alpha)/2(1 - \cos \alpha)$ in rhombohedral structures.

2.1. Simple method

In the simple method the pressure dependence of the intensities of a few selected reflections are obtained and from them values of $[d|F(\mathbf{H})|^2/dp]_{p=0}$ are deduced. Provided the crystal has not been compressed too greatly (so that the form factors change) the pressure derivatives are given by

$$\left(\frac{d|F(\mathbf{H})|^2}{dp}\right)_{p=0} = -2 \sum_{\pi} g_{\pi}(\theta, \lambda) \left(\frac{d\psi_{\mathbf{H}}^{\pi}}{dp}\right) \sin \chi_{\mathbf{H}}^{\pi} \quad (13)$$

on differentiating (1). The effect of inner compressibility will be seen only in those reflections that make $\psi_{\mathbf{H}}^{\pi}$ non-zero. From (7) we have

$$\frac{d\psi_{\mathbf{H}}^{\pi}}{dp} = \frac{\psi_{\mathbf{H}}^{\pi}}{p} = -2\pi[h_1 h_2 h_3] \begin{bmatrix} K_1^{\pi} \\ K_2^{\pi} \\ K_3^{\pi} \end{bmatrix} \quad (14)$$

and it is clear that if K_i^{π} is sought then a reflection with $h_i \neq 0$ must be observed.

Expressions for $|F(\mathbf{H})|^2$ (the zero-pressure value) and $pd|F(\mathbf{H})|^2/dp$ can be taken directly from Tables 6, 7 and 8 in C, since the second expression is formally identical to $\sigma d|F(\mathbf{H})|^2/d\sigma$. Values of $\chi_{\mathbf{H}}^{\pi}$ can be taken from Tables 3, 4 and 5 in the same paper. If the reflection indices are hkl the Cartesian forms relevant to (14) are

$[h_1, h_2, h_3]$

$$= \left[\frac{h-k}{\sqrt{3}}, \frac{h+k-2l}{2}, \frac{h+k+l}{3\delta} \right]$$

in rhombohedral structures

$$= \left[h, \frac{h+2k}{\sqrt{3}}, \frac{l}{\gamma} \right]$$

in hexagonal structures

$$= \left[h, \frac{k}{\beta}, \frac{l}{\gamma} \right]$$

in orthorhombic structures

$$= \left[h, k, \frac{l}{\gamma} \right]$$

in tetragonal structures,

where β and γ are b/a and c/a ratios and $\delta^2 = (1 + 2 \cos \alpha)/2(1 - \cos \alpha)$.

2.2. General method

In the general method, the structure of the crystal is determined at each of a number of pressures. At each pressure therefore a full set of atomic position coordinates is obtained. The pressure dependence of each of these is then found numerically and identifications with the appropriate inner compressibility component are made *via* (11).

This method will be essential for any crystal with five or more atoms per lattice point.

3. Illustrative examples

There have not been very many determinations of the variation of atomic position coordinates with pressure. An examination of the literature has revealed three elements for which adequate data are available. Three of these belong to a structure with two atoms per lattice point: arsenic, antimony and bismuth; two to a structure with three atoms: selenium and tellurium; and one, iodine, to a structure with four atoms per lattice point.

3.1. Arsenic, antimony and bismuth

These three elements were studied up to 3 kbar (0.3 GPa) by Morosin & Schirber (1969 for Sb and Bi, 1972 for As). Schirfel (1977) also studied antimony to 26 kbar (2.6 GPa). He found that dw/dp was linear over the whole range and in accord with the earlier measurements at lower pressure. The essential data for the evaluation of K_3 are: rhombohedral angles $54^{\circ}10'$, $57^{\circ}14'$ and $57^{\circ}19'$ leading to $\delta = 1.618$, 1.808 and 1.806. The values of dw/dp , assuming that the

variations for As and Bi are also linear, are 2.7(5), 1.2(2) and 2.6(5) in units of TPa^{-1} . Hence

$$K_3 = 8.7(1.6) \text{TPa}^{-1} \quad (\text{As})$$

$$K_3 = 4.3(0.7) \text{TPa}^{-1} \quad (\text{Sb})$$

and

$$K_3 = 9.4(1.8) \text{TPa}^{-1} \quad (\text{Bi}).$$

3.2. Selenium and tellurium

Selenium has been studied twice. McCann & Cartz (1972) determined the structure at five pressures, including zero, up to 5.2 GPa. A least-squares fitting of a quadratic to these results yields $du/dp = 9.8 \text{TPa}^{-1}$. From this

$$K_2^2 = 17.0 \text{TPa}^{-1} \quad (\text{Se}).$$

A later determination by Keller, Holzapfel & Schulz (1977) consisted of six sets of measurements at pressures up to 8.64 GPa, but excluding zero. A similar analysis yields $du/dp = 10.1 \text{TPa}^{-1}$, whence

$$K_2^2 = 17.5 \text{TPa}^{-1} \quad (\text{Se})$$

in most satisfactory agreement.

The same authors observed tellurium at ten pressures up to 3.82 GPa. A value of $du/dp = 8.0 \text{TPa}^{-1}$ was obtained and thus

$$K_2^2 = 13.9 \text{TPa}^{-1} \quad (\text{Te}).$$

3.3. Iodine

The principal investigation was undertaken by Shimomura, Takemura, Fujii, Minomura, Mori, Noda & Yamada (1978) and purported to extend to 206 kbar (20.6 GPa). A later publication by a subset of the authors, Takemura, Fujii, Minomura & Shimomura (1979), suggests that the earlier value was too large by 20 to 30 kbar. The results of the earlier paper are here assumed to refer to a pressure of 180 kbar. Relevant axial ratios are $\beta = 0.6567$ and $\gamma = 1.371$. The values of dv/dp and dw/dp are 2.22TPa^{-1} and 0.611TPa^{-1} (assuming linear variation which may well be unjustified). From these data it is found that

$$K_2^2 = -2.92 \text{TPa}^{-1}$$

and

(I).

$$K_3^4 = 1.68 \text{TPa}^{-1}$$

4. The internal strain tensors

The ultimate goal in C was to provide sufficient information to make possible a determination of all the components of the internal strain tensors. Measurements made under hydrostatic pressure can be useful in support of such a goal but do not yield values of specific components.

Putting the value for K_i^{π} obtained above and linear compressibilities quoted by the authors, or implicit in their work, into (12) we have the following connections between internal strain components.

$$8.7 = 2.2\bar{A}_{31} + 23.9\bar{A}_{33} \quad (\text{As})$$

$$4.3 = 8.8\bar{A}_{31} + 15.9\bar{A}_{33} \quad (\text{Sb})$$

$$9.4 = 13.6\bar{A}_{31} + 18.7\bar{A}_{33} \quad (\text{Bi})$$

$$17.5 = 27.4(\bar{A}_{21}^2 + \bar{A}_{22}^2) - 6.6\bar{A}_{23}^2 \quad (\text{Se})$$

$$13.9 = 25.1(\bar{A}_{21}^2 + \bar{A}_{22}^2) - 4.2\bar{A}_{23}^2 \quad (\text{Te})$$

and

$$-2.92 = 10.6\bar{A}_{21}^2 + 8.8\bar{A}_{22}^2 + 4.0\bar{A}_{23}^2 \quad (\text{I})$$

$$1.68 = 10.6\bar{A}_{31}^4 + 8.8\bar{A}_{32}^4 + 4.0\bar{A}_{33}^4$$

where factors of 10^{-12}Pa^{-1} have been cancelled throughout and tolerances on the experimental values have been omitted.

5. Concluding remarks

A knowledge of the internal strain tensors possessed by a crystal is essential if the relative displacements of atoms within the unit cell under an arbitrary uniform macroscopic strain are required. The components of these tensors are in principle most directly obtained by determining the change in structure factors under uniaxial stress. In reality there are difficulties in this approach because dislocation movement may introduce uncertainty, and slip or cleavage may make some measurements impossible. Partial avoidance of these difficulties is possible in some cases by making measurements under hydrostatic pressure, in which case certain combinations of internal strain components, weighted by linear compressibilities, are found. These have been called inner compressibilities and have been shown to be equivalent to pressure derivatives of atomic position parameters, multiplied in some instances by appropriate axial ratios. This has been illustrated by reference to the six elements for which pressure-dependent structural data exist.

Complementarily, if a theoretical model of atomic and electronic interactions exists for a particular crystal then the pressure dependence of the atomic position parameters may be obtained by applying the theory of inner elasticity.

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Adjustable Resolution Bragg Reflection Systems

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Abstract

In this paper is described the realization of an idea due to J. W. M. Dumond who, almost 50 years ago, suggested that Bragg diffraction peaks might be made narrower by multiple reflection [Dumond (1937). *Phys. Rev.* **52**, 872–883]. The optical elements which result belong to a family of harmonic free monochromators, X-ray and neutron polarizers whose properties make feasible many new Bragg diffraction optical systems.

Introduction

Nearly fifty years ago Kirkpatrick first suggested that the intrinsic width of the Bragg reflection from perfect single crystals might be reduced by making several successive reflections from different crystals. Dumond (1937) took up the idea and investigated the possibilities theoretically. Although Dumond calculated that a double Bragg reflection, successively from two calcite cleavage planes, could be used to reduce the width of the composite Bragg peak from $3\frac{1}{2}''$ to only $1\frac{1}{4}''$ at 0.71 Å wavelength he stated that Bollmann, Bailey & Dumond (1938) found experimentally that the attainable narrowing was insignificant. Dumond (1937) approximated the shape of the Bragg reflection peak with a Lorentzian $R_L(y) = 1/(1+y^2)$, where y represents the angle of incidence, and went on to show that no useful narrowing of the Bragg peak could be expected.

In this paper we show that Kirkpatrick's ideas can be successfully implemented with appropriate design and we demonstrate narrowing of the quadruply diffracted 422 rocking curve in silicon from 3.0'' to only 0.8'' at 1.54 Å wavelength. Two important

developments have made this work possible; ideally perfect crystals are now commercially available and the concept of monolithic construction with elastic adjustment Okkerse (1963) has been developed to achieve adequate stability and control in multiple Bragg reflection systems.

Theoretical and experimental background

Zero absorption approximation

The original Kirkpatrick–Dumond idea is indicated in Fig. 1. Taking two identical crystals whose reflectivities are given by

$$R_B(y) = R_1(y) = R_2(y + \Delta\theta) = ||y| - (y^2 - 1)^{1/2}|^2, \quad (1)$$

$$R(\Delta\theta) = R_1(y)R_2(y + \Delta\theta), \quad (2)$$

the double reflectivity profile [$R(\Delta\theta)$ in Fig. 1] may have a much lower angular spread than the Bragg peaks of the individual single crystals. This is the 'offset narrowing' concept which Kirkpatrick and Dumond proposed.

Dumond (1937) noted, as Fig. 1 shows well, that as the composite Bragg peak is narrowed (so that $\Delta\theta$ approaches 2 on the y scale) a progressively larger fraction of the integrated intensity resides in the tails of the peak. The corresponding decrease in signal-to-noise ratio when the narrowed peak is used as a probe is most unhelpful. Dumond also reported that 'Bollman and Bailey have found experimentally with three calcite crystals reflecting Mo K radiation on their cleavage planes and have subsequently verified by graphical integration with the theoretical diffraction patterns of Prins that the simple application of the principle of displaced superposition of diffraction patterns is not enough to give a "tool" adequate satisfactorily to reveal the Prins diffraction pattern of a third crystal' (Bollman, Bailey & Dumond, 1938). At long wavelengths, spectroscopists in the 1930's

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