Quasireciprocal relation between the Cs IV and β-Sn structures

Kuniyoshi Ebina and Tuto Nakamura
Department of Material Physics, Osaka University, Toyonaka, Japan
(Received 26 December 1984)

A quasireciprocal relation is pointed out between the Cs IV and β-Sn structures. This relation comes from a certain symmetry of the Madelung constant in a family of tetragonal diamond structures. The product of the axial ratios c/a for the two structures is predicted to be 2.0084, slightly lower than the experimental value 2.04–2.05 and very close to $(c/a)^2=2$ for the ideal diamond structure: a manifestation of the reciprocal relation.

The crystal structure of a high-pressure phase of cesium metal (Cs IV) has recently been determined by Takemura, Minomura, and Shimomura.[1] It has a tetragonal symmetry with four atoms in a rectangular unit cell and an axial ratio $c/a=3.73$. More recently it has been found that rubidium metal also shows a phase transition to a high-pressure phase (Rb V) with the Cs IV structure.[2]

The Cs IV structure is obtained from the diamond structure ($c/a=\sqrt{2}$) by stretching it along the c axis of the rectangular unit cell and is accordingly of the tetragonal diamond structure. Thus the Cs IV structure belongs to the same family as the crystal structure of β-Sn, which has $c/a=0.5456$.[3,4] The β-Sn structure is known to be the high-pressure form of Ge and Si,[5–7] where $c/a=0.55$.

In this Brief Report we wish to point out that the Cs IV and β-Sn structures are quasireciprocal to each other, with a certain generalization of the notion of reciprocal lattice. Thus the doublet of Cs IV and β-Sn structures may be compared to the known one of bcc and fcc, of which one is the reciprocal lattice of the other. We shall argue that the quasireciprocal relation may originate from some symmetry in the curve for the Madelung energy as a function of the axial ratio. This argument seems relevant in view of a recent study by Yin and Cohen.[7] According to these authors the Madelung energy plays a dominant role in determining the axial ratio for the high-pressure form of Ge and Si.

Following Heine and Weaire (HW),[8] we consider a self-reciprocal family of lattices where the reciprocal lattice of a member of the family also belongs to the same family. Since HW referred to families of the simple hexagonal structures and of the body-centered tetragonal ones as examples, we first describe the family of rhombohedral structures which is generated from simple cubic (sc) by rhombohedral distortions. For the product of the axial ratios c/a in a space lattice and its reciprocal one we have a constant value 3/2, referring to the hexagonal unit cell. The particular value $(c/a)_0=\sqrt{6}/2$ corresponds to the sc structure which is self-reciprocal or whose reciprocal lattice is identical with the space one. In the rhombohedral family the doublet of bcc and fcc appears at a pair of $c/a=\sqrt{6}/4$ and $c/a=\sqrt{6}$.

HW have shown that the Madelung energies of ions are nearly the same for two lattices satisfying the reciprocal relation,[8] with refinements of the earlier arguments by Weaire and Williams.[9] This is illustrated in Fig. 1 for the Madelung constant α_M of the rhombohedral structures, where α_M is defined by $E_M=\alpha_M/2R_0$ with E_M the Madelung energy of an ion of unit charge and with R_0 the radius of the sphere of the volume Ω_0 per ion.

We want to generalize HW's argument to a family of tetragonal diamond structures. We write down the Ewald-Fuchs formula[10] for the Madelung constant α_M:

$$\alpha_M=R_0\left[\frac{4\pi}{\Omega_0}\sum_{\mathbf{G}}{}'\frac{\exp(-G^2/4\eta)}{G^2}|S(\mathbf{G})|^2+\sum_{\mathbf{R}_j}{}'\frac{\mathrm{erfc}(\sqrt{\eta}R_j)}{R_j}-\left[\frac{2\sqrt{\eta}}{\sqrt{\pi}}+\frac{\pi}{\eta\Omega_0}\right]\right], \quad (1)$$

where $\mathbf{R}_j$ and $\mathbf{G}$ stand, respectively, for the space- and reciprocal-lattice vectors, and $\mathrm{erfc}(x)$ is the complementary error function

$$\mathrm{erfc}(x)=(2/\sqrt{\pi})\int_x^\infty e^{-x^2}dx \quad (2)$$

and $S(\mathbf{G})$ is the structure factor

$$S(\mathbf{G})=\frac{1}{n}\sum_j \exp(i\mathbf{G}\cdot\mathbf{R}_j), \quad (3)$$

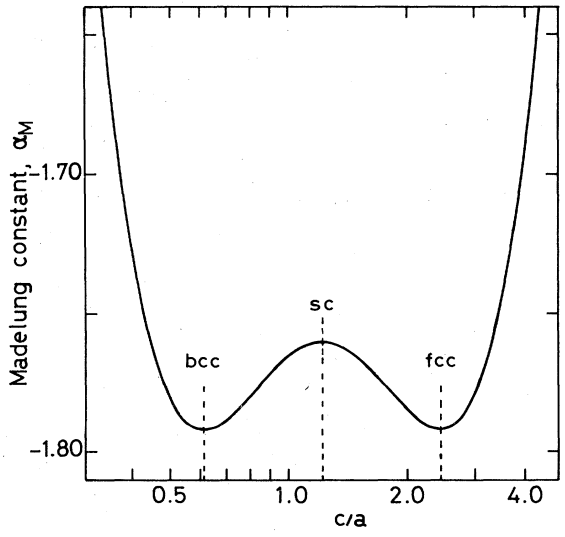

FIG. 1. Curve for the Madelung constant α_M for the rhombohedral structure as a function of c/a in logarithmic scale. The axes refer to the hexagonal unit cell.

where the summation is taken over n ions in the unit cell.

To show some improvement of the previous arguments, let us for a moment consider the Bravais lattice, where $S(\mathbf{G})=1$. For a self-reciprocal structure the sum over reciprocal-lattice vectors ($\mathbf{G}$ sum) and that over space-lattice vectors ($\mathbf{R}$ sum), both in Eq. (1), are identical in form,[9] if the complementary error function is replaced by its asymptotic expression

$$\mathrm{erfc}(x) \cong \frac{1}{\sqrt{\pi}} \frac{e^{-x^2}}{x} \quad . \tag{4}$$

HW observed that[8] if the Ewald parameter η is chosen to equate the convergence rates in the two summations of Eq. (1), then the factors of the $\mathbf{G}$ and $\mathbf{R}$ sums become approximately equal: They have a value of $\pi^{3/2}/6=0.928$ for the ratio of the two factors. However, a more detailed inspection on the equal convergence rates shows that the two factors above are exactly the same.

To examine the asymptotic series of the $\mathbf{G}$ sum in Eq. (1) we consider the contribution from $\mathbf{G}$ points lying far from the origin. In the considered region, $|S(\mathbf{G})|^2$ may be replaced by its average value, which is equal to $1/n$. With this average value taken into account as a weight, the effective density of $\mathbf{G}$ points proves equal to $(2\pi)^3/\Omega_0$, since the volume of a unit cell is $n\Omega_0$. From the volume for an effective reciprocal-lattice point we obtain the radius G_0 of its equivalent sphere as

$$G_0=(6\pi^2/\Omega_0)^{1/3} \quad , \tag{5}$$

which must correspond to another radius

$$R_0=(3\Omega_0/4\pi)^{1/3} \tag{6}$$

in the real space.

If we scale $\mathbf{G}$ and $\mathbf{R}_j$, respectively, by

$$\mathbf{G}=G_0\mathbf{g}, \quad \mathbf{R}_j=R_0\mathbf{r}_j \quad , \tag{7}$$

the weighted $\mathbf{g}$ points distribute with the same density as the $\mathbf{r}_j$ points in the reduced space. Then the $\mathbf{G}$ and $\mathbf{R}$ sums must have the same asymptotic series if the following identity holds for any distance ρ.

$$\frac{4\pi}{\Omega_0}\left(\frac{1}{G_0^2}\right)\exp(-G_0^2\rho^2/4\eta)=\frac{1}{\sqrt{\pi\eta}}\left(\frac{1}{R_0^2}\right)\exp(-\eta R_0^2\rho^2) \quad . \tag{8}$$

In writing down the right-hand side of Eq. (8) we use Eq. (4). The identity (8) proves to be satisfied by

$$\eta=G_0/(2R_0)=\pi/\Omega_0^{2/3} \quad . \tag{9}$$

It is noted that the above value minimizes the last term in parentheses of Eq. (1).

Substituting the value of η thus chosen into Eq. (1), we get the Madelung constant in the form

$$\alpha_M=\alpha_0+\alpha_s+\alpha_c \quad , \tag{10}$$

where

$$\alpha_0=-3\left(\frac{3}{4\pi}\right)^{1/3}=-1.861\,051 \quad , \tag{11}$$

$$\alpha_s=\left(\frac{4}{3\pi^2}\right)^{1/3}\left(\sum_{\mathbf{g}}{}'|S(\mathbf{g})|^2\frac{\exp(-\gamma g^2)}{g^2}+\sum_{\mathbf{r}_j}{}'\frac{\exp(-\gamma r_j^2)}{r_j^2}\right) \quad , \tag{12}$$

$$\alpha_c=\sum_{\mathbf{r}_j}{}'\left(\frac{\mathrm{erfc}(\sqrt{\gamma}r_j)}{r_j}-\frac{\exp(-\gamma r_j^2)}{\sqrt{\pi\gamma}r_j^2}\right) \quad , \tag{13}$$

where $\gamma=(9\pi/16)^{1/3}$.

We shall below consider the term α_s, leaving aside the correction α_c. For the Bravais lattices, the term α_s is symmetric with respect to the interchange of the space and re-

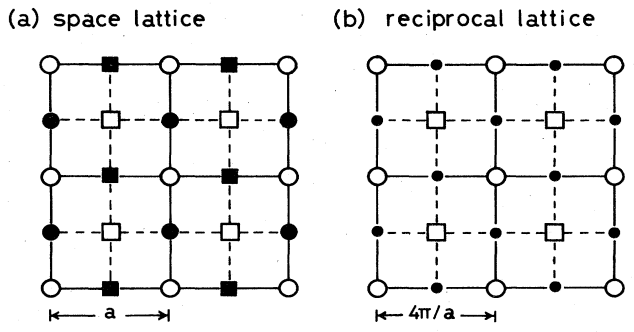

FIG. 2. (a) Tetragonal diamond lattice and (b) its weighted reciprocal lattice. In (a), open circles lie at $z=0$ plane, closed circles at $z=c/4$, open squares at $z=c/2$, and closed squares at $z=3c/4$, with the z axis vertical to the sheet. In (b), open circles lie at $\zeta=0$, closed circles at $\zeta=2\pi/c$, $6\pi/c$, and open squares at $\zeta=4\pi/c$, where ζ denotes the z component of the reciprocal-lattice vector $\mathbf{G}$. Closed circles are of weight $\frac{1}{2}$ and the others are of weight 1.

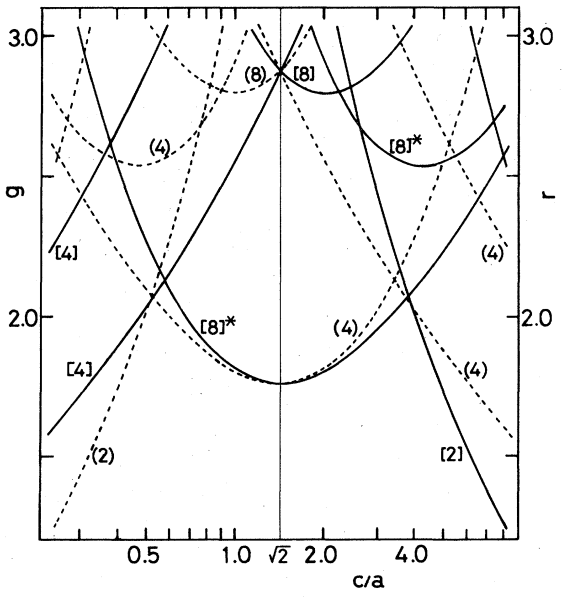

FIG. 3. Length of g and r vectors for tetragonal diamond structures as a function of c/a. Solid lines are drawn for g vectors, where the number of equivalent vectors is indicated by figures in brackets, and the g vectors with weight $\frac{1}{2}$ by asterisks. Broken lines are drawn for r vectors, with figures in parentheses indicating the number of equivalent vectors. (c/a in logarithmic scale.)

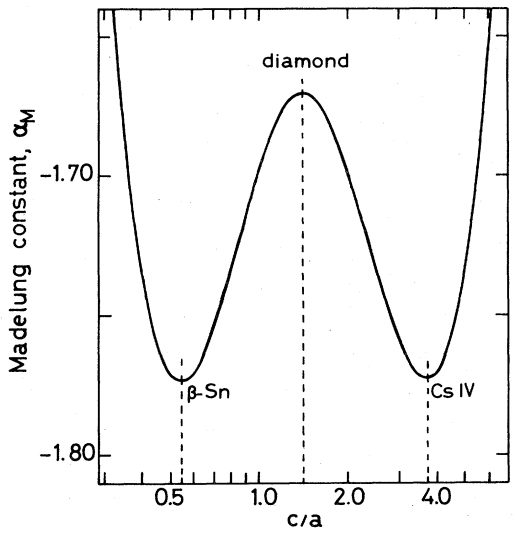

FIG. 4. Madelung constant α_M for tetragonal diamond structures as a function of c/a in logarithmic scale.

ciprocal lattices, and hence has the same value for two crystal lattices reciprocal to each other. For non-Bravais lattices we consider a reciprocal lattice where each lattice point **g** has a weight given by $|S(\mathbf{g})|^2$. Then we look for a space lattice for which the **r** sum is identified to the similar sum for a weighted reciprocal lattice. We consider this problem specifically for a family of tetragonal diamond structures.

For a tetragonal diamond structure, the space lattice and its weighted reciprocal lattice are illustrated in Fig. 2, which shows that a weighted reciprocal lattice belongs also to the family of tetragonal diamond structures as far as the lattice summation is concerned. Next we consider the length of the reciprocal- and space-lattice vectors, which are shown in Fig. 3 as a function of c/a in logarithmic scale. Notice in Fig. 3 that the solid (broken) lines on the right side are the reflection of the broken (solid) ones on the left side, with respect to the vertical line at the center corresponding to the ideal diamond lattice. Thus each of space-lattice vectors $\mathbf{r}_j$ for the crystal of an axial ratio c/a proves equal in magnitude to a reciprocal-lattice vector **g** for that of a different ratio c^*/a^* if we have the reciprocal relation

$$\left(\frac{c^*}{a^*}\right)\left(\frac{c}{a}\right)=2 \ . \tag{14}$$

Let us now consider Eq. (12), in which the **g** sum and **r** sum are interchanged with each other for two crystal lattices satisfying the reciprocal relation (14). Therefore the term α_s must be the same for the two crystal lattices above.

The minimum of the **g** sum occurs very nearly at the point where the low-lying reciprocal-lattice vectors cross. Referring to Fig. 3, we have 6(8) **g** points effectively at the crossing point $c/a=\sqrt{15}$ ($c/a=1/\sqrt{3}$) on the right (left) side. These numbers with interchange coincide, respectively, with the coordination numbers in the space lattice when the crossing occurs. However, the crossing point of the shortest r vectors shifts from that of the shortest g vectors (Fig. 3), in contradistinction to what happens in the family of simple rhombohedral lattices. This implies that the minimum point of the **r** sum is slightly different from the similar point of the **g** sum, for the tetragonal diamond structures. Though the numerical values of α_s remain the same, the minimum configurations of the Madelung energy appear at positions slightly different from those satisfying the reciprocal relation, owing to the correction term α_c.

In Fig. 4 we show the curve for the Madelung constant α_M, which is the logarithmic plot of the previous results.[4,6] For the minimum Madelung energy we have $\alpha_M=-1.773\,12$ at $c/a=0.5446$ and $\alpha_M=-1.772\,92$ at $c/a=3.6881$ with refinement of the values of c/a given by Hafner.[4] A close agreement of the Madelung constants above is comparable to that in the doublet of bcc ($-1.791\,86$) and fcc ($-1.791\,75$).[11]

The axial ratios c/a for the minimum Madelung energy are a little lower than the observed values, 0.55 for metallic Si and Ge (or 0.5456 for β-Sn) and 3.73 for Cs IV, respectively. These observed values are lying between the two axial ratios, one for the crossing of the shortest r vectors and the other for the crossing of the shortest g vectors. The ratios above are estimated, respectively, as 0.5164 and 0.5774 for the β-Sn and 3.464 and 3.873 for the Cs IV structures. The axial ratios observed are shifting from those for the minimum Madelung energy towards the crossing point of the g vectors.

We finally mention the reciprocal relation, Eq. (14). The product of c/a for the lowest structures of the Madelung energy proves to be 2.0084, which is closer to the ideal value 2 than to the experimental one 2.04–2.05.

We are grateful to Professor H. Miyagi for informing us of the Madelung constants for rhombohedral lattices.

[1]K. Takemura, S. Minomura, and O. Shimomura, Phys. Rev. Lett. **49**, 1772 (1982); **51**, 1603(E) (1983).
[2]H. Olijnyk and W. B. Holzapfel, Phys. Lett. **99A**, 381 (1983).
[3]J. Donohue, *The Structure of the Elements* (Wiley, New York, 1974).
[4]J. Hafner, Phys. Rev. B **10**, 4151 (1974).
[5]J. C. Jamieson, Science **139**, 762 (1963).
[6]D. Weaire, Phys. Status Solidi **42**, 767 (1970).
[7]M. T. Yin and M. L. Cohen, Phys. Rev. B **26**, 5668 (1982).
[8]V. Heine and D. Weaire, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 24, p. 249.
[9]D. Weaire and A. R. Williams, Philos. Mag. **19**, 1105 (1969).
[10]K. Fuchs, Proc. R. Soc. London, Ser. A **151**, 585 (1935).
[11]C. A. Sholl, Proc. Phys. Soc. London **92**, 437 (1967).