Can the Lennard-Jones Solid be Expected to be fcc?

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(Received 5 December 1990)

The structure of the Lennard-Jones solid, obtained by molecular-dynamics simulation of crystallization in the supercooled liquid, may be fcc, although the hcp structure is energetically more favorable. This could derive from the cubic symmetry of the fcc lattice, allowing lattice defects that are not possible in the hcp arrangement, but are essential to crystal growth in the simulated liquid. Two crossing stacking faults in a small fcc crystallite can produce nonvanishing, growth-promoting, but stacking-fault-resisting, surface steps.

PACS numbers: 61.20.Ja, 36.40.+d, 61.50.Cj

It is well known that the Lennard-Jones (LJ) potential favors the hcp structure over the fcc structure for the solid [1]. The difference in cohesive energy ($\approx 0.01\%$) appears to be too small, however, to provide a basis for an explanation of an observed preference for one of the two structures in molecular-dynamics (MD) simulations of crystallization in the supercooled LJ liquid. In fact, until very recently, such a preference has never been found [2–7], suggesting the inadequacy of the LJ potential to model the interatomic interactions in a simulation of either fcc or hcp crystal growth.

It is the purpose of this Letter to investigate the role that lattice defects may play in the simulated crystallization process, and, in particular, to demonstrate that growth-stimulating defects are much more probable to occur in fcc crystallites than in hcp crystallites. Moreover, it will be shown that such defects exclusively stimulate fcc growth, without further assumptions regarding the interatomic potential other than that it is isotropic and short ranged.

That growth characteristics can be decisive in the choice of crystal structure of a substance, rather than a difference in cohesive energy, can be illustrated by a comparison with the method of static lattice energy calculations, aimed at structure prediction. Here, the evaluation and subsequent minimization of lattice sums involves inclusion of all interactions between a representative central atom (the reference atom) with all its close and more distant neighbors within a limiting sphere. However, the reference atom has been incorporated in the crystal lattice under completely different conditions, notably in the absence of at least half of its ultimate neighbors. Moreover, according to accepted theories of crystal growth [8], the motions of surface-migrating atoms are governed by short-range forces and are rather insensitive to the detailed shape of the potential. Trapping sites that are (almost) equally favorable (but, possibly, not equivalent, as on close-packed faces of fcc or hcp crystals) will have equal *a priori* occupation probability. The possibility of complete layers of atoms shifting to "better" positions in response to the arrival of new neighbors can be ruled out.

Both the fcc and the hcp structures consist of plane hexagonal arrays of atoms that are stacked in an orderly way, with atoms in one layer over three-coordinated sites in the preceding layer. Consequently, each layer is parallel shifted with respect to the preceding layer by one of the six vectors $\mathbf{r}_i$ joining a particular atom with the three-coordinated sites surrounding it in its layer. The structure is fcc if each layer is shifted by the *same* vector $\mathbf{r}$ with respect to the preceding one, and hcp if the shifts are alternating $\mathbf{r}, -\mathbf{r}, \mathbf{r}, \ldots$. Apparently, in the latter case the odd layers are all in the same position, as are the even layers, and the stacking sequence is referred to as . . .*ABABAB*. . . . Similarly, fcc stacking is characterized by the sequence . . .*ABCABC*. . ., since the shifts $3\mathbf{r}$ and $0\mathbf{r}$ are equivalent. Omitting a layer from the fcc sequence introduces a shift $2\mathbf{r}$, equivalent to $-\mathbf{r}$.

Since the fcc arrangement has cubic symmetry, there are four different, but equivalent, stacking directions, along the body diagonals of the cubic unit cell; the hexagonal symmetry of the hcp lattice, on the other hand, allows only a single stacking direction. A small fcc crystal may be completely bounded by close-packed faces, as is the case, for example, when it is in the shape of a tetrahedron or an octahedron. The hcp crystal must exhibit other low-index faces as well.

There are two problems connected with the growth of an fcc crystal: (i) The close-packed faces do not offer favorable sites for surface nucleation, necessary to start a new layer, which practically excludes further growth under near-equilibrium conditions; and (ii) if surface nucleation did occur somehow, it could be easily in the wrong registry, e.g., *B* when the supporting layer is *C* and the new layer should be *A* to comply with the fcc sequence. Indeed, with a Lennard-Jones potential, the chances for "right" and "wrong" would be virtually equal. Both problems can be solved by introducing appropriate, but plausible, lattice defects, and considering their effects on growth modes, growth rates, and crystal symmetry.

If a close-packed face is only *partly* covered by a new layer, there will be a monatomic (full) step on the surface, and new atoms will be trapped in favorable five- and six-coordinated step and kink sites. Unfortunately, this process of accretion advances the step towards the end of the crystal, where it is annihilated, leaving a situation that is unfavorable for further growth. As was pointed out by Frank [9], this problem can be solved by observing the effect of a screw dislocation emerging from the surface. The dislocation has associated with it a full step that cannot run out of the crystal, but rather rotates, by accretion of atoms, about the intersection of the dislocation with the surface. The permanent availability of active surface sites clearly removes the growth-inhibiting difficulty of surface nucleation. However, since the origin of screw dislocations is believed to be in the inclusion of impurities in the crystal lattice, their role in computer simulations of the LJ liquid may be insignificant.

A simple stacking fault, on the other hand, is a very common defect in computer-generated structures, as is obvious in the frequently reported fcc/hcp mixtures [2-6]. Rather than a *full* step, the intersection of a stacking fault with a surface not parallel to it produces a *half* step (or, more generally, a nonintegral step) that cannot run out of the crystal either. This is illustrated schematically in Figs. 1(a)-1(d), where the effect of a single stacking fault in one of the three stacking directions not perpendicular to the (111) surface of an fcc crystal is considered. The steps provide the surface with rows of four-coordinated sites that would exhibit only three-coordinated sites otherwise. Consequently, the need for surface nucleation is not completely removed, but the resistance to island formation may be substantially reduced. It remains to be demonstrated that the steps help to initiate new layers in the correct fcc registry (*ABC*).

It is clear that the surface will be atomically flat (or can be made so by removing unfinished layers) if none of the three sets of close-packed layers that are inclined to the surface contains a stacking fault. Or, stated differently, the flatness of the surface guarantees the absence of a stacking fault in all three sets. Consequently, stacking faults can be avoided if the edge atoms of successive layers are forced to form a flat face. The situation depicted in Fig. 1(d) [which is identical to that of Fig. 1(b)] may be considered to represent a translation twin, in which both individuals had an atomically flat outer surface [parallel to the removed layer *B*, Fig. 1(a)] before they were joined. The misfit produces a step, which is an extension of either the "left" or the "right" surface. The individuals grow in turn, as they are on the lower side of the step, by accretion of a single layer on the free surface. The nucleation at the step guarantees the closing of the new layer to the step and, consequently, the extension of the flat interface between the twin individuals, implying correct stacking, as explained above. For example, in Fig. 1(d) the lower side of the $\frac{1}{3}$ step stimulates the nucleation of a *C* layer (and not a *B* layer, as is also apparent from the situation a few layers below the surface), that spreads to the right, simultaneously creating a $\frac{2}{3}$ step to the left. The detailed atomic arrangements near surface steps are shown in Fig. 2. Since each new layer is shifted by the *same* vector relative to the supporting layer, an *ABCABC*, rather than an *ABABAB*, sequence results.

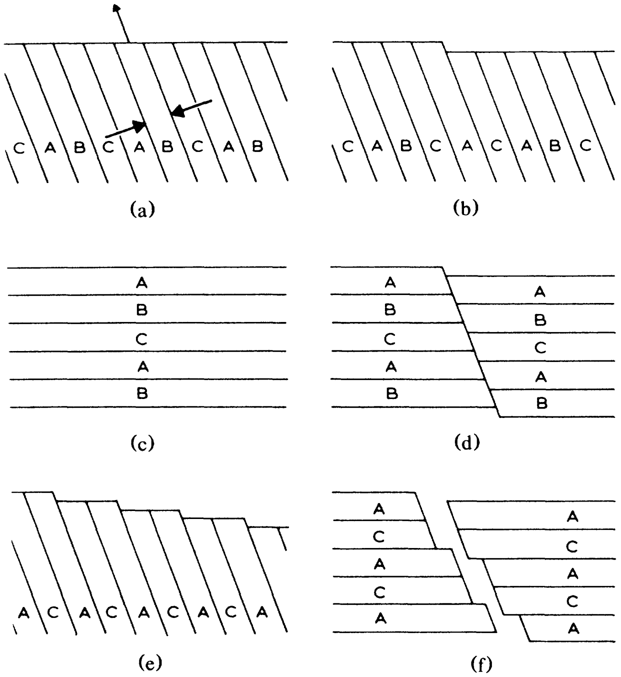

FIG. 1. (a)-(d) Origin of nonintegral surface steps in fcc crystals. The view is along the [110] direction, i.e., along the lines of intersection of two sets of crossing close-packed layers. (a),(b) A hcp stacking fault *CACA* may be viewed as resulting from the removal of a single *B* layer from a perfect crystal. The gap can be closed by pushing both crystal fragments together in the direction of the arrows, in order to make the facing *A* and *C* layers fit; the step height is $\frac{1}{3}d_{111}$. (c),(d) Same situation as (a),(b), but with emphasis on close-packed layers parallel to the surface. (e),(f) Comparison with hcp. (e) As (b), but with *all* *B* layers removed: hcp. The stepped surface is a $(10\bar{1}1)$ face (with no stacking ambiguity as on close-packed faces). An extra step would not influence the growth on this face significantly. (f) A nonintegral surface step on a (0001) close-packed face of a hcp crystal is not possible.

The single stacking direction in hcp crystals excludes a stacking fault in another direction and, consequently, a nonintegral step on a close-packed surface is not possible [Figs. 1(e) and 1(f)]. Even if it were possible, the result would be layer deposition in *ABC* stacking order, i.e., a conversion to fcc growth.

Isotropic fcc growth would require nonvanishing steps on *all* slow-growing faces, a condition easily met in an fcc crystal by introducing *two* crossing stacking faults. For example, in an octahedral crystal, one stacking fault, parallel to two faces, produces steps on the remaining six faces, and the second fault, parallel to one of these six faces, cuts the faces parallel to the first fault (cf. Fig. 3).

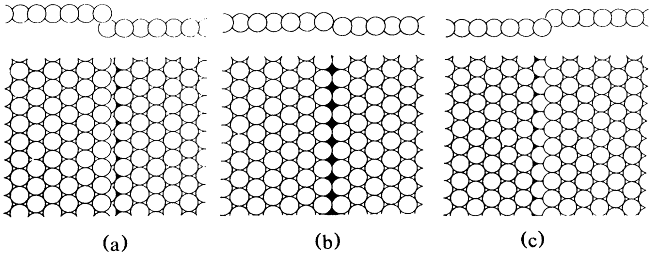

FIG. 2. Side and top views of atomic arrangement in the fcc (111) face with different kinds of steps. All accessible sites have three coordination, except as indicated for the sites marked in black. (a) Full step, five coordination; the layer will spread to the right, leaving an atomically flat surface. (b) $\frac{1}{3}$ step, four coordination; situation as in Fig. 1(d); if the marked sites are occupied first, a layer will spread to the right, to give (c) $\frac{2}{3}$ step, four coordination; if the marked sites are occupied first, a layer will spread to the left, leaving a situation as in (b), but parallel shifted by $\mathbf{r}=\frac{1}{6}a\langle 211\rangle$. The surface structures (b) and (c) can be recognized on the doubly faulted octahedron shown in Fig. 3.

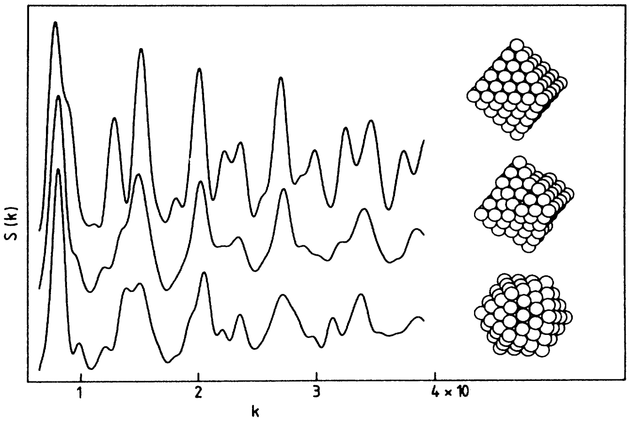

FIG. 3. Interference functions $S(k)$ at zero temperature for (from top to bottom) perfect fcc octahedron, fcc octahedron with two crossing stacking faults, and three-shell icosahedron. Reduced units, i.e., $k=2^{1/6}\sigma(4\pi/\lambda)\sin(\theta/2)$; peak positions would be at $k^2=2\pi^2(H^2+K^2+L^2)$ for an infinite fcc crystal.

A vacancy channel, surrounded by atoms with eleven, rather than twelve, neighbors at the line of intersection of the two faults causes a small loss in binding energy [10].

The smallest close-packed structure with two crossing stacking faults should contain some twenty atoms, and is not more or less likely to result from spontaneous structural fluctuations in the supercooled liquid than are perfect fcc nuclei. In contrast with a perfect nucleus, however, the permanent availability of active four-coordinated sites (that cannot be exhausted by occupation) on the surface of the faulted structure will make it fast growing, increasing its chances to leave the subcritical size region before disintegration (cf. Fig. 4).

The, supposedly indispensable, stacking faults in small crystallites may cause rather drastic changes in observable diffraction functions, as illustrated in Fig. 3, where the interference functions $S(k)=\sum(\sin kr_{ij})/kr_{ij}$ (summation over atom pairs i,j) of some small clusters of equal size are compared. The interference function of a faulted 146-atom fcc octahedral crystallite is significantly different from that of the perfect crystal, but similar to that of a three-shell 147-atom icosahedron, exhibiting fivefold symmetry. Growth based on icosahedral motives is believed to be a dominant feature in (rare) gas-phase nucleation in supersonic molecular beams [11-13].

The proposed qualitative scenario of crystal nucleation and growth unequivocally favors the fcc structure for the LJ crystal, to the extent that, if a nearly perfect crystal could be produced by an MD simulation of the supercooled LJ liquid, it is most likely fcc. The recently reported results of a simulation of a 10^6-atom liquid [14] are strongly in support of this view: It was found that originally defective hcp/fcc nucleation eventually resulted, after annealing, in nearly perfect fcc crystallites with some unidentified dislocations, including "planes of particles that do not line up with themselves" [cf. Fig. 1(d)]. Apparently, hcp stacking faults are unavoidable; presumably they are essential.

The foregoing discussion also suggests that conditions should be such that adsorbed atoms can stick only in sites that are at least four coordinated, but evaporate from three-coordinated sites [cf. $\exp(1/T^*)\approx 7$, at a reduced temperature $T^*=0.5$]. If not, there is no reason to expect the concentration of stacking faults to remain small, since then island formation in correct or incorrect registry would be equally probable. This condition would make growth of a perfect crystal virtually impossible, according to classical theories of growth. The same condition, however, hampers homogeneous nucleation and is liable to make the occurrence of a doubly faulted nucleus a rare event. This may be one of the reasons why a successful simulation requires some 10^6 atoms; it simultaneously suggests the possibility of an experimental verification of the proposed mechanism: The LJ liquid may be "seeded"

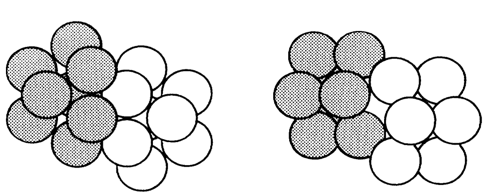

FIG. 4. Two views of a possible nucleus, supporting fcc growth. The 22-atom cluster consists of two incomplete 11-atom hcp anticuboctahedra (distinguished by shading). Its surface exposes three- as well as four-coordinated sites. If only the latter are occupied by new atoms, the cluster will grow into a nearly perfect fcc crystal, with not more than two (crossing) stacking faults. The four-coordinated sites cannot be exhausted, as occurs with a perfect fcc nucleus.

(e.g., by constraining the configuration of a group of atoms in the liquid to remain unchanged) with perfect fcc or hcp nuclei of approximately critical size, or alternatively with a defect structure like the one shown in Fig. 4. It should then be expected that the defect structure will initiate isotropic fcc growth, but that the perfect nuclei either remain unchanged or develop into disordered fcc/hcp mixtures.

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