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Glassy crystals III : X-ray determination of the structures of the plastic and glassy crystalline phases of cyclohexanol

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Abstract. — Single-crystal X-ray diffraction data were collected and interpreted for plastic (I) and glassy crystalline (I'G) phases of cyclohexanol. For phase I, the unit cell is face-centred cubic, the space group is Fm3m, (Z = 4), with parameter a = 8.809 Å at 275 K. A Monte Carlo method coupled with a rigid group least squares refinement led to a structural model (weighted residual WR = 1.05 %) in which both cyclohexanol conformers have equal occupancy factors: each isomer can occupy 48 equiprobable orientations at each crystalline site. The mass centres are not fixed, the molecular symmetry plane does not coincide with a symmetry element of the space group and each conformer is characterized by the oxygen atom position in the crystalline cell. The quality of phase I'G single crystals is not as good as for phase I. But the same structural model fits the X-ray data (WR = 2.6 %) with a = 8.608 Å at 121 K. Comparison of these results with NMR data suggests that the same large amplitude motions exist in phases I and I'G, with much lower frequencies in the glassy crystal.

In 1968, Seki and coworkers [1] observed long-time enthalpic relaxations when performing calorimetric measurements in a crystalline phase obtained by cooling the plastic phase, I, of cyclohexanol. Thus, they demonstrated that the phase transition observed by Kelley at 150 K on a similar cyclohexanol sample [2] was basically a glass transition. Analogous observations were made in a number of quenched so-called plastic phases [3], and Seki called these solids « glassy crystals » [1] within which the original orientational disorder is supposed to be trapped whereas the positional crystalline lattice is retained. Indeed, in 1955, Otsubo and Sugawara [4] had recorded similar X-ray photographs for cyclohexanol phase I at 285 K and for the same sample cooled down to 83 K, that is in the glassy crystalline state (that we will call Phase I'G). So, it could be inferred that phase I'G is most probably face-centred cubic (Fm3m) like phase I [5].

Recently, we have studied the diffuse X-ray scattering of phases I and I'G of cyclohexanol [6] and observed that phase I'G exhibits the same Bragg reflexions as phase I does, which confirms Otsubo and Sugawara’s findings. But the structure of diffusion patterns changes drastically from one phase to the other whatever the relative orientations of the incident X-ray beam and of the crystal. This led us to assume that strongly anisotropic short range intermolecular correlations characterize orientational disorder in phase I'G.

It was then necessary to determine the packings of phases I and I'G in order to know to what extent...
they differ. Furthermore, we need data to build models of disorder in these two phases; these models will eventually be tested against the X-ray diffuse scattering patterns we measured. The purpose of the present work was to determine these packing.

1. Experimental.

0.3 and 0.5 mm diameter Lindemann capillaries were filled with liquid cyclohexanol (Fluka purissimum, melting temperature = 295 K) and then sealed at both ends. Afterwards, the convenient capillary was fastened onto the goniometer head of a Syntex P2, four-circle diffractometer equipped with a molybdenum X-ray tube and a graphite monochromator ($\lambda_{K\alpha} = 0.7107$).

Temperature was controlled by means of a gaseous nitrogen flow cooling equipment which has already been described [7].

First, temperature was lowered down to $\sim 280$ K and a single crystal was grown in situ according to a zone melting procedure [8]. $\sim 1$ mm long single crystals were used to collect data.

Phase I crystalline lattice is face centred cubic. Values for the unit cell parameter, $a$, have been calculated with a local version of the PARAM (X-ray, 1972) program [9]. They are recorded in Table I as a function of temperature. The number of molecules per unit cell is 4 and $F(000) = 224$. The observed extinctions are compatible with space groups $F23$, $Fm3$, $F432$, $F43m$ and $Fm3m$. The first two ones were discarded because we found no significant differences between $(hkl)$ and $(khl)$ reflexion intensities. All the reflexions in a quarter-sphere of resolution have been measured up to $2\theta = 45^\circ$ using $\theta$-2$\theta$ scans with variable speeds ranging from 3 deg. min$^{-1}$ to 58.6 deg. min$^{-1}$, at 284, 258.5 (1) and 227 K (1). In a further experimental series, two data collections were recorded with the same single crystal at 275 and 258 K (1) with a 0.49 deg. min$^{-1}$ minimum speed.

Two standard reflexions were measured every fifteen reflexions.

At each temperature, a complete set of 38 independent reflexions have been recorded. The first 11 ones ($2\theta \leq 25^\circ$) had intensities $> 9 \sigma(I)$ and were considered as observed. All the others had intensities lower than 2 $\sigma(I)$, but were also taken into account in our calculations; however the reflexions that yielded negative neat counts were arbitrarily assigned zero intensities. Corrections for Lorentz and polarization effects were applied as usual. The more intense reflexions corresponding to samples of different sizes did not reveal any absorption or secondary extinction effects.

At these temperatures, phase I is metastable. In one example, a single crystal of phase I was kept down to 213 K without damage.

2. Determination of structure at 275 K.

Rigid group methods were used as convenient for plastic crystals, within which molecules reorientate between several positions at given crystalline sites. A molecular model has been built using the following bond lengths:

- C-C = 1.54 Å;
- C-H = 1.0 Å;
- C-O = 1.43 Å,

and tetrahedral bond angles ($109^\circ28'$) (see Fig. 1).

Corfield and Davies [10] assigned the dielectric absorption they measured to H-bonded hydroxyl group motions. Seki and coworkers explained a secondary (or $\beta$) dielectric dispersion domain by -OH rotational motions (11). Following these authors, we have assumed that the hydroxyl groups rotate around the C-O bonds, so that we are unable to locate them. Therefore, the hydrogen atoms of the -OH groups were not taken into account in calculations, which corresponds to neglect 4 electrons out of the 224 ones of the unit crystalline cell.

Furthermore, a Raman spectroscopic study by James et al. [12] has shown that the ratio of axial to equatorial cyclohexanol conformers (Fig. 1) remains constant throughout the whole phases I and I' ranges down to 14 K. So, in all calculations we have introduced both conformers, assigning each one a 0.5 weight. We shall come back later to this hypothesis. It is to be noticed that each conformer we used has only one symmetry element, that is the plane that contains the C-O bond and the C4 carbon atom of figure 1.

Fig. 1. — Representation of the two molecular conformers of cyclohexanol as they were used in our calculations: the hydrogen atom of the hydroxyl group has not been taken into account.
Several structural models were examined. The function minimized during refinements is
\[ \sum W( F_{\text{obs}} - F_{\text{calc}} )^2, \]
summing over all scanned independent reflexions; \( W \) is the weight we assigned
to each reflexion. As usual, the crystallographic residual \( R \) is defined as:
\[
R = \frac{\sum | F_{\text{obs}} | - | F_{\text{calc}} |}{\sum | F_{\text{obs}} |}
\]
and the weighted residual \( WR \) as:
\[
WR = \left( \frac{\sum W( F_{\text{obs}} - F_{\text{calc}} )^2}{\sum WF_{\text{obs}}^2} \right)^{1/2}
\]

2.1 Model with free rotation. — In this model,
molecules freely rotate around a fixed point. The scattering function for a spherically symmetric atom only
depends on the position of the rotation centre within the unit cell and on the distance from the atom to that
centre. It can be calculated using a formula given by James [13]. Only two parameters were refined: the
scale factor and an overall isotropic temperature factor. We got:
\[
R = 0.18; \quad WR = 0.17; \quad B = 22 \text{ Å}^2,
\]
which shows that there still exist important differences between calculated and observed structure factors and that such a model is not very probable.

2.2 Frenkel model. — After Frenkel [14], it can be assumed that, instead of freely rotating, the molecules occupy a discrete number of orientations. As the lattice site symmetry is m3m and as the only symmetry element of the molecule is a mirror plane (that may or may not coincide with a symmetry plane for the space group), all the orientations that a molecule can occupy must be related through the symmetry operations of the space group. Space groups F432 and F43m correspond to 24 orientations for a molecule in general position, space group Fm3m to 48 ones.

To get the number of molecular orientations, thermodynamic and spectroscopic data have to be considered. The entropy increment at phase transition II \( \rightarrow \) I, that is (1):
\[
S_{\text{II}\rightarrow\text{I}} = 33.25 \text{ J mol}^{-1} \text{ K}^{-1} \sim R \ln 53,
\]
implies, as a first approximation (15), that there should be \( \sim 50 \) as many equivalent molecular orientations in phase I than in phase II. James et al. [12] concluded that the equatorial isomer dominates the structures of phases II and III, but their Raman results reveal C-O-H stretching bands corresponding to axial conformers in both phases. Then, Ściesinska and Ściesinski [16] convincingly disputed their conclusion and showed that both conformers had to exist with equal concentrations to explain their infrared spectroscopic results in phases I, II and III. As the NMR second moment of phase II corresponds to rigid lattice value [17], we assume that cyclohexanol phase I space group is Fm3m as for cyclohexane [18] and quinuclidine [19]. Within this structure, a molecule (either axial or equatorial) can occupy 48 admitted equiprobable orientations, so that each molecular position has a 1/96 weight.

If we assume that the molecular mass centre is not fixed during molecular motions, 6 parameters per conformer (3 angles and 3 mass centre coordinates) are necessary to describe the molecule position within the crystalline cell. So, 12 parameters, plus one scale factor and an overall isotropic thermal factor, should be determined throughout refinements. Since the number of observed reflexions is very small, it was a matter of some difficulties that will be described presently.

Looking for 12 parameters at the same time seemed hopeless. So, we started with a « mean » cyclohexanol molecule in which the Cl carbon atom beared \((1/2 \text{ O} + 1/2 \text{ H})\) groups both in axial and equatorial positions; furthermore, the centre of the cyclohexyl cycle was constrained at the unit cell origin. To look for the remaining 3 (angular) parameters, program PYTHIE [20] was used. The algorithm of this program associates a Monte Carlo generation of molecular parameters and a rigid-group least-squares refinement using a variable small number of « low » angle Bragg reflexions. Each generation gives a structural model and the process is controlled through the evolution of the weighted residual. At that stage, each reflexion is assigned a \( W = (\lambda/\sin \theta)^2 \) weight and the overall thermal factor has been arbitrarily taken as 8 Å². Trials with PYTHIE converged towards a solution at 275 K.

A further rigid group refinement was performed with program ORION [21]. Three orientation parameters, the scale factor and an overall temperature factor were fitted taking into account all 38 experimental independent reflexions. This led to:
\[
R = 0.092; \quad WR = 0.067; \quad B = 21.7 \text{ Å}^2.
\]

Afterwards, instead of the fictitious « mean » molecule, each conformer has been individualized and the molecular orientations that were determined in the previous refinement were used as a starting point for the ensuing calculations.

Table I. — Values of the unit cell parameter, \( a \), and volume, \( V \), as a function of temperature for cyclohexanol phase I.

<table>
<thead>
<tr>
<th>( T/\text{K} )</th>
<th>( a/\text{Å} )</th>
<th>( v/\text{Å}^3 )</th>
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<td>689.7 (1.0)</td>
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<td>275</td>
<td>8.809 (6)</td>
<td>683.5 (1.3)</td>
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<tr>
<td>258.5</td>
<td>8.806 (4)</td>
<td>682.7 (0.8)</td>
</tr>
<tr>
<td>258</td>
<td>8.805 (4)</td>
<td>682.7 (0.9)</td>
</tr>
<tr>
<td>227</td>
<td>8.765 (5)</td>
<td>673.3 (1.2)</td>
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Three weighting schemes have been tried:
- equal weights;
- counting statistics weights, \( w = 1/\sigma^2(I) \);
- a Cruickshank type weighting [22],

\[ w = (a + b |F_{\text{obs}}| + c |F_{\text{obs}}|^2)^{-1}, \]

with \( a = 0.274, \quad b = 10^{-2} \) and \( c = 1.11 \times 10^{-5} \) for the observed reflections and \( a = 27.4, \quad b = 1 \) and \( c = 1.11 \times 10^{-3} \) for the others. This scheme downweights the contributions of strong reflections and takes into account weak ones (\( I < 2 \sigma(I) \)) without introducing too important a bias.

All three schemes led to equivalent results and, from now on, we will only refer to results obtained by using the Cruickshank type scheme.

At first, the mass centre of each conformer has been fixed at the origin of the crystalline cell and the angles defining each conformer orientation have been alternately refined. After several refinement trials, we got: \( R_1 = 0.0896, \quad (WR)_1 = 0.0437 \) and \( B_1 = 16.9 \) \( \text{Å}^2 \). These values are still high and there are still discrepancies between calculated and observed structure factors (table IIa).

So, the molecular mass centres were freed. As it was not possible to simultaneously refine all 14 necessary parameters, we had to use alternate refinements. Together with the scale and temperature factors, 3 angular parameters or 3 mass centre coordinates for each conformer have been optimized. During the last cycles, the six parameters corresponding to one conformer were optimized at the same time. This led to a solution with \( R_2 = 0.0475, \quad (WR)_2 = 0.0105 \) and \( B = 14.60 \) \( \text{Å}^2 \) (standard deviation = 0.38 \( \text{Å}^2 \)). The ratio \((WR)_2/(WR)_1\) is 4.162. According to Hamilton's statistical criteria [23], the constrained model with the mass centres fixed at the origin can be rejected at a level of significance better than 0.005. It can also be seen on table IIb that the agreement between calculated and observed structure factors has been improved. The corresponding atomic coordinates and molecular parameters are recorded on table III.

Then, we tried to determine whether the molecular symmetry plane could coincide with a symmetry plane of space group \( \text{Fm3m} \). Taking the previous results into account, we tested a model according to which the symmetry planes of the equatorial conformer and of the axial one coincide with planes of classes \{100\} and \{110\} respectively. Each molecule is described through 3 parameters, that are a rotation angle around a direction perpendicular to the symmetry plane and 2 coordinates for the mass centre within that plane. The refinements led to \( R_3 = 0.0685, \quad (WR)_3 = 0.0436 \) and \( B_3 = 21.3 \) \( \text{Å}^2 \). The ratio \((WR)_3/(WR)_1\) is equal to 4.152 which is much higher than \( R_6,24,0.005 = 1.432 \) [23], so that the latter model may be rejected.

Finally, the occupancy factors of axial and equatorial conformers have been tested. Starting with a calculated structural solution, the molecular parameters have been optimized together with the occupancy factors (that is one more variable) using an alternate procedure. The refinements consisted either in optimizing the initial values (50 \% for each conformer), or in starting with very different occupancy factors; for instance, we introduced 80 \% of equatorial

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Table II. — Observed and calculated structure factors for cyclohexanol phase I at 275 K : a) for molecules with mass centres fixed at the crystalline cell origin, b) for molecules in general position.

Table III. — Fractional atomic coordinates (\( \times 10^5 \)) for the structural model of cyclohexanol phase I at 275 K.
conformers and 20% of axial ones. All these calculations led to final occupancy factors very close to 50%, which supports our working hypothesis.

3. Structure of phase I at 275 K.

The time and space averaged structure of cyclohexanol phase I is reasonably well fitted by a model in which each conformer, corresponding to a 50% occupancy factor, can occupy 48 symmetry related equivalent orientations randomly populated at each lattice site.

The cyclohexyl cycle position cannot be determined with very great accuracy; different refinements performed with slightly different conditions (for instance different weighting schemes, different order in refinements of parameters,...) lead to slightly different atomic coordinates values with equivalent residuals. On the contrary, the position of the mass centre with respect to origin remains almost the same one ($d \approx 0.5$ Å for an equatorial molecule, $d \approx 0.35$ Å for an axial one).

Furthermore, the positions of the oxygen atoms, which play an important part in intermolecular contacts, hence in molecular motion correlations, can be assigned definite characteristics. For an equatorial conformer, the oxygen atom lies near a fourfold axis at $a \approx 0.52$ Å distance and at 2.71 Å from the origin. For an axial molecule, the oxygen atom is nearer a three-fold axis, with $d = 0.50$ Å, than a fourfold one ($d = 1.38$ Å), its distance from origin being 1.98 Å.

To study intermolecular contacts, every molecular orientation has to be taken into account. Each lattice site thus corresponds to 96 orientational states (48 for an axial conformer, 48 for an equatorial one) which are the same for every site. Each molecule is surrounded by 12 neighbouring ones (lying at the same distance, $a^{2}/2$) which may be deduced from itself through translations of the $(1/2, 1/2, 0)$ type. So, we have to describe how any one of 96 orientational states at one central site interacts with any one of the same 96 states at 12 neighbouring sites. Obviously, the interactions between a central molecule and any neighbouring one can be deduced through a rotation from the interactions between any other such couple. Then, it will be sufficient to study the contacts between a central molecule and its neighbour lying at $(1/2, 1/2, 0)$, and $96 \times 96 = 9216$ orientational state couples to be studied. Instead of describing the detailed intermolecular contacts, which would have been cumbersome, we chose to build a $96 \times 96$ matrix in which the value of element $A_{ij}$ defines steric compatibility between a molecule in orientational state $i$ at $(0, 0, 0)$ and a molecule in orientational state $j$ at $(1/2, 1/2, 0)$. $A_{ij} = 0$ when the two states are stericly compatible, $A_{ij} = 1$ when they are not. Any two cyclohexanol molecules were considered as sterically non compatible when any distance between two atoms belonging to one and the other molecules respectively was shorter than the sum of the van der Waals radii of the two atoms minus a given distance, $e$, which is supposed to take intermolecular interactions and motions into account. The van der Waals radii for carbon, oxygen and hydrogen were taken as 1.8, 1.4 and 1.2 Å respectively [24]. Values of 0, 0.1 and 0.2 Å for $e$ were considered. If $x$ represents the ratio of the number of compatible orientational state couples to the total number of couples (9216), the above values of $e$ correspond to $x = 60.9\%$, 68.2\% and 75.8\% respectively. Even in the more restrictive condition ($e = 0$), the number of stericly compatible orientational state couples is very great, which agrees with the great reorientational freedom in phase I as revealed by NMR measurements [17] for instance.

Such compatibility matrices will be used in further work to build models of disorder to be compared with diffuse X-ray scattering data.

4. Structure of the glassy crystalline phase of cyclohexanol.

To get single crystals of the glassy crystalline phase, we started with phase I single crystals prepared by in situ zone melting as previously described. The samples were first slowly cooled down to 245 K, then « quenched » to $\sim 140$ K with a $\sim -20$ K min$^{-1}$ cooling rate to by-pass the temperature domain ($\sim 220$ K) where recrystallisation towards phase II or III occurs, and finally cooled to 120 K where X-ray collections were attempted.

Except in some cases in which apparently fair phase I$_{C}$ single crystals were obtained, the samples seemed to stick to the Lindemann capillaries. This sticking, during the quenching process, resulted in a breakage of the inner part of the crystal and, most often, in the presence of some polycrystalline powder at its surface, which of course impaired the quality of the sample and even, at times, its stability as a function of time. We were unable to control the « unsticking » process.

We will now describe the results obtained with a « good » phase I$_{C}$ single crystal at 121 K.

As was already observed by Otsubo and Sugawara [4], the glassy crystal lattice is cubic. We observed no significant deformation with respect to phase I lattice, except thermal contraction. The unit cell parameter, as determined by means of program PARAM, is equal to 8.835 (4) Å at 283 K, 8.779 (9) Å at 249 K and 8.608 (9) Å at 121 K.

There are no important modifications in the intensity ratios for the eleven Bragg reflexions which were observed in phase I (table IV). For the studied sample, the reflexions were measured in a quarter-sphere of resolution, with a minimum scanning rate equal to 3 deg. min$^{-1}$, up to $2 \theta = 40^o$, which corresponds to 29 scanned reflexions at 121 K.

An overall weakening of intensities with respect to what was recorded for phase I is to be noticed. The weak reflexions have intensities very near $2 \sigma(I)$, respectively was shorter than the sum of the van der Waals radii of the two atoms minus a given distance, $e$, which is supposed to take intermolecular interactions and motions into account. The van der Waals radii for carbon, oxygen and hydrogen were taken as 1.8, 1.4 and 1.2 Å respectively [24]. Values of 0, 0.1 and 0.2 Å for $e$ were considered. If $x$ represents the ratio of the number of compatible orientational state couples to the total number of couples (9216), the above values of $e$ correspond to $x = 60.9\%$, 68.2\% and 75.8\% respectively. Even in the more restrictive condition ($e = 0$), the number of stericly compatible orientational state couples is very great, which agrees with the great reorientational freedom in phase I as revealed by NMR measurements [17] for instance.

Such compatibility matrices will be used in further work to build models of disorder to be compared with diffuse X-ray scattering data.

4. Structure of the glassy crystalline phase of cyclohexanol.

To get single crystals of the glassy crystalline phase, we started with phase I single crystals prepared by in situ zone melting as previously described. The samples were first slowly cooled down to 245 K, then « quenched » to $\sim 140$ K with a $\sim -20$ K min$^{-1}$ cooling rate to by-pass the temperature domain ($\sim 220$ K) where recrystallisation towards phase II or III occurs, and finally cooled to 120 K where X-ray collections were attempted.

Except in some cases in which apparently fair phase I$_{C}$ single crystals were obtained, the samples seemed to stick to the Lindemann capillaries. This sticking, during the quenching process, resulted in a breakage of the inner part of the crystal and, most often, in the presence of some polycrystalline powder at its surface, which of course impaired the quality of the sample and even, at times, its stability as a function of time. We were unable to control the « unsticking » process.

We will now describe the results obtained with a « good » phase I$_{C}$ single crystal at 121 K.

As was already observed by Otsubo and Sugawara [4], the glassy crystal lattice is cubic. We observed no significant deformation with respect to phase I lattice, except thermal contraction. The unit cell parameter, as determined by means of program PARAM, is equal to 8.835 (4) Å at 283 K, 8.779 (9) Å at 249 K and 8.608 (9) Å at 121 K.

There are no important modifications in the intensity ratios for the eleven Bragg reflexions which were observed in phase I (table IV). For the studied sample, the reflexions were measured in a quarter-sphere of resolution, with a minimum scanning rate equal to 3 deg. min$^{-1}$, up to $2 \theta = 40^o$, which corresponds to 29 scanned reflexions at 121 K.

An overall weakening of intensities with respect to what was recorded for phase I is to be noticed. The weak reflexions have intensities very near $2 \sigma(I)$,
Table IV. — Comparison between observed intensities in phases I and I’G of cyclohexanol; + arbitrary value for this reflexion which is the strongest one; × some equivalent reflexions have intensities lower than 2 \(\sigma(1)\).

<table>
<thead>
<tr>
<th>Reflexion</th>
<th>275 K (\times 10^4)</th>
<th>121 K (\times 10^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>100,0</td>
<td>100,0</td>
</tr>
<tr>
<td>200</td>
<td>73,2</td>
<td>63,7</td>
</tr>
<tr>
<td>220</td>
<td>3,5</td>
<td>5,8</td>
</tr>
<tr>
<td>331</td>
<td>10,7</td>
<td>10,2</td>
</tr>
<tr>
<td>222</td>
<td>22,5</td>
<td>20,4</td>
</tr>
<tr>
<td>400</td>
<td>7,8</td>
<td>5,5</td>
</tr>
<tr>
<td>331</td>
<td>5,2</td>
<td>2,9*</td>
</tr>
<tr>
<td>420</td>
<td>3,8</td>
<td>3,0*</td>
</tr>
<tr>
<td>422</td>
<td>4,6</td>
<td>4,4*</td>
</tr>
<tr>
<td>511</td>
<td>2,3</td>
<td>1,6*</td>
</tr>
<tr>
<td>333</td>
<td>3,6</td>
<td>3,8*</td>
</tr>
</tbody>
</table>

some equivalent reflexions of four observed ones were lower than 2 \(\sigma(1)\), but no « non observed » reflexion of phase I became observable in the glassy crystalline phase.

Because the experimental data quality was not as good as for phase I, refinements were not carried out as thoroughly as previously.

Anyway, our calculations show that the structural model we determined for phase I gives a satisfactory account of the intensities observed at 121 K (tables V and VI). The residuals are \(R = 0.055\) and \(WR = 0.026\) (\(W = 1\) for all reflexions), with \(B = 8.92\) Å\(^2\).

Table V. — Fractional atomic coordinates \((x 10^5)\) for the structural model of cyclohexanol phase I’G at 121 K.

<table>
<thead>
<tr>
<th>Equatorial conformer</th>
<th>Axial conformer</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1 - 482</td>
<td>3995</td>
</tr>
<tr>
<td>C2 - 1248</td>
<td>10916</td>
</tr>
<tr>
<td>C3 - 7481</td>
<td>- 6743</td>
</tr>
<tr>
<td>C4 - 3958</td>
<td>- 21048</td>
</tr>
<tr>
<td>C5 - 5688</td>
<td>- 11315</td>
</tr>
<tr>
<td>C6 - 11921</td>
<td>- 4938</td>
</tr>
<tr>
<td>O11 - 6369</td>
<td>120 28110</td>
</tr>
<tr>
<td>B12 - 9870</td>
<td>9167 14065</td>
</tr>
<tr>
<td>B21 - 8675</td>
<td>- 18134 8556</td>
</tr>
<tr>
<td>B22 - 9104</td>
<td>- 16089 2260</td>
</tr>
<tr>
<td>B31 - 17832</td>
<td>- 1571 11913</td>
</tr>
<tr>
<td>B32 - 8604</td>
<td>- 16424 19269</td>
</tr>
<tr>
<td>B41 - 10088</td>
<td>- 7083 31596</td>
</tr>
<tr>
<td>B51 - 14310</td>
<td>- 799 22085</td>
</tr>
<tr>
<td>B52 - 13115</td>
<td>- 26502 16576</td>
</tr>
<tr>
<td>B61 - 13044</td>
<td>24792 11249</td>
</tr>
<tr>
<td>B62 - 22272</td>
<td>9939 3893</td>
</tr>
</tbody>
</table>

Table VI. — Observed and calculated structure factors for cyclohexanol phase I’G at 121 K.

<table>
<thead>
<tr>
<th>h k l</th>
<th>FO</th>
<th>FC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 1 1</td>
<td>56.9</td>
<td>56.7</td>
</tr>
<tr>
<td>2 0 0</td>
<td>36.2</td>
<td>36.3</td>
</tr>
<tr>
<td>2 2 0</td>
<td>3.3</td>
<td>- 2.9</td>
</tr>
<tr>
<td>3 1 1</td>
<td>5.8</td>
<td>- 6.6</td>
</tr>
<tr>
<td>2 2 2</td>
<td>11.6</td>
<td>- 11.6</td>
</tr>
<tr>
<td>4 0 0</td>
<td>3.1</td>
<td>- 3.2</td>
</tr>
<tr>
<td>3 3 1</td>
<td>1.6</td>
<td>- 2.1</td>
</tr>
<tr>
<td>4 2 0</td>
<td>1.7</td>
<td>- 1.2</td>
</tr>
<tr>
<td>4 2 2</td>
<td>2.5</td>
<td>- 2.3</td>
</tr>
<tr>
<td>5 5 1</td>
<td>0.9</td>
<td>- 0.3</td>
</tr>
<tr>
<td>3 3 3</td>
<td>2.1</td>
<td>- 1.9</td>
</tr>
<tr>
<td>4 4 0</td>
<td>1.1</td>
<td>- 1.4</td>
</tr>
<tr>
<td>5 3 1</td>
<td>1.2</td>
<td>- 0.8</td>
</tr>
<tr>
<td>6 0 0</td>
<td>1.1</td>
<td>- 1.2</td>
</tr>
<tr>
<td>4 4 2</td>
<td>0.7</td>
<td>- 0.7</td>
</tr>
<tr>
<td>6 2 0</td>
<td>0.9</td>
<td>- 1.1</td>
</tr>
<tr>
<td>5 3 3</td>
<td>0.6</td>
<td>- 0.7</td>
</tr>
<tr>
<td>6 2 2</td>
<td>0.8</td>
<td>- 0.5</td>
</tr>
<tr>
<td>4 4 4</td>
<td>0.6</td>
<td>- 0.6</td>
</tr>
<tr>
<td>7 1 1</td>
<td>1.3</td>
<td>- 1.1</td>
</tr>
<tr>
<td>5 5 1</td>
<td>1.3</td>
<td>- 1.4</td>
</tr>
<tr>
<td>6 4 0</td>
<td>1.3</td>
<td>- 0.8</td>
</tr>
<tr>
<td>6 4 2</td>
<td>0.7</td>
<td>- 0.2</td>
</tr>
<tr>
<td>5 5 3</td>
<td>0.5</td>
<td>- 0.4</td>
</tr>
<tr>
<td>7 3 1</td>
<td>0.8</td>
<td>- 0.9</td>
</tr>
<tr>
<td>8 0 0</td>
<td>0.7</td>
<td>- 0.1</td>
</tr>
<tr>
<td>7 3 3</td>
<td>0.6</td>
<td>- 0.1</td>
</tr>
<tr>
<td>6 4 4</td>
<td>0.4</td>
<td>- 0.5</td>
</tr>
<tr>
<td>8 2 0</td>
<td>0.7</td>
<td>- 0.6</td>
</tr>
</tbody>
</table>

5. Conclusion.

Cyclohexanol phase I has been described by a structure in which each molecular conformer can occupy 48 equivalent orientational positions at each lattice site. These orientations are related to one another through all the symmetry operations of space group Fm3m, as no molecular symmetry has to be taken into account in the counting of accessible positions. Such a Frenkel model, the validity of which has long been acknowledged [25], can now be considered a matter of routine as far as structure solving is concerned. In fact, from that view point, the actual difficulties arise from the very low number of experimentally observable Bragg reflexions in such plastic phases.
In the case of glassy crystalline cyclohexanol, the quality of the experimental data was not as good as that corresponding to phase I. But there is little doubt that the time and space averaged structure of phase $I_G$ is similar to that of phase I; in particular, it contains the same number of positions accessible to each cyclohexanol conformer as phase I does. As NMR measurements [17, 26] reveal that large amplitude molecular motions still exist at temperatures lower than the glass transition temperature, it may be thought that every orientational position can effectively be attained within the glassy crystal through motions that are similar to those that exist in phase I but have much lower frequencies.

Moreover, the present results confirm that the modifications in diffuse X-ray scattering patterns between 289 and 120 K [6] are not to be assigned to some structural change. They must be related to changes in molecular motion correlations. This matter is now under study.

References