

The value of the χ^2 summation may be calculated from the expression

$$\chi^2 = C^2 a_{11} + 2CSa_{12} + S^2 a_{22} - 2Cv_1 - 2Sv_2 + v_3, \quad (A17)$$

where

$$v_3 = \sum_{i=1}^n w_i R_i^2. \quad (A18)$$

The correlation coefficient between C and S is

$$r(C, S) = b_{12}/(b_{11} b_{22})^{1/2}. \quad (A19)$$

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Use of a Statistical Distribution of Electron Density to Describe the Bragg Scattering from a Linearly Disordered Crystal

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Abstract

The modulated non-zero electron density distribution that results from linear disorder of iodine chains in systems of stacked planar organic molecules or metallomacrocycles partially oxidized by iodine is modeled by an integrable statistical distribution function. The contributions to the Bragg scattering of the iodine disorder are fit in an excellent manner with the use of at most two extra variables.

Introduction

Several highly conducting one-dimensional systems have been prepared by partial oxidation with iodine of planar organic molecules or metallomacrocycles (for a review see Hoffman, Martinsen, Pace & Ibers, 1982). These systems typically contain stacks of the oxidized species surrounded by linear chains of polyiodide anions that are disordered. The form of the iodine (e.g. I_2 , I_3^- , I_5^-) can be elucidated spectroscopically either by resonance Raman or Mössbauer methods (Marks,

1978), and in several cases structural information on the iodine species has been obtained by analysis of the diffuse X-ray scattering that results from the disorder (Endres, Keller, Mégnamisi-Bélombé, Moroni, Pritzkow, Weiss & Comès, 1976; Scaringe & Ibers, 1979; Schramm, Scaringe, Stojakovic, Hoffman, Ibers & Marks, 1980). Here, for several systems containing I_3^- we shall consider the effect of this disorder on the Bragg scattering.

In the systems Ni(Pc)I* (Schramm *et al.*, 1980), Ni(tbp)I (Martinsen, Pace, Phillips, Hoffman & Ibers, 1982) and $M(\text{bqd})_2I_{0.5}$ (Endres, Keller & Weiss, 1975; Brown, Kalina, McClure, Schultz, Ruby, Ibers, Kannewurf & Marks, 1979) the disorder of the I_3^- anions is not severe, perhaps because the spacing between macrocycles in the stack is short, less than 3.24 Å. All of the diffuse X-ray lines in these systems can be indexed on the basis of a superlattice spacing that is

* Abbreviations used: bqd, 1,2-benzoquinonedioximate; Pc, phthalocyaninate; tbp, tetrabenzporphyrinate; omtbp, 1,4,5,8,9,12-13,16-octamethyltetrabenzporphyrinate; tmp, 5,10,15,20-tetramethylporphyrinate; ϕ_4 DTP, tetraphenyldithiopyranilidene; TTT, tetrathiatetracene.

commensurate with the Bragg lattice and it is possible to describe the Bragg scattering from the iodine in the usual manner. The only structural manifestation of the disorder is an increase in the thermal parameter of iodine along the chain direction.

On the other hand, for the systems $\text{Ni(omtpb)}\text{I}_{1.08}$ (Phillips, Scaringe, Hoffman & Ibers, 1980) and $\text{Ni(tmp)}\text{I}$ (Pace, Martinsen, Ulman, Hoffman & Ibers, 1982), where the spacings between macrocycles in the stack are 3.78 and 3.47 Å, respectively, the diffuse X-ray lines are broad and irregular, indicative of short-range order only (Scaringe & Ibers, 1979). The disruption of the long-range order in the triiodide chains occurs because the macrocycles cause constrictions in the iodine channel that partially inhibit the iodine atoms from occupying an incommensurate superlattice and force some of them to occupy the commensurate (Bragg) lattice. The contribution of both the commensurate and incommensurate iodine atoms to the Bragg scattering results in maxima in electron density halfway between macrocycle positions while electron density adjacent to the macrocycle is lower, but much greater than zero. For disorder that is this severe it is not possible to use the usual thermal model to describe the Bragg scattering from the iodine scatterers. But if the metrical details of the macrocycles are to be derived from the Bragg scattering it is essential that the iodine scattering be handled in some effective manner.

An approach that was used for the iodine-oxidized organic conductors $(\varphi_4\text{DTP})\text{I}_x$, $x = 2.15, 3.09$ (Luss & Smith, 1980) and $(\text{TTT})_2\text{I}_3$ (Smith & Luss, 1977) involves the refinement of many partially occupied iodine positions to describe the iodine that is incommensurate with the organic sublattice, along with a fraction of iodine that is commensurate with the organic sublattice. However, this method requires many variables, and it is doubtful whether physical significance can be attached to the results. A more facile approach that requires fewer variables to describe the disordered iodine atoms is discussed here.

Results

The approach we have taken is to describe the electron density from the disordered iodine chains by a statistical distribution $\rho(z)$, where

$$\rho(z) = \alpha_1 f(z) + \alpha_2. \quad (1)$$

Here $f(z)$ is an integrable function chosen by trial and error to provide a good fit to the observed distribution of electron density.

With the electron density along z defined in this way, the structure factor takes the following form:

$$F(hkl) = \Omega f_1 T \exp[-2\pi i(hx + ky)] \int_{\epsilon_2}^{\epsilon_1} \rho(z) \{ \cos(2\pi lz) - i \sin(2\pi lz) \} dz, \quad (2)$$

where f_1 is the atomic scattering factor for iodine, T is the usual isotropic thermal term $\exp(-B\lambda^{-2} \sin^2 \theta)$, Ω is the occupancy factor, and the limits ϵ_1 and ϵ_2 depend upon the space-group symmetry. In this description, in addition to the usual occupancy parameter Ω that describes the iodine-to-macrocycle ratio, it is convenient to introduce two additional variables, α_1 and α_2 ; only the ratio of these variables is independent. The two physically interpretable variables, Ω and α_2/α_1 , are refined simultaneously with the usual structural parameters that describe the macrocyclic moieties. This method has been utilized successfully for both the systems $\text{Ni(omtpb)}\text{I}_{1.08}$ (Phillips *et al.*, 1980) and $\text{Ni(tmp)}\text{I}$ (Pace *et al.*, 1982), and these will be discussed separately.

$\text{Ni(omtpb)}\text{I}_{1.08}$

The iodine atoms are disordered along $\frac{1}{4}, \frac{1}{4}, z$ in space group $D_{4h}^{11}-P4_2/nbc$ and display maxima of electron density at $z = 0$ and $z = \frac{1}{2}$. Because of the $\frac{1}{4}, \frac{1}{4}, z$ $[8(f)]$ special position, the statistical distribution will contribute only to the $h + k = 2n, l = 2n$ reflections. The first distribution tested was triangle shaped and takes the form

$$\rho(z) = \left(\frac{4\Omega}{\alpha_1 + 2\alpha_2} \right) [\alpha_1(1 - 4z) + \alpha_2] \quad \text{for } 0 \leq z \leq \frac{1}{4}. \quad (3)$$

The contribution of the triangular distribution centered at $\frac{1}{4}, \frac{1}{4}, 0$ to the structure factor is then

$$F(hkl) = 4\Omega f_1 T \cos \frac{\pi}{2} (h + k) \quad \text{for } l = 0$$

$$F(hkl) = \frac{32\Omega f_1 T \cos \frac{\pi}{2} (h + k)}{\pi^2 l^2 (1 + 2\alpha_2/\alpha_1)} \quad (4)$$

for $l = 2n \neq 4n \neq 0$

$$F(hkl) = 0 \quad \text{for all other reflections}$$

where the ratio $\text{Ni(omtpb)}:\text{I}$ is $1:\Omega$.

The second distribution tested was cosine shaped and of the form

$$\rho(z) = \left(\frac{2\Omega}{2\alpha_1/\pi + \alpha_2} \right) [\alpha_1 \cos(2\pi z) + \alpha_2]. \quad (5)$$

The contribution of this distribution (centered at $\frac{1}{4}, \frac{1}{4}, 0$) to the structure factor is

$$F(hkl) = 4\Omega f_1 T \cos \frac{\pi}{2} (h + k) \quad \text{for } l = 0$$

$$F(hkl) = \frac{(-1)^l 4\Omega f_1 T \cos \frac{\pi}{2} (h + k)}{(1 - l^2)(2 + \pi\alpha_2/\alpha_1)} \quad \text{for } l = 2n \neq 0 \quad (6)$$

$$F(hkl) = 0 \quad \text{for all other reflections.}$$

The fit of either the cosine or the triangular distribution to the experimental data is satisfactory (Fig. 1), and the structural parameters of the Ni(omtbp) molecule are insensitive to the iodine model used. However, a better agreement index resulted from refinement of the cosine distribution ($R = 0.050$) than from the triangular distribution ($R = 0.059$), and so the former was used to complete the structural determination. A value of $\Omega = 1.08$, in good agreement with results from elemental analysis, was derived from the $hk0$ reflections, reflections unaffected by the disorder of the iodine chains. Before introduction of the distribution function the R index for the $l \neq 0$ reflections was 0.14; after addition and refinement of the distribution it was 0.050. The corresponding reduction in estimated standard deviations of conventional parameters, and hence the increase in the precision of the structure, was equally dramatic.

Ni(tmp)I

The iodine disorder is along $\frac{1}{4}, \frac{1}{4}, z$ in space group $D_{4h}^{19}P4/nnc$, with two different maxima of electron

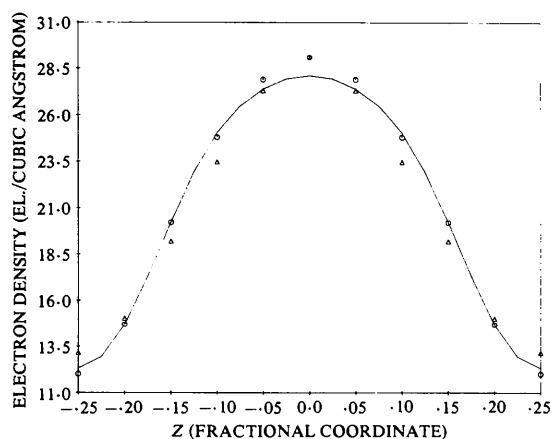


Fig. 1. A plot of observed (—) vs calculated ($\Delta =$ triangle, $\circ =$ cosine) electron density along the line $\frac{1}{4}, \frac{1}{4}, z$ for Ni(omtbp)I_{1.08}.

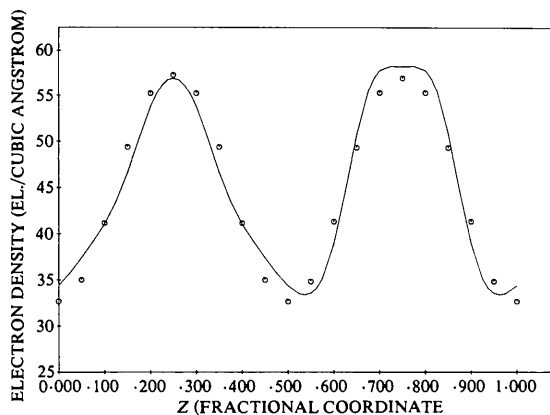


Fig. 2. A plot of observed (—) vs calculated ($\circ =$ sine-squared) electron density along the line $\frac{1}{4}, \frac{1}{4}, z$ for Ni(tmp)I.

density, one at $z = \frac{1}{4}$ and one at $z = \frac{3}{4}$ [special positions 2(a) and 2(b), respectively]. Atoms along the iodine channel, $\frac{1}{4}, \frac{1}{4}, z$ [special position 4(e)], contribute only to the $h + k + l = 2n$ reflections. Severe correlation problems made it impossible to refine independently two different distributions centered at $z = \frac{1}{4}$ and $z = \frac{3}{4}$, so the two distributions were constrained to be identical. As a result the contribution to the structure factor for $h + k = 2n + 1, l = 2n + 1$ reflections of an iodine atom at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ is equal in magnitude but opposite in sign to the contribution of an iodine atom at $\frac{1}{4}, \frac{1}{4}, \frac{3}{4}$, and we need to consider only the $h + k = 2n, l = 2n$ reflections.

A satisfactory fit to the observed electron density for Ni(tmp)I was achieved with a sine-squared distribution (Fig. 2) of the form

$$\rho(z) = \left(\frac{4\Omega}{\alpha_1 + 2\alpha_2} \right) [\alpha_1 \sin^2(2\pi z) + \alpha_2]. \quad (7)$$

The contribution of this distribution to the structure factor is

$$F(hkl) = 2\Omega f_1 T \cos \frac{\pi}{2} (h+k) \quad \text{for } l=0$$

$$- \Omega f_1 T \cos \frac{\pi}{2} (h+k)$$

$$F(hkl) = \frac{\quad}{1 + 2\alpha_2/\alpha_1} \quad \text{for } l=2 \quad (8)$$

$$F(hkl) = 0 \quad \text{for all other reflections.}$$

A value of $\Omega = 1.11$, derived from the refinement, is larger than that of 0.99, derived from chemical analysis of the bulk material, possibly because we were unable to refine independently the two different distributions at $z = \frac{1}{4}$ and $z = \frac{3}{4}$. But again the efficacy of the method is apparent: the R index for the $l \neq 0$ reflections was 0.20 before introduction of the distribution and 0.047 afterwards.

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Analysis of the Diffuse X-ray Scattering from Substitutionally Disordered Molecular Crystals: Monoclinic 9-Bromo-10-methylanthracene

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Abstract

Model calculations of random and correlation distributions of diffuse X-ray scattering are used to determine the correlations between molecular sites of a substitutionally disordered molecular crystal. The correlation coefficients are varied until qualitative agreement is obtained between the calculated diffuse scattering and that measured using Weissenberg film techniques. This procedure was used to determine the correlation coefficients of the monoclinic form of 9-bromo-10-methylanthracene, $C_{15}H_{11}Br$. The four nearest-neighbour correlations were found to be $a = 0.4$ (0.1), $b = 0.20$ (0.05), $c = 0.0$ (0.05) and $d = 0.05$ (0.03), respectively. These values imply that the probability of bromine–methyl contacts between neighbouring molecules is greater than that for a random distribution of molecules and that the probabilities of bromine–bromine and methyl–methyl contacts are smaller than for the random distribution.

Introduction

The diffuse intensities of X-rays which are scattered by a disordered molecular crystal contain information about the correlations between the displacements of pairs of nuclei and, in the case of substitutional disorder, information about the pair distribution function of the crystal (Guinier, 1963; Amorós & Amorós, 1968; De Ridder, 1978; Fouret, 1979).

The monoclinic form of 9-bromo-10-methylanthracene is one example of a class of substituted anthracene crystals which is substitutionally disordered. The orthorhombic form is also disordered and is the subject of a separate study (Welberry, Jones & Epstein, 1982). Each site of the crystal may be occupied by one of two types of molecule, labelled *A* and *B*, respectively. *A* and *B* differ only in the positions of the bromine and methyl substituents and, in effect, represent two orientations of the same molecule, related by a twofold rotation about the long axis of the anthracene frame. Within the resolution of the measured Bragg diffraction data, the anthracene frame is ordered, but the bromine and methyl substituents at the 9- and 10-positions are disordered. For the monoclinic form 64.3% of the sites are occupied by molecules of type *A*, with the Br substituent at the 9-position, and 35.7% of the sites are occupied by molecules of type *B*, with the CH_3 substituent at the 9-position (Jones & Welberry, 1980). The average crystal structure has space group $P2_1/c$ with four molecules per unit cell.

From the diffuse intensities of X-rays scattered by such a disordered crystal the *A–A*, *A–B*, *B–A* and *B–B* pair distribution functions may be obtained. As the degree of substitutional disorder in the crystalline phase is independent of temperature (*i.e.* no exchange occurs between molecules of different types), these pair distributions reflect the intermolecular interactions which have occurred during crystal growth.

A preliminary analysis of the diffuse intensities in the