FAST COMMUNICATIONS

Acta Cryst. (1989). A**45**, *FC29–FC32*

Magic strains in face-centered and body-centered cubic lattices

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(Received 24 May 1989; accepted 6 July 1989)

Abstract. An orthorhombic strain is shown to transform a f.c.c. lattice into itself. A related transformation takes the b.c.c. lattice into itself. The energy barriers for two f.c.c. systems are found to be of the order of the melting temperature. Possible connections with melting, liquid structure and crystal growth are discussed.

Introduction. It is well known that the energy of a stable crystal increases for any small lattice strain. One might expect the energy to increase monotonically with increasingly larger strain, but this is not true in general. A certain large strain is shown to transform a f.c.c. lattice into another f.c.c. lattice, *i.e.*, with no net change in energy, while a related strain transforms a b.c.c. lattice into itself. Close-packed systems are often well described by simple pair potentials. The energy barrier for the f.c.c. transformation has been computed for two such systems; a Lennard-Jones (rare-gas) model and a rigid-ion model for NaF. In both cases the energy barrier (per atom) is on the order of the melting temperature. For a finite-sized cube-shaped crystal, the transformation creates an approximate fivefold angle, suggesting it as a possible mechanism for nucleating fivefold symmetries.

The magic strain. An orthorhombic strain in a cubic crystal is conveniently expressed as a product of three matrices

$$T(a,b,c)=\begin{bmatrix} a/a_0 & 0 & 0 \\ 0 & a/a_0 & 0 \\ 0 & 0 & a/a_0 \end{bmatrix}$$

$$\times\begin{bmatrix} (1+b)^{-1/3} & 0 & 0 \\ 0 & (1+b)^{-1/3} & 0 \\ 0 & 0 & (1+b)^{2/3} \end{bmatrix}\begin{bmatrix} 1 & c & 0 \\ c & 1 & 0 \\ 0 & 0 & 1/(1-c^2) \end{bmatrix} \quad (1)$$

whose restoring stress, for small strains, is proportional to the bulk modulus, the C_{11}–C_{12} shear modulus and the C_{44} shear modulus respectively. The constant a_0 is defined to be half the usual lattice constant, *i.e.*, $2^{1/2}a_0$ is the nearest-neighbor separation in a f.c.c. lattice. When $c=c_0=(1-2^{1/2})/(1+2^{1/2})$ and $b=b_0=(1+c_0)^3-1$,

$$T_0\equiv T(a_0,b_0,c_0)=\tfrac{1}{2}\begin{bmatrix} 1+2^{1/2} & 1-2^{1/2} & 0 \\ 1-2^{1/2} & 1+2^{1/2} & 0 \\ 0 & 0 & 2^{1/2} \end{bmatrix} \quad (2)$$

and the f.c.c. lattice is transformed into another f.c.c. lattice, with the atoms (at lattice sites) rearranged according to (2). The cubic axes of the transformed lattice are along the (1, –1, 0), (1, 1, $-2^{1/2}$) and (1, 1, $2^{1/2}$) directions, which can be obtained from the original axes by a 45° rotation about z followed by another 45° rotation about the new x axis. This becomes apparent by applying T_0 to the vectors which become second-neighbor positions in the transformed lattice. Specifically, $T_0(1, -1, 0) = (2^{1/2}, -2^{1/2}, 0)$, $T_0(1, 1, -2) = (1, 1, -2^{1/2})$ and $T_0(1, 1, 2) = (1, 1, 2^{1/2})$. Two of the second-neighbor atoms in the transformed lattice were first neighbors and the other four were third neighbors. Obviously, T_0 is not a simple rotation because separations between atom pairs, in general, are changed. Relative to the atom at the origin, atoms in neighboring shells are exchanged as follows: two from the nearest-neighbor shell ($S1$) go to the second-neighbor shell ($S2$), two $S2$ go to $S1$, four $S2$ go to $S3$, four $S3$ go to $S2$, eight $S3$ go to $S5$, and the exchange becomes more complex for further neighbors. An equivalent f.c.c. transformation is obtained for $c = -c_0$. This just changes the sign of the off-diagonal elements of T_0.

The transformation which takes a b.c.c. lattice into itself is also given by the general form of (1). The 'magic' values in this case are $c = \pm c_0$ and $b = (1 - c_0)^3 - 1$. The b.c.c. transformation occurs for a particular positive value of b $\{[11(2^{1/2}) - 7]/[7 + 5(2^{1/2})] \simeq 0.6081\}$ while the f.c.c. transformation occurs for a particular negative value, $b_0 = [1 - 5(2^{1/2})]/[7 + 5(2^{1/2})] \simeq -0.4315$. The b.c.c. (f.c.c.) transformation expands (contracts) the lattice in the z direction. Thus, second neighbors along the z direction become third (first) neighbors of the transformed b.c.c. (f.c.c.) lattice. For the b.c.c. transformation four $S1$ go to $S2$, four $S2$ go to $S1$, two $S2$ go to $S3$, two $S3$ go to $S2$, eight $S3$ go to $S4$, and of course, the exchange becomes more complex for further neighbors. We note that ten of the twelve $S1$ neighbors in the f.c.c. lattice remain $S1$ neighbors of the transformed f.c.c. lattice, while only four of the eight $S1$ neighbors of the b.c.c. lattice remain $S1$ neighbors in the transformed b.c.c. lattice.

Energy barrier. A f.c.c. lattice of atoms interacting *via* the pair potential $4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ is known to melt at a temperature of $T_m \simeq 0.67\varepsilon/k$, where k is the Boltzmann constant. At that temperature the lattice is expanded to $a \simeq 1.04a_0$, where $a_0 = 0.7711\sigma$ is the zero-temperature equilibrium value (Hansen & Verlet, 1969; Broughton & Gilmer, 1983). The energy per atom $E(a_0, b, c)$ relative to the zero-temperature unstrained value, $E(a_0, 0, 0) = E(a_0, b_0, c_0)$ is shown as a contour plot in Fig. 1. The associated energy barrier is $\sim 0.37\varepsilon$ per atom, about half kT_m. With $a = 1.04a_0$ the barrier is reduced to $\sim 0.2\varepsilon$.

The NaCl structure is transformed into itself by T_0 provided we also displace the Cl sublattice (Na is assumed at the origin) by $a_0(\frac{1}{2}, \frac{1}{2}, 0)$. The energy barrier for this transformation was computed for NaF using previously published potentials (Boyer, 1981) derived by the method of

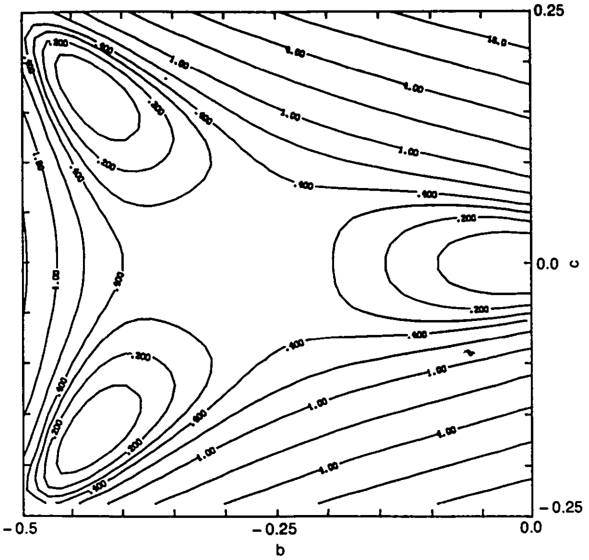

Fig. 1. Contour plot of the energy $E - E_0$ of a Lennard-Jones f.c.c. lattice for fixed volume ($a = a_0 = 0.7711\sigma$) as a function of strains b and c. Energy contours are relative to the ground-state energy $E_0 = E(a_0, 0, 0) = E(a_0, b_0, c_0) = -8.583\varepsilon$ and have values 0.1, 0.2, 0.3, 0.4, 0.6, 1.0, 2.0, 4.0, 8.0 and 16.0 in units of ε.

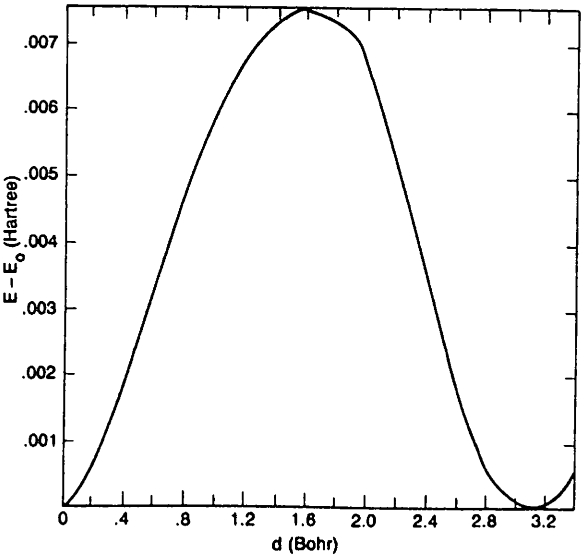

Fig. 2. Minimum energy, $E(d, a, b, c) - E_0$, for a Gordon-Kim model of NaF as a function of sublattice displacement d along the (1,1,0) direction. The ground-state energy, $E_0 = -0.3590235$ Hartree, occurs at $a_0 = 4.38689$ Bohr, with $d = 0$ or $d = 2^{1/2}a_0/2$.

Gordon & Kim (1972). Of the alkali halides, NaF was selected because the overall agreement between theory and experiment for elastic and equation-of-state properties, including molecular-dynamics simulation of melting (Boyer & Pawley, 1988), is remarkably good. The static energy per molecule (E) is a function of sublattice displacement (d) and the strain parameters a, b and c. A plot of the minimum $E(d, a, b, c)$, relative to the absolute minimum $E_0 = E(0, a_0, 0, 0) = E(2^{1/2}a_0/2, a_0, b_0, c_0)$, is shown in Fig. 2 as a function of d. A corresponding plot of the strain parameters which minimize E is given in Fig. 3. In temperature units (1 Hartree $k^{-1} \simeq 3.26 \times 10^5$ K) the barrier is ~1250 K per atom, approximately the melting temperature. The energy required to expand the static lattice to $1.05a_0$, approximately the value for the solid at the melting temperature, is ~750 K per atom. Thus the barrier is substantially reduced at melting.

Discussion. The above analysis suggests that such transformations should be considered in developing models for melting, liquid structure and crystallization. Several features of the transformation are well suited for modeling liquid structure. Equivalent transformations are formed by selecting the x or y axes for compression, rather than the z axis, and an additional choice is in the sign of the remaining strain: the off-diagonal element can be plus or minus (see results in Fig. 1). Thus, six equivalent transformations are available which, if applied many times at random, could produce the appearance of liquid-like diffusion. Moreover, in such a random sequence of transformations, the crystallographic axes would lose any apparent relation to the original axes. In reality, of course, microdomains would develop to further enhance diffusion and create disorder. Finally, we note that the shape of a finite crystal undergoes a rather drastic change in each transformation, which is analogous to a liquid's lack of resistance to shear stress. This brings us to one more intriguing observation.

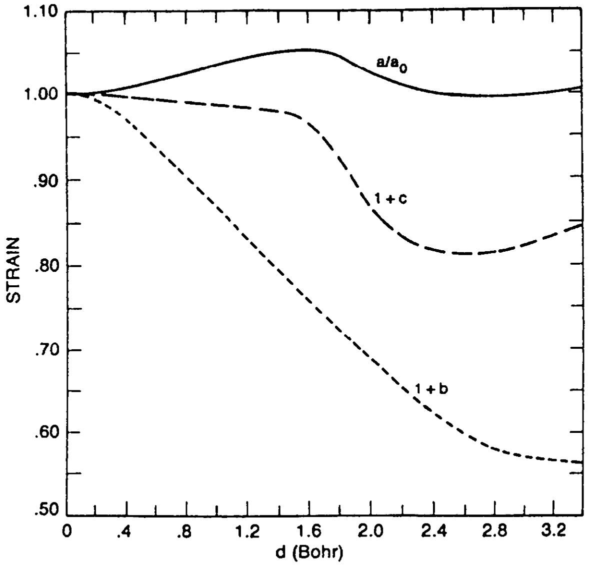

Fig. 3. Values for volume- and the two shear-strain parameters a, b and c, corresponding to the minimum-energy curve in Fig. 2.

If T_0 is applied to a finite-sized cube-shaped crystallite, the shape of the transformed crystallite in the xy plane is a parallelogram with the small interior angle having a cosine of 1/3, or a value of ~70.5°; only 1.5° from 1/5 of a circle. Atomic structures with fivefold symmetry have been the subject of intense investigation since their discovery in aluminium alloys (Shechtman, Blech, Gratis & Cahn, 1984). The detailed nature of their structure is still the subject of debate (Steinhardt, 1986; Janot & Dubois, 1988), although a growing body of evidence suggests they are three-dimensional analogs of two-dimensional Penrose tilings, so called 'quasicrystals', rather than elaborate twinned structures, both of which can have fivefold symmetry. Regardless of the true nature of their structure, there must be some physical mechanism which nucleates the fivefold symmetry from the liquid. The transformations described above could possibly provide this mechanism. In this regard, the *approximate* fivefold angle could be significant in two respects: (1) the angle must be close enough to 72° to nucleate fivefold structures, and (2) the imperfect fivefold angle might explain why these structures are only formed by rapid-quench techniques, and consequently, why they transform to a f.c.c. ground state when heated sufficiently.

The form of the strain tensor used above was derived by M. J. Mehl for calculating elastic constants in cubic systems (Mehl, Hemley & Boyer, 1986; Chen, Boyer, Krakauer & Mehl, 1988). The special values of b and c were discovered through an ongoing collaborative effort with P. J. Edwardson and R. E. Cohen to calculate electrostrictive coefficients in alkali halides. Helpful discussions with J. Q. Broughton and W. T. Elam are gratefully acknowledged.

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