

LETTER TO THE EDITOR

A Cluster Model for the Cubic Plastic Phase of Ethanol

R. Fayos* and J. Fayos†

*Instituto de Estructura de la Materia, Consejo Superior de Investigaciones Científicas, Serrano 123, E-28006 Madrid, Spain; and

†Instituto de Química Física Rocasolano, Consejo Superior de Investigaciones Científicas, Serrano 119, E-28006 Madrid, Spain

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A structural model, built by crystalline packing of optimized clusters of 12 ethanol molecules (C_2OH_6), reproduces well the observed neutron-diffraction spectrum of the plastic phase. Besides fitting the observed bcc Bragg peaks of a 5.4 Å cubic cell, this model produces a multitude of weak peaks in between, which approaches the observed background. Thus, the partially random molecular orientation in the cluster is the main contributor to that background. The centers of mass of the 12 independent molecules are at the reticular bcc points (cell of 5.4 Å), while their mutual orientations are optimized to have a minimum packing energy. The molecules link together through hydrogen bonds, forming *trans-gauche* molecular dimers. © 1997 Academic Press

INTRODUCTION

Data derived from X-ray and Raman scattering unveiled the existence of an orientationally disordered cubic bcc phase in ethanol at 97 K (besides the liquid, glass, and monoclinic crystal phases), with two molecules per unit cell and a lattice constant of 5.4 Å (1,2). A preliminary study of the structure of the different phases (3) and a more detailed study using higher resolution in neutron and X-ray experiments (4) have been performed recently. The shape of the diffraction spectrum $I(2\theta)$ and the radial distribution function $D(r)$ suggest the presence of a plastic phase, with translational order of the centers of mass (CM) of ethanol molecules but with orientational disorder of molecules.

MODELIZATION

We realized that there is a simple deformation from the monoclinic cell to the plastic phase cell. The monoclinic-phase lattice, having $a_m = 5.377$, $b_m = 6.872$, $c_m = 8.255$ Å, and $\beta = 102.2^\circ$ (5), can be deformed into a tetragonal lattice of similar values, $a_t = 5.40$, $b_t = 5.40\sqrt{2} = 7.637$, and

$c_t = 5.40\sqrt{2} = 7.637$ Å, by

$$\begin{pmatrix} \mathbf{a}_t \\ \mathbf{b}_t \\ \mathbf{c}_t \end{pmatrix} = \begin{pmatrix} \frac{5.40}{|a_m|\sin(\beta)} & 0 & \frac{5.40}{-|c_m|\tan(\beta)} \\ 0 & \frac{5.40\sqrt{2}}{|b_m|} & 0 \\ 0 & 0 & \frac{5.40\sqrt{2}}{|c_m|} \end{pmatrix} \begin{pmatrix} \mathbf{a}_m \\ \mathbf{b}_m \\ \mathbf{c}_m \end{pmatrix}$$

with an increase in volume of 5%. The latter lattice is the diagonal one of the 5.4 Å cubic lattice observed for the plastic phase. In addition, the CM of the four molecules in the monoclinic lattice is close (0.27 to 0.60 Å) to forming a bcc distribution in the plastic cubic cell. Both facts suggest a displacive phase transition. We tried to model that transition by proposing a structural model for the plastic phase and by suggesting a structural mechanism for this transition. First we modeled a cluster of 36 randomly oriented molecules to fill a bcc crystalline lattice; the corresponding calculated $I(2\theta)$ showed no peaks, with the exception of the largest one (110), as we can see in Fig. 1. Hence, we concluded that there must be some orientational order in the plastic phase. So it is reasonable to model an acceptable set of molecular orientations inside a cluster which, extended to the bulk, represents the plastic phase and reproduces the observed $I(2\theta)$. The observed diffraction pattern, as shown in Fig. 1, has some Bragg peaks and a continuous background; between the more important effects contributing to the background are the lattice imperfections of various kinds (6).

In our work we find a crystal-type model for the plastic phase, formed by clusters of molecules that fill the bulk by three-dimensional translations. This model both reproduces the observed Bragg peaks and contributes to the observed background. For technical reasons (7) the size of our cluster was of 12 molecules, corresponding to a volume of 944.7 Å³,

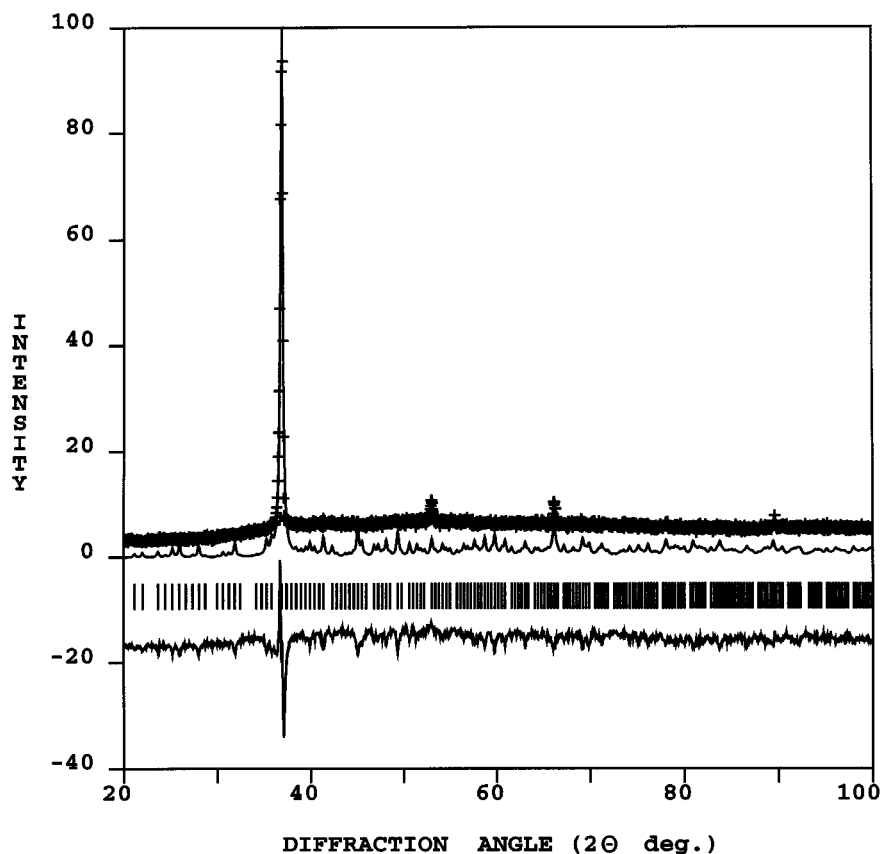


FIG. 1. The upper curve, with crosses, is the experimental neutron spectrum ($\lambda = 2.398 \text{ \AA}$). The second is the calculated spectrum from a random model of 36 molecules, with all allowed reflections displayed with vertical bars below. The third curve at the bottom is the difference (observed) – (calculated), where the zero difference is at -20 in the intensity axis.

which is six times larger than the 5.4 \AA cubic cell containing two molecules. We chose the packing energy as the acceptance criterion for the relative orientation of the molecules. A central force field was considered, with van der Waals, hydrogen bond (both of Lennard Jones type), and coulombic terms (7). We considered charges only for atoms involved in hydrogen bonds: $O(\text{COH}) = -0.7$, $H(\text{COH}) = 0.435$, and $C(\text{COH}) = 0.265$ (in electron units) (8). To validate this potential we minimized the reported monoclinic structure, allowing the change in the cell parameters and all translations and rotations of the four molecules in the cell. The minimized structure differs by only 1% from the original monoclinic phase, in terms of the cell axis and molecular displacements. Then, starting from an initial set of orientations, we minimized the packing energy of the plastic phase in the space of 12×3 molecular-rotational variables, considering interactions up to 7 \AA and monitoring the calculated $I(2\theta)$ (7).

The first starting model tried was built by translating the CM of the molecules of the monoclinic phase to the bcc reticular points, preserving their orientations and hydrogen bond linking. This packing was minimized but did not

reproduce the $I(2\theta)$ well. Then, considering that the X-ray spectrum only has one peak (200) (besides the dominant (110)) and that the heavy atoms are the main contributors to it, we built a second starting initial model where hydrogen-bonded dimers *trans-gauche* (3) fill the (200) planes, with the C–C–O groups on them. In this model the 36 rotations converged to a minimum for the packing energy $E = -10.2 \text{ kcal/mol}$, compared to $E = -18.7 \text{ kcal/mol}$ for the monoclinic phase; this also reproduces well the observed neutron $I(2\theta)$, as shown in Fig. 2. (A Debye Waller factor of $B = 3 \text{ \AA}^2$ was used). Figure 3 shows the model where some molecules are linked forming *trans-gauche* dimers and others form chains linking the dimers together through hydrogen bonds between the *gauche* molecules. The large difference in energy would explain the experimental difficulty in obtaining the plastic phase from the monoclinic phase. The failure of the first model, combined with the success of the second, suggests a mechanism for the phase transition in which small molecular translations allow simultaneously large molecular rotations and which could be related to a possible melt phase observed in between (2).

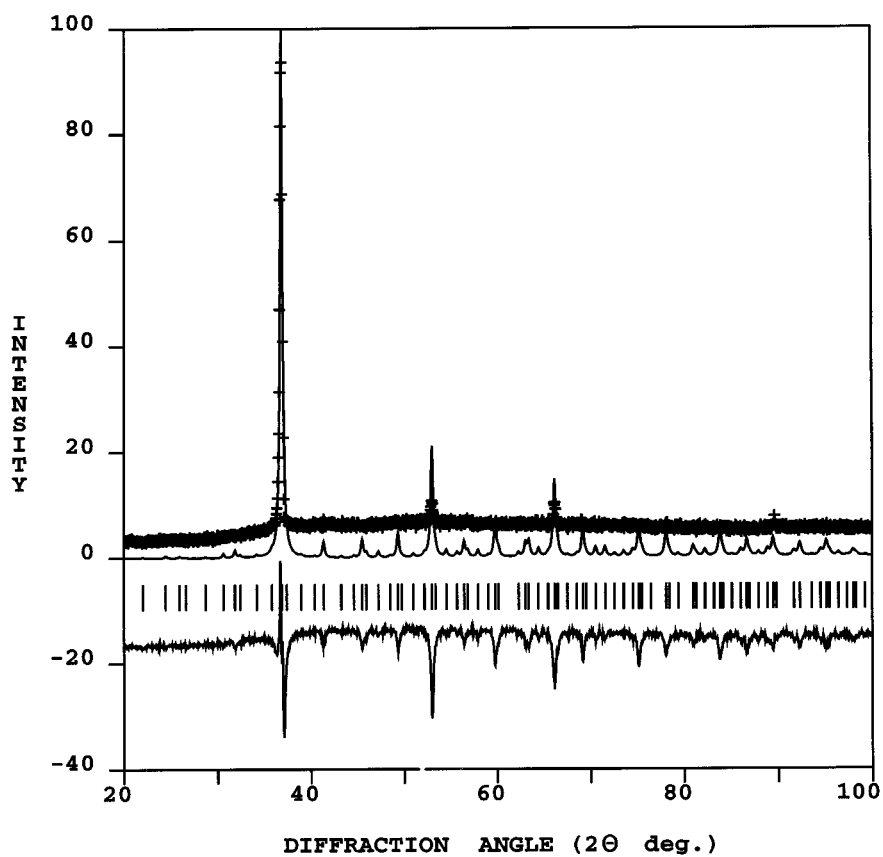


FIG. 2. The upper curve is the experimental spectrum, the second is the spectrum calculated from the simulated model, with all allowed reflections below, and the third curve is the difference (observed) - (calculated).

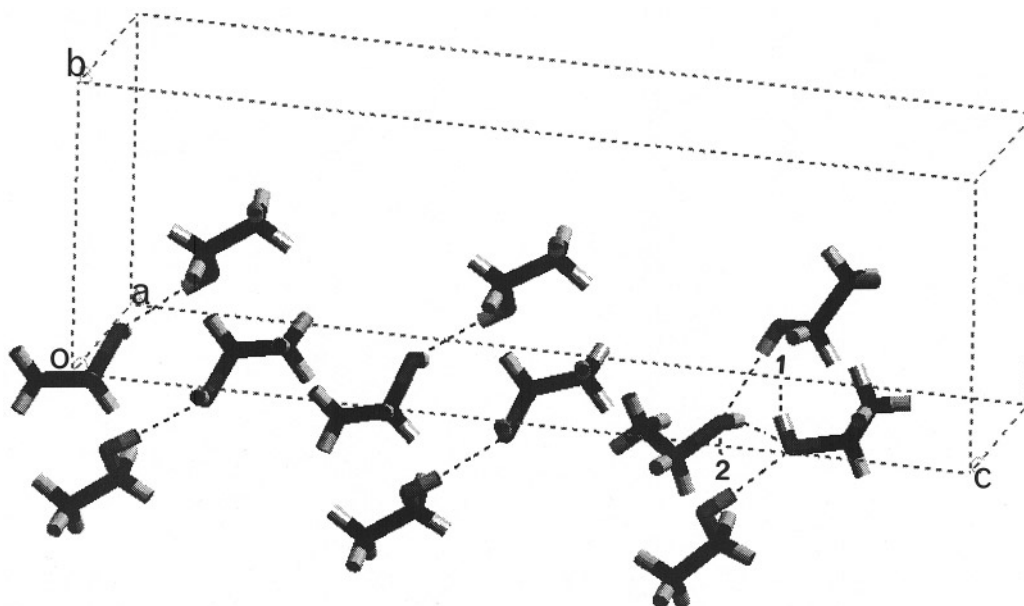


FIG. 3. Simulated cluster for the plastic phase in a cell of $a_1 = 5.40$, $b_1 = 5.40\sqrt{2}$, and $3c_1 = 3 \times 5.40\sqrt{2} \text{ \AA}$. 1 to 2 shows the hydrogen-bond linking *gauche* molecules.

Due to the large cell considered for the 12 molecules and their different orientations, many peaks in the calculated $I(2\theta)$ occur between the observed peaks. Note that our model, besides reproducing the observed bcc peaks (for a cell of 5.4 Å), produces a pattern of weak peaks in between, which contribute to the observed background. If the molecules are rotated out of their optimal orientations, not only does the fit to the observed peaks fail, but some of those weak peaks become higher than the observed background. The number of these weak peaks will increase with the size of the cluster and we could expect that a larger optimized cluster would fill the observed background with the envelope of those peaks. Besides, there is no wonder that a plastic phase, where the molecular random orientation breaks the bcc condition and the 5.4 Å translation, would produce such peaks contributing to the background.

On the other hand, the observed $D(r)$ shows a break of the orientational disorder below 4 Å (3), which would justify the small size chosen for our cluster. The long-range disorder would be due to a larger cluster size or to a multi-twinning packing of clusters. The latter material, like quasicrystals, although not being a real crystal, would produce a multitude of diffraction peaks, which in our case would contribute to the observed background.

The $D(r)$ calculated with our model (Fig. 4) reproduces approximately the peaks up to 4 Å; the difference from the observed intensities could be due to any periodic spurious peaks (6) created when the direct Fourier transform of the experimental $I(2\theta)$ was performed. Above that value the period of the oscillations is about 3.7 Å = d_{110} in both cases, but the sinusoidal shape differs progressively from the soft curve observed, probably due to considering only 12 molecules in our model, as we saw occurred for a random model when we took 36 molecules instead of 12.

The presence of a broad (110) peak in the $I(2\theta)$ of the glass phase was explained (3) by a residual bcc plastic structure. We suggest that the remaining similarities observed in the $I(2\theta)$ of both phases are also due to residual plastic structure in the glass, which would contribute to $I(2\theta)$ as "quasiBragg planes" (9).

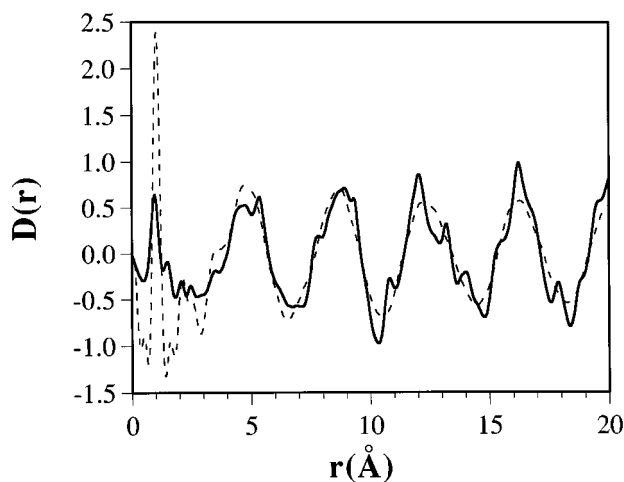


FIG. 4. $D(r)$ of the calculated plastic (solid line) compared to the experimental one (dotted line).

In summary, we have developed here a cluster model, with a minimum calculated packing energy, that accounts for the plastic configuration of ethanol.

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