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The Elastic Strain Energy and Stability of Some Idealized Lead–Bismuth Sulphides

K. AIZAWA AND E. IGUCHI

Department of Metallurgical Engineering, Faculty of Engineering, Yokohama National University, Tokiwadai 156, Hodogaya-ku, Yokohama 240, Japan

AND R. J. D. TILLEY

School of Materials Science, University of Bradford, Bradford BD7 1DP, West Yorkshire, England

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The elastic strain energy of idealized structures related to the homologous series of chemically twinned phases xPbS · Bi_2S_3, which includes the naturally occurring sulphides lillianite, $Pb_3Bi_2S_6$, and heyrovskyite, $Pb_6Bi_2S_9$, have been calculated using the Fourier transform method and an ionic model to represent the bonding. The elastic strain energy depends critically upon the distribution of the Pb and Bi atoms over the sites in the twin planes and the PbS-like matrix between the twin planes. The elastic strain energy terms so calculated do not explain why lillianite and heyrovskyite are the only stable compounds but do account for the fact that doping with other atoms can stabilize members of the homologous series not found in the pseudo-binary PbS–Bi_2S_3 system.

Introduction

The increasing use of high resolution electron microscopy, combined with precision X-ray diffraction studies, has revealed that many compounds which were once believed to be nonstoichiometric phases with extensive composition ranges instead consist of a succession of discrete phases. These phases are often members of homologous series and each compound has a structure closely related to that of its neighbors. A very commonly occurring crystallographic pattern is one in which each member of the series consists of slabs of a parent structure which are united along planar boundaries. The composition of the material is determined by the width of the slabs of parent structure and by the nature of the interfaces between them. Materials of this general type have been the subject of a recent review article (*1*).

Since the discovery of such series of phases there has been considerable speculation on the forces responsible for ordering in these materials as they must act over what are often appreciable distances in the solid. In addition, experiment has shown that often some members of a particular homologous series seem to be more stable than others although structural differences between stable and unstable phases are slight. One factor which has been shown to be important in controlling the microstruc-

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tures of such phases and which seems to contribute appreciably to both the ordering of the phases and their relative stabilities is elastic strain energy. To date elastic strain energy calculations have almost entirely been restricted to crystallographic shear structures, but there is no doubt that the calculations seem to successfully explain some of the puzzling details of microstructure mentioned above (*2–8*) for these compounds. It is important though, to extend the calculations to as many alternative systems as possible to check on their general applicability.

In this report we describe the calculations of elastic strain energy in some chemically twinned (CT) phases. We have made the calculations for idealized structures which are closely related to minerals which occur in the pseudo-binary $PbS-Bi_2S_3$ system, namely heyrovskyite, $Pb_6Bi_2S_9$, and lillianite, $Pb_3Bi_2S_6$. For compactness of expression we will use the terms heyrovskyite and lillianite throughout this report to refer to these idealized structures, but it should be kept in mind that the real structures, as detailed in the following section, are considerably different in some ways. In addition, we have chosen to use an ionic model to represent the bonding in our hypothetical compounds. This allows a clearer picture to be obtained of the effects of changing the structures themselves without the complexity of changes in bonding obscuring the results. The results are discussed in terms of the crystal chemistry of the phases and also compared to the situation found in the naturally occurring materials, which are best described in terms of nonionic bonding.

Crystal Chemistry

The phases occurring in the $PbS-Bi_2S_3$ system have been investigated a number of times, in view of the economic importance of lead minerals. Although some aspects of the phase relations remain obscure, it is agreed that in the composition region near to PbS, two ternary phases occur, heyrovskyite, $Pb_6Bi_2S_9$, and lillianite, $Pb_3Bi_2S_6$. The structures of these phases are known (*9, 10*) and we will first consider them in an idealized form. These are illustrated in Fig. 1, together with the PbS structure. It is seen that both heyrovskyite and lillianite consist of slabs of the PbS structure joined along twin planes. These planes are on (010) referred to the unit cells of heyrovskyite and lillianite, and on (311) with respect to the PbS structure. The cations in these two phases are difficult to locate with precision, because of their similar X-ray scattering factors. However, the investigations made to date suggest that the Bi and Pb atoms are located at random in octahedral sites in the matrix between twin planes. The trigonal prismatic sites in the twin planes appear to be occupied only by Pb atoms.

The major difference between heyrovskyite and lillianite is in the width of the PbS-like slabs of structure between the twin planes. It is easy to see that if these widths are varied in a regular fashion we can generate a homologous series of phases, of general formula M_mS_{m+1}. The crystal chemistry of these phases was first described by Takéuchi and Takagi (*11*) and in more detail by Makovicky and Karup-Møller (*12–14*). Although a multiplicity of phases is readily constructed theoretically, a recent study has shown that only the two phases, lillianite and heyrovskyite, seem to form in the $PbS-Bi_2S_3$ system (*15*) although other members of the series may occur in the $Ag_2S-PbS-Bi_2S_3$ system (*12–14*). For the purposes of the calculations it is useful to relate the overall composition of the phases to the separation between the twin planes. This is easily done, and it found that each member of the series has a composition given by xPbS + Bi_2S_3, where x takes on integral values 1, 2, 3, . . . , etc. The

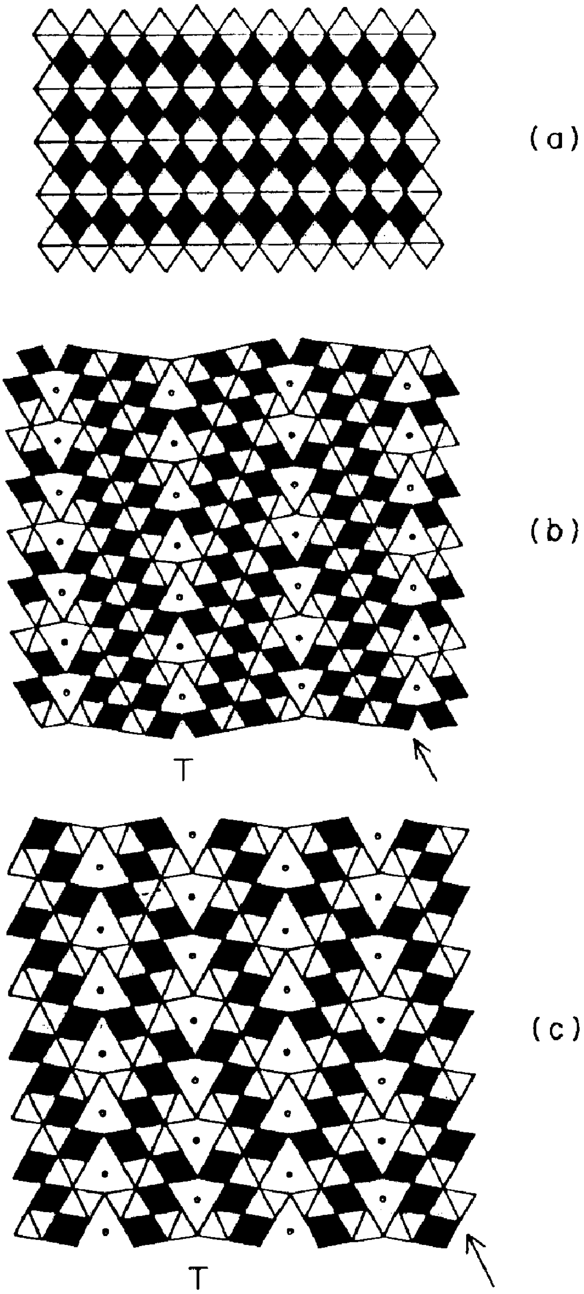

FIG. 1. The structures of (a) PbS projected onto (110), (b) heyrovskyite projected onto (001), and (c) lillianite projected onto (001). The structures are shown as packings of metal–sulfur octahedra; those at a lower level are light and those at a higher level are dark. The structures (b) and (c) can be regarded as made up of slabs of PbS structures joined along twin planes, marked T, which contain cations in trigonal prismatic coordination. The separation between the twin planes can be expressed in terms of the number of octahedra separating them, n, counted in the direction of the arrows. For heyrovskyite, $n = 7$ and for lillianite, $n = 4$.

formula of these phases is then given by the expression $Pb_xBi_2S_{3+x} = M_mS_{m+1}$, where $m = x + 2$. The separation between the twin planes, in terms of octahedra, in the directions indicated by the arrows in Fig. 1, is n, where $n = m - 1$. For example, heyrovskyite has a formula $M_8S_9 = Pb_6Bi_2S_9$ and the number of octahedra in the PbS-like slabs between each twin plane is seven.

When we come to consider the real structures, it is found that they are somewhat distorted compared to the idealized forms. This is because Bi, and to a lesser extent Pb, are both lone-pair ions, and, as is typical with such elements, coordination polyhedra are often irregular so as to accommodate the lone-pair electron cloud with a minimum of unfavorable interactions. Hence the octahedra tend towards square pyramidal form and the PbS-like layers are no longer cubic.

The compounds are covalent and to a large extent their structures are dominated by lone-pair interactions. Particularly the distortion of the metal sulphur coordination polyhedra and the aggregation of the Bi coordination polyhedra into larger groups depends critically on the Pb to Bi ratio and the ability of the lone-pair electrons to occupy "empty" regions of structure (*23*). We should recall that in fact the structures of these compounds are very complex and even the PbS-like slabs are not cubic, but distorted variants of this structure. The models must therefore be taken to be considerably simplified.

Theory

The elastic strain energy in the structures that we are discussing will arise at the twin boundaries, where a certain amount of misfit between atoms is found. In addition, the interactions between the Bi and S atoms, and Pb and S atoms in the triangular tunnels of the twin planes will be different than the same interactions in the PbS-like matrix between the twin planes. The result of these factors can be described in terms of a force, which we call the defect force, arising in the twin planes. The effect of these defect forces will be to strain the matrix between the twin planes. In addition, the forces in each twin plane will interact with all the other defect forces in the crystal. The first of these results in a strain energy, denoted by E_S, and the second term is regarded as a relaxation energy E_R. The total strain energy E_T is regarded as the summation of E_S and E_R, i.e., $E_T = E_S - E_R$.

To calculate E_S and E_R we can use classical elasticity theory. When a unit-volume element deforms reversibly by a strain increment $d\varepsilon_{ij}$, the strain energy density function is obtained by the integration of the work that the stress does on the element, i.e.,

$$W = \int \sigma_{ij} d\varepsilon_{ij} = (\tfrac{1}{2}) C_{ijkl} \varepsilon_{ij} \varepsilon_{kl} \qquad (1)$$

where C_{ijkl} is the elastic constant in tensor form. Thus the strain energy density for a cubic elastic continuum has the form

$$\begin{aligned} W = {} & (\tfrac{1}{2}) C_{11}(\varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2) \\ & + C_{12}(\varepsilon_{22}\varepsilon_{33} + \varepsilon_{33}\varepsilon_{11} + \varepsilon_{11}\varepsilon_{22}) \\ & = 2C_{44}(\varepsilon_{23}^2 + \varepsilon_{31}^2 + \varepsilon_{12}^2). \qquad (2) \end{aligned}$$

The displacement in the αth direction of the ion at $\mathbf{r}$, $u_\alpha(\mathbf{r})$, caused by the βth component of the force at $\mathbf{r}'$, $F_\beta(\mathbf{r}')$ is given, by using the elastic Green's function $G_{\alpha\beta}(\mathbf{r} - \mathbf{r}')$, as

$$u_\alpha(\mathbf{r}) = \sum_{\mathbf{r}'} \sum_{\beta} G_{\alpha\beta}(\mathbf{r} - \mathbf{r}') F_\beta(\mathbf{r}'). \qquad (3)$$

If the defect forces repeat periodically in an infinite matrix, we can employ the Fourier transform treatment in calculating the strain energy. The transformed defect forces $\tilde{F}_\beta(\mathbf{q})$ and Green's function $\tilde{G}_{\alpha\beta}(\mathbf{q})$ can be written

$$F_\beta(\mathbf{r}') = (1/N) \sum_{\mathbf{q}} \tilde{F}_\beta(\mathbf{q}) e^{-i\mathbf{q}\mathbf{r}'}$$

$$G_{\alpha\beta}(\mathbf{r}-\mathbf{r}') = (1/N)\sum_{\mathbf{q}} \tilde{G}_{\alpha\beta}(\mathbf{q})e^{-i\mathbf{q}(\mathbf{r}-\mathbf{r}')} \quad (4)$$

where N is the number of primitive unit cells in the periodic unit cell. We can obtain $u_\alpha(\mathbf{r})$ by substituting Eq. (4) into Eq. (3), thus

$$u_\alpha(\mathbf{r}) = (1/N)\sum_{\mathbf{q}} e^{-i\mathbf{q}\mathbf{r}} \sum_{\beta} \tilde{G}_{\alpha\beta}(\mathbf{q})\tilde{\mathrm{F}}_\beta(\mathbf{q}). \quad (5)$$

The *hk*th component of the strain ε_{hk} is related to the component of the displacement by

$$\varepsilon_{hk} = \left(\frac{1}{2}\right)\left(\frac{\partial u_h}{\partial x_k} + \frac{\partial u_k}{\partial x_h}\right) \quad (6)$$

so ε_{hk} at $\mathbf{r}$ in the matrix is given by

$$\varepsilon_{hk} = -(i/2N)\sum_{\mathbf{q}} e^{-i\mathbf{q}\mathbf{r}} \sum_{\beta} (\mathbf{q}_k\tilde{\mathrm{G}}_{h\beta}(\mathbf{q}) + \mathbf{q}_h\tilde{\mathrm{G}}_{k\beta}(\mathbf{q}))\tilde{F}_\beta(\mathbf{q}). \quad (7)$$

We can now assess the E_S and E_R terms in the following way. We assume that the total strain energy E_S in one periodic unit cell is given as

$$E_\mathrm{S} = \sum_{\mathbf{r}} (4\pi r_\mathbf{r}^3/3)W(\mathbf{r}) \quad (8)$$

where $\sum_{\mathbf{r}}$ indicates the summation of the strain of all atoms in a periodic unit cell, $W(\mathbf{r})$ denotes the strain energy density of an iron at $\mathbf{r}$, the atomic radius of which is written as $r_\mathbf{r}$.

When the defect force $F_\alpha(\mathbf{r}')$ does work on an atom at $\mathbf{r}'$, on the other hand, the displacement of this atom $u_\alpha(\mathbf{r}')$ induced by another force $F_\beta(\mathbf{r}'')$ at $\mathbf{r}''$ can be expressed in a form similar to Eq. (5), viz.,

$$\begin{aligned} u_\alpha(\mathbf{r}') &= \sum_{\mathbf{r}''}\sum_{\beta} G_{\alpha\beta}(\mathbf{r}'-\mathbf{r}'')F_\beta(\mathbf{r}'') \\ &= (1/N)\sum_{\mathbf{q}} e^{-i\mathbf{q}\mathbf{r}'} \sum_{\beta} \tilde{G}_{\alpha\beta}(\mathbf{q})\tilde{\mathrm{F}}_\beta(\mathbf{q}). \quad (9) \end{aligned}$$

The total relaxation energy E_R in a periodic unit cell then has the form

$$E_\mathrm{R} = (1/N)\sum_{\mathbf{r}'}\sum_{\alpha} F_\alpha(\mathbf{r}') \sum_{\mathbf{q}} e^{-i\mathbf{q}\mathbf{r}'}\tilde{\mathrm{G}}_{\alpha\beta}(\mathbf{q})\tilde{\mathrm{F}}_\beta(\mathbf{q}) \quad (10)$$

where $\sum_{\mathbf{r}'}$ has the same meaning as in Eq. (8).

Calculations

Periodic Unit Cells

To make use of the Fourier transform method, it is necessary to construct periodic unit cells for each phase investigated. In the main these unit cells will correspond to the idealized crystallographic unit cells. Two examples are shown in Fig. 2, which represents the projection of the unit cells onto the (001) plane. The unit cells of the

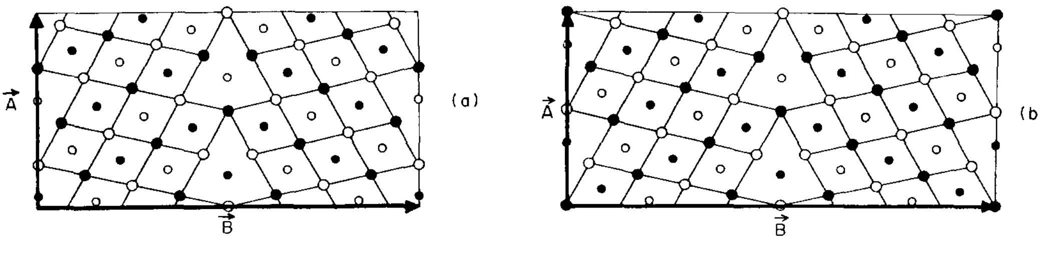

FIG. 2. The periodic unit cells of two phases in the xPbS · Bi_2S_3 homologous series, (a) 5PbS · Bi_2S_3, and (b) 6PbS · Bi_2S_3, heyrovskyite. Large circles represent S^{2-} ions and small ones cations (Bi^{3+} or Pb^{2+}). Two (001) planes, the ions on one of them being represented as open circles and the ions on another one closed circles, are stacked in turn along the direction parallel to the vector C.

other hypothetical phases are similar, differing from the two shown only in the separation of the twin planes and the width of the PbS-like slabs.

Each periodic unit cell is defined by vectors **A, B,** and **C** which can be constructed from a linear combination of primitive translation vectors **a, b,** and **c** which we can relate to the lattice constant of PbS by geometrical methods. If we write the vectors **a, b,** and **c** as the product of unit vectors **i, j,** and **k** along the three orthogonal axes and the absolute values a, b, and c, so that

$$\mathbf{a} = a\mathbf{i} \qquad \mathbf{b} = b\mathbf{j} \qquad \mathbf{c} = c\mathbf{k} \tag{11}$$

and take the lattice parameter of PbS to be 0.59362 nm (*16*) we find that a = 0.37782 nm, b = 0.091438 nm, and c = 0.20988 nm. In terms of the primitive translation vectors **a, b,** and **c** we can also write

$$\begin{aligned} \mathbf{A} &= 36\mathbf{a} \\ \mathbf{B} &= (8 + 4n)\mathbf{b} \\ \mathbf{C} &= 18\mathbf{a} + \mathbf{c} \end{aligned} \tag{12}$$

where n represents the number of octahedra in the PbS-like slab between the twin planes, as specified in Fig. 1.

From these unit cell data we can construct the macroscopic structure of each of the hypothetical idealised $x\mathrm{PbS} \cdot \mathrm{Bi_2S_3}$ phases by using the formal geometrical transformation **T** given by

$$\mathbf{T} = n_1\mathbf{A} + n_2\mathbf{B} + n_3\mathbf{C}. \tag{13}$$

As the defect forces must repeat under the translation **T,** all transforms $\tilde{F}(\mathbf{q})$ of the forces in Eq. (4) vanish unless **q** reflects this translation. That is,

$$F(\mathbf{r} + \mathbf{T}) = (1/N) \sum_{\mathbf{q}} \tilde{F}(\mathbf{q})e^{-i\mathbf{q}(\mathbf{r}+\mathbf{T})} = F(\mathbf{r}). \tag{14}$$

Therefore

$$\exp(-i\mathbf{q}\mathbf{T}) = 1 \tag{15}$$

and

$$\mathbf{q}\mathbf{T} = 2\pi x(\text{integer})$$

Each component of the wave vector **q** can be written

$$\begin{aligned} \mathbf{q} &= L\mathbf{q}_1 + M\mathbf{q}_2 + N\mathbf{q}_3 \\ &= q_x\mathbf{i} + q_y\mathbf{j} + q_z\mathbf{k} \end{aligned} \tag{16}$$

where

$$\begin{aligned} \mathbf{q}_1 &= 2\pi \frac{\mathbf{B} \times \mathbf{C}}{\mathbf{A}(\mathbf{B} \times \mathbf{C})} = (\pi/18a)\mathbf{i} - (\pi/c)\mathbf{k} \\ \mathbf{q}_2 &= 2\pi \frac{\mathbf{C} \times \mathbf{A}}{\mathbf{B}(\mathbf{C} \times \mathbf{A})} = \{\pi/(4 + 2n)b\}\mathbf{j} \\ \mathbf{q}_3 &= 2\pi \frac{\mathbf{A} \times \mathbf{B}}{\mathbf{C}(\mathbf{A} \times \mathbf{B})} = (2\pi/c)\mathbf{k} \end{aligned} \tag{17}$$

and L, M, and N are integers and **i, j,** and **k** are unit vectors along the x, y, and z axes, respectively. From these relations, $q_x = L\pi/18a$, $q_y = M\pi/(4 + 2n)b$, and $q_z = (2N - L)\pi/c$. The elastic strain energy is then obtained by a summation over the first Brillouin zone of the lattice, i.e.,

$$-\pi/a \leq q_x < \pi/a \qquad -\pi/b \leq q_y < \pi/b \qquad -\pi/c \leq q_z < \pi/c$$

and the number of primitive unit cells per periodic unit cell is

$$N = \frac{\mathbf{A}(\mathbf{B} \times \mathbf{C})}{\mathbf{a}(\mathbf{b} \times \mathbf{c})} = 36(8 + 4n) \tag{18}$$

Use of an Ionic Model

As outlined in the introduction, we are exploring the effects of elastic strain energy on the stability of various members of a homologous series of CT phases. Because of this, it seems reasonable to begin with a model which allows the elastic strain energy to be easily calculated. There is no doubt that an ionic model fits this role well. The interactions are easily visualized and because ionic radii in oxides are fairly precisely defined and are partly defined for sulphides (*21, 22*) they can be quantified. It is

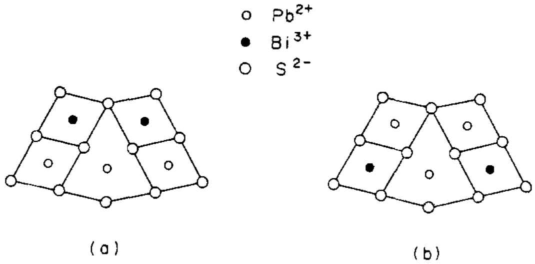

FIG. 3. The two models chosen for cation distribution around the twin plane trigonal prismatic sites in the xPbS · Bi_2S_3 phases: (a) model 1, (b) model 2.

important, though, to remember that the results so calculated will, as they stand, be more relevant to hypothetical "ionic" type phases similar to oxides or fluorides than to covalent or metallic sulfides.

It is useful, however, to draw attention to one feature of the calculations which does not depend upon the bonding model used. This is that the elastic strain energy does not depend upon the *direction* of the defect forces, only on their magnitude. Clearly the tension in a lattice, to a first approximation, does not depend upon whether the lattice is slightly dilated or slightly compressed. In terms of the calculations this is taken care of by using $|F^2|$ terms in the equations rather than F terms for the force involvement. Because of this, the ionic model is rather more applicable to other bonding situations than may appear at first sight.

Ionic Distribution

In the real structures of heyrovskyite and lillianite the Pb and Bi atoms in the PbS-like regions are distributed at random or partially at random over the available positions. It is impossible to calculate the elastic strain energy using the Fourier transform method with random atom distributions. Because of this we have had to distribute the ions around the trigonal pyramidal twin plane sites in a regular fashion, and have chosen two models for this distribution. The first distribution, model 1, is illustrated in Fig. 3(a) and the second distribution, model 2, is illustrated in Fig. 3(b). We should also note that in the phase 2PbS · Bi_2S_3 the distribution model 2 is not possible, and we are only able to calculate the elastic strain energy for the distribution model 1. For all the other phases, both distributions are possible.

Defect Forces and Strain Energies

To calculate the elastic strain energy in these phases we have employed the same Green's function used by Stoneham and Durham (*17*) for a cubic elastic continuum, as PbS is cubic itself. In the Green's function we have employed the elastic constants for PbS reported by Ramachandran and Wooster (*18*), that is,[1]

$$C_{11} = 63.66 \text{ eV} \cdot \text{nm}^{-2}$$

$$C_{12} = 23.72 \text{ eV} \cdot \text{nm}^{-2}$$

$$C_{44} = 15.60 \text{ eV} \cdot \text{nm}^{-2}.$$

To calculate the defect forces we have considered the Coulomb and Born-Mayer interactions between nearest neighbor ions, i.e.,

$$f = z_i z_j e^2/r_{ij}^2 + A_{ij}B_{ij} \exp(-B_{ij}r_{ij}) \quad (19)$$

where $z_i e$ and $z_j e$ denote the charges on neighboring ions i and j, and r_{ij} is the separation of these ions. The constants A_{ij} and B_{ij} are estimated following Huntington (*19*) and, for the interaction between Pb and S

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[1] eV = 1.602×10^{-19} J.

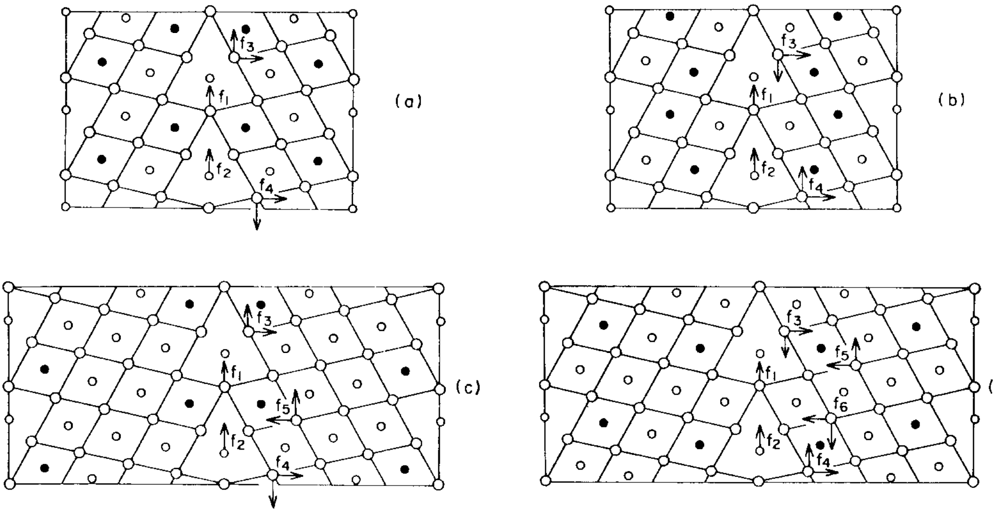


FIG. 4. The defect forces, shown as arrows, acting in two members of the xPbS · Bi_2S_3 phases. (a) represents the lillianite structure and refers to ions distributed as in model 1, and (c) the heyrovskyite structure in which ions are distributed as in model 1; (b) represents the lillianite structure and refers to ions distributed as in model 2, and (d) the heyrovskyite structure and model 2.

atoms, are found to be $A = 5.5977 \times 10^6$ eV, $B = 55.7$ nm^{-1}. The Born–Mayer parameter A, between Bi and S atoms, was obtained by a scaling procedure (*20*) and the parameter B for Bi–S interactions was assumed to be equal to that for Pb–S interactions. Thus, for Bi–S we have employed $A = 2.9192 \times 10^6$ eV and $B = 55.7$ nm^{-1}.

The ionic radii used in these and other calculations were $Pb^{2+} = 0.118$ nm, $Bi^{3+} = 0.102$ nm, $S^{2-} = 0.184$ nm (*21*).

The defect forces generated in this way for heyrovskyite and lillianite, for the atomic distribution models 1 and 2, are shown in Fig. 4, and the numerical values of the forces are indicated in Table I. The defect forces for the other hypothetical phases are similar to those for heyrovskyite and lillianite.

Results and Discussion

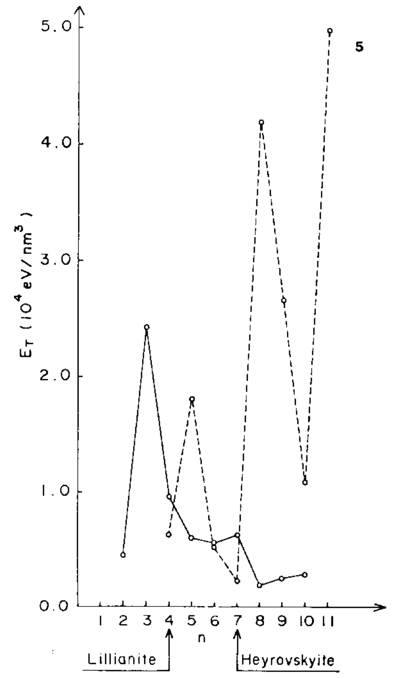
The results of the calculations of the elastic strain energy $E_T = E_S - E_R$ are shown in Fig. 5, where models 1 and 2 (denoted by A and B) refer to the two different cation distributions shown in Fig. 3. We can point out that the strain energy for both models of cation distribution is the same for the phase with $n = 2$, i.e., the hypothetical $PbBi_2S_4$. For the other phases, model 1 shows that the phase with $n = 8$, i.e., $Pb_7Bi_2S_{10}$, has the lowest strain energy. In terms of model 2, as mentioned above, the strain energy of the phase at $n = 3$, i.e., $Pb_2Bi_2S_5$, cannot be calculated, but of the other phases, heyrovskyite has the lowest strain energy, and lillianite has only a slightly lower strain energy than the phase with the second lowest strain energy at $n = 6$, i.e., $Pb_5Bi_2S_8$.

An interesting result, and one which is immediately apparent, is that the rather small change in cation distribution described in Fig. 3 and used in this report makes a great deal of difference to the elastic strain energy of these phases. If we could therefore adjust the cation positions with complete flexibility, we could change the elastic strain energy almost at will between the bounds set by the limiting cation

TABLE I

THE DEFECT FORCES IN LILLIANITE AND HEYROVSKYITE

Compound		Model 1 (eV · nm)		Model 2 (eV · nm)	
		f_x	f_y	f_x	f_y
Lillianite	f_1	0.121030	0.0	0.389791	0.0
	f_2	0.234351	0.0	0.234351	0.0
	f_3	0.363857	0.321985	−0.218439	0.430401
	f_4	−0.618908	0.197023	0.142542	0.955852
Heyrovskyite	f_1	0.121030	0.0	0.389791	0.0
	f_2	0.234351	0.0	0.234351	0.0
	f_3	0.363857	0.321985	−0.218439	0.430401
	f_4	−0.618908	0.197023	0.276923	0.630631
	f_5	−0.134381	0.325221	−0.447916	−0.216804
	f_6			0.134381	0.325221



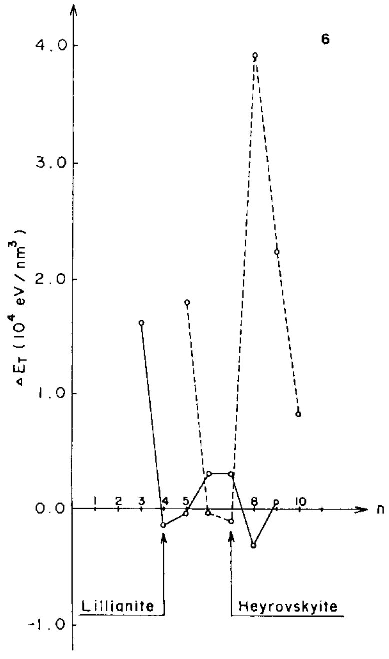


FIG. 5. The elastic strain energy in eV nm^{-3} for the homologous series of phases xPbS · Bi_2S_3, plotted against the number of octahedra separating the twin planes, n in these phases. The naturally occurring phases lillianite and heyrovskyite correspond to $n = 4$ and $n = 7$, respectively. The full line refers to cations distributed as in model 1, and the dotted line to cations distributed as in model 2. The value for $n = 2$ is the same in both models.

FIG. 6. Stability of members of the homologous series of phases xPbS · Bi_2S_3, ΔE_T, plotted against the number of octahedra separating the twin planes, n in these phases. Only those phases with negative values of ΔE_T are stable with respect to disproportionation. The full line refers to cations distributed as in model 1, and the dotted line to cations distributed as in model 2.

distributions. A change in the cation distribution models will thus be expected to have equally large effects on the elastic strain energy. We can note from Fig. 3 that in the two ionic distributions chosen we have constrained Bi^{3+} to the octahedral sites. If we allow the Bi^{3+} to move into the trigonal sites in the twin planes separating the rocksaltlike slabs, then an even greater degree of flexibility would be anticipated. There seems little doubt, therefore, that a cation distribution could be found which would give almost any one of these structures minimum elastic strain energies.

Before considering the implications of this result in more detail it is of interest to obtain an estimate of the relative stabilities of these phases with respect to elastic strain energy. To do this we have considered whether the total strain energy of a system would increase or decrease if the crystals were to disproportionate into the neighboring phases. In the present case we would therefore consider a disproportionation of the type

$$2x\mathrm{PbS} \cdot \mathrm{Bi_2S_3} \rightarrow (x+1)\mathrm{PbS} \cdot \mathrm{Bi_2S_3} + (x-1)\mathrm{PbS} \cdot \mathrm{Bi_2S_3}.$$

If the total strain energy falls during this change we consider that the $x\mathrm{PbS} \cdot \mathrm{Bi_2S_3}$ phase would decompose, while if the elastic strain energy increases the $x\mathrm{PbS} \cdot \mathrm{Bi_2S_3}$ phase would be stable.

The results of this calculation are shown in Fig. 6, where it should be noted that only those phases with negative values of ΔE_T are stable. In terms of model 1 for the cation distribution, the phases $n = 4$, 5, and 8 are stable, while the $n = 9$ phase is only marginally unstable. In the case of model 2 we have more restricted data which show only the phases $n = 6$ and 7 to be stable, which is almost the converse of the result for model 1. It is interesting that in neither model are both the naturally occurring phases heyrovskyite and lillianite stable. In model 1 lillianite, $n = 4$, is stable while in model 2, heyrovskyite, $n = 7$, is stable.

The results show that the elastic strain energy of these phases, and their stability, in so far as this depends upon elastic strain energy, is very dependent upon cation distribution. If we consider the elastic strain energy, we see that for one cation distribution this term falls steadily as the size of the rocksalt slabs increase while in the other situation explored the elastic strain energy seems to increase. It is of interest to consider whether this would cause the cation distributions to change in the solid, so as to achieve a minimum strain energy. This seems reasonable, as another fairly small energy term, crystal field stabilization, does act in this way and does seem to control cation distribution in oxides such as spinels. In the same way, if we replace a cation by a dopant we will get a change in elastic strain energy and stability. Hence doping may well have a significant effect upon which phases may form in nature. Thus the results reported by Mackovicky and Karup-Møller (*12–14*), in which the presence of silver in naturally occurring phases stabilizes some structures, are understandable in these terms, although other explanations are also possible.

The results obtained do not explain why the phases heyrovskyite and lillianite are the preferred phases found in nature. This fact underlines the shortcomings of the ionic model in such obviously covalent compounds. However, they do show that an ionic material with n equal to 2 should be fairly stable. This is found to be so, as the material is $\mathrm{CaTi_2O_4}$, a well-known and relatively ionic phase. The model also suggests that for such fairly ionic materials, n values from 3 to 7 should be unfavorable, but compounds with n equal to 8 or above may form. If the degree of ionicity is decreased, and the compounds become more covalent in nature, the elastic strain energy as we have calculated it will decrease. This is because the defect forces which cause the strain originate in the repulsion and attraction of ionic species. Hence if elastic strain is important in stabilizing these materials, the effects will be more pronounced in more ionic materials. It would therefore be of some interest to try to prepare these homologs in oxide or fluoride systems.

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