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ON THE EXISTENCE OF TAILS OR SMEAR EFFECTS IN THE DIFFRACTION PHOTOGRAPHS OF MESOGENIC MATERIALS

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An attempt was made to explain the diffuse streaks or tails present in the X-ray diffraction photographs of liquid crystalline materials. Due to anisotropy of thermal motion, the placement of the atoms in the linear molecules of the mesogenic materials no longer corresponds to an ideal lattice at each instant. The scattering by such anisotropically vibrating molecules which can be treated as diffraction by standing waves, essentially alters the diffraction condition, which is the reason for certain diffusion spots to pick up diffuse tails or streaks depending upon the anisotropy of vibration of the molecules.

1. Introduction

It has been observed ever since the first diffraction photograph of liquid crystalline material was obtained by Bernal and Crowfoot [1] that these mesogenic materials, especially nematogenic and cholesterol derivatives with long side chains, normally show smear effects instead of giving sharp reflections unlike most of the other molecular crystals. Also, the smear effects are predominent in certain reflections only and the rest being free from tail formations. The crystalline structures with low R values of the mesogenic organic materials reveals that the smear effect is not due to any disorder but must be due to a systematic dynamical effect. Here an attempt has been made to explain the same.

2. Theoretical discussion

From the few molecular structure data of liquid crystalline molecules which are available, we can draw the conclusion that almost[1] all organic molecules which exhibit mesogenic phases are essentially linear and the neighbouring molecules are weakly bound by van der Waals type of interaction. Also, the phenyl groups of the mesogenic materials are essentially rigid and the principal anisotropic temperature factors of the atoms com-

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[1] There are mesogenic linear molecules (disc-like).

prising these groups have almost the same magnitude. This indicates closeness to sphericity, whereas the atoms in the end groups viz, alkyl chains have strong anisotropy in particular planes in relation to the planes of the phenyl groups [2–4]. For these reasons, the alkyl parts of the molecules, and in turn the atoms have a tendency to have thermal motion in a preferential plane, that is, there is anisotropy of thermal motion. In addition the thermal wave parameters such as amplitude, etc., for the end groups which are normally alkyl chains, will be different from those for the central phenyl groups. Due to the thermal motion, the placement of crystal atoms no longer corresponds to an ideal lattice at each instant. Suppose an atom in the k^{th} position of the L^{th} unit cell is shifted by the vector, δ_k^L, from its ideal position. This atom gives an elementary wave of the same amplitude f_k. However, the phase of the wave will change relative to that which existed in the ideal lattice by the value $(k-k_0)\cdot\delta_k^L = s\cdot\delta_k^L$. Thus, the amplitude of the wave sent by an atom displaced from its equilibrium position should be represented by

$$g_k^L = f_k \exp(is\cdot\delta_k^L).$$

The structural amplitude becomes

$$F_L = \sum g_k^L \exp(is\cdot r_k).$$

The experimental intensities will be determined by the average values of the structural factor, since the time of measurement is fairly large compared to the period of vibration of the atom ($\sim 10^{-13}$ sec) and this vibration period is very large compared to the period of the electromagnetic X-ray wave (10^{-18} sec). Hence it is justifiable to consider the electromagnetic field of the instantaneous distribution of matter in the lattice. So in addition to considering the elastic scattering of an X-ray photon by a crystal governed by the wave vector relation rule [5]

$$k' = k+G,$$

where G is a vector in the reciprocal lattice, k is the wave vector of the incident photon and k' the wave vector of the scattered photon, must consider the scattering from vibrating

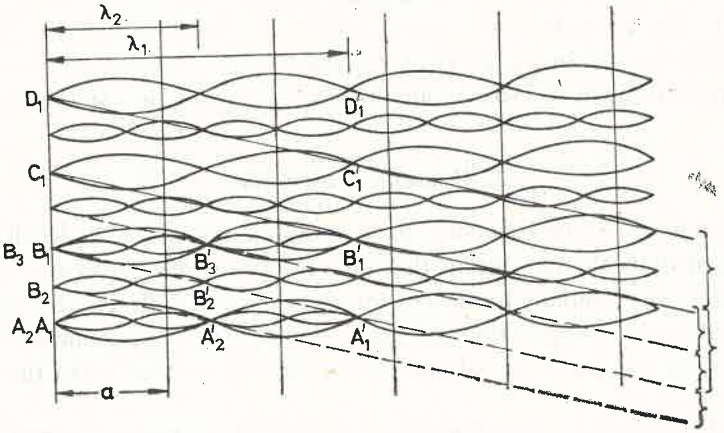

Fig. 1. Generation of additional nodal planes by the different thermal vibrations

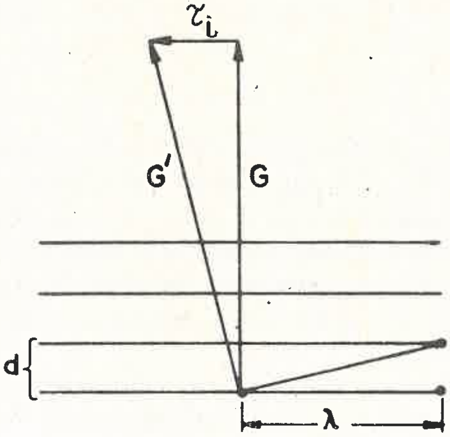

Fig. 2. Condition of diffraction due to heat waves

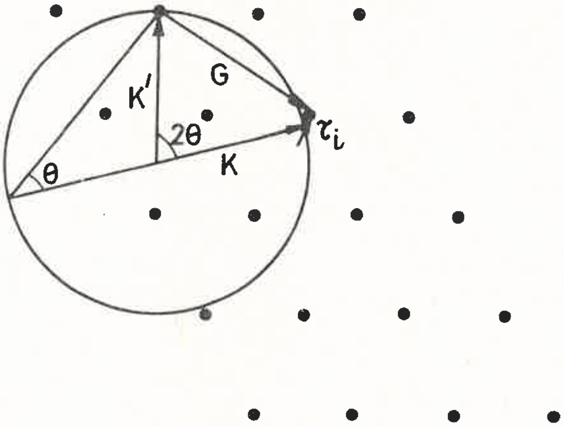

Fig. 3. Interpretation of diffraction due to heat waves by means of a reciprocal lattice

molecules which can be taken as the diffraction by standing waves. The standing waves of thermal vibrations impose a superlattice on the static pattern with a period equal to the length of the thermal wave. Also we have to consider several superlattices or additional nodal planes (Fig. 1) as depending upon the lengths of the thermal waves which are determined by varying degrees of vibration in the end groups of linear molecules. Each of the waves will have its own superlattices. Thus, the diffraction spot will pick up a diffuse streak due to anisotropy of vibration.

The condition for diffraction from heat waves should have the form

$$G' = k' - k,$$

where $G' = G + \tau_i$, τ_i being the thermal wave vector. Because of the preferential vibration of the molecule in a plane, the magnitude of the thermal wave vector changes with fixed direction depending upon the length of the thermal wave. Thus, the condition for diffraction (Fig. 2) becomes

$$G+\tau_i = k'-k.$$

In Fig. 3 we have shown the geometrical sense of the condition that diffraction from the thermal waves of a crystal in a given direction occurs if the thermal wave vector joins the end of the vector, k, with the nearest reciprocal point. The zone of each reciprocal lattice point can be characterized by the scattering intensity as a function of $G+\tau_i$ and the streaks can be generated. Therefore, we can comprehend the streaks to be formed by the heat wave scattering by the assembly of anisotropically vibrating molecules in addition to elastic scattering by the atom.

The onset of the smear effect in certain reflections only can be explained by determining the plane of the vibration of the alkyl chains with reference to the plane of the phenyl groups. The gradual decrease in the intensity of the tail as we go away from the centre of the reflection can be accounted for by the varying magnitudes of amplitudes of vibration of atoms away from the central rigid phenyl groups.

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REFERENCES

[1] J. D. Bernal, D. Crowfoot, *Trans. Faraday Soc.* **29**, 1032 (1933).
[2] J. Shashidhara Prasad, *Acta Crystallogr.* **B35**, 1404 (1979).
[3] J. Shashidhara Prasad, *Acta Crystallogr.* **B35**, 1407 (1979).
[4] J. Shashidhara Prasad, P. K. Rajalakshmi, *J. Phys.* (France) **40**, 309 (1979).
[5] C. Kittel, *Introduction to Solid State Physics*, John Wiley & Sons, New York-London-Sydney-Toronto.