Computer Simulation of the Plastic-to-Crystalline Phase Transition in SF_6

G. S. Pawley
Department of Physics, University of Edinburgh, Edinburgh EH9 3JZ, Scotland

and

G. W. Thomas
Distributed Array Processor Support Unit, Queen Mary College, London E1 4NS, England

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A simple but realistic model for the condensed phases of SF_6 gives a plastic phase at 80 K in a molecular-dynamics simulation. Equilibration of a sample of 4096 molecules at 25 K and at zero pressure results in a transition to a polycrystal. The crystal structure found is triclinic $P\bar{1}$, $Z = 3$, but is pseudo-orthorhombic, a result not inconsistent with recent spectroscopic measurements. It is suggested that, to avoid bias, a large size is necessary for modeling the plastic-to-crystalline phase transition.

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The realistic modeling of solid-state phase transitions with molecular dynamics requires a sample large enough that the nucleating phase is in no way restricted or determined by the imposed boundary conditions. With a large enough sample separate grains can grow and compete and each can be large enough to exhibit the structural pattern of the new phase. Because of its extreme anharmonicity the plastic crystalline[1] phase of matter, characterized by a positionally ordered but orientationally disordered arrangement of molecules, is difficult to study analytically. Theoretical progress can thus best be made through molecular-dynamics computer simulations. Ideally any model for the plastic phase of a system should be capable of reproducing the phase change to the crystalline form, thus furnishing an excellent tool for the study of such transitions. We report here what may well be the first realistic example of such a transition found by this technique, yielding a crystal structure of considerable complexity.

It has been pointed out that the selection of a good potential function is of central importance to this work,[2] and it is argued that the simple Lennard-Jones F-F atom-atom potential as already used for the plastic-phase simulation of SF_6 has all the requirements to produce a plastic-to-crystal transition.[3] Molecules are assumed to move as rigid units under interactions with eight nearest and six next-nearest neighbors only. Each intermolecular interaction involves 36 F-F interactions, so that the force field on any one molecule depends on 504 F-F interactions. The dynamical equations followed Beeman's algorithm[4] using the quaternion formulation.[5] The resulting model reproduced the crystallographic result for the plastic phase in which molecules are arranged on average on a body-centered cubic lattice, and perform occasional reorientational jumps as expected in this phase. The temperature of the calculation was 80 K.

Harmonic lattice dynamical calculation for the body-centered-cubic phase gave evidence of a very unstable model, as only the longitudinal acoustic modes had positive eigenvalues.[3] The transverse-acoutic modes had negative eigenvalues, indicating that the structure was unstable with respect to any shear, and instability associated with any molecular rotational displacement was similarly shown by the absence of any librational positive definite modes at any point in the Brillouin zone. This was thought to be an attribute for the model as the cubic phase is not a truly crystalline phase.

A sample of roughly 13 × 13 × 13 body-centered unit cells was used in this calculation. This sample makes full use of the 4096 parallel processors of the International Computers Ltd. distributed-array processor[6] (DAP) which has recently been installed at Queen Mary College, London. The processing elements (PE's) of the DAP are hard wired in a 64 × 64 array, and through the use of software it is very easy to implement cyclic boundary conditions for any desired topology.[7] All PE's work simultaneously on the data for the molecule that each represents, and can exchange information between themselves on the intermolecular interactions. The DAP is thus ideally suited to condensed-phase matter simulations, and as one time step for the present work takes only 3 sec, the DAP is effectively competitive with the fastest of modern computers.

In the work on the dynamics of Rb Parrinello and Rahman[8] have reported a crystal-to-crystal phase transition induced in a molecular-dynamics calculation. With the right conditions evidence of a transition was immediate but the transition itself was slow before the rapid move to completion. This result prompted us to run the SF_6 simulation at a low temperature (25 K) for a long time (3 h) in the hope of a similar event. The temperature of the sample slowly drifted upwards, requiring a continuous extraction of energy from the system. The total potential of the system fell accordingly, and the volume of the constant-pressure sample decreased. This behavior pointed to a gradual ordering process, the geometry of which was quite unknown. No sudden move to completion was observed.

The time step used in this calculation was 0.015 psec, perhaps rather small for a calculation at 25 K, but it had been found to be necessary for runs at 150 K. An earlier calculation[8] on a sample of 54 molecules was quite stable with a time step of 0.025 psec, but such a time step gave problems with the larger sample, eventually producing a close and catastrophic intermolecular contact. Such events were presumably inhibited in the smaller sample by the artificial constraints of the cyclic boundary conditions. Constant pressure was maintained as follows. The displacement of each molecule was measured from its individual origin, these origins being arranged on a body-centered-cubic lattice. The size of the lattice spacing was systematically adjusted to maintain zero pressure, but no attempt was made to distort the basic lattice as done by Parrinello and Rahman.[8] Such distortions relieve shear stresses in the sample, but such stresses should be automatically relieved when the structure suffers a transition by the nucleation of a number of crystallites in various different orientations, provided the sample used for modeling such transitions is large enough for the natural development of a mosaic. If this is not the case the possible new structures for the nucleating phase may be arbitrarily constrained. These considerations are not of such importance if the transition structural change is known in advance. In such cases, as with Rb,[8] it is possible to have the cyclic boundary conditions so that they are consistent with both phases, and then the onset of the transition will be swift at the moment when one grain dominates and the sample becomes a single crystal.

The structure of the natural crystalline phase of SF_6 is not yet known, though recent spectroscopic measurements[9] lead to a conjecture that the phase is orthorhombic. The transition from the plastic phase takes place at 92 K for the natural system, and so a temperature of 25 K is reasonable for a long calculation to search for a crystalline phase. As mentioned above, ordering of the sample took place slowly, and when it appeared that most of the transition was accomplished, about one quarter of the sample was drawn out in layers by the computer, the molecules being represented by octahedra. The layers contain molecules on cubic (100) planes, close molecules therefore being next-nearest neighbors. Part of one typical layer is reproduced in Fig. 1, where the ordering is clearly apparent. In this figure there are two major crystal grains, both with ordering along the diagonal lines parallel to *AB*. The three molecules nearest *B* on *AB* have an orientation (orientation 1) which is not repeated until three rows distant. The intervening two rows contain molecules of orientation 2. Molecules of orientation 1 occupy symmetry inversion centers, utilizing the centrosymmetry of the octahedral molecules. Molecules of orientation 2 do not use the molecular symmetry, but are related in pairs about inversion centers. A primitive unit cell thus comprises one molecule of orientation 1 and two of orientation 2, and is tri-

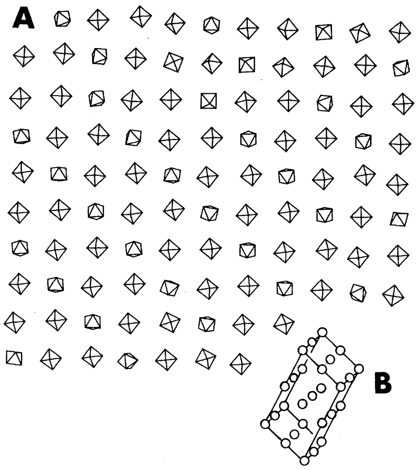

FIG. 1. A part of one (100) layer of the polycrystalline SF_6 at 25 K. Order occurs along rows parallel to *AB*, repeating every three rows. The primitive triclinic cell is shown near *B*, where the open circles denote centers of symmetry. These lie in the plane of the diagram and in two parallel planes, the upper of which is in the next plane of molecules. Twinning occurs as seen by the existence of a local twofold axis perpendicular to the plane of the diagram, situated between molecules 4 and 5 on the line *AB*.

clinic, $P\bar{1}$ $(Z=3)$. This result is consistent with the instability with respect to shear in the cubic phase. A unit cell is outlined in Fig. 1, where the circles denote inversion centers; the upper part of the cell is related to the layer of nearest neighbors above that of Fig. 1, and the inversion centers relating these two layers are also shown.

A more convenient centered unit cell can be chosen as follows. The shortest axis on Fig. 1, that between layers, has a vector $\vec{c}=(d/2, d/2, d/2)$ expressed in terms of the underlying cubic grid of spacing d. Two other axes can be chosen which are orthogonal in the true cubic arrangement, $\vec{b}=(d, -d, 0)$ and $\vec{a}=(d, d, -2d)$. A typical cell of these dimensions has been chosen from the middle of a large grain and is shown projected down $\vec{a}$ in Fig. 2. As this is a "snapshot," the symmetry-related molecules do not appear exactly identical. The molecules labeled + and − are at approximately $+\vec{c}/3$ and $-\vec{c}/3$. The unit cell is

$$(a, b, c)=(14.1, 7.7, 4.70)\ \text{Å}\ ,$$

$$(\alpha, \beta, \gamma)=(89.4°, 91.9°, 88.1°)$$

and is pseudo C-face centered orthorhombic. This is quite consistent with recent spectroscopic measurements on the natural material.[9]

It has been suggested[10] that structural complexity is likely to characterize plastic crystals in their ordered phases. The developing triclinic cell can nucleate in any of 48 possible orientations, thus giving a large entropy contribution at the transition. Furthermore the choice of origin of the unit cell introduces a further factor of 3 as there are three molecules in the unit cell, and it is therefore not surprising that ordering in the simulation is not abrupt. However, the fundamental ordering in each grain has been found to be identical.

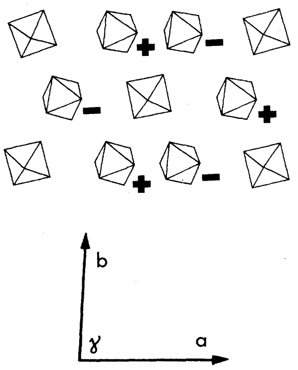

FIG. 2. A pseudo C-face centered orthorhombic cell extracted from a large crystal grain. The axes below show the definition of the triclinic cell. The molecules at + and − are approximately at $+\frac{1}{3}\vec{c}$ and $-\frac{1}{3}\vec{c}$, the other molecules (orientation 1) being in the plane of the diagram.

The annealing of grains will be considerably frustrated by twinning which is likely to occur in a number of ways. The layer of Fig. 1 has been chosen because it displays twinning, as can be seen by careful observation. Of the seven molecules in the row AB, the fourth and fifth are related by a twofold axis perpendicular to the diagram. This twin axis relates a large number of molecules in the two ordered grains, both in the plane of the diagram and on several parallel planes.

A count of the number of molecules in the larger grains gives a value of about 300, indicating a grain diameter of roughly eight nearest-neighbor distances. As this is well short of the cyclic repeat distance, it is clear that the observed transition is not driven by cyclic boundary constraints.

Further work is planned both to solve the natural structure experimentally and to study the simulation phase transition in depth. To monitor the sample on cooling we can follow Parrinello and Rahman[8] and scan the radial distribution function. Figure 3 shows the first peak in the S-S radial distribution function at 25 K; if this were in the cubic phase there would be only one peak centered at 4.77 Å. For observing the transition on warming, the triclinic angles α, β, and γ for a single crystal can be used as order parameters. It is amusing to note that a single-crystal sample will require a multiple of 3 (therefore 4095) molecules, and careful programming will be necessary to discard just one molecule ![6]

We believe that the large size of the molecular-

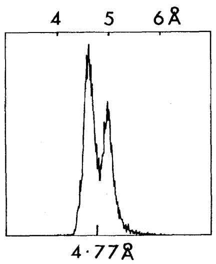

FIG. 3. The nearest-neighbor molecular center-center (S-S) radial distribution function in the sample at 25 K. If this sample were in the plastic phase there would be only one peak, at 4.77 Å.

dynamics cell has made it possible, for the first time, to model a realistic transition from the plastic to the crystalline phase. Many other systems are within the power of the DAP, and it should soon be possible to perform a comprehensive unifying analysis of the wide variety of experimental data available for many of these systems. Furthermore such simulations should stimulate experimental work—the present result clearly indicates the point in the Brillouin zone of the cubic phase which should show evidence of the transition through x-ray diffuse scattering —that is, if the simulation has developed the true natural structure.

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Calculation of the Γ-Δ Electron-Phonon and Hole-Phonon Scattering Matrix Elements in Silicon

Orest J. Glembocki and Fred H. Pollak
Department of Physics, Brooklyn College of the City University of New York, Brooklyn, New York 11210

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With use of the "rigid-pseudoion" model, the first calculation of the electron-phonon and hole-phonon scattering matrix elements for the TO, LO, TA, and LA phonon-assisted indirect transitions (Γ-Δ) in Si has been performed. Excellent agreement with experimental values for the TO phonon is found. Based on the present results, the intensities of the entire Γ-Δ indirect spectrum of this material can be accurately described, thereby rigorously testing the model.

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Although intervalley electron-phonon (e-ph) and hole-phonon (h-ph) interactions play a crucial role in many of the optical[1] and transport[2-4] properties of semiconductors, little is known about them either experimentally or theoretically. For example, absorption (and luminescence) in indirect-gap semiconductors proceeds via two scattering mechanisms involving e-ph as well as h-ph interactions. The intensity of a given transition is proportional to the square of the sum of terms involving e-ph and h-ph matrix elements, $S_{\text{e-ph}}$ and $S_{\text{h-ph}}$, respectively, and hence is strongly affected by the constructive or destructive interference that can occur between the two mechanisms. Despite nearly three decades of research into processes which involve e-ph and h-ph interactions, the matrix elements ($S_{\text{e-ph}}$ and $S_{\text{h-ph}}$) were never explicitly evaluated. Recent piezospectroscopic studies of the fundamental absorption edges in Si (Ref. 5) and GaP (Ref. 6) have yielded the magnitudes and phases of the e-ph and h-ph matrix elements for the TO (Γ-Δ) phonon process in Si, and the LA and TA (Γ-X) phonons of GaP.[1] However, to date there has been no theoretical effort in this area.

In this Letter, we present the first theoretical calculation of the magnitudes and phases of $S_{\text{e-ph}}$ and $S_{\text{h-ph}}$ for the TO, LO, TA, and LA indirect-phonon-assisted (Γ-Δ) transitions in Si. We have used the "rigid-ion" model to represent the interactions, as well as pseudopotential wave functions and form factors ($V_{\vec{q}}$) for the potential (the "rigid-pseudoion" model[7]). Within the context of the model, this was a first-principles calculation.

For the TO phonon, our results are in excellent agreement with the experimental values in both magnitude and phase. In addition, using the calculated numbers for $S_{\text{e-ph}}$ and $S_{\text{h-ph}}$ for the various phonons, we have correctly accounted for the relative as well as absolute intensities of all four phonon-assisted indirect transitions in