JOURNAL OF SOLID STATE CHEMISTRY **133,** 322–326 (1997)
ARTICLE NO. SC977494

The Rotation-Induced Relaxation Mechanism for Strains: Application to Boron-Rich Crystals

Koun Shirai

ISIR, Osaka University, 8-1, Mihogaoka, Ibaraki, Osaka 567, Japan

Received May 19, 1997; accepted May 27, 1997

A relaxation mechanism for externally applied strains has been studied for those crystals which have molecular units in the unit cell. In many classes of such crystals, it is proven that rotations of the molecular units are capable to relax the strain substantially. This effect is particularly significant, if noncentral forces are ignored for the interatomic forces. This paper illustrates this mechanism by taking a simple 2-dimensional square lattice as example. Boron-rich crystals furnish further examples, in which subtle variations in the structures and in forces are crucial for this mechanism. © 1997 Academic Press

I. INTRODUCTION

Recently, the elastic properties of boron-rich solids have been studied by the present author (1). In the course of the study, a general mechanism of the relaxation for external strains has been found for those crystals which have molecular units in the unit cell. Rotational motions of the molecular units are able to relax an external strain substantially. This mechanism is closely related to the rotation phenomenon in the high-temperature phase of fullerenes (2). It was fortunate that the crystals of α-boron modifications were suitable for illustrating this mechanism. This class of crystals has a variety of polymorphic modifications, suitable for testing the mechanism by changing interatomic forces and the crystal structure.

This rotation-induced relaxation mechanism is sensitive to the details of the crystal structure. Even for the α-boron modifications, the relationship between the mechanism and the geometry is not quite obvious. More simple examples would be more helpful for intuitive understanding of the mechanism. The first purpose of this paper is to give a more simple example of a 2-dimensional square crystal. The second purpose is to give further pictorial illustrations of the mechanism by using examples of α-boron modifications.

II. ROTATION-INDUCED RELAXATION MECHANISM FOR EXTERNAL STRAINS

First, we summarize the theorems proven in Ref. (1). In general, when an external strain is applied to a nonprimitive crystal, the internal shift among the basis atoms is induced in order to relax the external strain. Owing to this degree of freedom, the elastic responsibility is divided into two parts. In terms of the elastic constant $c_{\mu\alpha,\nu\beta}$, these are expressed in the form (3)

$$c_{\mu\alpha,\nu\beta} = [\mu\nu, \alpha\beta] + [\alpha\nu, \mu\beta] - [\alpha\mu, \nu\beta] + (\mu\alpha, \nu\beta). \quad [1]$$

The first three terms on the right-hand side represent the contribution of the homogeneous external deformation. The last term represents the contribution of the internal shift. Here, α, β, μ, and ν refer to the Cartesian coordinates.

For the internal shift, only selected optical modes are induced. Which type *ra* of optic mode couples with the external deformation $u_{\mu\alpha}$ is determined by the selection rule. Here, the label *r* denotes an irreducible representation of the point group of the crystal, and the label *a* denotes a different vector belonging to the same irreducible representation. The pair of indices $\mu\alpha$ is transformed as the symmetrized product of the Cartesian coordinates, *i.e.*, $(\Gamma_p \times \Gamma_p)_s$. Hence, the following selection rule can be expressed:

THEOREM (I). *Only symmetric Raman-active modes can be induced as the internal shift by the external strain.*

The selection rules between external strains and the induced internal shift have been known for limited classes of crystals, such as alkali halides (4, 5). The above theorem (I) has the most general form, which holds for any class of crystals. Derivation of this theorem is not difficult. But, it is a surprising matter that, as far as the author is aware, there has been no description in the literature.

The magnitude of contribution of a specific optic mode *ra* is determined by the inverse of the dynamic matrix for the zone-center modes. From this, it follows that:

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THEOREM (II). *If the crystal has a librational mode, and if the librational mode is Raman active, then the librational mode is able to greatly reduce the strain energy.*

Librational modes are based on rotations of molecular units. The symmetry of rotation is represented by the anti-symmetrized product of the Cartesian coordinates, $(\Gamma_p \times \Gamma_p)_a$, which are frequently consonant with the symmetry of Raman activity, $(\Gamma_p \times \Gamma_p)_s$. Hence, the conditions of (II) are often met for those crystals which have molecular units in the unit cell. Since the frequency ω_l of the librational mode is usually dominated by noncentral forces, the property (II) drastically appears as the noncentral forces are decreased.

Now let us examine the above mechanism for a 2-dimensional square lattice, as shown in Fig. 1a. Probably, this example is the smallest one that is large enough to exhibit the rotation-induced mechanism. The point group of this crystal is C_{4v}. We assume central forces α and α' for the intramolecular and intermolecular interactions, respectively. The isolated square molecule has four distinct eigenvibrations: $A_1 + B_1 + B_2 + E$. In the present two-force-constant model, the frequency of the B_1 mode is zero, while the frequencies of the A_1, B_2, and E modes are accidentally all the same, $\sqrt{2\alpha/m}$. Then the deformation energy U becomes,

$$U = \alpha^*(a + b)^2(\varepsilon_{xx} + \varepsilon_{yy})^2/(4\Omega_0), \qquad [2]$$

along the same line as in Ref. (6). Here, Ω_0 is the volume of the unit cell, and $\alpha^* = \alpha\alpha'/(\alpha + \alpha')$. The diagonal components of the elastic constants are then obtained as

$$c_{11} = c_{22} = c_{12} = \alpha^*(a + b)^2/(2\Omega_0), \qquad [3]$$

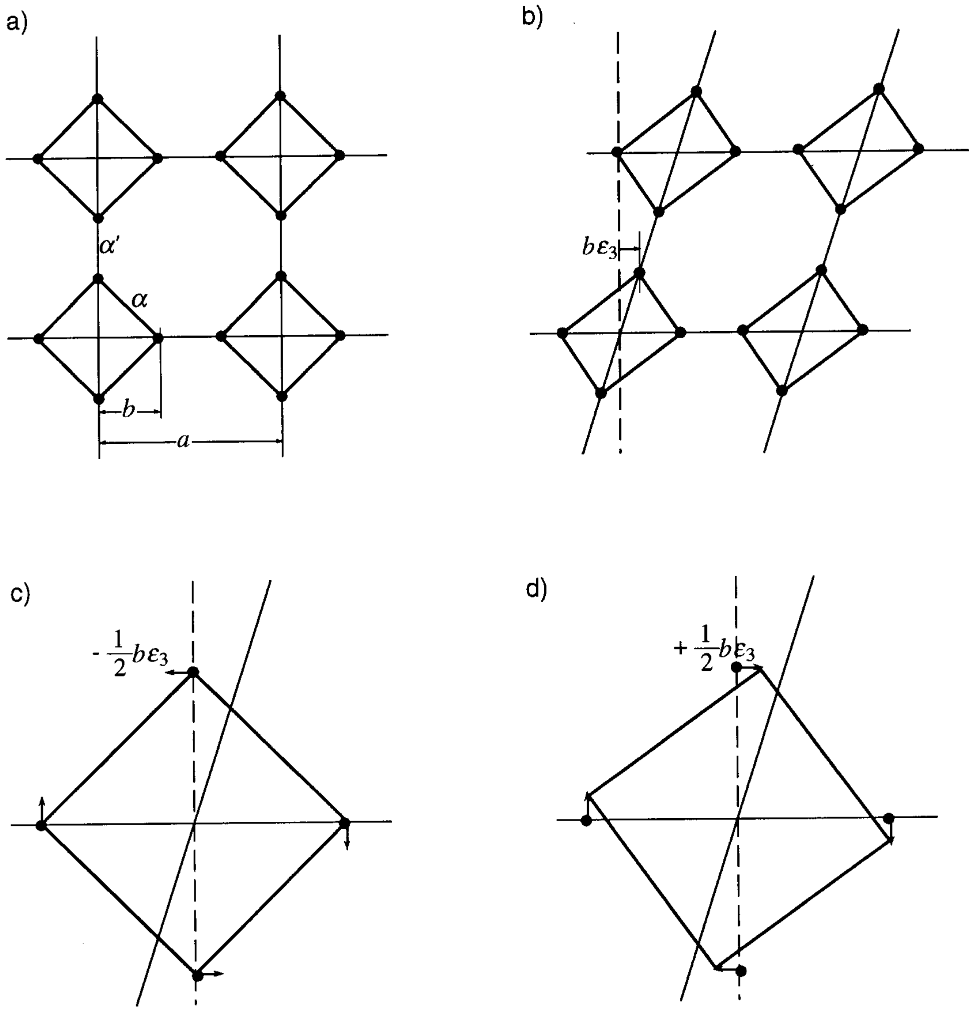

FIG. 1. A relaxation mechanism for the 2-dimensional square lattice, the equilibrium configuration being shown in (a). When a shear strain $\varepsilon_3 = \varepsilon_{yx}$ is applied, the lattice vectors are deformed as in (b). Then, the internal shift B_2 is induced in the square molecule as in (c). Consequently, the net displacements of the basis atoms are given by the sum of (b) and (c), which turn to a free rotation of the molecule, as shown in (d).

This equality shows that the isotropic condition holds. Hence, this model exhibits higher symmetry than the original symmetry of the cubic system. Such situations sometimes occur when the Cauchy relations hold (3, 5). In addition, it immediately follows from Eq. [2] that the c_{33} component, which is the elastic response for a shear strain $\varepsilon_3 \equiv \varepsilon_{xy}$, vanishes. Hence, a Cauchy relation $c_{33} = c_{12}$ does not hold in this case. This example shows that extra symmetry can occur even when the Cauchy relations do not hold.

We can understand what happens with the vanishing c_{33}, on the basis of the above theorems. Although all the normal modes are Raman active and thereby could participate in the relaxation, only the B_2 mode is induced for a shearstrain ε_{xy}, since B_2 is transformed as a quadric term xy. The B_2 mode is shown in Fig. 1c. The actual displacements of atoms are sum of the external displacements and the internal shift. To which extent the internal shift is induced is determined as to retain the deformation energy minimum. The magnitude of the induced internal shift q_{B2} is found to be $-b\varepsilon_{xy}$. As seen in Fig. 1d, it is clear that this condition leads to a pure rotation of the square molecule. In this situation, all the intramolecular and intermolecular bonds retain their equilibrium lengths.

Some comments are needed concerning the properties that are special with this simplest example. First, the induced optic mode, B_2, is apparently quite different from a free rotation of the molecule, although the final displacements are perfect rotations. The rotational motion belongs to the A_2 symmetry and thereby is incapable to participate in the internal relaxation. This is a special consequence that the structure of the square lattice is quite simple. As the structure is more complicated, the induced optic mode itself will exhibit a rotational character.

Second, the induced optic mode, B_2, is not a librational mode. Actually, it is one of the highest modes. Nevertheless, there is no choice; the selection rule allows only this mode for a shear strain ε_{xy}. Even a highest mode is able to cancel completely a shear strain ε_{xy} in this case. This example shows that theorem (I) always holds, whereas (II) is most likely to hold but not necessarily.

From the figure, we can see that, even if intramolecular angle-bending forces are introduced, the situation about the rotations cannot be changed. To suppress the rotations, intermolecular angle-bending forces are necessary.

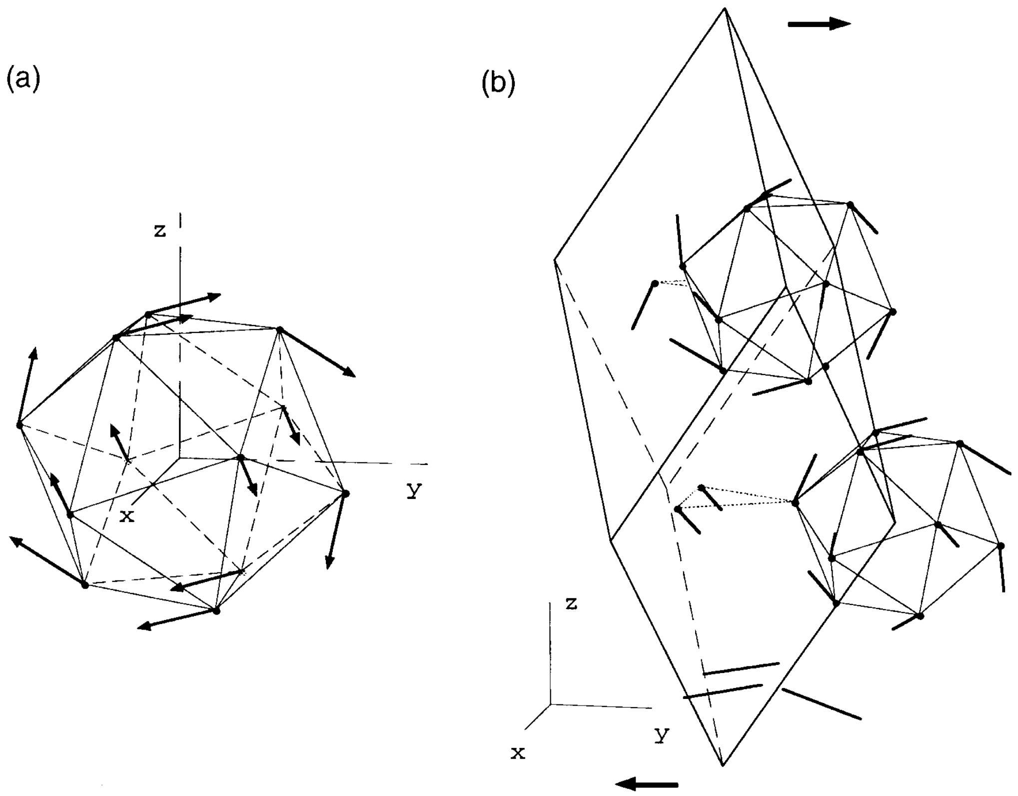

FIG. 2. A relaxation for a shear strain ε_4 in α-boron. The central forces only are assumed. (a) shows the internal shift induced on the icosahedron alone, whereas (b) shows the net displacements, which include the contribution of the external displacement. The external contribution is shown relatively by taking the center of the main diagonal as the origin. $\varepsilon_4 = 0.2$ is assumed. The arrows in (b) indicate the direction of the shear strain ε_4.

III. ILLUSTRATIONS FOR THE α-BORON MODIFICATIONS

We will examine how the foregoing mechanism work by using the crystals of the α-boron modifications. We use the Voigt notation for elastic constants and strains.

First, let us ignore any noncentral force. The forgoing theory predicts that rotational motions drastically appear. Figure 2 shows the elastic response of α-boron for a shear strain ε_4. The used parameters are the same as those of model (I) of Table I in Ref. (1). The external contribution is shown relatively by taking the center of the main diagonal as the origin, and the same is applied for the following illustrations. The selection rule tells that only the E_g2 (the second partner of the E_g symmetry) mode is induced in this case. There are six E_g modes. Among them, the lowest librational mode E_g corresponds to the rotational motion. This librational mode is slightly different from a pure rotational motion. In a similar way to the 2-dimensional square lattice, adding the contribution of the external strain completes the pure rotation. Any strain energy disappears, and this leads to $c_{44} = 0$, as in the square lattice. The instability of the crystal of α-boron can be understood on this basis.

It is also noted that there is a special condition in which this relaxation mechanism does not effectively act on. If the rhombohedral atoms are located just on the lattice vector of the rhombohedral frame, the condition for the perfect cancellation of the shear strain would break. This is proven in Ref. (1). A small deviation of the polar angle $\Delta\theta$ formed between the rhombohedral site and the lattice vector is essential for the mechanical stability.

Next, let us apply the compression in the x and y directions. Figure 3 shows the elastic response of boron carbide for a compression in the x and y direction (ε_1 and ε_2). The selection rule tells that the A_{1g} and E_g2 modes are induced in this case. There are five A_{1g} and seven E_g modes. Again, the lowest librational mode E_g has a dominant role on the relaxation, as seen in Fig. 3. The second partner of the E_g mode corresponds to the rotation about the x axis. It is noted that both directions of the compression, x and y, induce the same orientation of rotation. But, the direction of rotation is reversed for ε_1 and ε_2. For α-boron, the directions of rotations are opposite to those of boron carbide. Compare the present figure (boron carbide) with Fig. 3 (α-boron) of Ref. (1). In this way, we understand that the rotational response stands on subtle conditions about balance of forces. A small change in the structure or a change in the

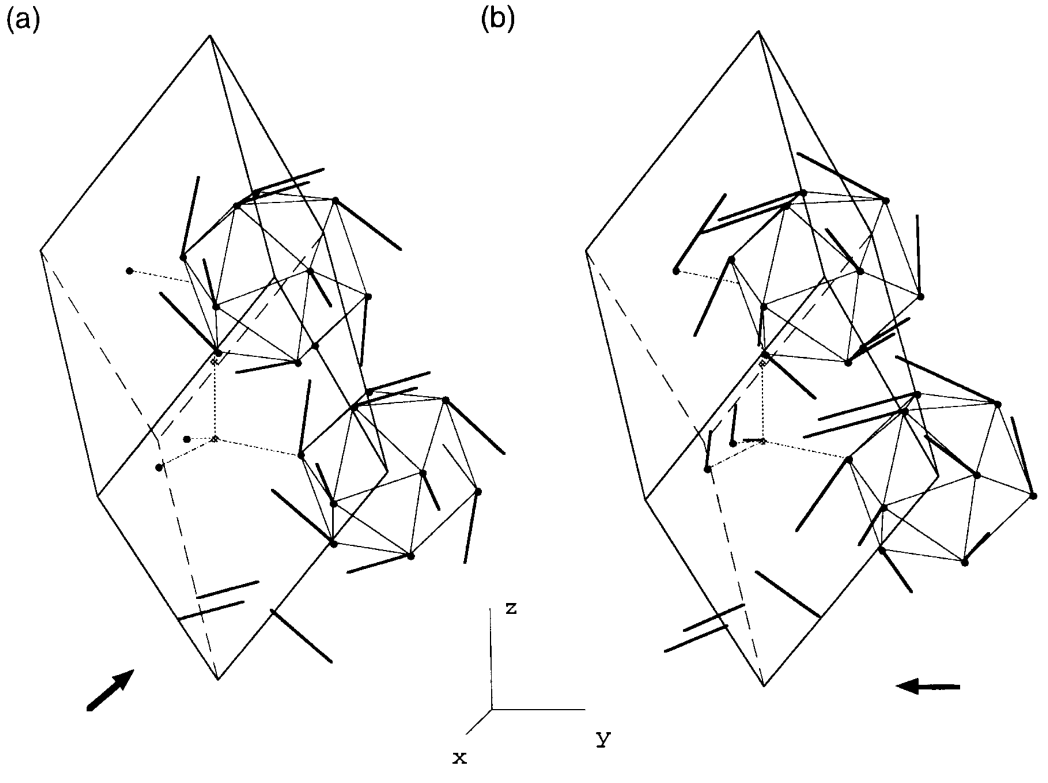

FIG. 3. The relaxation in boron carbide (a) for the compression in the x direction ε_1, (b) for the compression in the y direction ε_2. The central forces only are assumed. $\varepsilon_i = 0.2$ is assumed. The thick arrows outside the cell indicate the direction of compression.

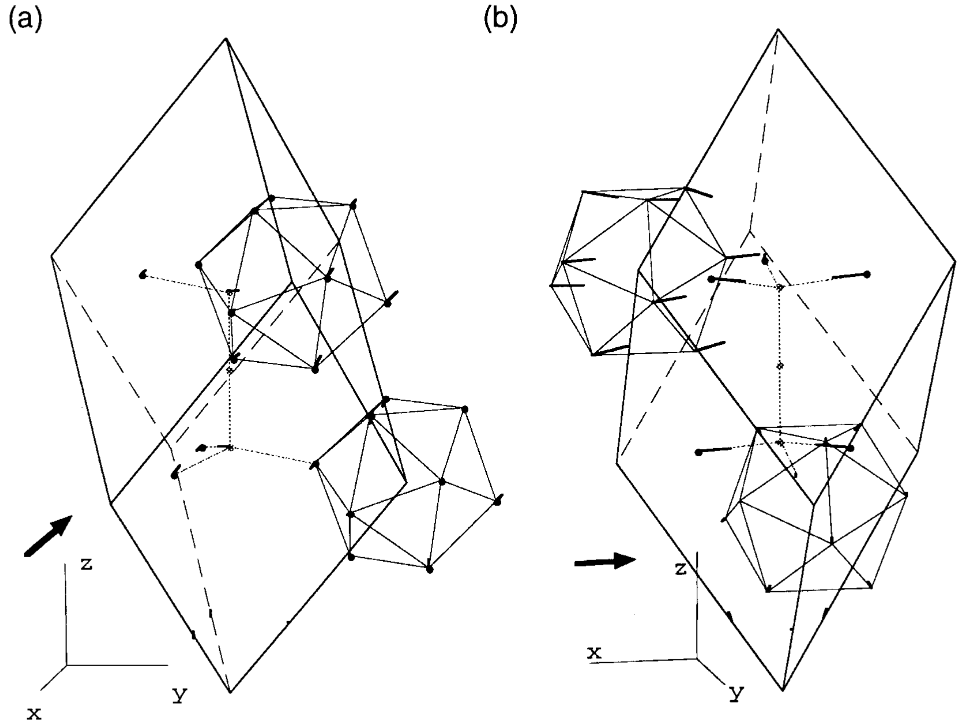

FIG. 4. The relaxation in boron carbide for the compression in the x direction ε_1. The conditions are the same as those in Fig. 3a, but only small noncentral forces are applied. For convenience, the result is illustrated from two different viewpoints.

direction of the perturbation could cause a significant change in rotations.

Now, let us introduce small noncentral forces and examine what happens about rotations. Figure 4 shows the elastic response for ε_1 in boron carbide in this case. The applied noncentral forces are the same as those of model (III) of Table III in Ref. (1). Compared to Fig. 3a, we can see that adding small angle-bending forces has a great influence on the rotational response. The mathematical basis underlying this profound effect is the nonlinearity of the contribution of the internal shift for strains; it contributes to the relaxation through the inverse of the dynamical matrix, which is nearly singular.

REFERENCES

1. K. Shirai, *Phys. Rev. B* **55,** 12235 (1997).
2. H. Ehrenreich and F. Spaepen (Eds.), "Fullerenes: Solid State Physics," Vol. 48. Academic Press, San Diego, 1994.
3. M. Born and K. Huang, "Dynamical Theory of Crystal Lattices." Oxford Univ. Press, Oxford, 1954.
4. A. A. Maradudin, E. W. Montroll, G. H. Weiss, and I. P. Ipatova, "Theory of Lattice Dynamics in the Harmonic Approximation," 2nd ed. Academic Press, New York, 1971.
5. P. Brüesch, "Phonons: Theory and Experiments I". Springer-Verlag, Berlin, 1982.
6. P. N. Keating, *Phys. Rev.* **145,** 637 (1966).