

Site symmetry and internal strains

R SRINIVASAN and G LAKSHMI

Department of Physics, Indian Institute of Technology, Madras 600036

MS received 23 October 1975; after revision 7 January 1976

Abstract. The determination of the internal strains on the coupling parameter approach becomes very involved particularly when the number of atoms per unit cell is very large. It is shown in this paper that a knowledge of the site symmetry of the atoms helps one in determining the number of non-vanishing internal strain coefficients easily. The internal strain coefficients of two symmetry connected atoms can also be related. Examples are shown to illustrate these ideas.

Keywords. Site symmetry; internal strains; Lagrangian strains; inversion symmetry.

1. Introduction

When a crystal lattice is macroscopically strained, there is a relative displacement between the sublattices. If we indicate a given sublattice by the symbol K , then the displacement $u_i \left(\frac{L}{K} \right)$ of an atom of this sublattice in cell L under a macroscopic strain is given by

$$u_i \left(\frac{L}{K} \right) = \sum_j \eta_{ij} R_j \left(\frac{L}{K} \right) + W_i(K) \quad (1.1)$$

Here i, j are component indices, $\vec{R} \left(\frac{L}{K} \right)$ is the position vector of atom $\left(\frac{L}{K} \right)$ in the unstrained state, η_{ij} are the Lagrangian strain components and $\vec{W}(K)$ the internal displacement of the K th sublattice. The η_{ij} are defined in terms of the deformation components $\epsilon_{ij} = \delta x_i' / \delta x_j$ (x_i' are the coordinates of a particle in the strained state and x_j are the coordinates in the unstrained state) by

$$\eta_{ij} = \frac{1}{2} (\epsilon_{ij} + \epsilon_{ji} + \sum_k \epsilon_{ki} \epsilon_{kj}). \quad (1.2)$$

The internal displacement $\vec{W}(K)$ can be expanded as a power series in the macroscopic strain η_{ij} as

$$W_i(K) = \sum_{ik} \Gamma_{i,jk}(K) \eta_{jk} + \sum_{jk,lm} \Gamma_{i,jk,lm}(K) \eta_{jk} \eta_{lm} \quad (1.3)$$

However it has been shown by Born and Huang (1968) for second order elastic constants and piezoelectric constants and by Srinivasan (1966) for third order elastic constants, that only the first term in the above expansion is important. The constants $\Gamma_{i,jk}(K)$ are determined either by minimising the elastic energy density with respect to internal displacements in the method of homogeneous deformation or by solving for the first order equation of motion in the method of long

waves. However a straightforward application of this method involves the inversion of a $(3n - 3) \times (3n - 3)$ matrix where n is the total number of sublattices present (*i.e.*), the number of atoms in the unit cell. This is a very cumbersome procedure when the number of atoms in the unit cell is large, for example, eight in V_3Si and ten in Calcite.

The internal displacements can be observed by x-ray diffraction. In displacive transitions a knowledge of the type of internal displacements caused by anisotropic thermal expansion (if the transition is temperature induced) or by pressure (if it is pressure induced) is useful.

In this paper it is shown that the site symmetry of an atom completely fixes the number of non-vanishing coefficients of $\Gamma_{i,jk}(K)$ and so one could get useful information about these internal displacements from symmetry consideration. A knowledge of the number of non-vanishing coefficients and the way the internal displacement components of two symmetry connected atoms are related reduces the labour involved in expressing $\Gamma_{i,jk}(K)$ in terms of the force constants of a model.

Section 2 deals with site symmetry and the internal strains and relations among internal strain coefficients $\Gamma_{i,jk}(K)$ of symmetry related atoms. Section 3 illustrates the application of the results in section 2 to a few crystals.

2. Symmetry and internal strain coefficients $\Gamma_{i,jk}(K)$

The internal strain coefficient $\Gamma_{i,jk}(K)$ is a third rank polar tensor having the symmetry $\Gamma_{i,jk}(K) = \Gamma_{i,kj}(K)$. This tensor is similar to the piezoelectric constant tensor tabulated in Cady (1964) and Nye (1960) for the 32 point groups. However this tensor will not depend on the point group of the crystal as a whole but on the site symmetry of the given atom in the crystal which will be a subgroup of the point group. For example a crystal like CaF_2 has the O_h point group and so the piezoelectric tensor is zero for this crystal. However the point group symmetry at the site of F is T_d and so $\Gamma_{i,jk}(F)$ is not identically zero. So to find the non-vanishing components of $\Gamma_{i,jk}(K)$ we have to find the point group representing the site symmetry at K and then look up the tables of the piezoelectric tensor for this point group. In particular if the site symmetry of an atom involves a centre of inversion then there will be no internal displacement for this sublattice.

Let S be a symmetry operation of the crystal which carries a sublattice K to a sublattice K' . If S_{ij} are the elements of the 3×3 matrix representing the transformation S , then,

$$\Gamma_{i,jk}(K') = \sum_{lmn} S_{il} S_{jm} S_{kn} \Gamma_{l,mn}(K) \quad (2.1)$$

This is the law of transformation of a third rank polar tensor. Using this we may determine the internal strain coefficients of one sublattice from that of another symmetry related sublattice.

3. Application of the above results to a few crystals

(i) $NaCl$ and $CsCl$ structures

Here the metal and chlorine ions are both situated at centres of inversion

symmetry. So the internal strain coefficients are zero for both sublattices. In these crystals a macroscopic strain does not cause any internal displacements.

(ii) *Germanium structures*

There are two atoms in the unit cell Ge (1) and Ge(2). The site symmetry of the germanium atom is T_d . From the tables of the piezoelectric constants in Cady, the only non-vanishing internal strain coefficients are

$$\Gamma_{x,yyz}(K) = \Gamma_{y,xyz}(K) = \Gamma_{z,xyx}(K)$$

where $K = 1$ or 2 . This shows that a shear strain η_{yz} causes a displacement of the germanium atom along the x axis. Since Ge (1) sublattice is carried to Ge (2) sublattice by inversion about a point midway between the Ge (1) and its nearest neighbour Ge (2),

$$\Gamma_{i,jk}(2) = -\Gamma_{i,jk}(1) \tag{3.1}$$

So there is only one internal strain coefficient to be determined in this case. This is in agreement with the lattice dynamical calculations on germanium by Srinivasan (1967).

(iii) *CaF₂ structure*

As already pointed out Ca is at a centre of inversion symmetry and each of the two fluorine sublattices have a site symmetry T_d . The sublattice F_1 is carried to the sublattice F_2 by inversion at calcium. So

$$\Gamma_{i,jk}(F_1) = -\Gamma_{i,jk}(F_2) \tag{3.2}$$

and the only non-vanishing coefficient of $\Gamma_{i,jk}(F_1)$ is $\Gamma_{x,yyz}(F_1)$ and

$$\Gamma_{x,yyz}(F_1) = \Gamma_{y,xyz}(F_1) = \Gamma_{z,xyx}(F_1). \tag{3.3}$$

This is in agreement with Srinivasan's (1968) results on CaF₂.

(iv) *V₃Si structure*

This lattice is cubic. It has eight atoms in the unit cell. Si (1) is located at the corners of a cube while Si (2) is at the body centre. V(1) and V(2) are situated on either side of the centre of the (100) face of the cube at a distance $a_0/2$ from the centre on a line parallel to the y axis. V (3) and V (4) are similarly situated on the (010) face on a line parallel to the z axis and V (5) and V (6) are situated on the (001) face on a line parallel to the x axis.

The position coordinates of the ions are given in table 1 for reference. The site symmetry at Si (1) and Si (2) has a centre of inversion symmetry. So

$$\Gamma_{i,jk}(\text{Si}(1)) = \Gamma_{i,jk}(\text{Si}(2)) = 0 \tag{3.4}$$

The silicon atoms suffer no internal displacement on applying a macroscopic strain. The site symmetry at the site of V(1) is C_{2v} with the two fold axis along y and mirror planes yz and yx . From Cady's tables we have

$$\Gamma_{x,yyz}(V(1)), \Gamma_{y,xyz}(V(1)), \Gamma_{y,yyz}(V(1)), \Gamma_{y,xyz}(V(1)), \Gamma_{z,xyx}(V(1))$$

as the only non-vanishing coefficients. Also we get V (2) from V (1) by inversion

Table 1. Position coordinates of the atoms in V_3Si

Atom	Position
Si (1)	$a_0 (0, 0, 0)$
Si (2)	$a_0 (1, 1, 1)$
V (1)	$a_0 (0, 1/2, 1)$
V (2)	$a_0 (0, 3/2, 1)$
V (3)	$a_0 (1, 0, 1/2)$
V (4)	$a_0 (1, 0, 3/2)$
V (5)	$a_0 (1/2, 1, 0)$
V (6)	$a_0 (3/2, 1, 0)$

$2a_0$ is the lattice constant of the crystal.

at a point midway between them. So

$$\Gamma_{i,jk} (V (2)) = -\Gamma_{i,jk} (V (1)) \quad (3.5)$$

i.e., for a given strain the sublattices V (1) and V (2) will be displaced in opposite directions by an equal amount. So also for V (3) and V (4), V (5) and V (6). The non-vanishing elements of the internal strain coefficients for V (3) and V (5) can be obtained from those for V (1) by finding the symmetry operations which carry the V (1) sublattice to the V (3) and V (5) sublattices respectively. The symmetry operation is a rotation by 120 and 240° about the three-fold axis along the (111) direction. This gives the following relations:

$$\begin{aligned} \Gamma_{\sigma,xy} (V (1)) &= \Gamma_{y,y\sigma} (V (3)) = \Gamma_{z,\sigma z} (V (5)) \\ \Gamma_{y,\sigma z} (V (1)) &= \Gamma_{\sigma,yy} (V (3)) = \Gamma_{\sigma,\sigma\sigma} (V (5)) \\ \Gamma_{y,yy} (V (1)) &= \Gamma_{\sigma,\sigma z} (V (3)) = \Gamma_{\sigma,\sigma z} (V (5)) \\ \Gamma_{y,\sigma z} (V (1)) &= \Gamma_{\sigma,\sigma z} (V (3)) = \Gamma_{\sigma,yy} (V (5)) \\ \Gamma_{\sigma,y\sigma} (V (1)) &= \Gamma_{\sigma,\sigma\sigma} (V (3)) = \Gamma_{y,\sigma y} (V (5)). \end{aligned} \quad (3.6)$$

So we see that symmetry considerations tell us that out of the 144 possible internal strain coefficients only five are non-zero and independent. Recently Prabhakaran Nayar and Viswanathan (1975) have calculated the internal strain coefficients of V_3Si by the method of long waves on a model using the DeLaunay's central and non-central force constants for nearest neighbour V-V and Si-V interactions and the results obtained by them are in complete agreement with the symmetry relations obtained above. In fact irrespective of the model used the above relations among the internal strain coefficients should be satisfied. The long wave method as mentioned in the introduction is cumbersome and involves the inversion of matrices of large order. However the same internal strain coefficients can be calculated from a knowledge of the relations derived from symmetry above and using the homogeneous deformation method of Born and Huang. The strain energy density will now involve only the five independent internal strain coefficients which can be obtained by minimising the strain energy with respect to the corresponding

internal displacements. The internal displacements in V_3Si have been calculated by us using the above procedure and the expressions are in complete agreement with those of Prabhakaran Nayar and Viswanathan (1975).

(v) *Calcite structure*

Calcite belongs to the trigonal system and has a point group symmetry D_{3d} . The z -axis is a three-fold axis of symmetry and there are ten atoms in the rhombohedral unit cell, two calciums, two carbons and six oxygens. Figure 1 shows the arrangement of atoms in the unit cell. We choose the x -axis to be along C (1)-O (3). The site symmetries at various sites are as follows: (a) The two calciums are located at sites of inversion symmetry. So

$$\Gamma_{i,jk}(\text{Ca (1)}) = \Gamma_{i,jk}(\text{Ca (2)}) = 0 \quad (3.7)$$

They do not undergo any internal displacements when the lattice is strained. (b) The C (1) has a site symmetry of D_3 . From Cady's tables for the piezo-electric tensor we have the following non-vanishing coefficients:

$$\Gamma_{x,xx}(\text{C (1)}) = -\Gamma_{x,yy}(\text{C (1)}) = -\Gamma_{y,yy}(\text{C (1)}) \quad (3.8)$$

$$\Gamma_{x,yz}(\text{C (1)}) = -\Gamma_{y,xz}(\text{C (1)}). \quad (3.9)$$

So to describe the internal displacement of C (1) we need only two independent constants.

We also see that C (1) and C (2) are related by inversion about Ca (1). So

$$\Gamma_{i,jk}(\text{C (1)}) = -\Gamma_{i,jk}(\text{C (2)}) \quad (3.10)$$

(c) The oxygen O (3) lies along the x -axis on a two-fold axis of symmetry. Its site symmetry is C_2 . We have therefore

$$\Gamma_{x,xx}(\text{O (3)}), \Gamma_{x,zz}(\text{O (3)}), \Gamma_{x,yy}(\text{O (3)}), \Gamma_{y,zz}(\text{O (3)}), \Gamma_{y,xy}(\text{O (3)})$$

$$\Gamma_{y,zz}(\text{O (3)}), \Gamma_{x,yy}(\text{O (3)}), \Gamma_{x,zz}(\text{O (3)}).$$

From O (3) we may go to O (2) by a 120° rotation about the three-fold axis through

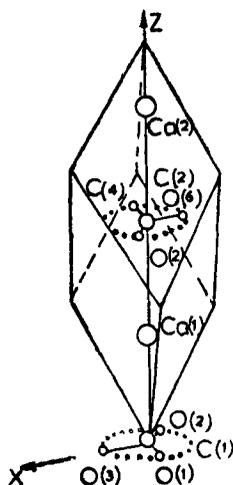


Figure 1. Unit cell of calcite.

C (1). The law of transformation leads to the non-vanishing constants of O (2) in terms of the constants for O (3). We give below two such relations:

$$\Gamma_{\sigma, \nu\sigma}(\text{O (2)}) = \frac{1}{4}(\Gamma_{\sigma, \nu\sigma}(\text{O (3)}) - 3 \Gamma_{\nu, \sigma\sigma}(\text{O (3)})) \quad (3.11)$$

$$\Gamma_{\sigma, \sigma\sigma}(\text{O (2)}) = \frac{-1}{8}(\Gamma_{\sigma, \sigma\sigma}(\text{O (3)}) + 3 \Gamma_{\sigma, \nu\nu}(\text{O (3)}) + 6 \Gamma_{\nu, \sigma\nu}(\text{O (3)})) \quad (3.12)$$

The internal strain coefficients $\Gamma_{i,jk}$ (O (1)) can be obtained similarly. The internal strain coefficients of O (4), O (5) and O (6) can be obtained by inverting O (1) O (2) and O (3) through Ca (1). So

$$\begin{aligned} \Gamma_{i,jk}(\text{O (1)}) &= -\Gamma_{i,jk}(\text{O (4)}); & \Gamma_{i,jk}(\text{O (2)}) &= -\Gamma_{i,jk}(\text{O (5)}) \\ \Gamma_{i,jk}(\text{O (3)}) &= -\Gamma_{i,jk}(\text{O (6)}). \end{aligned} \quad (3.13)$$

Thus in calcite the number of non-vanishing independent internal strain coefficients are ten.

The above examples suffice to illustrate the usefulness of the symmetry arguments. There is one point to be made here. If an atom lies at a special position in the lattice, then a hydrostatic stress will not move the atom from this special position. So we must expect the $\Gamma_{i,jk}(K)$ for such atoms to satisfy the condition $\sum_j \Gamma_{i,jj}(K) = 0$. This may actually be apparent from the coefficients deduced by the application of symmetry. For example, C (1) in calcite for which

$$\Gamma_{\sigma, \sigma\sigma}(\text{C (1)}) = -\Gamma_{\sigma, \nu\nu}(\text{C (1)}) \quad \text{and} \quad \Gamma_{\sigma, \sigma\sigma}(\text{C (1)}) = 0. \quad (3.14)$$

On the other hand there will be cases where this condition is in addition to that demanded by symmetry. For example in $V_3\text{Si}$

$$\Gamma_{\nu, \nu\nu}(\text{V (1)}) + \Gamma_{\nu, \sigma\sigma}(\text{V (1)}) + \Gamma_{\nu, \sigma\sigma}(\text{V (1)}) = 0 \quad (3.15)$$

because V (1) is at a special position in the lattice. In fact any calculation of these coefficients from a force constant model must satisfy the above condition.

References

- Born M and Huang K. 1968 *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford)
 Cady W G 1964 *Piezoelectricity* (Dover Publication Inc., New York)
 Nye J F 1960 *Physical Properties of Crystals* (Clarendon Press, Oxford)
 Prabhakaran Nayar S R and Viswanathan K S 1975 To appear in *Indian J. Pure Appl. Phys.*
 Srinivasan R 1966 *Phys. Rev.* **144** 620
 Srinivasan R 1967 *J. Phys. Chem. Solids* **28** 2385
 Srinivasan R 1968 *Phys. Rev.* **165** 1054