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To cite this version:
Alain H. Fuchs, G.S. Pawley. Molecular dynamics simulation of the plastic to triclinic phase transition in clusters of SF6. Journal de Physique, 1988, 49 (1), pp.41-51. <10.1051/jphys:0198800490104100>. <jpa-00210673>

HAL Id: jpa-00210673
https://hal.archives-ouvertes.fr/jpa-00210673
Submitted on 1 Jan 1988

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Molecular dynamics simulation of the plastic to triclinic phase transition in clusters of SF$_6$

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(Reçu le 26 mars 1987, révisé le 17 août 1987, accepté le 16 septembre 1987)

Résumé. — Une simulation de la dynamique moléculaire a été effectuée sur des agrégats de 512 molécules de SF$_6$ à l'aide d'un modèle de molécules rigides interagissant selon un potentiel atome-atome de Lennard-Jones. Les calculs ont été effectués sur les ordinateurs parallèles DAP. Les résultats sont présentés sous la forme de diagrammes de distribution d'orientations et de spectres de diffraction. A haute température, les deux couches externes des globules fondent en premier. Lorsqu'un agrégat de la phase plastique est refroidi, une transition est observée vers la phase basse température, la nucléation s'effectuant à partir du centre. Les agrégats de la phase basse température sont généralement des cristaux doubles de différents types et qui sont parfois des macles ou pseudo-macles. Un recuit de ces cristaux vers 100 K conduit à la forme la plus stable de ces pseudo-macles. Ce phénomène n'est pas observé dans des agrégats de taille plus petite (128 molécules), ceux-ci formant des monocristaux. La simulation de plus gros agrégats n'a pas été entreprise.

Abstract. — Clusters of 512 SF$_6$ molecules in their condensed phases are simulated by molecular dynamics on the DAP computers, using a Lennard-Jones rigid-molecule model. The results are presented in the form of orientational distribution plots (dot-plots) and powder diffraction patterns. As the clusters approach melting, the outermost two molecular layers appear to melt first. Cooling the melt gives rise only to a glassy phase. However, nucleation can be identified in a cluster being cooled from the plastic phase, showing that the growth of the true crystal is initiated in the inner regions of the cluster. The crystalline clusters form generally as polycrystals, often bi-crystals, and these can be classified in terms of three different types of pseudo-twins. Attempts to anneal these clusters to give perfect single crystals failed below 100 K, and even above 100 K annealing tended to produce the more stable forms of pseudo-twin. Smaller clusters of 128 molecules readily formed perfect single crystals; the simulation of clusters substantially larger than 512 would be computationally very demanding.

1. Introduction.

For some years the study of atomic and molecular clusters has become an important area for research in condensed matter physics, and for a coverage of much of this work the reader is referred to the review given by Bartell [1]. For the present computer simulations a SIMD (single instruction multiple data) computer was used, as the highly parallel computer architecture of the ICL Distributed Array Processor (DAP) is well suited for constant pressure Molecular Dynamics (MD) simulations of finite systems such as clusters [2].

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Liquid sulphur hexafluoride, SF$_6$, forms on cooling what is known as a plastic crystal. The molecules are ordered on a body-centred cubic lattice but have considerable dynamic orientational disorder. At temperatures below ca. 50 K a stable triclinic structure is known to exist and has been observed by electron diffraction [3] and neutron diffraction [4]. This phase has also been obtained by MD simulation [5]. An intermediate phase has been observed, around 85 K, by electron diffraction [3] and MD simulation [6], but not by neutron diffraction [4] and N.M.R. [7].

Some preliminary MD runs [2] on clusters of 128 molecules showed qualitatively that the properties of SF$_6$ clusters do not differ much from the bulk. Both the low temperature triclinic and the plastic bcc structures were obtained. This is confirmed by some recent electron diffraction results [8].
The present work is aimed at modelling the low temperature plastic to triclinic phase transition which was found to be easily simulated with the DAP computer [2]. The advantages of using clusters allow us to study melting, and the nucleation of the crystal phase on cooling and its subsequent annealing. We have also discovered stable twinings in a variety of forms.

2. Simulation details.

The calculations have been performed on the ICL Distributed Array Processors (DAP) at the Edinburgh Regional Computing Centre. The DAP is an array of 4096 interconnected processing elements which work in lock-step, each processor simultaneously performing the same operation on its own individual data set (SIMD).

As in previous MD studies of SF₆ [2, 9, 10], the intermolecular potential V (r) was modelled by using a Lennard-Jones atom-atom potential for the interaction of any pair of fluorine atoms separated by a distance r. By summing the forces that this potential gives, intermolecular forces and torques can easily be found. The potential function

\[ V(r) = -\frac{A}{r^6} + \frac{B}{r^{12}} \]

contains two parameters and these were fixed by using the cubic lattice parameter and the sublimation enthalpy, thus giving no further adjustable parameter for the model [9];

\[ A = 216.81 \text{ kcal/g-mole } \AA^{-6} \]
\[ B = 83984.2 \text{ kcal/g-mole } \AA^{-12}. \]

The potential gives rise to forces between molecules which are assumed to move as rigid units, their orientational motion being governed by the use of quaternions.

A spherical sample was made by taking a plastic phase configuration from the earlier work and carving out a spherical cluster containing either 128 or 512 molecules. Each F atom of each molecule of the cluster is assumed to interact with all the other F atoms in the sample following the procedure described elsewhere [2]. For the 512 molecule cluster, each time-step therefore involves the calculation of about 5 million interactions and takes about 15 s in the DAP. The calculation times vary as the square of the number of molecules in the cluster. No boundary conditions are required as the system is a cluster in free space.

Time steps of 0.015 ps were used. The plastic to triclinic transition was simulated with two different clusters of 128 molecules and four clusters of 512 molecules. Each simulation was carried out for about 5200 time-steps corresponding to a simulated time of \( \approx 78 \text{ ps} \). The annealing and melting phenomena were simulated with two different clusters of 512 molecules, each of them for a total simulated time of about 100 ps.

3. Results.

3.1 The dot-plot representation. — Each simulated cluster configuration will be shown on diagrams constructed as follows. Each molecule gives rise to three dots in the diagram, found by first projecting the six S-F vectors on to a unit sphere. The intersections in the lower hemisphere are discarded, and those three in the upper hemisphere are projected on to the equatorial plane using the equal area projection. We have shown in figure 1a the dot-

Fig. 1. — a) S-F bond direction dot-plots for a 512 cluster of SF₆ molecules in the plastic phase at 150 K. The most probable S-F bond directions are along the cartesian axes; b) a similar cluster after forming a near-perfect single crystal at 85 K. The dot-density in the maxima have roughly two values in the ratio 1:2, showing that the single crystal has molecules in this ratio in different orientations.
plot of a 512 molecule plastic phase configuration at 150 K. At the time of the cluster construction the mean S-F bond directions lay along the cartesian axes. In figure 1b, we have shown the cluster configuration after a few minutes of computer time which had equilibrated at 85 K. It is apparent from the figure that a single crystal of a lower phase has grown in which there is one set of octahedral directions with a third of the molecular population, and another set with two-thirds of the population. This is in agreement with the earlier simulation results [2] where the crystal phase was identified as triclinic with three molecules in the primitive unit cell, two of which are related by a centre of symmetry. The same triclinic structure has been obtained by simulation of 128 and 320 molecule clusters, and this structure is identical to that obtained by MD simulation in a single « infinite » crystal [5] and in natural SF₆ [4]. There is also good agreement with the N.M.R. work of Garg [7] which is summarised in the appendix.

3.2 SIMULATION OF THE PLASTIC TO TRICLINIC PHASE TRANSITION. — Figure 1 already indicates that the simulation can produce clusters which undergo a solid state phase transition to the ordered triclinic structure. In figure 2, we follow the development of the dot-plots as a function of time during which the single crystal develops. Figure 2a starts from a plastic phase 512-molecule cluster at 100 K, and at this stage the S-F bonds are preferentially ordered along the cartesian directions. Figure 2b results after a period of 512 time-steps (7.68 ps) following a procedure in which energy is removed from the cluster by rescaling the velocities (linear and angular) to agree with a temperature of 50 K, this being done at the start of each period. The remaining two stages shown in this figure occur after a further rescaling and simulation period.

In figure 2b the formation of the weaker peaks which result from the molecules reorienting into the less common (one-third) sites can be discerned and this becomes much clearer in figure 2c. After figure 2d very little further variation occurred, and it is clear that the less common site corresponds to molecules of somewhat higher thermal motion.

Although the dot-plots give an easily assimilated representation of the orientational ordering within.

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Fig. 2. — The formation of a single crystal cluster from a plastic phase cluster a) at 100 K; each of b), c) and d) are at periods of 512 time-steps later, there being temperature readjustments to 50 K at the start of each 7.68 ps period.
the cluster, they do not provide any information about translational order. To investigate the latter we have calculated the spherically averaged diffraction pattern from a cluster following the analytic procedure outlined by Bartell [1].

Figure 3 shows these diffraction scans for the corresponding cluster configurations represented in figure 2. The range of the total scattering angle $2 \theta_n$ is from 10° to 130°, the wavelength is 1.6 Å, and the S and F scattering lengths are taken to be equal. What we observe in this run sequence is the gradual change from the symmetrical single peaks of the cubic structure to the complex multiple peaks of the triclinic structure.

Figure 3 shows the difficulty in establishing the low-temperature structure of real SF$_6$, either by neutron diffraction or by electron diffraction from clusters. The figure well represents the latter in terms of the resolution available from the technique, but even with the neutron scattering technique the best resolution yet available cannot fully resolve the 6 triclinic peaks corresponding to the cubic (110) and the 3 peaks corresponding to the cubic (200) peak, these being the first two peaks in figure 3a.

3.3 Finite size effects and melting. — The earlier work on SF$_6$ clusters [2] was done with only 128 molecules. Although it is not easy to define temperature satisfactorily for clusters of varying surface-to-volume ratios, it was quite clear that the solid state transition occurred at roughly the same temperature for the 128 and 512 molecule clusters. However, on warming up to melting we found that the larger clusters melted at a significantly higher temperature. We have not studied this property in detail; there is no difficulty whatsoever in simulating melting, though the implication of this is that the search for a cause for melting would be very difficult. On the other hand we have tried patiently but unsuccessfully to take a liquid cluster back into the plastic phase; failure in this could well be indicative of the unrealistic purity of our simulated sample, which always becomes a glass.

The method we have found to be the most informative on the approach to melting is as follows. First, a word about the sample and the computational technique. To form the sample initially by carving out from an infinite crystal (as mentioned earlier) requires the identification of an origin, and the molecules are then ordered with respect to their distance from this origin. Storage in the DAP takes the form of 64-component vectors (other problems use 4096-component matrices), and so the molecular information is stored radially in 8 such vectors. Averaging over any one vector is therefore averaging over a shell of the cluster containing 64 molecules, and this makes it very easy to analyse the clusters in terms of these shells. Analysis then takes the form of finding the average distance $d(t)$ travelled by each of the 64 molecules in any one shell from its position at $t = 0$. 

$\langle |d(t)| \rangle_{\text{shell}}$

Figure 4 shows the variation of $\langle |d(t)| \rangle_{\text{shell}}$ at 100, 150 and 200 K. One test of the accuracy of the simulation program is that the cluster, once set up with zero angular momentum, conserves angular momentum, which therefore remains zero. It is quite clear, especially from figure 4a, that there is no uniform rotational motion contributing to $\langle |d(t)| \rangle_{\text{shell}}$.

In all the plots of figure 4, obtained after some equilibration, the lowest curve corresponds to the innermost shell, and we see from a) that all the shell averages reach stable values within about 128 time-steps (2 ps) at 100 K. Although this gradation of $\langle |d(t)| \rangle_{\text{shell}}$ with shell number is not unexpected, it is interesting to note that there is a distinction between the outer 3 shells and the inner 5. This is
Fig. 4. — Plot of $\langle |d(t)| \rangle_{\text{shell}}$ versus time $t$ for the 8 shells of a cluster at a) 100 K, b) 150 K and c) 200 K. Measurements are taken after 8 $n$ and 64 $n$ time-steps ($n = 1, 2, \ldots, 8$), giving a time range of 512 time-steps, 7.68 ps.

demonstrated dramatically in b); without b) the distinction in a) may have been considered as a fluctuation. As the outer three shells correspond quite closely to two layers of molecules, we can deduce that the extra activity of the surface molecules penetrates two molecular layers.

At 150 K the extra activity of the outer two layers (3 shells) is clear, and there is perhaps a distinction between the outermost layer and the second layer, the latter probably reaching a stable value of $\langle |d(t)| \rangle$ of $\sim 2 \text{ Å}$ after $\sim 10$ ps. At 200 K the outer two layers show no sign of stabilising, indicating that these two layers are melting, while the next two layers are behaving like the surface molecules did at 150 K. However, figure 4c does suggest that the inner regions remain in the plastic phase, although no orientational order can be discerned from a dot-plot at the end of the simulation run, the temperature being well above that for figure 1a.

3.4 LOWER PHASE NUCLEATION. — Let us now return to the plastic to crystalline transformation and attempt to identify the crystallisation nucleation process. We analyse in detail the phase transformation for two 512 molecule clusters by following the change of molecular orientations as a function of time of the one-third molecule component only, since these molecules are those experiencing the greater change during the transition. We have calculated, for each molecule, the scalar product of its quaternion at time $t$ with the quaternion corresponding to the final equilibrium configuration where the whole cluster has transformed into the triclinic structure. Figure 5 shows, for two different clusters (obtained from two different equilibrium 100 K plastic crystal starting configurations), how the molecules gradually find their final orientation as a function of the simulated time during 3 periods (23.04 ps). The symbols that are used instead of numbers have been chosen so that they get darker as the quaternion scalar product tends to unity. In both cases a few molecules find their final orientation (denoted $H$) very rapidly ($t \approx 7$ ps). Among them one or two pairs of molecules are nearest neighbours along $\langle 111 \rangle$ directions in the initial plastic phase. These pairs presumably indicate the seed for crystallisation towards the triclinic structure.

In order to analyse the nucleation in detail, we have indexed all the molecules in terms of their equivalent position on a lattice corresponding to the plastic cubic phase, but with a cube spacing at $a/2$. This means that if one molecule is at (000), the molecule at $(1,1,1)$ is its nearest neighbour in the $(111)$ direction and is related by the vector $(1,1,1)$ $a/2$. By ordering the molecules in figure 5 radially outwards, it is possible to see at a glance that the nucleation and growth starts in the inner regions of the cluster, these being the upper parts of the figure. The quaternion scalar product does not vary very much as a molecule undergoes the final adjustment.
indication of nucleation in a) the crystallisation of figure 2 and b) an independent crystallisation under the same conditions. The symbols $-$, $+$, $H$, indicate the progress of the quaternion value. The top of the figures correspond to the innermost molecule. The time-span also corresponds to figure 2, and is $3 \times 512$ time-steps or 23.04 ps.

on ordering. When it is within $16^\circ$ ($23^\circ$, $28^\circ$) of its final orientation, the scalar product is $0.99$ ($0.98$, $0.97$), and its representation in figure 5 is $H(+ - )$. The following is an analysis of the molecules in the two examples studied.

Figure 5a
First two to reach within $16^\circ$:

$17(2, 0, 2)$ and $67(3, 1, 3)$.

These are related by the vector $(1, 1, 1)$ i.e. $(1, 1, 1) a/2$.

Neighbouring molecules to these also along $(1, 1, 1)$:

$238(4, 2, 4)$ orients fairly late,
$4(1, -1, 1)$ orients very late.

Next 3 to reach within $16^\circ$ simultaneously are related by

$(1, 1, 1) : 40(1, 1, -3), 53(2, 2, -2), 63(0, 0, -4)$.

Neighbouring molecules to these also along $(1, 1, 1)$:

$69(3, 3, -1)$ orients fairly late,
$147(-1, -1, -5)$ orients very late.

In a more extensive analysis we find that almost all of the « one-third » molecules belong to one-dimensional channels situated along the (111) crystallographic direction. However no evidence can be found that the propagation of the transition takes place preferentially along these channels once the seed has formed. The kinetics of the phase transition is most probably driven by the small distortion of the initial cubic structure involving the other « two-thirds » molecules component. Each cluster crystallisation studied is statistically independent, as shown by the fact that the seeds are not formed from the same molecules, but they are always situated in the inner regions of the cluster. It is clear from figure 5 that the phase transition is initiated and grows from the internal part of the clusters rather than from the surface; this result was not immediately intuitively obvious.

3.5 DOUBLE CRYSTAL FORMATION AND ANNEALING EXPERIMENT SIMULATION. — In our simulations which gave rise to figure 2 we often had examples where multiple crystal growth occurred. In fact figure 2 is not a typical result; a more typical result is given by figure 6 and later figures. Figure 6 starts at an independent 512 molecule configuration at 100 K with rescaling as for figure 2 to 50 K at the start of each 512 time-step period. Some molecules of the one-third component are apparent in part c), and a number of these do not remain in this orientation by part d) where the dominant one-third component orientation is clear. Competition between possible orientations for the two-thirds component is being resolved in part e) and complete in part f) where a single crystal results.

Some further configurations obtained as a function of time are shown in figure 7 starting with the 512 molecule cluster of figure 2 at 100 K. The procedure used was exactly the same as that described above and which gave rise to figure 2 except that the scaling after each 7.68 ps period was to 25 K. In this case, the phase transition clearly leads to two crystals with different orientations in the cluster. This event is not too surprising since we saw in the
Fig. 6. — a) An independent starting configuration at 100 K for a 512 molecule cluster; b), c) etc. result after one period of 512 time-steps with scaling performed at 50 K at the start of each period; d) shows competition between two different crystallites; e) shows a little competition still present in the two-thirds molecule components, and f) shows a perfect single crystal.
Fig. 7. — a) Starting configuration at 100 K [same as Fig. 2a] ; b) etc., after 512 time-step periods with scaling to 25 K at the start of each period ; d) stable coexistence of two crystallites.

preceding section that the size of a seed is small in comparison with the size of the whole cluster. However this is not the case for a 128 molecule cluster, where we should bear in mind that the outer two molecular layers are probably in too much turmoil to produce seeds. Indeed, in our simulation of the smaller clusters we did not encounter multiple crystal formation.

The double crystal configuration of figure 7d was apparently stable at 25 K as it did not change perceptibly during subsequent periods. We then tried to anneal this double crystal by slowly heating it up in stages to 105 K in about 50 ps and then slowly cooling it from the various stages back down to 50 K, constantly monitoring the dot-plot and the diffraction pattern. The diffraction pattern showed no perceptible change in this warming sequence.

The results of the slow warming are shown in figure 8, where a) is that obtained at 95 K and b) subsequently at 100 K. Although one might expect that some annealing would take place before 95 K, this was not found to happen even after considerable simulation at 95 K, whereas at 100 K the dominance of one crystal orientation over the other is established. The fact that this is still not a single crystal is discussed in the following section.

The annealing just mentioned is the result of a careful search for a temperature at which transition takes place. Temperature was raised in 5° intervals; the use of smaller intervals would demand much more computational time and would probably only be of value in a study of a large number of independent clusters. Thus our estimate is $97.5 \pm 2$ K for the annealing of clusters of diameter about 50 Å, and this could indicate a transition to the intermediate phase where one third of the molecules become hindered rotators. Although this is not the transition to the cubic phase, the temperature found for the annealing does compare well with that of the electron diffraction of Farges et al. [12] whose results indicate the triclinic/cubic transition between 70 and 100 K.

3.6 TWINNING. — To describe the bi-crystals that have been produced by these simulations as « polycrystalline » is not fully accurate. The grains in a
poly-crystal have no special relationship one with another, whereas the simulated bi-crystals enjoy a translational periodicity even if the molecular orientations do not follow any symmetry pattern. Consequently one could argue that the bi-crystals are "twins", but, as we shall see, there are a number of different ways in which twinning can occur.

The bi-crystals form in such a way that there is no symmetry in the twin-plane. The question we now ask is whether figure 8b corresponds to a twin with a definite twin-plane symmetry. To answer this question we quote from the earlier paper [2] where the angles between the mean S-F points on a 25 K single crystal dot-plot have been measured. Figure 9a shows the dot-plot and 9b the angular measurements around the appropriate great circles from the peak positions for the one-third component to the peak positions for the major two-thirds component. Half-way between two of these latter peaks a pole is marked 0, and the corresponding great-circle has the arc carrying the measurement of $79^\circ$. The reliability of the measurements on this figure is not better than $2^\circ$, so we can see that there is an approximate $2/m$ pseudosymmetry defined by the pole just mentioned. Measuring the angle around the great circle between the one-third component peak and the pseudosymmetric peak gives $180 - 2 \times 79 = 22^\circ$. In other words, the minor peak is $\pm 11^\circ$ from the great circle between two major peaks.

Cooling the cluster of figure 8b gave figure 10 at 50 K. This cluster has formed as a twin, and the dot-plot shows the central major peak split into two equal parts separated by about $18^\circ$. This is identifiable as the $22^\circ$ arc, within the error of the analysis of

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Fig. 8. — Dot-plots after annealing attempts on the cluster of figure 7d. a) Prolonged simulation at 95 K; b) prolonged subsequent simulation at 100 K.

Fig. 9. — a) Dot-plot from reference 1 for a single crystal (128 molecules, 4 different moments in time) at 25 K; b) angular measurements between the peaks of a) around the great circles of the equal-area projection. The great circle showing the angle $79^\circ$ has its pole at 0.
the previous paragraph, and indicates that the twin is formed from two crystallites with the one-third component molecules all identically aligned and the major two-thirds component split equally between the pseudosymmetric orientations. The twin-plane in this case is therefore determined by the pseudosymmetry rather than by a true symmetry subgroup as in classical twinning; remember that there is no possible symmetry subgroup for a triclinic (albeit P1) crystal.

Thus there is an extension of the concept of twinning through the use of pseudosymmetry and translational periodicity, but there is yet another form of twinning that can occur in this system which we found only after a very meticulous analysis. This is demonstrated by the subtle differences between figures 11a and b. These dot-plots correspond to different clusters, both at 25 K exhaustively equilibrated. The peaks in a), especially the minor peaks, appear to be slightly more extended, but as the density about the peaks is the same for both a) and b) we must accept that the clusters do have the same temperature. In a) there are a small number of molecules, about 15 in number, which are persistently misaligned about the minor peaks. A detailed search of the computer file led to the following explanation.

In a perfect single crystal cluster (Fig.11b) the molecules can be thought of as being in strings along a certain (formerly cubic) (111) direction. These strings can be subdivided into 3 sets, one set (set A) for the one-third component and two sets for the major two-thirds component. Although the latter two sets of strings correspond to molecules of the same orientation, they are distinguishable; let us label them B and C. In the cluster giving rise to figure 11a, the sets of strings labelled A, B, C on one side of the cluster became B, C, A on the other side of a plane across the strings. Thus the string starting B and finishing C contained molecules all of the same orientation, whereas the strings A → B and C → A experienced an orientation change on crossing the twin-plane. The dot-plots indicate those few molecules positioned in this twin-plane.


These calculations are possibly the most extensive simulations yet made on molecular clusters in a number of condensed phases. In the liquid phase it should be possible to extend the work on atomic clusters [13] (drops) to include the extra problems presented by extended molecules. A detailed analysis of melting has not been done, but initial experiments seem to indicate that melting first takes place in the outer two molecular layers. Nucleation for the growth of the crystal phase from the plastic
phase is shown to take place in the inner regions of the cluster, but spontaneous nucleation of the liquid to give the plastic phase has not been observed.

Clusters with 512 molecules were prone to make some form of bi-crystal, the clusters that we have generated have contained two components of equal size. We can conclude that such « balanced » bi-crystals do not anneal into a single crystal at any temperature below 100 K. In comparison with this we cite figure 6 where, in the later stages of growth, the larger crystal component is gaining molecules from the other. Thus we might expect annealing to become more likely in much larger samples where the larger crystal component is gaining molecules from the other. This argument leads to the conclusion that there may be a range of cluster size in which balanced bi-crystals occur, and that outside this range, for both smaller and larger clusters, fully ordered arrangements become more likely. On the other hand, our conclusion that defective clusters are bi-crystals should not be accepted without caution, bearing in mind that some twinnings, as in figure 11a, are very hard to substantiate.

When the clusters were cooled more slowly in an attempt to make a large perfect crystal, two forms of twinning have been observed. We have argued that the bi-crystals are a cruder form of twinning as the underlying translational pseudosymmetry is not broken. All these phenomena indicate the enormous complexity of this system in which a structure of the highest symmetry (Im3m) becomes one with the lowest symmetry (P1) after minimal distortion [4, 5]. It may well be that this complexity masks the intermediate phase when we attempt to find this phase in a bulk powder [4]. To finish on an enigmatic note, could it be that the onset of annealing observed at 100 K and above is characterised by rapid « isotropic » reorientation (v_r \gg 10 kHz) of the molecules. Here « isotropic » means that all the intramolecular magnetic dipolar interactions are averaged to zero by the motion. As melting is approached (T > 180 K) the self diffusion frequency becomes \sim 10 kHz.

At 90 K the plastic phase undergoes a transition on cooling to a phase where the molecules occupy two different sites in a ratio which, within Garg's experimental error, could be 2:1. Most of the molecules are ordered, v_r \approx 10 kHz, but the smaller fraction still undergoes rapid reorientation. Garg determined a ratio 3:1 by deconvolution of the absorption line, and although an improved method may be deconvolute the free induction decay, thus finding the equilibrium magnetisation for each site, any improvement would most probably not distinguish 3:1 from 2:1.

Below 90 K, v_r for those molecules still undergoing rapid reorientation decreases on cooling and at 45 K, v_r \sim 10 kHz. On further cooling the linewidth increases, reaching the so-called « rigid lattice » value, for which all large amplitude molecular motions have v_r \ll 10 kHz. There is no phase change at 45 K according to N.M.R.; at this temperature the rate of reorientation simply becomes commensurate with the line-width.

5. Acknowledgments.

We wish to acknowledge the support given by the Science and Engineering Research Council (G.B.) to the maintenance of the two DAP computers in Edinburgh, on which all this work was done. A. H. Fuchs wishes to thank the Royal Society for a study visit award in the European Science Exchange Programme.

Appendix A.

The N.M.R. work of Garg [7] shows that liquid SF_6 forms a plastic phase at \sim 220 K which persists to 90 K, characterised by rapid « isotropic » reorientation (v_r \gg 10 kHz) of the molecules. Here « isotropic » means that all the intramolecular magnetic dipolar interactions are averaged to zero by the motion. As melting is approached (T > 180 K) the self diffusion frequency becomes \sim 10 kHz.

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