

both maxima occurring at $2\theta = 85^\circ$. These numbers are appreciably larger than found for alanine (Table 3; Fig. 4); most of the increase comes from the tails, and may be due to the different method of treating the least-squares fit to the Cauchy function. The 2θ dependence of the truncation losses indicated by the citrinin data is similar, but by no means identical, to that shown in Fig. 4, emphasizing once more that these corrections must be considered entirely empirical.

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Equations for Diffuse Scattering from Disordered Molecular Crystals

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Abstract

General equations are presented for diffuse scattering due to static substitutional and orientational disorder in molecular crystals. Scattering due to displacements, both static and dynamic, and molecular librations is treated separately. Examples of a pair of isostructural isomers of dibromodiethyldimethylbenzene, which show very different disorder diffuse scattering, are given. Procedures for data analysis and

separation of various diffuse scattering components are discussed.

Introduction

Since the early experiments of Wilchinsky (1944), Cowley (1950) and Warren, Averbach & Roberts (1951), most quantitative studies of diffuse X-ray and neutron scattering from disordered materials have been carried out on metallic alloys. The techniques for data and error analysis have become reasonably well established; see Borie & Sparks (1971), Gragg, Hayakawa & Cohen (1983), Hayakawa & Cohen

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(1975), Tibballs (1975), Khanna (1984) for the latest procedures. Recently there has been interest in the study of disorder in organic molecular crystals (*e.g.* Amorós & Amorós, 1968; Glazer, 1970; Gierren & Lamm, 1980; Epstein, Welberry & Jones, 1982; Welberry & Siripitayananon, 1986, 1987) where the occurrence of disorder is governed by short-range intermolecular interactions which can be well modelled theoretically (Kitaigorodsky & Ahmed, 1972; Ramdas & Thomas, 1978). Many molecular crystals exhibit static substitutional disorder effects as a result of either two different molecules of the same shape or the same molecule in (two or more) different orientations being able to occupy the same crystallographic site (Flack, 1970; Welberry, Jones & Epstein, 1982). The general diffraction equations for alloys cannot be applied directly to analyse diffuse scattering from disordered molecular crystals. Although the same principles are involved, there are some basic differences between analysing diffuse scattering from molecular crystals and that from metallic alloys. The atomic scattering factors which are used in the analysis for alloys are replaced by molecular structure factors in the case of molecular crystals. These are, in general, complex and rapidly varying functions in reciprocal space and depend strongly on the position vectors of the various atoms constituting the molecule. The molecules may have different orientations in different sublattices, thus causing the molecular structure factor to vary from one sublattice to another. In the case of orientational disorder, the position vectors of only a few atoms in the molecule may change from one orientation to another while the positions of the rest of the atoms remain unchanged. In addition, alloys basically tend to have simple structures of high symmetry whereas molecular crystals often have low symmetry with complex arrangements of intermolecular contacts. The modelling of the size-effect and thermal-vibration contributions to the diffuse scattering is much more difficult to quantify for molecular crystals. A redeeming feature for some molecular crystals in which disorder is introduced at growth is that the degree of substitutional disorder is independent of temperature (*i.e.* no exchange occurs between molecules of different type), unlike the case for alloys. Here the pair distribution functions reflect the intermolecular interactions which would have occurred during crystal growth.

Most studies of diffuse X-ray scattering from disordered molecular crystals have been either qualitative or semi-quantitative and, in general, have neglected contributions from displacement disorder. In this paper, general equations for diffuse scattering from disordered molecular crystals are derived. The general equations for alloys, due to Hayakawa & Cohen (1975), were used as the starting point for this work and we derived the modifications necessary for use with molecular crystals. Specific examples of two

isomers of dibromodiethylmethylbenzene are considered. A basic procedure to separate the various contributions is presented.

1. General theory

From kinematic theory, the total scattering intensity in electron units (I_{tot}) can be written as

$$I_{\text{tot}} = \sum_m \sum_{\mu} f_{m\mu} \exp [i\mathbf{K} \cdot (\mathbf{r}_m + \mathbf{r}_{\mu} + \mathbf{u}_{m\mu})] \\ \times \sum_n \sum_{\nu} f_{n\nu}^* \exp [-i\mathbf{K} \cdot (\mathbf{r}_n + \mathbf{r}_{\nu} + \mathbf{u}_{n\nu})] \quad (1)$$

where m, n and μ, ν are lattice and sublattice indices respectively. f represents the molecular structure factor and is in general complex, depending upon the position vectors of the various atoms of the molecule. \mathbf{r} is the position vector of the centre of mass of a molecule at a lattice point with respect to an arbitrary origin and \mathbf{u} represents small displacements with respect to the lattice point. \mathbf{K} is the diffraction vector. Let x_{μ}^i be the fraction of molecules of type i on the sublattice μ and $P_{\mu\nu}^j$ be the conditional probability of finding a j -type molecule on the ν th sublattice associated with the n th lattice point. Equation (1) may then be written as

$$I_{\text{tot}} = \sum_{\substack{m,n \\ \mu,\nu \\ i,j}} x_{\mu}^i f_{i\mu} f_{j\nu}^* \langle \exp (i\mathbf{K} \cdot \mathbf{U}_{\mu\nu}^j) \rangle P_{\mu\nu}^j S_{\mu\nu} A_{mn}, \quad (2)$$

where $A_{mn} = \exp [i\mathbf{K} \cdot (\mathbf{r}_m - \mathbf{r}_n)]$, $S_{\mu\nu} = \exp [i\mathbf{K} \cdot (\mathbf{r}_{\mu} - \mathbf{r}_{\nu})]$ and $\exp [i\mathbf{K} \cdot \mathbf{U}_{\mu\nu}^j] = \exp [i\mathbf{K} \cdot (\mathbf{u}_{m\mu}^i - \mathbf{u}_{n\nu}^j)]$. The average of the displacement term is taken for each set of intermolecular vectors whose total probability is $x_{\mu}^i P_{\mu\nu}^j$. The molecular orientation may differ from one sublattice to another, leading to a distinct molecular structure factor for each sublattice. I_{tot} can be separated into two sums: one due to the average structure, I_{ave} , and the other due to the local order I_{LO} ,

$$I_{\text{tot}} = I_{\text{ave}} + I_{\text{LO}}, \quad (3a)$$

$$I_{\text{ave}} = \sum_{\substack{m,n \\ \mu,\nu \\ i,j}} x_{\mu}^i x_{\nu}^j f_{i\mu} f_{j\nu}^* \langle \exp (i\mathbf{K} \cdot \mathbf{U}_{\mu\nu}^j) \rangle S_{\mu\nu} A_{mn}, \quad (3b)$$

$$I_{\text{LO}} = \sum_{\substack{m,n \\ \mu,\nu \\ i,j}} x_{\mu}^i x_{\nu}^j f_{i\mu} f_{j\nu}^* \langle \exp (i\mathbf{K} \cdot \mathbf{U}_{\mu\nu}^j) \rangle \\ \times [(P_{\mu\nu}^j / x_{\nu}^j) - 1] S_{\mu\nu} A_{mn}. \quad (3c)$$

The sum over i and j in (3c) can be further simplified

by employing the following relationships:

$$x_\nu^i = 1 - \sum_{j(\neq i)} x_\nu^j, \quad (4a)$$

$$P_{\mu\nu}^{ii} = 1 - \sum_{j(\neq i)} P_{\mu\nu}^{ij}, \quad (4b)$$

$$I_{LO} = \sum_{\substack{m,n \\ \mu,\nu \\ i,j}} x_\mu^i x_\nu^j f_{i\mu} [f_{i\nu}^* \langle \exp(i\mathbf{K} \cdot \mathbf{U}_{\mu\nu}^i) \rangle - f_{j\nu}^* \langle \exp(i\mathbf{K} \cdot \mathbf{U}_{\mu\nu}^j) \rangle] \alpha_{\mu\nu}^{ij} S_{\mu\nu} A_{mn}. \quad (5)$$

We now assume that the displacements of the molecules are small and that the averages over odd powers of the displacements vanish for large intermolecular vectors. In the presence of strain fields, both static and dynamic, molecules can undergo two types of movements:

(1) Libration of the molecule about an axis, or axes, passing through its centre of mass. Depending on the axis of libration, one half of the molecule moves in one direction while the other half moves in the opposite direction. Librations shift the position vectors of the various atoms constituting the molecule by different amounts, thereby affecting the molecular structure factor, *i.e.* $f \rightarrow f + \Delta f$. If one assumes that the average contribution from odd powers of Δf vanishes, librations result in an addition to the terms in the diffuse scattering which contains $\Delta f \Delta f^*$ (Krivoglaз, 1969).

(2) Translation of the molecule as a whole. The displacements referred to in (1) belong to this class of molecular motion.

In the method of Hayakawa & Cohen (1975), $\langle \exp(i\mathbf{K} \cdot \mathbf{U}_{\mu\nu}^i) \rangle$ can be approximated by

$$\begin{aligned} \langle \exp(i\mathbf{K} \cdot \mathbf{U}_{\mu\nu}^i) \rangle &= \exp[-\frac{1}{2} \langle (\mathbf{K} \cdot \mathbf{U}_\mu^i)^2 \rangle] \\ &\quad \times \exp[-\frac{1}{2} \langle (\mathbf{K} \cdot \mathbf{U}_\nu^j)^2 \rangle] \\ &\quad \times \exp[\langle \mathbf{K} \cdot \mathbf{U}_\mu^i \mathbf{K} \cdot \mathbf{U}_\nu^j \rangle] \\ &\quad \times [1 + i \langle \mathbf{K} \cdot \mathbf{U}_{\mu\nu}^i \rangle]. \end{aligned} \quad (6)$$

This expansion is correct out to quadratic terms. With $f_{i\mu}^*$ implying $f_{i\mu} \exp[-\frac{1}{2} \langle (\mathbf{K} \cdot \mathbf{U}_\mu^i)^2 \rangle]$, the intensity may be written in terms of the moments of expansion.

$$I_{ave}^0 = \sum_{\substack{m,n \\ \mu,\nu \\ i,j}} x_\mu^i x_\nu^j f_{i\mu}^* f_{j\nu}^* S_{\mu\nu} A_{mn} \quad (7a)$$

$$I_{ave}^1 = \sum_{\substack{m,n \\ \mu,\nu \\ i,j}} x_\mu^i x_\nu^j f_{i\mu}^* f_{j\nu}^* \langle \mathbf{K} \cdot \mathbf{U}_{\mu\nu}^i \rangle S_{\mu\nu} A_{mn} \quad (7b)$$

$$I_{ave}^2 = \sum_{\substack{m,n \\ \mu,\nu \\ i,j}} x_\mu^i x_\nu^j f_{i\mu}^* f_{j\nu}^* \langle \mathbf{K} \cdot \mathbf{U}_\mu^i \mathbf{K} \cdot \mathbf{U}_\nu^j \rangle S_{\mu\nu} A_{mn} \quad (7c)$$

$$I_{ave}^L = \sum_{\substack{m,n \\ \mu,\nu \\ i,j}} x_\mu^i x_\nu^j \Delta f_{i\mu} \Delta f_{j\nu}^* S_{\mu\nu} A_{mn}. \quad (7d)$$

I^L represents the contribution to the diffuse scattering from the molecular librations. For local-order terms, we have

$$I_{LO}^0 = \sum_{\substack{m,n \\ \mu,\nu \\ i \neq j}} x_\mu^i x_\nu^j f_{i\mu}^* (f_{i\nu}^* - f_{j\nu}^*) \alpha_{\mu\nu}^{ij} S_{\mu\nu} A_{mn} \quad (8a)$$

$$I_{LO}^1 = \sum_{\substack{m,n \\ \mu,\nu \\ i \neq j}} x_\mu^i x_\nu^j f_{i\mu}^* (f_{i\nu}^* \langle \mathbf{K} \cdot \mathbf{U}_{\mu\nu}^i \rangle - f_{j\nu}^* \langle \mathbf{K} \cdot \mathbf{U}_{\mu\nu}^j \rangle) \alpha_{\mu\nu}^{ij} S_{\mu\nu} A_{mn} \quad (8b)$$

$$I_{LO}^2 = \sum_{\substack{m,n \\ \mu,\nu \\ i \neq j}} x_\mu^i x_\nu^j f_{i\mu}^* (f_{i\nu}^* \langle \mathbf{K} \cdot \mathbf{U}_\mu^i \mathbf{K} \cdot \mathbf{U}_\nu^j \rangle - f_{j\nu}^* \langle \mathbf{K} \cdot \mathbf{U}_\mu^i \mathbf{K} \cdot \mathbf{U}_\nu^j \rangle) \alpha_{\mu\nu}^{ij} S_{\mu\nu} A_{mn} \quad (8c)$$

$$I_{LO}^L = \sum_{\substack{m,n \\ \mu,\nu \\ i \neq j}} x_\mu^i x_\nu^j \Delta f_{i\mu} (\Delta f_{i\nu}^* - \Delta f_{j\nu}^*) \alpha_{\mu\nu}^{ij} S_{\mu\nu} A_{mn}. \quad (8d)$$

Equations (8a)–(8d) clearly bring out the distinct contributions from molecules belonging to different sublattices. As will be seen in the following sections, this feature plays an important role in data analysis. Equation (7a) represents the Bragg peaks. The sum over i and j in (8a) can be further simplified as

$$\begin{aligned} \sum_{i>j} f_{i\mu}^* (f_{i\nu}^* - f_{j\nu}^*) &= \sum_{i>j} [f_{i\mu}^* (f_{i\nu}^* - f_{j\nu}^*) + f_{j\mu}^* (f_{j\nu}^* - f_{i\nu}^*)] \\ &= \sum_{i>j} (f_{i\mu}^* - f_{j\mu}^*) (f_{i\nu}^* - f_{j\nu}^*). \end{aligned} \quad (9)$$

I_{SRO} , given by (8a), can now be written as

$$I_{SRO} = \sum_{\substack{m,n \\ \mu,\nu \\ i>j}} x_\mu^i x_\nu^j (f_{i\mu}^* - f_{j\mu}^*) (f_{i\nu}^* - f_{j\nu}^*) \alpha_{\mu\nu}^{ij} S_{\mu\nu} A_{mn}. \quad (10)$$

The ‘Laue monotonic’ scattering is given by the $m\mu = n\nu$ term,

$$I_{LM} = N \sum_{\substack{\mu \\ i>j}} x_\mu^i x_\nu^j (f_{i\mu}^* - f_{j\mu}^*) (f_{i\mu}^* - f_{j\mu}^*) \quad (11)$$

where N represents the total number of lattice points. Unlike the case of alloys, scaling of the observed intensity by I_{LM} is not very useful for disordered molecular crystals and even complicates data analysis in all but a few special cases. The desired scaling may differ from one crystal to another and has to be determined specifically. For molecular crystals, the sum over m, n, μ and ν cannot, in general, be replaced by N times a single sum over intermolecular vectors as the structure factors differ from one sublattice to another owing to different molecular orientations. However, if the molecular orientations are identical in all sublattices, which they may be for some particular 2D projections, then such a changeover is permissible.

The first moment of the diffuse scattering from both local order and the average lattice arises because of static displacements and can be written as

$$\begin{aligned}
 I^1 &= I_{\text{ave}}^1 + I_{\text{LO}}^1 \\
 &= i \sum_{\substack{m,n \\ \mu,\nu \\ i}} \left[x_{\mu}^i x_{\nu}^j f'_{i\mu} f'_{j\nu}{}^* \langle \mathbf{K} \cdot \mathbf{U}_{\mu\nu}^i \rangle \right. \\
 &\quad + \sum_{j(\neq i)} x_{\mu}^i x_{\nu}^j f'_{i\mu} f'_{j\nu}{}^* \langle \mathbf{K} \cdot \mathbf{U}_{\mu\nu}^i \rangle \\
 &\quad + \sum_{j(\neq i)} x_{\mu}^i x_{\nu}^j f'_{i\mu} f'_{j\nu}{}^* \langle \mathbf{K} \cdot \mathbf{U}_{\mu\nu}^i \rangle \alpha_{\mu\nu}^{ij} \\
 &\quad \left. - \sum_{j(\neq i)} x_{\mu}^i x_{\nu}^j f'_{i\mu} f'_{j\nu}{}^* \langle \mathbf{K} \cdot \mathbf{U}_{\mu\nu}^j \rangle \alpha_{\mu\nu}^{ij} \right] S_{\mu\nu} A_{mn}. \quad (12)
 \end{aligned}$$

If we define

$$F_{\mu\nu}^{ii} = x_{\mu}^i f'_{i\mu} f'_{i\nu}{}^* \left(x_{\nu}^i + \sum_{j(\neq i)} x_{\nu}^j \alpha_{\mu\nu}^{ij} \right) \quad (13a)$$

and

$$F_{\mu\nu}^{ij} = x_{\nu}^i x_{\nu}^j f'_{i\mu} f'_{j\nu}{}^* (1 - \alpha_{\mu\nu}^{ij}), \quad (13b)$$

then (12) becomes

$$I^1 = \sum_{\substack{m,n \\ \mu,\nu \\ i,j}} F_{\mu\nu}^{ij} \langle \mathbf{K} \cdot \mathbf{U}_{\mu\nu}^j \rangle S_{\mu\nu} A_{mn}. \quad (14a)$$

Second moments, which represent scattering due to both thermal and static displacements, can be written as

$$I^2 = \sum_{\substack{m,n \\ \mu,\nu \\ i,j}} F_{\mu\nu}^{ij} \langle \mathbf{K} \cdot \mathbf{U}_{\mu}^i \mathbf{K} \cdot \mathbf{U}_{\nu}^j \rangle S_{\mu\nu} A_{mn}. \quad (14b)$$

I^L , the contribution from molecular librations, can be written as

$$\begin{aligned}
 I^L &= I_{\text{ave}}^L + I_{\text{LO}}^L \\
 &= \sum_{\substack{m,n \\ \mu,\nu \\ i}} \left[x_{\mu}^i x_{\nu}^i \Delta f_{i\mu} \Delta f_{i\mu}{}^* + \sum_{j(\neq i)} x_{\mu}^i x_{\nu}^j \Delta f_{i\mu} \Delta f_{j\nu}{}^* \right. \\
 &\quad + \sum_{j(\neq i)} x_{\mu}^i x_{\nu}^j \Delta f_{i\mu} \Delta f_{j\nu}{}^* \alpha_{\mu\nu}^{ij} \\
 &\quad \left. - \sum_{j(\neq i)} x_{\mu}^i x_{\nu}^j \Delta f_{i\mu} \Delta f_{j\nu}{}^* \alpha_{\mu\nu}^{ij} \right] S_{\mu\nu} A_{mn}. \quad (15)
 \end{aligned}$$

If we define

$$\Delta F_{\mu\nu}^{ii} = x_{\mu}^i \Delta f_{i\mu} \Delta f_{i\nu}{}^* \left(x_{\nu}^i + \sum_{j(\neq i)} x_{\nu}^j \alpha_{\mu\nu}^{ij} \right) \quad (16a)$$

and

$$\Delta F_{\mu\nu}^{ij} = x_{\mu}^i x_{\nu}^j \Delta f_{i\mu} \Delta f_{j\nu}{}^* (1 - \alpha_{\mu\nu}^{ij}), \quad (16b)$$

(15) can now be written as

$$I^L = \sum_{\substack{m,n \\ \mu,\nu \\ i,j}} \Delta F_{\mu\nu}^{ij} S_{\mu\nu} A_{mn}. \quad (17)$$

The vector products can be further simplified by using the equations

$$\mathbf{K} = 2\pi(h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3), \quad (18a)$$

$$\mathbf{U}_{\mu}^i = U_{\mu}^{i1}\mathbf{a}_1 + U_{\mu}^{i2}\mathbf{a}_2 + U_{\mu}^{i3}\mathbf{a}_3, \quad (18b)$$

where \mathbf{a} and \mathbf{b} represent unit vectors in real and reciprocal space respectively. The total diffuse intensity can now be written as

$$I_D = I_{\text{SRO}} + \sum_p^3 Q_p h_p + \sum_p^3 R_p h_p^2 + \sum_p^3 S_{p,p+1} h_p h_{p+1} \quad (19a)$$

where

$$I_{\text{SRO}} = \sum_{\substack{m,n \\ \mu,\nu}} \bar{\alpha}_{\mu\nu} S_{\mu\nu} A_{mn} \quad (19b)$$

$$Q_p = i \sum_{\substack{m,n \\ \mu,\nu}} \bar{\gamma}_{\mu\nu}^p S_{\mu\nu} A_{mn} \quad (19c)$$

$$R_p = \sum_{\substack{m,n \\ \mu,\nu}} [\bar{\delta}_{\mu\nu}^p(1) + \bar{\delta}_{\mu\nu}^p(2)] S_{\mu\nu} A_{mn} \quad (19d)$$

$$S_{p,p+1} = \sum_{\substack{m,n \\ \mu,\nu}} [\bar{\epsilon}_{\mu\nu}^{p,p+1}(1) + \bar{\epsilon}_{\mu\nu}^{p,p+1}(2)] S_{\mu\nu} A_{mn} \quad (19e)$$

with

$$\bar{\alpha}_{\mu\nu} = \sum_{i>j} x_{\mu}^i x_{\nu}^j (f'_{i\mu} - f'_{j\mu})(f'_{i\nu}{}^* - f'_{j\nu}{}^*) \quad (20a)$$

$$\bar{\gamma}_{\mu\nu}^p = 2\pi \sum_{i,j} F_{\mu\nu}^{ij} \langle U_{\mu\nu}^{p,ij} \rangle \quad (20b)$$

$$\bar{\delta}_{\mu\nu}^p(1) = 4\pi^2 \sum_{i,j} F_{\mu\nu}^{ij} \langle U_{\mu}^{p,i} U_{\nu}^{p,j} \rangle \quad (20c)$$

$$\bar{\delta}_{\mu\nu}^p(2) = 4\pi^2 \sum_{i,j} \Delta F_{\mu\nu}^{p,i,pj} \quad (20d)$$

$$\bar{\epsilon}_{\mu\nu}^{p,p+1}(1) = 8\pi^2 \sum_{i,j} F_{\mu\nu}^{ij} \langle U_{\mu}^{p,i} U_{\nu}^{p+1,j} \rangle \quad (20e)$$

$$\bar{\epsilon}_{\mu\nu}^{p,p+1}(2) = 8\pi^2 \sum_{i,j} \Delta F_{\mu\nu}^{p,i,p+1j}. \quad (20f)$$

In (19a) the contributions from librations and displacements have been collected together as they have similar \mathbf{K} dependence (see Appendix 1). Equations (19) and (20) have a form similar to that of equations (22) and (23) of Hayakawa & Cohen (1975). However, the above equations clearly bring out the sublattice dependence of the various structure factors, a feature not present in Hayakawa & Cohen's paper.

2. Application to specific molecular crystals

As an example we consider a pair of isostructural isomers of dibromodiethylmethylbenzene, BEMB1 (1,4-dibromo-2,5-diethyl-3,6-dimethylbenzene) and BEMB2 (1,3-dibromo-2,5-diethyl-4,6-dimethylbenzene). Diffuse scattering data have recently been reported for both BEMB1 and BEMB2 (Welberry & Siripitayananon, 1986, 1987). These molecules form

disordered structures in which a molecular site can be occupied by either of two molecular orientations. The two different configurations (labelled *A* and *B*) differ in the position of the substituent Br- and CH₃- groups about the diethylbenzene nucleus (see Fig. 1). Within the resolution of the measured diffraction data, the diethylbenzene nucleus is ordered but the Br and CH₃ substituents are disordered. The average crystal structure is monoclinic (space group *P2*₁) with two molecules per unit cell. The molecules in the two sublattices of the unit cell are oriented differently [see Fig. 4 of Wood, Welberry & Puza (1984)], a feature which rather complicates the separation of the various diffuse-scattering components. We next consider BEMB1 and BEMB2 individually.

2.1. BEMB2

Let $\mathbf{X}_1 [= (x_1, x_2, x_3)]$ and $\mathbf{Y}_1 [= (y_1, y_2, y_3)]$ represent the position vectors of Br atoms in crystallographic fractional coordinates with respect to the centre of mass of the molecule in orientation *A* located at sublattice 1 of the unit cell. $\mathbf{X}_2 [= (x_1, -x_2, x_3)]$ and $\mathbf{Y}_2 [= (y_1, -y_2, y_3)]$ will then be the corresponding position vectors of Br in sublattice 2. Let f_1 and f_2 represent the structure factors of the ordered diethylbenzene nucleus in sublattices 1 and 2 respectively. The structure factor of the molecule in the different orientations can now be written for sublattice 1 as

$$f_{A1} = f_{\text{Br}}[\exp(i\mathbf{K} \cdot \mathbf{X}_1) + \exp(i\mathbf{K} \cdot \mathbf{Y}_1)] + f_{\text{CH}_3}[\exp(-i\mathbf{K} \cdot \mathbf{X}_1) + \exp(-i\mathbf{K} \cdot \mathbf{Y}_1)] + f_1 \quad (21a)$$

$$f_{B1} = f_{\text{Br}}[\exp(-i\mathbf{K} \cdot \mathbf{X}_1) + \exp(-i\mathbf{K} \cdot \mathbf{Y}_1)] + f_{\text{CH}_3}[\exp(i\mathbf{K} \cdot \mathbf{X}_1) + \exp(i\mathbf{K} \cdot \mathbf{Y}_1)] + f_1 \quad (21b)$$

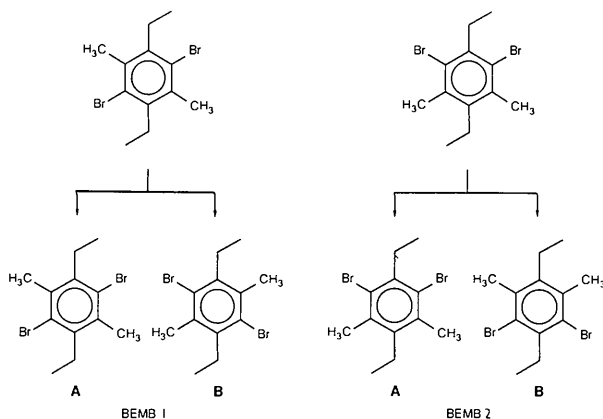


Fig. 1. Molecular structures of two isomers BEMB1 and BEMB2 which possess static orientational disorder. Two possible orientations, *A* and *B*, are shown in the figure.

and for sublattice 2

$$f_{A2} = f_{\text{Br}}[\exp(i\mathbf{K} \cdot \mathbf{X}_2) + \exp(i\mathbf{K} \cdot \mathbf{Y}_2)] + f_{\text{CH}_3}[\exp(-i\mathbf{K} \cdot \mathbf{X}_2) + \exp(-i\mathbf{K} \cdot \mathbf{Y}_2)] + f_2 \quad (21c)$$

$$f_{B2} = f_{\text{Br}}[\exp(-i\mathbf{K} \cdot \mathbf{X}_2) + \exp(-i\mathbf{K} \cdot \mathbf{Y}_2)] + f_{\text{CH}_3}[\exp(i\mathbf{K} \cdot \mathbf{X}_2) + \exp(i\mathbf{K} \cdot \mathbf{Y}_2)] + f_2. \quad (21d)$$

For calculating I_{SRO} , we need the difference in the structure factors

$$f_{A1} - f_{B1} = 4i(f_{\text{Br}} - f_{\text{CH}_3}) \sin[\mathbf{K} \cdot (\mathbf{X}_1 + \mathbf{Y}_1)/2] \times \cos[\mathbf{K} \cdot (\mathbf{X}_1 - \mathbf{Y}_1)/2] \quad (22a)$$

$$f_{A2} - f_{B2} = 4i(f_{\text{Br}} - f_{\text{CH}_3}) \sin[\mathbf{K} \cdot (\mathbf{X}_2 + \mathbf{Y}_2)/2] \times \cos[\mathbf{K} \cdot (\mathbf{X}_2 - \mathbf{Y}_2)/2]. \quad (22b)$$

The sinusoidal, or cosinusoidal, modulations observed in (22) are a typical feature of diffuse scattering from molecular crystals and can help a great deal in data analysis. If we assume that molecules of a given type do not have a specific sublattice (sub) preference, *i.e.* $x'_i = x'_j = \frac{1}{2}x_i$ and $x'_j = x'_i = \frac{1}{2}x_j$, where x_i and x_j are total fractions of *i*- and *j*-type molecules, the Laue monotonic intensity can be written as

$$I_{\text{LM}} = 4x_i x_j (f_{\text{Br}} - f_{\text{CH}_3})^2 \{ \sin^2[\mathbf{K} \cdot (\mathbf{X}_1 + \mathbf{Y}_1)/2] \times \cos^2[\mathbf{K} \cdot (\mathbf{X}_1 - \mathbf{Y}_1)/2] + \sin^2[\mathbf{K} \cdot (\mathbf{X}_2 + \mathbf{Y}_2)/2] \times \cos^2[\mathbf{K} \cdot (\mathbf{X}_2 - \mathbf{Y}_2)/2] \}. \quad (23)$$

There are two different types of vectors for BEMB2. The first ones are between the pairs sub1-sub1 and sub2-sub2 of the different unit cells and the second ones are between sub1-sub2 of the same or different unit cells. Direct substitution of (22) in (20a) for type 1 vectors yields

$$\bar{\alpha}_{\mu\nu} = 4x_i x_j (f_{\text{Br}} - f_{\text{CH}_3})^2 \{ \sin^2[\mathbf{K} \cdot (\mathbf{X}_1 + \mathbf{Y}_1)/2] \times \cos^2[\mathbf{K} \cdot (\mathbf{X}_1 - \mathbf{Y}_1)/2] + \sin^2[\mathbf{K} \cdot (\mathbf{X}_2 + \mathbf{Y}_2)/2] \times \cos^2[\mathbf{K} \cdot (\mathbf{X}_2 - \mathbf{Y}_2)/2] \} \alpha_{mn}^{AB} \quad (24a)$$

and for type 2 vectors

$$\bar{\alpha}_{\mu\nu} = 8x_i x_j (f_{\text{Br}} - f_{\text{CH}_3})^2 \{ \sin^2[\mathbf{K} \cdot (\mathbf{X}_1 + \mathbf{Y}_1)/2] \times \cos[\mathbf{K} \cdot (\mathbf{X}_1 - \mathbf{Y}_1)/2] \sin[\mathbf{K} \cdot (\mathbf{X}_2 + \mathbf{Y}_2)/2] \times \cos[\mathbf{K} \cdot (\mathbf{X}_2 - \mathbf{Y}_2)/2] \} \alpha_{mn}^{AB}. \quad (24b)$$

It is to be noticed that the coefficients $\bar{\alpha}$ in the present form are strongly \mathbf{K} dependent. Division by I_{LM} removes the \mathbf{K} dependence of only type 1 vectors. This problem arises because of the different molecular orientations in the different sublattices. For this reason the Borie & Sparks (1971) method cannot be directly applied to disordered molecular crystals. If we proceed in the same manner, the coefficients $\bar{\gamma}$ of the size-effect modulation for type 1 vectors can be

written as

$$\begin{aligned} \bar{\gamma}_{\mu\mu}^x = 2\pi \sum_{\mu=1}^2 [F_{\mu\mu}^{AA} \langle U_{\mu\mu}^{AA}(x) \rangle + (F_{\mu\mu}^{AB} + F_{\mu\mu}^{BA}) \langle U_{\mu\mu}^{AB}(x) \rangle \\ + F_{\mu\mu}^{BB} \langle U_{\mu\mu}^{BB}(x) \rangle] \end{aligned} \quad (25a)$$

and for type 2 vectors

$$\begin{aligned} \bar{\gamma}_{\mu\nu}^x = 4\pi [F_{12}^{AA} \langle U_{12}^{AA}(x) \rangle + (F_{12}^{AB} + F_{12}^{BA}) \langle U_{12}^{AB}(x) \rangle \\ + F_{12}^{BB} \langle U_{12}^{BB}(x) \rangle]. \end{aligned} \quad (25b)$$

The explicit forms of various F 's are tabulated in Appendix 2. The γ 's are in general \mathbf{K} dependent and have a very complex form. The point to be noted at this stage is that the ordered part of the molecule, *i.e.* the diethylbenzene nucleus, makes a contribution to the size-effect modulation but does not affect I_{SRO} . Scaling of the γ 's by I_{LM} again does not remove their \mathbf{K} dependence. We next evaluate the coefficients $\bar{\delta}(1)$ and $\bar{\varepsilon}(1)$ involving the mean square and cross products of the displacements respectively. For type 1 vectors

$$\begin{aligned} \bar{\delta}_{\mu\mu}^x(1) = 4\pi^2 \sum_{\mu=1}^2 \{F_{\mu\mu}^{AA} \langle [U_{\mu\mu}^{AA}(x)]^2 \rangle \\ + (F_{\mu\mu}^{AB} + F_{\mu\mu}^{BA}) \langle [U_{\mu\mu}^{AB}(x)]^2 \rangle \\ + F_{\mu\mu}^{BB} \langle [U_{\mu\mu}^{BB}(x)]^2 \rangle\} \end{aligned} \quad (26a)$$

and for type 2 vectors

$$\begin{aligned} \bar{\delta}_{12}^x(1) = 8\pi^2 \{F_{12}^{AA} \langle [U_{12}^{AA}(x)]^2 \rangle \\ + (F_{12}^{AB} + F_{12}^{BA}) \langle [U_{12}^{AB}(x)]^2 \rangle \\ + F_{12}^{BB} \langle [U_{12}^{BB}(x)]^2 \rangle\}. \end{aligned} \quad (26b)$$

The coefficients $\bar{\varepsilon}(1)$ for type 1 vectors can be written as

$$\begin{aligned} \bar{\varepsilon}_{\mu\mu}^x(1) = 8\pi^2 \sum_{\mu=1}^2 [F_{\mu\mu}^{AA} \langle U_{\mu\mu}^{AA}(x) U_{\mu\mu}^{AA}(y) \rangle \\ + (F_{\mu\mu}^{AB} + F_{\mu\mu}^{BA}) \langle U_{\mu\mu}^{AB}(x) U_{\mu\mu}^{AB}(y) \rangle \\ + F_{\mu\mu}^{BB} \langle U_{\mu\mu}^{BB}(x) U_{\mu\mu}^{BB}(y) \rangle] \end{aligned} \quad (27a)$$

and for type 2 vectors

$$\begin{aligned} \bar{\varepsilon}_{12}^x(1) = 16\pi^2 [F_{12}^{AA} \langle U_{12}^{AA}(x) U_{12}^{AA}(y) \rangle \\ + (F_{12}^{AB} + F_{12}^{BA}) \langle U_{12}^{AB}(x) U_{12}^{AB}(y) \rangle \\ + F_{12}^{BB} \langle U_{12}^{BB}(x) U_{12}^{BB}(y) \rangle]. \end{aligned} \quad (27b)$$

At this stage no attempt is made to simplify these relations. We now evaluate the contributions from the libration terms $\delta(2)$ and $\varepsilon(2)$. BEMB2 is not symmetric about the centre of mass (CM) of the molecule. At present we consider librations about three mutually perpendicular axes passing through the CM and concentrate on the positions of the Br atoms. Libration of the molecule about an axis perpendicular to the plane of the molecule moves two Br atoms differently, *i.e.* although the magnitude of

the displacement u is identical for both atoms, its direction is different. Movement about an axis passing through two diethyl groups moves the two Br atoms in opposite directions. A movement about the third axis along the perpendicular bisector of the vector joining Br and CH_3 causes the two Br atoms to move in the same direction by the same amount. For a general libration movement there may not be a well defined relationship between the displacements of the two Br atoms. The same holds true for other atoms of the molecule. However, a pair of atoms symmetric about the CM always move in opposite directions by the same amount. The modified structure factor of the molecule may be written as

$$\begin{aligned} f_{A1} + \Delta f_{A1} = f_{\text{Br}} \{ \exp [i\mathbf{K} \cdot (\mathbf{X}_1 + \Delta\mathbf{X}_1)] \\ + \exp [i\mathbf{K} \cdot (\mathbf{Y}_1 + \Delta\mathbf{Y}_1)] \} \\ + f_{\text{CH}_3} \{ \exp [-i\mathbf{K} \cdot (\mathbf{X}_1 + \Delta\mathbf{X}_1)] \\ + \exp [-i\mathbf{K} \cdot (\mathbf{Y}_1 + \Delta\mathbf{Y}_1)] \} + f_1 + \Delta f_1 \end{aligned} \quad (28)$$

where $\Delta\mathbf{X}_1$ and $\Delta\mathbf{Y}_1$ are the positional changes and Δf_1 is the change in the structure factor of the ordered diethyl nucleus. For small displacements

$$\begin{aligned} \Delta f_{A1} \approx i\mathbf{K} \cdot \Delta\mathbf{X}_1 [f_{\text{Br}} \exp (i\mathbf{K} \cdot \mathbf{X}_1) - f_{\text{CH}_3} \exp (-i\mathbf{K} \cdot \mathbf{X}_1)] \\ + i\mathbf{K} \cdot \Delta\mathbf{Y}_1 [f_{\text{Br}} \exp (i\mathbf{K} \cdot \mathbf{Y}_1) \\ - f_{\text{CH}_3} \exp (-i\mathbf{K} \cdot \mathbf{Y}_1)] + \Delta f_1 \end{aligned} \quad (29)$$

and similarly for Δf_{B1} , Δf_{A2} and Δf_{B2} . Explicit forms of $\delta(2)$ and $\varepsilon(2)$ can then be obtained by substituting (29) in (20d) and (20f) respectively.

2.2. BEMB1

BEMB1 differs from BEMB2 only in the position of the substituents Br and CH_3 . With the same notation as for BEMB2, let the vectors \mathbf{X}_1 and $-\mathbf{X}_1$ represent the position of Br atoms with respect to the centre of mass of the molecule in orientation A located on sublattice 1. \mathbf{Y}_1 and $-\mathbf{Y}_1$ then represent the position vectors of CH_3 . The structure factor of the molecule in the different orientations can then be written as

$$\begin{aligned} f_{A1} = f_{\text{Br}} [\exp (i\mathbf{K} \cdot \mathbf{X}_1) + \exp (-i\mathbf{K} \cdot \mathbf{X}_1)] \\ + f_{\text{CH}_3} [\exp (i\mathbf{K} \cdot \mathbf{Y}_1) + \exp (-i\mathbf{K} \cdot \mathbf{Y}_1)] + f_1 \end{aligned} \quad (30a)$$

$$\begin{aligned} f_{B1} = f_{\text{Br}} [\exp (i\mathbf{K} \cdot \mathbf{Y}_1) + \exp (-i\mathbf{K} \cdot \mathbf{Y}_1)] \\ + f_{\text{CH}_3} [\exp (i\mathbf{K} \cdot \mathbf{X}_1) + \exp (-i\mathbf{K} \cdot \mathbf{X}_1)] + f_1 \end{aligned} \quad (30b)$$

and for sublattice 2

$$\begin{aligned} f_{A2} = f_{\text{Br}} [\exp (i\mathbf{K} \cdot \mathbf{X}_2) + \exp (-i\mathbf{K} \cdot \mathbf{X}_2)] \\ + f_{\text{CH}_3} [\exp (i\mathbf{K} \cdot \mathbf{Y}_2) + \exp (-i\mathbf{K} \cdot \mathbf{Y}_2)] + f_2 \end{aligned} \quad (30c)$$

$$f_{B2} = f_{Br}[\exp(i\mathbf{K} \cdot \mathbf{Y}_2) + \exp(-i\mathbf{K} \cdot \mathbf{Y}_2)] \\ + f_{CH_3}[\exp(i\mathbf{K} \cdot \mathbf{X}_2) + \exp(-i\mathbf{K} \cdot \mathbf{X}_2)] + f_2. \quad (30d)$$

The difference in structure factors can be written as

$$f_{A1} - f_{B1} = 4(f_{Br} - f_{CH_3}) \sin[\mathbf{K} \cdot (\mathbf{X}_1 + \mathbf{Y}_1)/2] \\ \times \sin[\mathbf{K} \cdot (\mathbf{X}_1 - \mathbf{Y}_1)/2] \quad (31a)$$

$$f_{A2} - f_{B2} = 4(f_{Br} - f_{CH_3}) \sin[\mathbf{K} \cdot (\mathbf{X}_2 + \mathbf{Y}_2)/2] \\ \times \sin[\mathbf{K} \cdot (\mathbf{X}_2 - \mathbf{Y}_2)/2]. \quad (31b)$$

Comparing (22) and (31) we observe that in some directions of reciprocal space, I_{SRO} for BEMB1 and BEMB2 will be complementary to each other, one of them being sinusoidal in nature and the other cosinusoidal. The experimental results of Welberry & Siripitayanon (1986, 1987) corroborate this observation. The Laue monotonic intensity for BEMB1 can be written as

$$I_{LM} = 4x_i x_j (f_{Br} - f_{CH_3})^2 \{ \sin^2[\mathbf{K} \cdot (\mathbf{X}_1 + \mathbf{Y}_1)/2] \\ \times \sin^2[\mathbf{K} \cdot (\mathbf{X}_1 - \mathbf{Y}_1)/2] + \sin^2[\mathbf{K} \cdot (\mathbf{X}_2 + \mathbf{Y}_2)/2] \\ \times \sin^2[\mathbf{K} \cdot (\mathbf{X}_2 - \mathbf{Y}_2)/2] \}. \quad (32)$$

As is the case for BEMB2, there are two types of interatomic vectors for BEMB1. Direct substitution of (30) into (20a) yields, for type 1 vectors,

$$\bar{\alpha}_{\mu\mu} = 4x_i x_j (f_{Br} - f_{CH_3})^2 \{ \sin^2[(\mathbf{X}_1 + \mathbf{Y}_1)/2] \\ \times \sin^2[(\mathbf{X}_1 - \mathbf{Y}_1)/2] + \sin^2[(\mathbf{X}_2 + \mathbf{Y}_2)/2] \\ \times \sin^2[(\mathbf{X}_2 - \mathbf{Y}_2)/2] \} \quad (33a)$$

and, for type 2 vectors,

$$\bar{\alpha}_{\mu\nu} = 8x_i x_j (f_{Br} - f_{CH_3})^2 \{ \sin[(\mathbf{X}_1 + \mathbf{Y}_1)/2] \\ \times \sin[(\mathbf{X}_1 - \mathbf{Y}_1)/2] \sin[(\mathbf{X}_2 + \mathbf{Y}_2)/2] \\ \times \sin[(\mathbf{X}_2 - \mathbf{Y}_2)/2] \}. \quad (33b)$$

General expressions for γ , δ and ϵ , as given by (24)–(27), are identical for BEMB1 and BEMB2. However, the general forms of various F 's are different and have been tabulated in Appendix 2. Since BEMB1 is a symmetrical molecule, the contribution from libration has a simpler form for BEMB1 than for BEMB2. The modified structure factor for BEMB1 can be written as

$$f_{A1} + \Delta f_{A1} = f_{Br} \{ \exp[i\mathbf{K} \cdot (\mathbf{X}_1 + \Delta\mathbf{X}_1)] \\ + \exp[-i\mathbf{K} \cdot (\mathbf{X}_1 + \Delta\mathbf{X}_1)] \} \\ + f_{CH_3} \{ \exp[i\mathbf{K} \cdot (\mathbf{Y}_1 + \Delta\mathbf{Y}_1)] \\ + \exp[-i\mathbf{K} \cdot (\mathbf{Y}_1 + \Delta\mathbf{Y}_1)] \} + f_1 + \Delta f_1 \quad (34a)$$

$$\Delta f_{A1} \approx +2i[\mathbf{K} \cdot \Delta\mathbf{X}_1 f_{Br} \sin(\mathbf{K} \cdot \mathbf{X}_1) \\ + \mathbf{K} \cdot \Delta\mathbf{Y}_1 f_{CH_3} \sin(\mathbf{K} \cdot \mathbf{Y}_1)] + \Delta f_1 \quad (34b)$$

and similarly for Δf_{A2} , Δf_{B1} and Δf_{B2} .

3. Separating the various contributions to diffuse scattering

It is obvious from the various expressions developed in the previous sections that the Borie–Sparks method cannot be used directly for analysing diffuse scattering data from molecular crystals. Since the coefficients α , γ , δ and ϵ have a fairly complex \mathbf{K} dependence, summations in (19a) cannot be represented as simple Fourier series. As these coefficients depend strongly on the nature of the molecule, the basic procedure for data analysis may differ from one system to another. Here the examples of BEMB1 and BEMB2 discussed above will be employed. As a first step we assume that the major contribution to the diffuse scattering comes from short-range order and attempt to remove the \mathbf{K} dependence of α in some special regions of reciprocal space. Other coefficients are assumed to be small and to vary slowly with \mathbf{K} . I_{SRO} is then obtained from the observed data by the Borie–Sparks method modified for use with low-symmetry monoclinic crystals. As I_{SRO} vanishes in some regions of reciprocal space owing to the oscillatory nature of the molecular structure factors, the displacement coefficients can be further optimized. This procedure can be repeated several times until a satisfactory fit is obtained.

The main problem in the analysis of diffuse scattering data from BEMB1 and BEMB2 arises from the different molecular orientations in the two sublattices. We first try to separate the contributions to I_{SRO} from the two sublattices. From (22) and (31) we note that the contribution from vectors associated with sub1 will be zero for the following set of \mathbf{K} vectors:

BEMB 2

$$\mathbf{K} \cdot (\mathbf{X}_1 + \mathbf{Y}_1)/2 = n\pi \text{ and } \mathbf{K} \cdot (\mathbf{X}_1 - \mathbf{Y}_1)/2 = (m + \frac{1}{2})\pi, \quad (35)$$

which yields

$$h_1(x_1 + y_1) + h_2(x_2 + y_2) + h_3(x_3 + y_3) = n, \quad (36a)$$

$$h_1(x_1 - y_1) + h_2(x_2 - y_2) + h_3(x_3 - y_3) = (m + \frac{1}{2}), \quad (36b)$$

where n and m are integers;

BEMB 1

$$\mathbf{K} \cdot (\mathbf{X}_1 + \mathbf{Y}_1)/2 = n\pi \text{ and } \mathbf{K} \cdot (\mathbf{X}_1 - \mathbf{Y}_1)/2 = m\pi, \quad (37)$$

which yields

$$h_1(x_1 + y_1) + h_2(x_2 + y_2) + h_3(x_3 + y_3) = n, \quad (38a)$$

$$h_1(x_1 - y_1) + h_2(x_2 - y_2) + h_3(x_3 - y_3) = m. \quad (38b)$$

The contribution to I_{SRO} from vectors associated with sub2 vanishes for the following set of \mathbf{K} vectors:

BEMB 2

$$\mathbf{K} \cdot (\mathbf{X}_2 + \mathbf{Y}_2)/2 = n\pi \text{ and } \mathbf{K} \cdot (\mathbf{X}_2 - \mathbf{Y}_2)/2 = (m + \frac{1}{2})\pi, \quad (39)$$

which yields

$$h_1(x_1 + y_1) - h_2(x_2 + y_2) + h_3(x_3 + y_3) = n, \quad (40a)$$

$$h_1(x_1 - y_1) - h_2(x_2 - y_2) + h_3(x_3 - y_3) = m + \frac{1}{2}; \quad (40b)$$

BEMB 1

$$\mathbf{K} \cdot (\mathbf{X}_2 + \mathbf{Y}_2)/2 = n\pi \text{ and } \mathbf{K} \cdot (\mathbf{X}_2 - \mathbf{Y}_2)/2 = m\pi, \quad (41)$$

which yields

$$h_1(x_1 + y_1) - h_2(x_2 + y_2) + h_3(x_3 + y_3) = n, \quad (42a)$$

$$h_1(x_1 - y_1) - h_2(x_2 - y_2) + h_3(x_3 - y_3) = m. \quad (42b)$$

For the set of vectors represented by (36) and (38), for BEMB2 and BEMB1 respectively, I_{SRO} will have a contribution only from intermolecular vectors belonging to sub2-sub2. If the observed data at these points are scaled by a portion of I_{LM} arising from sub2-sub2 vectors, the coefficients $\bar{\alpha}$ thus obtained will be \mathbf{K} independent.

Owing to the low symmetry of monoclinic BEMB1 and BEMB2, it is not possible to simplify greatly the general expression for I_D [(19)], thus necessitating measurement of the diffuse scattering in extensive regions of reciprocal space. I_D , the total diffuse intensity, may be written as

$$\begin{aligned} I_D(h_1, h_2, h_3) = & I_{\text{SRO}}(h_1, h_2, h_3) + h_1 Q_x(h_1, h_2, h_3) \\ & + h_2 Q_y(h_1, h_2, h_3) + h_3 Q_z(h_1, h_2, h_3) \\ & + h_1^2 R_x(h_1, h_2, h_3) \\ & + h_2^2 R_y(h_1, h_2, h_3) \\ & + h_3^2 R_z(h_1, h_2, h_3) \\ & + h_1 h_2 S_{xy}(h_1, h_2, h_3) \\ & + h_2 h_3 S_{yz}(h_1, h_2, h_3) \\ & + h_3 h_1 S_{zx}(h_1, h_2, h_3). \end{aligned} \quad (43)$$

The validity of (43) is not just restricted to the special region of reciprocal space being discussed above, but is true over all reciprocal space. From symmetry considerations, the phase factors $S_{\mu\nu} A_{mn}$ can be considerably simplified in summations (19b)-(19e). At this stage, *i.e.* for the special regions of reciprocal space, it is permissible to replace the sum over μ, ν, m and n by N times a single sum over the intermolecular vector $la_1 + ma_2 + na_3$, giving

$$I_{\text{SRO}}(h_1, h_2, h_3) = \sum_{l,m,n} \bar{\alpha}'_{lmn} \cos 2\pi(h_1 l + h_2 m + h_3 n) \quad (44a)$$

$$Q_x(h_1, h_2, h_3) = - \sum_{l,m,n} \bar{\gamma}'_{lmn} \sin 2\pi(h_1 l + h_2 m + h_3 n) \quad (44b)$$

$$R_x(h_1, h_2, h_3) = \sum_{l,m,n} \bar{\delta}'_{lmn} \cos 2\pi(h_1 l + h_2 m + h_3 n) \quad (44c)$$

$$S_{xy}(h_1, h_2, h_3) = \sum_{l,m,n} \bar{\epsilon}'_{lmn} \cos 2\pi(h_1 l + h_2 m + h_3 n). \quad (44d)$$

The primed coefficients in these Fourier series are the coefficients in (19) scaled by I_{LM} from sub2-sub2 vectors.

The series in (44) have a periodicity of one. However, only a limited number of \mathbf{K} vectors permitted by (36) and (38) can be used in data analysis. The real periodicity will be governed by the magnitudes of \mathbf{X}_1 and \mathbf{Y}_1 . Let m_1, m_2 and m_3 represent the basic periodicities along the three reciprocal-lattice directions

$$\begin{aligned} m_1 &= n_1/h_1(x_1 + y_1), \quad m_2 = n_2/h_2(x_2 + y_2), \\ m_3 &= n_3/h_3(x_3 + y_3). \end{aligned} \quad (45)$$

n_1, n_2 and n_3 are the smallest integers for which the right-hand side of (45) approaches an integer. The various terms in (43) can then be separated as follows:

$$\begin{aligned} R_x(h_1, h_2, h_3) = & [I_D(h_1 + m_1, h_2, h_3) \\ & - 2I_D(h_1, h_2, h_3) \\ & + I_D(h_1 - m_1, h_2, h_3)]/2m_1^2 \end{aligned} \quad (46a)$$

$$\begin{aligned} S_{xy}(h_1, h_2, h_3) = & [I_D(h_1, h_2, h_3) - I_D(h_1 - m_1, h_2, h_3) \\ & - I_D(h_1, h_2 - m_2, h_3) \\ & + I_D(h_1 - m_1, h_2 - m_2, h_3)]/m_1 m_2 \end{aligned} \quad (46b)$$

$$\begin{aligned} Q_x(h_1, h_2, h_3) = & [I_D(h_1, h_2, h_3) - I_D(h_1, h_2 - m_2, h_3) \\ & - (2m_1 - m_1^2) R_x(h_1, h_2, h_3) \\ & - m_2 h_2 S_{xy}(h_1, h_2, h_3) \\ & - m_3 h_3 S_{xz}(h_1, h_2, h_3)]/m_1 \end{aligned} \quad (46c)$$

and similarly for the other terms. Once Q, R and S are known, I_{SRO} can be obtained from (43) and the coefficients α due to sub2-sub2 vectors can then be evaluated. The coefficients α due to sub1-sub2 vectors are expected to be identical to the coefficients due to sub2-sub2 vectors. The contribution to I_{SRO} from type 1 vectors (sub1-sub1; sub2-sub2) can then be calculated over all reciprocal space from (10) and deducted from the observed diffuse scattering data. The remaining data contain the contribution to I_{SRO} from sub1-sub2 vectors and displacement scattering. These data are then scaled by I_{LM} due to sub1-sub2 vectors and the various terms separated by the procedure outlined above. This basic periodicity will now be one as there are no specific restrictions on \mathbf{K} vectors.

4. Concluding remarks

General equations for diffuse scattering from disordered molecular crystals and a data-analysis scheme for separating its various components have

been presented. The separation of components is severely handicapped by the presence of different molecular orientations in the different sublattices. The assumption of treating the various displacement coefficients (γ , δ and ϵ) as \mathbf{K} independent could be a major source of error in the processed data. However, this error can be evaluated and rectified to some extent by making measurements at two different temperatures. Terms higher than quadratic in \mathbf{K} have also been neglected in the present treatment and may be an additional source of error.

Unlike the case of alloys, the concept of the minimum-volume cell is not particularly useful for molecular crystals. These crystals in general have low symmetry and the diffuse-scattering data need to be measured in extended regions of reciprocal space. Owing to the complexity of the equations involved, no attempt is made at this stage to separate the contributions due to displacements and librations. The effect of the various terms will be further evaluated for some special cases through computer simulation and optical-diffraction experiments.

APPENDIX 1

Let f_n be the atomic scattering factor of an atom n of the molecule and \mathbf{r}_n be its position vector with respect to the centre of mass of the molecule. Let \mathbf{u}_n represent the displacement of atom n due to librations. The change in structure factor of the molecule can then be written as

$$\begin{aligned}\Delta f &= \sum_n f_n \exp [i\mathbf{K} \cdot (\mathbf{r}_n + \mathbf{u}_n)] - \sum_n f_n \exp (i\mathbf{K} \cdot \mathbf{r}_n) \\ &= \sum_n f_n \exp (i\mathbf{K} \cdot \mathbf{r}_n) [\exp (i\mathbf{K} \cdot \mathbf{u}_n) - 1] \\ &\approx i \sum_n (\mathbf{K} \cdot \mathbf{u}_n) f_n \exp (i\mathbf{K} \cdot \mathbf{r}_n)\end{aligned}$$

for small displacements. Substitution of Δf into (17) results in a K^2 -dependent contribution from molecular librations.

APPENDIX 2

The general expression for $f_{i\mu} f_{j\nu}^*$ of BEMB2 is given below.

$$\begin{aligned}f_{i\mu} f_{j\nu}^* &= 4(f_{\text{Br}} + f_{\text{CH}_3})^2 \cos [\mathbf{K} \cdot (\mathbf{X}_1 + \mathbf{Y}_1)/2] \\ &\quad \times \cos [\mathbf{K} \cdot (\mathbf{X}_1 - \mathbf{Y}_1)/2] \cos [\mathbf{K} \cdot (\mathbf{X}_2 + \mathbf{Y}_2)/2] \\ &\quad \times \cos [\mathbf{K} \cdot (\mathbf{X}_2 - \mathbf{Y}_2)/2] \\ &\quad + 4(f_{\text{Br}} - f_{\text{CH}_3})^2 \sin [\mathbf{K} \cdot (\mathbf{X}_1 + \mathbf{Y}_1)/2] \\ &\quad \times \cos [\mathbf{K} \cdot (\mathbf{X}_1 - \mathbf{Y}_1)/2] \sin [\mathbf{K} \cdot (\mathbf{X}_2 + \mathbf{Y}_2)/2] \\ &\quad \times \cos [\mathbf{K} \cdot (\mathbf{X}_2 - \mathbf{Y}_2)/2] \\ &\quad + 4i(f_{\text{Br}}^2 - f_{\text{CH}_3}^2) \cos [\mathbf{K} \cdot (\mathbf{X}_1 - \mathbf{Y}_1)/2]\end{aligned}$$

$$\begin{aligned}&\quad \times \cos [\mathbf{K} \cdot (\mathbf{X}_2 - \mathbf{Y}_2)/2] \\ &\quad \times \{\sin [\mathbf{K} \cdot (\mathbf{X}_1 + \mathbf{Y}_1)/2] \cos [\mathbf{K} \cdot (\mathbf{X}_2 + \mathbf{Y}_2)/2] \\ &\quad - R_{\mu\nu} \sin [\mathbf{K} \cdot (\mathbf{X}_2 + \mathbf{Y}_2)/2] \\ &\quad \times \cos [\mathbf{K} \cdot (\mathbf{X}_1 + \mathbf{Y}_1)/2]\} \\ &\quad + 2(f_{\text{Br}} + f_{\text{CH}_3}) \{f_{\mu} \cos [\mathbf{K} \cdot (\mathbf{X}_2 + \mathbf{Y}_2)/2] \\ &\quad \times \cos [\mathbf{K} \cdot (\mathbf{X}_2 - \mathbf{Y}_2)/2] \\ &\quad + f_{\nu}^* \cos [\mathbf{K} \cdot (\mathbf{X}_1 + \mathbf{Y}_1)/2] \\ &\quad \times \cos [\mathbf{K} \cdot (\mathbf{X}_1 - \mathbf{Y}_1)/2]\} \\ &\quad - 2iR'_{ij}(f_{\text{Br}} + f_{\text{CH}_3}) \{f_{\mu} \sin [\mathbf{K} \cdot (\mathbf{X}_2 + \mathbf{Y}_2)/2] \\ &\quad \times \cos [\mathbf{K} \cdot (\mathbf{X}_2 - \mathbf{Y}_2)/2] \\ &\quad + f_{\nu}^* \sin [\mathbf{K} \cdot (\mathbf{X}_1 + \mathbf{Y}_1)/2] \\ &\quad \times \cos [\mathbf{K} \cdot (\mathbf{X}_1 - \mathbf{Y}_1)/2]\} + f_{\mu} f_{\nu}^*\end{aligned}$$

where

$$\begin{aligned}R_{\mu\nu} &= 1 \text{ when } \mu = \nu \\ &= -1 \text{ otherwise}\end{aligned}$$

and

$$\begin{aligned}R'_{ij} &= +1 \text{ for } i = j = A \\ &= -1 \text{ otherwise.}\end{aligned}$$

The expression for $f_{i1} f_{j1}^*$ can be obtained from $f_{i\mu} f_{j\nu}^*$ by changing \mathbf{X}_2 to \mathbf{X}_1 and \mathbf{Y}_2 to \mathbf{Y}_1 and the other way round for $f_{i2} f_{j2}^*$. The coefficients F can then be calculated from (13).

For BEMB1, $f_{i\mu} f_{j\nu}^*$ ($i \neq j$) can be written as

$$\begin{aligned}f_{i\mu} f_{j\nu}^* &= 4[f_{\text{Br}} \cos (\mathbf{K} \cdot \mathbf{Y}_1) + f_{\text{CH}_3} \cos (\mathbf{K} \cdot \mathbf{X}_1)] \\ &\quad \times [f_{\text{Br}} \cos (\mathbf{K} \cdot \mathbf{X}_2) + f_{\text{CH}_3} \cos (\mathbf{K} \cdot \mathbf{Y}_2)] \\ &\quad + 2f_{\mu} [f_{\text{Br}} \cos (\mathbf{K} \cdot \mathbf{X}_2) + f_{\text{CH}_3} \cos (\mathbf{K} \cdot \mathbf{Y}_2)] \\ &\quad + 2f_{\nu}^* [f_{\text{Br}} \cos (\mathbf{K} \cdot \mathbf{Y}_1) + f_{\text{CH}_3} \cos (\mathbf{K} \cdot \mathbf{X}_1)] \\ &\quad + f_{\mu} f_{\nu}^*.\end{aligned}$$

The expression for $f_{i1} f_{j1}^*$ ($i \neq j$) can be obtained by changing \mathbf{X}_2 to \mathbf{X}_1 and \mathbf{Y}_2 to \mathbf{Y}_1 and $f_{i1} f_{i1}^*$ by changing \mathbf{X}_2 to \mathbf{Y}_1 and \mathbf{Y}_2 to \mathbf{X}_1 ; and similarly for $f_{i2} f_{j2}^*$. Note that the expressions for BEMB1 and BEMB2 are completely different.

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Refinement of the Orientational Distribution Function in Plastic *n*-Butane Guided by Computer Simulations

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Abstract

Neutron powder diffraction data for the plastic crystalline phase of *n*-butane are refined with a model suggested from molecular dynamics (MD) computer simulation work. A small decrease in the *R* factor is achieved, corresponding to a reduction of the discrepancy between fit and experiment of about 30%. This supports the MD result that the orientational distribution function (ODF) describing the disorder is an asymmetric sum of four angular Gaussian distributions, one of which is dominant. The orientational disorder is uniaxial about the axis between the end C atoms of a molecule. Refinement of the four-Gaussian function is stable, and results in a distribution closely related to that obtained from the MD work. It is suggested that the ODF is temperature dependent, and that this dependence could be found by a further series of high-quality experiments.

Introduction

Although *n*-butane (CH₃CH₂CH₂CH₃) is a very simple well known molecule, its crystal structures were not successfully studied until recently. Our analysis of neutron powder diffraction data obtained with perdeuterobutane yielded the structures of three phases (Refson & Pawley, 1986; paper I). The phase below the melt, phase I, is a plastic crystal phase showing orientational disorder about a unique axis, and it is this phase which is now the subject of further analysis. The other phases which occur on cooling

are a metastable phase II followed by a stable truly crystalline structure, phase III, which persists to very low temperatures.

A considerable body of information from model calculations has been built up since the work of paper I concerning the possible nature of the disorder in the plastic phase. The aim of the present work is to examine whether there is any experimental evidence to confirm the results from the model, and whether there is enough information in the experimental results to justify further structure refinements guided by the model.

Our work on *n*-butane started with computer simulations of the condensed phases using molecular dynamics (MD). The MD model consisted of 2048 molecules in a volume with periodic boundary conditions, each molecule interacting with its neighbours through atom–atom potentials between all its C and D atoms. Three torsional internal degrees of freedom were included, though it was found later that the two methyl-group torsions had no effect on the cooperative dynamics and could have been omitted. Simulations were performed before any of the true structures were determined in the hope that the structures found by MD would be as in nature and thus of great help in the crystallographic determination (Refson & Pawley, 1987*a*; paper II).

The model predicted three phases as found in nature, but with incorrect structures. Consequently the determination of the natural structures and their refinements, paper I, was done without the aid of MD simulations. The structures so found have since been used as the start for further simulations which have proved the model to be good (Refson & Pawley, 1987*b*; paper III). The results from the simulation

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