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# Anharmonic strain effects in crystals and mixed valence states

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**We modify Friedel's discussion of the elastic model of alloys by showing that "impurities" of different sizes can attract each other when the strains involved are very large. This fact has applications in various physical phenomena. An example is the metal-insulator transitions of SmS, SmSe, and SmTe under pressure. Our theory explains why the transition in SmS is much less continuous than that of SmSe and SmTe. Other applications are also discussed.**

## I. INTRODUCTION

This paper is an attempt to explain a variety of physical phenomena in terms of the interaction of atoms via anharmonic strain effects. For example, recently[1] it was discovered that Sm in $SmB_6$ exists as a mixture of $Sm^{2+}$ and $Sm^{3+}$ ions in a ratio of 40 to 60. In this mixed-valence state, it seems to undergo a metal-insulator transition, with properties we do not attempt to discuss here. Various other Sm compounds undergo more or less gradual metal-insulator transitions apparently involving valence changes as well. There are also a number of Fe compounds which undergo gradual transitions from $Fe^{++}$ to $Fe^{+++}$ or from high to low spin under pressure, as described by Drickamer and Slichter.[2]

The classical theory of metal alloys, due to Friedel,[3] discusses the elastic interaction between atoms of different sizes in an elastic medium. The major component of this is the elastic energy of interaction between volume defects, which has two properties that are rather unique: (i) the interaction between like defects is necessarily *attractive*; (ii) the force is the only interaction known which is truly infinitely long range. This follows from the fact that a volume change in a perfectly elastic lattice leads to a uniform dilatation when surface effects are included. But an attractive force leads to a tendency to segregate, as for instance in Friedel's[3] well-known discussion of Hume-Rothery's rule that metals of sufficiently different atomic sizes will not dissolve in each other. That is, such a force will lead, in a compound with components 1 and 2: $(1)_{x_1}(2)_{x_2}$ $(x_1+x_2=1)$ to an energy like $-c(x_1-x_2)^2$, which is *never* a minimum at any intermediate concentration $x_1 \neq 1$ or 0. Thus this force tends to make all alloys segregate. If we suppose that different valence states of the same atom have the character of different volume defects, this would also tend to make all transitions between valence states be first order at low temperatures and would be expected to prevent mixtures of valences at low temperatures in all crystals.

The experimental data on the Sm and Fe compounds require a *repulsive* force, i.e., with *positive* curvature in the $Sm^{2+}$ concentration, so that the mixture can be in equilibrium. The infinite-range character of the elastic force is, however, ideal: no ordering takes place experimentally, as would have been expected from most types of repulsive forces, such as Coulomb or exchange repulsion, or the Friedel-oscillation forces discussed by Blandin and Deplante.[4] It is also suggested that the phenomenon of mixed valence takes place most clearly in the elastically rigid hexaboride lattice. We are proposing here that consideration of the *anharmonic* effects of substituting atoms of different sizes can reverse the sign of the Friedel potential. This amounts essentially to taking into account in the interaction the change in elastic constants caused by a substitution as well as the volume defect. We show that this can be estimated to be of the right order and that it explains much of the data, at least qualitatively.

## II. MODEL

We shall use a model in which holes of volume $V_n$ have been scooped out of an anharmonically elastic medium, and into them are put spheres of the same material but of size $V_n+\Delta V$. The sphere that we are putting into the hole will be our impurity of "wrong" valence; e.g., in the case of $SmB_6$, we shall take the medium as $Sm^{3+}B_6$; scoop out a $Sm^{3+}$ and put back in a $Sm^{2+}$. We then try to compare the energy of the two situations. Of course, it might be a simpler model if the inserted sphere and the medium were not allowed to be of the same elastic constant, but the above model has the attractiveness of being simple and not too far from reality. We emphasize that we must use an *anharmonic* medium because substitution of a different atom or valence state is by no means a small perturbation. In Sec. III we shall try to evaluate the total elastic energy $U_{int}$ involved, viz.,

$$U_{int}=\frac{1}{2}\int C^{ijhl}\, e_{ij}\, e_{hl}\, dv$$

$$+\frac{1}{6}\int C^{ijhlmn}\, e_{ij}\, e_{hl}\, e_{mn}\, dv \quad , \qquad (2.1)$$

where the $C$'s are the elastic constants and the $e$'s are the strains produced by inserting the spheres into the holes. The stress $p_{ij}$ is defined as $\partial U/\partial e_{ij}$. In writing (2.1) we have used the notation of Brugger.[5] The reader is referred to Ref. 5 for further discussion of these elastic constants.

In this section we shall try to find out what the strains are when the impurities are put in. Calling the displacement from equilibrium $u$ and using the fact that the divergence of the stress tensor is zero, one has, in the pure harmonic (Hooke's law) case,

$$\mu\nabla^2\vec{u} + (\lambda+\mu)\,\vec{\nabla}(\vec{\nabla}\cdot\vec{u}) = 0 \quad . \qquad (2.2)$$

In writing (2.2) we have made the simplifying assumption that the elastic medium is isotropic and the stress can be expressed in terms of the strain as

$$p_{ij} = \lambda e_{mm}\delta_{ij} + 2\mu e_{ij} \quad .$$

We shall continue to make the assumption of isotropy in what follows. Cubic anisotropy does not lead to long-range effects of the Friedel type. The solution with only one impurity is (the case for more than one impurity can be obtained by superposition because of linearity)

$$\vec{u}_h = \begin{cases} C_0\vec{r}/r^3 + \vec{u}^I, & r > r_0 \\ b\vec{r}\,, & r < r_0 \end{cases} \qquad (2.3)$$

where $4\pi C_0 = \Delta V/\gamma$, $\gamma = (3k+4\mu)/3k$, and $k$ is the bulk modulus. $\vec{u}^I$ is the so-called image term and comes from the fact that the stress at the boundary of the medium is zero. When anharmonic effects are included, Eq. (2.1) is changed to a correspondingly complicated form. The spherically symmetric case is discussed in Appendix A. In that case, the displacement $\vec{u}_a$ is given by Eq. (A6′) where $f(r) = u(r)$:

$$\vec{u}_a = \begin{cases} \sum \dfrac{C_n\vec{r}}{r^{3\times 2^n}} + \vec{u}^I\,, & r > r_0 \\ a\vec{r}\,, & r < r_0\,. \end{cases} \qquad (2.4)$$

Here the $C_n$'s are given by Eqs. (A8) and (A15); $a$ is given by Eq. (A19). For our applications of interest $u_a$ is not very much different from the harmonic values $u_h$, i.e., the first term in the series dominates.

When more than one impurity is present in the anharmonic case the solution can no longer be superimposed linearly (in principle); thus when two impurities are present, the total $u$ should be $\vec{u}_1 + \vec{u}_2 + \Delta\vec{u}$, causing a strain $\overleftrightarrow{e}_1 + \overleftrightarrow{e}_2 + \Delta\overleftrightarrow{e}$.

If the impurities are not very dense, $\vec{u}$ decreases to zero fairly rapidly with distance from an impurity. When $\vec{u}_1$ is large, $\vec{u}_2$ is small; thus $\Delta u$, produced by $\vec{u}_1 \cdot \vec{u}2$, is small compared with $\vec{u}_1$ and hence also $\vec{u}_1 + \vec{u}_2$. Careful investigation (see Appendix B) shows that indeed the contribution of $\Delta\vec{u}$ to the interaction energy is not important.

The net result of these two approximations and the model is that the calculation of interactions is very simple, because it amounts to assuming that each impurity displaces the lattice just as it would if the lattice were uniform and the elasticity linear, and only the final calculation of the energy brings in the anharmonic terms. This is a reasonably good approximation, in addition to giving us a very simple physical picture of the phenomena. Let the volume density of impurities be $n$. Concentrate on a particular impurity, say the one nearest the origin, and call it $S$; the total displacement can approximately be written as

$$\vec{u} = \vec{u}^S + \vec{u}^T \quad , \qquad (2.5)$$

$$\vec{u}^S = \begin{cases} \dfrac{C_0}{r^3}\,\vec{r} + \dfrac{4}{3}\pi C_0 \dfrac{1}{V}(\gamma-1)\,\vec{r}\,, & r > r_0 \\ a\vec{r}\,, & r < r_0 \end{cases} \qquad (2.6)$$

$$\vec{u}^T = \begin{cases} \frac{4}{3}\pi C_0 n\gamma\vec{r} - u_S\,, & r > r_0 \\ \frac{4}{3}\pi C_0 n(\gamma-1)\,\vec{r}\,, & r < r_0 \quad . \end{cases} \qquad (2.7)$$

Here $u^S$ is the strain due to the $S$th impurity and $u^T$ is that due to the other impurities; $n$ is the concentration of the impurities. Equation (2.7) for $u^T$ is analogous to Eshelby's[3] Eq. (8–16) and neglects the granular nature of the impurities. The exact solution should have in addition to (2.7) small ripples separated by the interimpurity distance. As discussed in Appendix A, (2.7) is a good approximate solution to the elastic equation (A5).

## III. INTERACTION ENERGY

From (2.1) the interaction energy between two systems $S$ and $T$ can be written as $(e = e^S + e^T)$

$$U_{\text{int}} = \tfrac{1}{6}\int C^{ijk}\,(e_i^S e_j^T e_k^T + e_i^S e_j^S e_k^T + e_i^S e_j^T e_k^S + e_i^T e_j^S e_k^S + e_i^T e_j^T e_k^S + e_i^T e_j^S e_k^T)\,dv \quad , \qquad (3.1)$$

where the Voigt[6] notation has been used for the indices, i.e., 1 stands for $xx$, 2 for $yy$, 3 for $zz$, and 4 for $yz$, etc. Transforming into spherical coordinates and with $u_r^S = f(r)$, $u_\theta^S = u_\varphi^S = 0$, $u_r^T = g(r)$, and $u_\theta^T = u_\varphi^T = 0$, we obtain

$$U_{\text{int}}^{\text{S,T}} = \int dv\,\left(\frac{1}{r^3}(f^2g + g^2f)(\overline{C} + 3d) + \frac{1}{r^2}(f'g^2 + g'f^2 + 2f'fg + 2g'gf)(e+d) + \frac{1}{r}(fg'^2 + 2ff'g + 2gf'g' + gf'^2)(\tfrac{1}{2}d) + \tfrac{1}{2}\,\overline{C}\,(f'^2g' + g'^2f')\right) \quad , \qquad (3.2)$$

where $e$, $d$, and $\overline{C}$ are elastic constants as defined in Appendix A, and primes denote differentiation. Taking $u^S$ and $u^T$ as defined in (2.6) and (2.7), the total interaction energy of a system of $n$ impurities is thus

$$\tfrac{1}{2} n U^{S,T} = U_I \quad . \tag{3.3}$$

We shall confine our interest to terms in $U_I$ that are of the order $n^2$ because (i) in some applications, $n$ is small; (ii) the contribution to the $n^3$ term contains the quartic harmonic terms and we do not have any physical feeling for these; (iii) the $n^2$ term gives us enough qualitative insight into what is happening, and we do not hope for quantitative results.

Writing

$$\overline{g} = \tfrac{4}{3}\pi C n \gamma r \ , \quad r > r_0$$

$$\overline{g} = g \ , \qquad r < r_0 \ ;$$

$$\vec{u}^S = f \vec{e}_r \ ,$$

then

$$g = \overline{g} - f \ \text{ for } r > r_0 \quad . \tag{3.4}$$

Collecting terms of $U_I$ that are of the order $n^2$, we obtain

$$U_I = \tfrac{1}{2} n \left( - \int_{r_0}^{\infty} dv f^2 \overline{g} \frac{1}{r^3} (\overline{C} + 3d) + \frac{1}{r^2} (f^2 \overline{g}' + 2 f' f \overline{g}) (e + d) + \frac{1}{r} (2 f f' \overline{g}' + f'^2 \overline{g}) (\tfrac{1}{2} d) + \tfrac{1}{2} \overline{C} (f'^2 \overline{g}') \right.$$
$$\left. + \int_0^{r_0} dv f^2 \overline{g} \frac{1}{r^3} (\overline{C} + 3d) + \frac{1}{r^2} (f^2 \overline{g}' + 2 f' f \overline{g}) (e + d) + \frac{1}{r} (2 f f' \overline{g}' + f'^2 \overline{g}) \tfrac{1}{2} d + \tfrac{1}{2} \overline{C} (f'^2 \overline{g}') \right) \quad . \tag{3.5}$$

Substituting $f$ and $\overline{g}$ we have

$$U_1^a = -\tfrac{1}{2} n^2 [\tfrac{1}{9}(6\xi + \nu)] \frac{1}{V_0} \left(\frac{\Delta V}{\gamma}\right)^3 \gamma$$
$$- \tfrac{1}{2} n^2 (\zeta + \tfrac{1}{9}\nu) \frac{1}{V_0} \left(\frac{\Delta V}{\gamma}\right)^3 (\gamma - 1) \quad . \tag{3.6}$$

The superscript $a$ indicates the anharmonic contribution to the interaction energy. The symbols $\zeta$, $\nu$, and $\xi$ are elastic constants. Their relationship to the symbols $\overline{C}$ and $d$, etc. are given in Eq. (A5). The second term on the right-hand side of (3.6) has a simple physical interpretation. It is just the modification of the self-energy of the impurities when anharmonic effects are included. In fact, from Appendix C, $\zeta + \frac{1}{9}\nu$ is just $dk/dv$. Note that because $\xi$, $\zeta$, and $\nu$ are in general negative, the $U_I$ that we have calculated in positive if $\Delta V/V$ is positive.

## IV. APPLICATIONS: METAL-INSULATOR TRANSITION IN SmSe, SmTe, and SmS

The first application is to investigate the insulator-metal transition of SmS, SmSe, and SmTe under pressure.[7,8] It was found that as pressure is increased SmS goes through a discontinuous transition at $P = 6.5$ kbar; SmSe, a continuous transition around $P = 30-60$ kbar. According to the conventional idea of the Mott transition[9] the insulator-metal transition should be first order. The reason can be seen more clearly than in the usual discussion simply by considering the energy of the electron-hole gas of a metal as a function of its density, i.e., of the number of excited electrons in bands. This may be written[10] as

$$E = E(T) n - E_{ex}(n) n^{4/3} + E_k(n) n^{5/3} + E_2 n^2 + \cdots , \tag{4.1}$$

$E(T)$ represents the band gap and $E_k$ represents the kinetic energy. Here at high densities $E_{ex}$ is just the standard exchange energy (equal to $\sim 1/r_s$ per particle, $r_s$ being the conventional dimensionless volume parameter in the free-electron-gas problem), but even at low densities one may give excellent arguments that the exchange-correlation term is of similar form, i.e., singular (by singular we mean it has a branch point) as $n \rightarrow 0$, and is negative. That it is not possible for dielectric effects due to reduced gaps to modify this result is shown by Anderson, Chui, and Brinkman,[10] who point out that even where no free electrons and holes are present, the dielectric effects of the excitons themselves lead to a negative (attractive) interaction term; i.e., even $E_2$ is likely to be negative (and even neglecting molecular binding forces).

While the interactions caused by strains are always of the form $n^2$ and thus contribute only to $E_2$ (and thus cannot outweigh the exchange attraction, which is singular as a function of $n$, at low enough densities), they may turn out to be considerably larger for reasonable densities of carriers, and thus may, except for very precise measurements at very low temperatures, effectively control whether the metal-insulator transition is first order or gradual. Very simply, if the dominant term beyond the linear one is negative (attractive), the transition must be of the first order, since states with finite $n$ will first have lower free energy than those with $n = 0$; and vice versa for repulsive forces.

Let us call the anharmonic contribution to the $n^2$ term $E_4 n^2$, and the harmonic one $E_3 n^2$. If $E_4$ is sufficiently positive, then, we go towards a more continuous transition. The more deformed the elastic medium, the larger are $E_4$, $E_3$, and

$E_4/E_3$. As it happens SmS has a rather small band gap ~0.1 eV,[11] so the transition occurs at a smaller pressure and hence smaller volume deformation, the anharmonic term is not large enough, and a first-order transition results. SmSe and SmTe have a much larger band gap (~0.5 eV),[10] so the transition occurs at a higher pressure and larger volume deformation, anharmonic terms dominate, and a more continuous transition results.

TABLE I. Various distances of interest concerning the summarium salts, that are used in the calculation in Table II.

Ionic radii of various ions of interest[a]

| (Å) | $Sm^{2+}$ | $Sm^{3+}$ | $S^{=}$ | $Se^{=}$ | $Te^{=}$ |
|---|---|---|---|---|---|
| | 1.143 | 0.964 | 1.84 | 1.91 | 2.11 |

Interionic distance in Sm$X$ compounds at zero pressure[b]

| (Å) | Sm–S | Sm–Se | Sm–Te | $P=0$ |
|---|---|---|---|---|
| | 2.99 | 3.1 | 3.3 | |

Change in Sm$X$ distance ($\Delta R/R$) at transition[c]

| $\delta$(Sm–S) | $\delta$(Sm–Se) | $\delta$(Sm–Te) |
|---|---|---|
| 0.01982 | 0.0497 | 0.0488 |

[a] The ionic radii is obtained from A. Iandelli, in *Rare Earth Research*, edited by E. V. Kleber (MacMillan, New York, 1961), p. 40.

[b] The interionic distance is obtained from data of A. Jayaraman *et al.*

[c] By at the transition point, we mean 6.1 kbar for SmS (right before the discontinuous transition takes place), 40 kbar for SmSe, and 45 kbar for SmTe; for these two latter substances, because the transition is continuous it is difficult to judge exactly where the transition starts and where it ends. A point midway between was chosen. A slight change of the deformation should not change the result qualitatively.

TABLE II. The volume mismatches. See Sec. IV.

"Natural" interionic distance (in Å) for $Sm^{2+}X$ and $Sm^{3+}X$

$R(Sm^{2+})+R(S^{=})=1.143+1.84=2.983$
$R(Sm^{2+})+R(Se^{=})=1.143+1.91=3.053$
$R(Sm^{2+})+R(Te^{=})=1.143+2.11=3.253$

$R(Sm^{3+})+R(S^{=})=0.964+1.84=2.804$
$R(Sm^{3+})+R(Se^{=})=0.964+1.91=2.874$
$R(Sm^{3+})+R(Te^{=})=0.964+2.11=3.074$

"Real" interionic distance (in Å) for $Sm^{2+}X$ and $Sm^{3+}X$ at transition

$R(\mathrm{SmS})=2.9307$
$R(\mathrm{SmSe})=2.9459$
$R(\mathrm{SmTe})=3.139$

Volume mismatches at transition[a]

$(\Delta V/V)_1$ SmS: $3\times\dfrac{2.983-2.9307}{2.983}=0.053$
SmSe: $3\times\dfrac{3.053-2.9459}{3.073}=0.11$
SmTe: $3\times\dfrac{3.253-3.139}{3.253}=0.11$

$(\Delta V/V)_2$ SmS: $3\times\dfrac{2.804-2.9307}{2.804}=-0.14$
SmSe: $3\times\dfrac{2.874-2.9459}{2.874}=-0.75$
SmTe: $3\times\dfrac{3.074-3.139}{3.074}=-0.063$

[a] The index 1 stands for $Sm^{2+}X$; index 2 stands for $Sm^{3+}X$.

We feel that the question of whether the mixed-valence transition and the metal-insulator transition are the same is a very complicated one, involving such complicated possibilities as heavy excitons (by that we mean the hole mass is very heavy) in the case of the Sm compounds. We are here merely trying to identify an important component of the interactions which works in the correct direction. In Table I is listed the zero-pressure Sm-$X$ ionic separation, the ionic radius of the cation, the ionic radii of $Sm^{2+}$ and $Sm^{3+}$, and the Sm-anion distances when the transitions occur. We have decided to use ionic radii because we believe the bond is mainly an ionic bond. In Table II is listed the "natural" $Sm^{n+}$-$X$ distance before compression and the volume compression when the transition occurs. The hole size of our model should be that for $Sm^{2+}$ at zero pressure. At higher pressure both $Sm^{2+}$ and $Sm^{3+}$ will not fit into the hole. In order to compare the situation of the $Sm^{3+}$'s the strain energy for both valences is calculated and compared. The volume mismatches for both the 2+ and the 3+ valences are also listed in Table II. The harmonic strain energy to order $n^2$, $n$ being the volume density of the 2+, is

$$\tfrac{1}{2}Kn^2(\gamma-1)\frac{V_1V_2}{\gamma}\left[-\left(\frac{\Delta V_1}{V_1}\right)^2\left(\frac{V_1}{V_2}\right)-\left(\frac{\Delta V_2}{V_2}\right)^2\left(\frac{V_2}{V_1}\right)+\left(\frac{\Delta V_1}{V_1}\right)\left(\frac{\Delta V_2}{V_2}\right)\right], \tag{4.2}$$

where the 2+–2+, 2+–3+, and 3+–3+ interactions are included. The index 1 refers to the $Sm^{2+}X$; index 2 refers to the $Sm^{3+}X$. Similarly the anharmonic term is

$$-\frac{1}{2}n^2\left[\left(\frac{6}{9}\xi+\frac{\nu}{9}\right)\frac{1}{2}+\left(\zeta+\frac{\nu}{9}\right)\left(\frac{\gamma-1}{\gamma^3}\right)\right]V_1V_2 \times\left[\left(\frac{V_1}{V_2}\right)\left(\frac{\Delta V_1}{V_1}\right)^3+\left(\frac{\Delta V_2}{V_2}\right)^3\left(\frac{V_2}{V_1}\right)\right]. \tag{4.3}$$

TABLE III. Numerical evaluations for the quantities $x$ and $y$ in Eqs. (4.4) and (4.5).

| | $x$ | $y$ |
|---|---|---|
| SmS | $-0.0084973$ | $-0.0018404$ |
| SmSe | $-0.0139412$ | $0.0019279$ |
| SmTe | $-0.01417$ | $0.0020621$ |

These formulas are obtained by expanding the energy as $E_a n^2 + E_b(1-n)^2 + E_c n(1-n)$ and by collecting the $n^2$ term.

When the numerical values for $\Delta V_1/V_1$, etc., are plugged in, we find the result listed in Table III. The $x$ and $y$ are defined as follows:

$$E_3 = \text{harmonic term}$$

$$= x\tfrac{1}{2} K n^2 V_1 V_2 \gamma(\gamma-1) \quad , \tag{4.4}$$

$$E_4 = \text{anharmonic term}$$

$$= -y\tfrac{1}{2}\left[\left(\frac{6}{9}\xi + \frac{\nu}{9}\right)\frac{1}{\gamma^2} + \left(\zeta + \frac{\nu}{9}\right)\left(\frac{\gamma-1}{\gamma^2}\right)\right] \quad . \tag{4.5}$$

Since the $\xi$'s are negative, it is at once obvious that the anharmonic term is positive for SmSe and SmTe, whereas it is negative in the case of the sulphide. We have no exact experimental information on the elastic constants, so further numerical comparison is difficult. An order-of-magnitude estimate can be made, however. According to Slater,[12] if we write $(\Delta V/V) = \bar{a}P + \bar{b}P^2$, then $\bar{b}/\bar{a}^2 = 2.5$ for nearly all materials. Inverting, we find

$$P \approx \frac{1}{1-a}\left[\left(\frac{\Delta V}{V}\right)5 - 12.5\left(\frac{\Delta V}{V}\right)^2 - \cdots\right] \quad , \tag{4.6}$$

so that $(\zeta + \frac{1}{9}\nu) = -2.5$.

Empirically we find $\xi \sim \zeta$,[13] so that the factor in the square brackets in Eq. (4.5) is $-5$. Thus $E_3 \simeq E_4$ (see Table III) in the case of the selenides and the tellurides, and the anharmonic term can indeed overwhelm the harmonic term. This is not the case in the sulphides. Because we can not make detailed calculations, we shall remark here that an estimate shows that $E_2$[10] is of the same order of magnitude as $E_3$ and $E_4$.

## V. HEXABORIDE

As is mentioned in Sec. I, our problem here is to explain why the system prefers to remain in a mixed-valence state. We believe that because of the rigidity of the hexaboride lattice and the large size of the Sm ions, the $Sm^{2+}(B_6)^{--}$ state is not stable, as one would naively expect from the calculation of Longuet-Higgins and Roberts.[14] (For a more detailed description of the properties of $SmB_6$, the reader is referred to an article by Nickerson *et al.*[15] and reference therein.) In $SmB_6$, the Sm ion sits at the center of a cube, at each corner of which are octahedras of B atoms. One might argue that as the electrons are removed from the $Sm^{2+}$ ion, the size of the cation increases and this would squeeze back on the $Sm^{2+}$ ion itself and thus there is no net gain in strain energy. However, as the electrons are squeezed out of the $Sm^{2+}$, at least for small $n$, the local increase in size is very small so that one would expect that this would not affect the strain energy very much. In fact, the band electrons occupy both sites in unknown ratios. It is irrelevant whether the band electrons are considered to be partially covalent; the resulting energies will vary smoothly with $Sm^{3+}/Sm^{2+}$, and will not change the qualitative picture that we are going to propose. We believe that because of the strain energies discussed in Sec. IV, when $Sm^{2+}$ ions are put into the hexaboride lattice some electrons will be squeezed out.

The electronic structure and metal-insulator transition in $SmB_6$ is a very complex subject, and we feel new ideas beyond the scope of this work are necessary for their understanding. What is striking, however, is that according to various rather sound experimental arguments (chemical shifts, steric, etc.) the ratio $Sm^{3+}/Sm^{2+}$ does not change while the transition is taking place. This seems to us to be strong evidence that some extra forces are overwhelmingly large and enforce a fixed ratio, and the best candidate for such forces is the strain energy discussed in Sec. IV, since the hexaborides are elastically very stiff. We *assume*, then, that whatever purely electronic energies are involved are relatively small.

Since we do not know the numerical value of the third-order elastic constant and since we do have a very clear picture of the electronic structure of the hexaborides, we shall not attempt a calculation that would give us the 2+, 3+ mixture in the correct ratio. Instead, we shall just indicate how the anharmonic force can be repulsive in the case of the hexaborides. The metallic radii of $Sm^{2+}$ and $Sm^{3+}$ are 2.1 and 1.8 Å, respectively.[16] (We believe that a metallic radius, rather than an ionic radius, would be more appropriate here.[17])

$$\Delta V/V_0 = 0.588 = [(2.1)^3 - (1.8)^3]/(1.8)^3 \quad ,$$

the magnitude of the ratio of the harmonic to the anharmonic term $E_3/E_4$ is given by

$$\frac{E_3}{E_4} \sim \tfrac{1}{2}K(\Delta V)^2\,\frac{\gamma-1}{\gamma}\Bigg/\left\{\frac{1}{2}\left[\left(\frac{6}{9}\xi + \frac{\nu}{9}\right)\frac{1}{\gamma^2} + \left(\zeta + \frac{\nu}{9}\right)\left(\frac{\gamma-1}{\gamma^3}\right)\right](\Delta V)^2\left(\frac{\Delta V}{V}\right)\right\} \sim \frac{1}{0.6\times 5} \sim \tfrac{1}{3} \quad .$$

The system thus will not segregate. One can also assume that since the system likes to stay as a mixture with a ratio $4f^5 : 4f^6 = 40 : 60$, the "natural" hole radius is not that of $Sm^{3+}$ but is $0.4\ Sm^{2+} + 0.6\ Sm^{3+}$. In this case, the volume mismatch between the $Sm^{2+}$ ion and the natural hole $(\Delta V/V)'$ is 0.32 and $E_3/E_4$ is 1/1.5; one still has a mixture.

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## APPENDIX A

In this appendix we shall first derive the equation for the anharmonic strain, solve it, and then try to fit the boundary conditions. We shall use the model as discussed in Sec. II and shall not repeat its description here.

When nonlinear effects are included, the equations are in general very difficult to solve. We pick the case of spherical symmetry which roughly approximates the situation of interest and use spherical coordinates. Then

$$p^{ij}\,|\,j = 0 \quad , \tag{A1}$$

where $|\,j$ denotes covariant differentiation with respect to $x_j$ (sum over $j$ is implied for repeated indices). The stress $p^{ij}$ is obtained from the energy whose anharmonic component is given by

$$U_2 = \frac{1}{6} \sum C_{ijklmn}\, e_{ij}\, e_{kl}\, e_{mn} \quad . \tag{A1$'$}$$

Assuming that the displacement from equilibrium is $u_r = f(r)$, $u_\theta = 0$, and $u_\varphi = 0$, with the strain $e_{\alpha\beta}$ defined by

$$e_{\alpha\beta} = \tfrac{1}{2}\left(u_\alpha\,|_\beta + u_\beta\,|_\alpha + u^\gamma\,|_\alpha u_\gamma\,|_\beta\right) \tag{A2}$$

we have

$$\begin{aligned} e_{rr} &= f' + \tfrac{1}{2}(f')^2 \quad , \\ e_{\theta\theta} &= rf + \tfrac{1}{2}f^2 \quad , \\ e_{\varphi\varphi} &= r(\sin^2\theta)f + \tfrac{1}{2}(\sin^2\theta)f^2 \quad ; \end{aligned} \tag{A3}$$

all other components of $e$ are zero.

The anharmonic $C$'s in Eq. (A1$'$) can be expressed in terms of three independent elastic constants $\xi$, $\zeta$, and $\nu$ in the case that the medium is isotropic. We shall make this simplifying assumption in what follows. These constants are given by Eq. (14–14) of Ref. 2. (Similarly, the harmonic $C$'s can be related to two parameters $\lambda$ and $\mu$.)

Restricting our attention to the $i = r$ component, which, as it turns out, is the only component that gives interesting information, one has

$$\alpha f + 2\alpha\left(\frac{f}{r}\right)' + \left(\tfrac{1}{2}\bar{C} + \tfrac{1}{2}\alpha\right)(f'^2)' + \frac{8d}{6}\left(\frac{f'f}{r}\right)'$$

$$+ \left(\tfrac{1}{3}e + \beta\right)\left(\frac{f^2}{r^2}\right) + A\frac{f^2}{r^3} + B\frac{f'^2}{r} + C\frac{ff'}{r^2} = 0 \ , \tag{A4}$$

where $\alpha = \lambda + 2\mu$,

$$\bar{C} = 2\zeta + 4\xi \ , \quad d = 2\zeta \ , \quad e = 2\zeta - 2\xi + \nu \quad , \tag{A5}$$

$$\begin{aligned} &A = (-6\bar{C} - 6d + 4e)\tfrac{1}{6} \ , \quad B = (-2d + 6\bar{C}) \ , \\ &C = (-4d + 8e)\tfrac{1}{6} \quad . \end{aligned} \tag{A6}$$

Assuming

$$f = \sum \frac{C_n}{r^{3\times 2^n} - 1} \quad (r > r_0) \quad , \tag{A6$'$}$$

we have, with

$$\begin{aligned} \bar{C}' &= \tfrac{1}{2}\bar{C} + \tfrac{1}{2}\alpha \quad , \\ d' &= \tfrac{8}{6}\, d \quad , \\ e' &= \tfrac{1}{3}e + \beta + \tfrac{1}{3}d \quad , \end{aligned} \tag{A7}$$

$$\frac{C_{n+1}}{C_n^2} = \frac{\{2(3\times 2^n)[\bar{C}'(3\times 2^n - 1)^2 - d'(3\times 2^n - 1) + e'] + A + B(3\times 2^n - 1)^2 - (3\times 2^n - 1)C\}}{\alpha(3\times 2^{n+1} - 3)(3\times 2^{n+1})} \quad . \tag{A8}$$

The radius of convergence $R$ of (A6$'$) is given by

$$\left[\left(\frac{6\bar{C}' + 3B}{4\alpha}\right) C_0^2\right]^{1/3} \quad . \tag{A9}$$

As will be shown, $4\pi C_0$ is of the order of $(\Delta V)$. If we further assume that (see Sec. IV) $\zeta \sim \xi \sim 2.5\alpha$, then

$$R \sim 2\delta r \sim \tfrac{1}{5} r_0 \quad , \tag{A10}$$

where $r_0$ is the radius of the impurity sphere. Thus our solution is valid outside the impurity sphere. Inside the sphere, the solution is

$$\vec{u} = f\vec{e}_r = -a\vec{r} \quad , \tag{A11}$$

where $a$ is an arbitrary constant.

The full solution is obtained if we further require that the outside surface of the medium is free. This produces an image volume $\Delta V^I$ given by

$$\Delta V^I = \frac{1}{3K'}\left(\int p_{ij}\, x_i\, dS_j\right) \quad , \tag{A12}$$

where the prime on the bulk modulus $K$ is to draw attention to the fact that it is the average bulk modulus in the compressed state. We shall approximate it by

$$K' = K \quad 1 - 2.5 \left(\frac{\Delta V_0}{V_0}\right) \quad . \tag{A13}$$

(As discussed in Sec. IV, this is a result of the work of Slater and is due to the fact that the lattice is anharmonic.) To obtain a better approximation, one has to solve Eq. (A 1) better; but for reasons mentioned in the text, we are content in obtaining qualitative results, and the above approximation is then adequate. The total volume change is thus $\Delta V = 4\pi\gamma C_0 = V_{\text{mis}}$, where

$$\gamma = \frac{3K' + 4\mu}{3K'} \quad . \tag{A14}$$

$C_0$ is determined by observing (as in Ref. 1, p. 115) that the total volume change should be zero;

$$C_0 = \frac{V_{\text{mis}}}{4\pi\gamma} \quad . \tag{A15}$$

$a$ is next determined from the observation that the pressure exerted by the medium on the impurity is equal to that by the impurity on the medium. With the volume of the impurity given by

$$\Delta V_1 = -a r_0^3 4\pi \tag{A15a}$$

and that of the medium by

$$\Delta V_2 = 4\pi C_0 + 4\pi C_1 / r_0^3 \tag{A15b}$$

(we neglect all higher powers in $1/r$). We have

$$-K\Delta V_1 \left[1 - 2.5 \left(\frac{\Delta V_1}{V_0}\right)\right] = K\Delta V_2 \left[1 - 2.5 \left(\frac{\Delta V_2}{V_0}\right)\right] . \tag{A16}$$

If we call $\Delta V_2 [1 - 2.5 \Delta V_2 / V_0] = \delta$, then

$$\Delta V_1 = \tfrac{1}{5} V_0 \{1 - [1 + (\delta / V_0) 10]^{1/2}\}$$
$$(\simeq \delta \text{ when } \delta / V_0 \text{ is small}) . \tag{A17}$$

$\delta$ can be obtained from (A15b); in fact,

$$\Delta V_2 / V_0 \approx 4\pi C_0 / V_0 \approx 1/10 \quad , \tag{A18}$$

and hence $\delta \simeq \frac{3}{4} V_0$. From (A17) we finally have

$$a = \tfrac{1}{3} \delta / V_0 \simeq \tfrac{1}{4} \quad . \tag{A19}$$

A form for $u^I$ can also be written: It is just

$$\tfrac{4}{3} \pi (1/V)(\gamma - 1) r \quad , \tag{A20}$$

$V$ being the volume of the medium. It satisfies Eq. (A6′), produces the right volume change $\Delta V^I$, and thus is our candidate.

Finally, it should be remarked that our solution [Eqs. (A8), (A1), and (A20)] is unique, because of the uniqueness theorem[18] of an ordinary differential equation.

## APPENDIX B

In this appendix we shall show that for the applications we have in mind, linear superposition is really not a bad approximation, even in the anharmonic case.

Suppose we denote by $u_1$ and $u_2$ the displacement due to a particular impurity and the rest of the impurities, respectively, as given approximately by (2.6) and (2.7). When both $u_1$ and $u_2$ are present, the true solution should be $u_1 + u_2 + \Delta u$. We want to show $u_1 + u_2 \gg \Delta u$ for all values of $r$. As a side remark, we want to point out that $\frac{4}{3}\pi C_0 n \gamma \vec{r}$ and $u_s$ both satisfy Eq. (A5) and the true solution for $r > r_0$ should be $\frac{4}{3}\pi C_0 n \gamma \vec{r} - u_s + \langle \Delta u \rangle$. That $\langle \Delta u \rangle$ is small follows from the same kind of reasoning that we are going to present below.

First, for $r < r_0$, we find $\Delta u = 0$, as is obvious by substituting $u_1 + u_2$ into Eq. (A4). For $r > r_0$, the order of magnitude of $\Delta u$ is estimated from (A4) as

$$\tilde{\alpha}(\Delta u)'' \sim \tilde{C} \, \frac{(\frac{4}{3}\pi C_0 n \gamma) C_0 / r^2}{r^2} \quad , \tag{B1}$$

where $\tilde{\alpha}$ denotes some sort of an average of the coefficients multiplying the linear terms in (A4) and $\tilde{C}$ denotes the average of the coefficients of the anharmonic terms. From the discussion in Sec. IV we expect the ratio of these two numbers to be about 2.5; that is,

$$(\Delta u) \sim \frac{C_0}{r^2} \left(\frac{\tilde{C}}{\tilde{\alpha}} \frac{4}{3} \pi C_0 n\right)$$
$$\sim \frac{C_0}{r^2} \left(\frac{\tilde{C}}{\tilde{\alpha}} \frac{(\Delta V)}{6 V_0}\right) \tag{B2}$$
$$\sim \frac{1}{20} (u_1 + u_2) \quad . \tag{B3}$$

In going from (B1) to (B2) we have made the approximations that $n \sim 1/2V_0$ (we assume an impurity concentration of 50%), $4\pi C_0 \sim \Delta V/\gamma$, and $\Delta V / V \sim \frac{1}{10}$.

## APPENDIX C

We would like to show that

$$\frac{dK}{dV} = \zeta + \tfrac{1}{9}\nu \quad .$$

From Ref. 5, for uniform strains $\eta_1 = \eta_2 = \eta_3 = \frac{1}{3}\delta$, the third-order change in energy $u^3$ is given by

$$u^3 = \tfrac{1}{3}\delta^3 (\zeta + \tfrac{1}{9}\nu) \quad .$$

This should be equal to $\frac{1}{3}(dK/dV)\delta^3$; thus

$$dK/dV = \zeta + \tfrac{1}{9}\nu \quad .$$

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