A computer-simulation study of the 'white-line effect' in diffraction patterns of mixed charge-transfer salts. By T. R. Welberry and N. J. Fox, Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

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Abstract

Computer simulations have been carried out to test the theory of the origin of the 'white-line effect' in diffraction patterns of some mixed charge-transfer salts put forward by Ravy, Pouget & Comès (1992) [J. Phys. I France, 2, 1173-1190]. The diffraction patterns shown confirm that the pinning of charge-density waves to defects is responsible for the effect. The magnitudes of the atomic displacements, which were assumed to be small in development of the theory, are shown to be crucial for the effect to be observed. For displacements of ~0.008 Å, the phenomena are clearly visible, but for magnitudes of only ~0.08 Å they become masked by higher-order diffraction effects.

Introduction

A characteristic feature of the diffraction patterns of one-dimensional conductors such as the charge-transfer salts of the TTF-TCNQ family is the presence of diffuse planes of scattering that occur, normal to the one-dimensional conducting direction, at wave vectors \( q = \pm 2k_F \) from the layers of Bragg reflections (see e.g. Comès, 1982). These planes, which appear as lines on diffraction patterns, can be directly attributed to a Peierls distortion that occurs in one-dimensional metal (Peierls, 1955; see also Kittel, 1976). In a recent paper, Ravy et al. (1992) described a distinctive variation of this X-ray scattering effect that they observed in the diffraction patterns of crystals of some mixed charge-transfer salts, \((TTF)_x(TSF)_{1-x}TCNQ\) and \((HMTTF)_x(HMTSF)_{1-x}TCNQ\,*\) where selenium- and sulfur-based donor molecules are alloyed (Pouget, Ravy & Henion, 1991; Ravy et al., 1992). In these mixed crystals, broad regions of scattering due to substitutional disorder overlay the regions where the \( \pm 2k_F \) lines should be. On close inspection, however, the diffuse lines are still visible but there is a marked asymmetry between the \(+2k_F\) and \(-2k_F\) lines. Now, at \(+2k_F\), the lines have an intensity minimum visible at the expense of the diffuse background (giving the appearance of a 'white line') and at \(-2k_F\) an intensity maximum. The explanation for this effect is that the white \(+2k_F\) lines originate from a subtraction of a diffuse intensity term, due to lattice fluctuations in the electron gas, from the so-called Laue 'monotonic' scattering due to the HMTTF/HMTSF disorder, while the dark \(-2k_F\) lines originate from an addition. Such negative and positive interferences were demonstrated to result from phase coherence between the positions of the impurities and the lattice distortions. That is, the charge-density waves are pinned to the defect molecules.

In the theoretical treatment given, atomic displacements were, however, assumed to be sufficiently small that a number of simplifying approximations could be made. While the origins of the white-line effect were convincingly demonstrated, the range of applicability of the approximation and the resulting effects when the approximations break down were not explored.

A second reason for our interest in the white-line effect is that it is clearly closely related to the so-called 'atomic size effect', an understanding of which played an important rôle in our recent studies of cubic stabilized zirconias (Butler, Withers & Welberry, 1992; Welberry, Butler, Thompson & Withers, 1993). In this work, rather similar white lines were observed (in fact, in our work we have invariably used positive prints of X-ray patterns, so that regions of low intensity were black and such lines were therefore termed 'dark lines'). As for the present case, the effect was found to be due to the coupling of atomic displacement patterns to the occupancies of particular sites.

Simulations

For our computer simulations, a square array of \( 512 \times 512 \) lattice sites was used. On these sites, two types of atom, \( A \) (10%) and \( B \) (90%) were distributed at random. The positions...
of all the atoms were represented as departures from the ideal lattice positions by displacement variables \(X(n, m)\) and \(Y(n, m)\), which were initially all set to zero. Then, periodic perturbations were applied to the variables in the form

\[
Y(n, m + l) = Y(n, m + l) + K \exp \left(-|l|/\xi \right) \times \sin \left(2\pi l q' + \phi \right)
\]

for longitudinal waves and

\[
X(n, m + l) = X(n, m + l) + K \exp \left(-|l|/\xi \right) \times \sin \left(2\pi l q' + \phi \right)
\]

for transverse waves. Perturbations were applied for every site, \((m, n)\), that contained a defect \((A)\) atom, and over values of \(l\) extending from \(-60\) to \(60\). Here, the exponential factor provides a range of coherence for each modulation dependent on the parameter \(\xi\). This had a value of 10.5 for the examples shown below in Fig. 1. \(q'\) is the modulation wave vector, which was chosen arbitrarily to be 0.204, \(\phi\) is the phase of the modulation at the pinning defect and \(K\) is an amplitude. After summation of the contributions to \(X\) or \(Y\) from all such waves, these variables were normalized to have zero mean and unit variance. Different average modulation amplitudes were then obtained by multiplication of these normalized variables by an appropriate scale factor. For convenience, the atomic scattering factors for the two species \(A\) and \(B\) were chosen as \(f_A = f_{ae}\) and \(f_B = f_s\) (i.e. \(f_A > f_B\)).

From the atomic coordinates generated for this model lattice, diffraction patterns were computed using the program ‘DIFFUSE’ (Butler & Welberry, 1992). Patterns, examples of which are shown in Fig. 1, were computed over a range in reciprocal space \((h = -4 \rightarrow 4; k = -4 \rightarrow 4)\) on a grid consisting of 400 \(\times\) 400 pixels. In displaying these calculated patterns, we follow our usual practice of using positive prints in which low intensity is black and high intensity is white. The Bragg peak positions have been marked by white dots for reference.

**Results**

In Fig. 1, we show calculated diffraction patterns of simulations containing longitudinal modulations (Figs. 1a and b) and transverse modulations (Figs 1c and d), with two different modulation amplitudes. For the examples shown in Figs 1(a) and (c), the r.m.s. amplitude was 0.2% of the cell spacing, while for Figs. 1(b) and (d), it was 2%. For a unit-cell spacing of 4 \(\AA\), these displacements correspond to 0.008 and 0.08 \(\AA\), respectively. Beneath each figure is a plot of the horizontal intensity integrated along each vertical line in the figures. For Figs. 1(a) and (b), the integration is over the whole range shown in the figure \((h = -4 \rightarrow 4)\), while for Figs 1(c) and (d), it is over the range \((h = -4 \rightarrow 0)\).

The value of the phase \(\phi\) was zero for all four figures, and it can be seen that in Fig. 1(a) the \(-2k_F\) line has an intensity added on to the diffuse background (Laue monotonic) intensity, while the \(+2k_F\) line has an intensity subtracted from the background level. This figure is in broad agreement with the case illustrated in the lower half of Fig. 4 of Ravy et al. (1992). The lines associated with the \(k = 0\) row of Bragg peaks are barely visible.

Fig. 1(c) shows a comparable pattern for transverse modulations and this is in broad agreement with the diagram in the lower left of Fig. 6 of Ravy et al. (1992). One difference noted here, however, is that the switch in polarity in crossing the \(h = 0\) line is not abrupt as indicated schematically in their diagram. The visibility of the lines against the diffuse background diminishes as the \(h = 0\) line is approached, and the lines can hardly be discerned at all for values of \(h\) less than about 0.5.

Some significant changes are seen in Figs. 1(b) and (d), for which the modulation amplitudes were increased to 2%. In Fig. 1(b), although around the \(k = 1\) line of Bragg peaks the positive \(-2k_F\) and negative \(+2k_F\) lines appear much as before (although much stronger), around higher \(k = 2, 3\) etc. lines, new features are observed. In particular, the negative \(+2k_F\) line associated with the \(k = 2\) Bragg peaks has now been superposed by a more sharply peaked positive line, an effect that is even more pronounced near the \(k = 3\) peaks. In addition, broader relatively weak lines of scattering can now be seen running along the \(k = 2, 3\) etc. rows of Bragg peaks. Similar effects can be observed in the corresponding transverse pattern of Fig. 1(d), except that the extra sharp peaks within the dark lines, as well as the broader peaks along the Bragg rows, occur for all values of \(k\) but are observed to increase in intensity as \(|h|\) increases. In Fig. 1(b), the \(\pm 2k_F\) lines around the \(k = 0\) line are now clearly visible and in Fig. 1(d) the visibility of the lines extends much closer to the \(k = 0\) line. It may be possible to interpret the broad diffuse lines that run along the rows of Bragg peaks as being due to small uncorrelated longitudinal displacements of the modulation chains themselves, but no such simple explanation of the narrow positive lines is available. These represent a new and unexpected feature of this type of scattering.

A number of other simulations were carried out to test the various properties predicted by the theory developed by Ravy et al. (1992). For example, it was confirmed that interchanging the two scattering factors (so that \(f_A < f_B\)) results in an interchange of the light and dark satellite lines. The same effect was also achieved by setting the phase \(\phi\) to a value \(\pi\). The effect of using molecular scatterers instead of the single atoms shown here was also tested.

The effect of changing the coherence parameter \(\xi\) was also tested in some detail. In addition to the expected effect that as \(\xi\) increased the width of the lines decreased, it was found that, for a given modulation amplitude, both the broad diffuse lines running along the rows of Bragg peaks and the narrow positive lines occurring within the negative satellites appear together at the same order of \(k\), more or less independently of the value of \(\xi\).

Some calculations were made at a much higher resolution than those shown in Fig. 1, in order to estimate the widths of the extra narrow lines compared to the main \(-2k_F\) lines, but the amount of computation involved precluded a complete survey. For the peaks around the \(k = 2\) Bragg rows in the 2% amplitude examples, it was found that full-width at half-maximum measurements of the narrow lines at \(+2k_F\) ranged from \(\sim0.6\) to 0.75 of the values for the main \(-2k_F\) lines as \(\xi\) varied from 5.25 to 21.0.

**Discussion**

Our simulation results provide confirmation of the theory of the origins of the white-line effect given by Ravy et al. (1992). For a defect concentration of 10%, it was found that the simple
white-line effect, as described by the theory of Ravy et al., provided a good description of the observed patterns when the modulation amplitude was 0.2% of the cell parameter or 0.008 Å for a 4 Å cell. This figure agrees well with the magnitude of the displacements resulting from the Peierls distortion in some other nondisordered one-dimensional conductors. For displacement amplitudes of 2% and higher, substantial higher-order effects are observed and the white-line effect may then only be observed near the lowest-order Bragg reflections.

Fig. 1. Calculated diffraction patterns. See text for details.
It should also be noted that it might be expected purely from the difference in size (van der Waal’s radius) between selenium and sulfur that local size-effect distortions of ~2–3% (~0.1 Å) would be induced by the alloying. Size-effect distortions of this magnitude have been observed in some closely related systems (Liu, Ravy, Pouget, Johannsen & Bechgaard, 1993). Such large distortions would produce substantial sinusoidal modulations of the Laue monotonic scattering. However, it is unclear whether this would prevent observation of the white-line effect. It is possible that the presence of the one-dimensional metallic state inhibits such large local departures from a perfectly regular lattice, but alternatively it is possible that the periodic lattice distortion takes advantage of the size effect to relax further the atoms in the neighbourhood of an impurity. The possibility of observing or not the white-line effect in such a situation would be of key interest for the understanding of pinning effects in charge-density-wave materials.

The diffuse-scattering images shown in Fig. 1 were computed on a Fujitsu VP-2200 supercomputer using a grant from the Australian National University Supercomputer Facility. One of us (NJF) is grateful to the Australian National University for the granting of a Vacation Scholarship during the tenure of which this work was carried out.

References


Lysozyme solubility in H2O and D2O solutions as a function of sodium chloride concentration. By Isabelle Broutin,* Madeleine Riês-Kautt and Arnaud Ducruix, Laboratoire de Cristallochimie, Institut de Chimie des Substances Naturelles, Laboratoire de Biologie Structurale CNRS, Bâtiment 34, 91198 Gif sur Yvette CEDEX, France

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Abstract

Some spectroscopic methods require solubilization or crystallization of proteins in heavy water because of the large difference in neutron scattering properties between protons and deuterons. In order to quantify the impact of slightly different physical properties of D2O and H2O, lysozyme solubility curves have been measured for these solvents, using 0.2 to 3.0 M sodium chloride in 0.050 M sodium acetate buffer (pH 4.5) at 291 K. After four months of crystallization, solubility data were measured within 9% error and showed that the lysozyme solubility in H2O is 1.3 times that in D2O.

1. Introduction

Many techniques require the use of heavy water to study proteins, because of the large difference in neutron scattering properties between protons and deuterons. For example, in neutron crystallographic studies, crystals are soaked in deuterated water to increase the coherent signal-to-noise ratio.

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