

Diffuse X-ray Scattering from Cubic ZnS Crystals having Substitutional Elastic Distortion Centres*

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Abstract

Diffuse X-ray scattering is studied theoretically from a crystal of cubic ZnS having distortion centres at the sulphur sites (having T_d symmetry). The atomic displacement due to a distortion centre is expressed as a sum of components consisting of radial functions combined with the appropriate Cubic Harmonics (KH) of Von der Lage & Bethe [*Phys. Rev.* (1947), **71**, 612–622]. The final expression for the intensity from the distorted crystal is used to study the shape of the diffuse spot around the (0,0, l) reciprocal lattice point. For isotropic distortion, the diffuse spot has cylindrical symmetry about the reciprocal z axis and there is no diffuse intensity in the reciprocal plane passing through (0,0, l) and normal to the z axis. For anisotropic distortion, however, the diffuse spot has fourfold symmetry about the reciprocal z axis. In particular, the reciprocal plane normal to the z axis and passing through (0,0, l) has four diffuse regions midway between the reciprocal x and y axes.

Introduction

In diamond structures, in which all the atoms are located at special positions having the point symmetry $\bar{4}3m$, the atomic charge density departs from perfect spherical symmetry and acquires the tetrahedral symmetry ($\bar{4}3m$) of the atomic site (Dawson, 1967*a,b,c*). Point symmetry of the atomic site is also imposed on the lattice vibrations of the atoms; recently the anharmonicity of atomic vibrations has been studied in white tin in which the atoms lie at sites of symmetry $\bar{4}2m$ (Merisalo & Jarvinen, 1977). In principle, the site symmetry of an elastic distortion centre in a crystal should also be imposed on the distorted crystal, even though the anisotropy of distortion may generally be too small to be detected experimentally. In case of appreciable anisotropy,

however, the symmetry would be reflected in the diffuse X-ray scattering from the distorted crystal. In the present paper, the form of the diffuse reflexions from crystals having anisotropic elastic distortion centres is studied theoretically, taking for illustration cubic ZnS structure having distortion centres at the sulphur sites.

Intensity formula

The intensity $J_2(\mathbf{S})$ of diffuse scattering at a point defined by the vector \mathbf{S} in reciprocal space is given by (Cochran, 1956; Cochran & Kartha, 1956)

$$J_2(\mathbf{S}) = N \exp(-2M) |T(\mathbf{S})|^2, \quad (1)$$

where N is the number of defects, $T(\mathbf{S})$ the transform of each defect and $M = 2\pi^2 \bar{u}^2 S^2$, \bar{u}^2 being the mean square displacement of an atom due to the combined effect of all the distortion centres. The defect is defined as consisting of positive atoms at positions to which they have moved due to the distortion centre and negative atoms at positions in the perfect structure.

Cubic ZnS has the diamond structure in which Zn and S atoms are surrounded tetrahedrally by atoms of the other type. Taking the origin at the S site and referring the face-centred crystal to a primitive rhombohedral cell, we get

$$T(\mathbf{S}) = \sum_n f(\mathbf{S}) [-\exp(2\pi i \mathbf{S} \cdot \mathbf{a}_n) + \exp\{2\pi i \mathbf{S} \cdot (\mathbf{a}_n + \mathbf{u}_n)\}], \quad (2)$$

where $f(\mathbf{S}) = f^S + f^{\text{Zn}} \exp(2\pi i \mathbf{S} \cdot \boldsymbol{\epsilon})$. In the above, $\boldsymbol{\epsilon}$ is the vector distance between S and an adjacent Zn atom, \mathbf{a}_n is the vector from the origin to the n th lattice point and \mathbf{u}_n is the vector displacement of the S and Zn atoms of the n th unit cell; it is assumed that \mathbf{a}_n and \mathbf{u}_n are parallel and that the displacements of the pair of atoms S and Zn are equal. The latter approximation is not justified for atoms near the distortion centre but appears reasonable for atoms further away; it is, however, not expected to alter the results materially since we are interested in the diffuse intensity near the

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reciprocal lattice points only where the influence of the atoms which are near the distortion centre is small.

On expanding $\exp\{2\pi i \mathbf{S} \cdot (\mathbf{a}_n + \mathbf{u}_n)\}$ and retaining only the first-order term in \mathbf{u}_n , we get

$$T(\mathbf{S}) = 2\pi i f(\mathbf{S}) \sum_n \mathbf{S} \cdot \mathbf{u}_n \exp(2\pi i \mathbf{S} \cdot \mathbf{a}_n). \quad (3)$$

Ewald's transformation (Ekstein, 1945) gives

$$T(\mathbf{S}) = \frac{4}{v} 2\pi i f(\mathbf{S}) \sum_{\mathbf{H}} \int \mathbf{S} \cdot \mathbf{u}(\mathbf{r}) \exp\{2\pi i (\mathbf{S} - \mathbf{H}) \cdot \mathbf{r}\} dv. \quad (4)$$

In the above, v is the volume of the cubic unit cell, \mathbf{H} is the vector to a reciprocal lattice point and the summation excludes the reciprocal lattice points corresponding to systematically absent reflexions. It is convenient to work with the cubic unit cell since the direct and reciprocal axes coincide in this case.

Putting $2\pi(\mathbf{S} - \mathbf{H}) = \mathbf{k}$, and retaining only that term of the summation which corresponds to the reciprocal lattice point which is nearest to the point defined by \mathbf{S} , we get

$$T(\mathbf{S}) = \frac{8\pi f(\mathbf{S})|\mathbf{S}|}{v} G(\mathbf{k}), \quad (5)$$

where $G(\mathbf{k}) = i \int \mathbf{u}(\mathbf{r}) \cos \mathbf{H}\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) dv$. In the above, $\cos \mathbf{S}\mathbf{r}$ is replaced by $\cos \mathbf{H}\mathbf{r}$ since \mathbf{H} and \mathbf{S} nearly coincide in the neighbourhood of a reciprocal lattice point.

Let (l_1, l_2, l_3) be the direction cosines of the vector \mathbf{H} , and (r, θ, φ) and (x, y, z) the spherical and Cartesian coordinates respectively of the point defined by vector \mathbf{r} with respect to the axes of the cubic unit cell. Then

$$\cos \mathbf{H}\mathbf{r} = l_1 \sin \theta \cos \varphi + l_2 \sin \theta \sin \varphi + l_3 \cos \theta. \quad (6)$$

Using the Cubic Harmonics of Von der Lage & Bethe (1947) and truncating the expansion at fourth-order terms, $\mathbf{u}(\mathbf{r})$ can be expressed as

$$\mathbf{u}(\mathbf{r}) = \bar{u}_c(r) + u_{a,3}(\mathbf{r}) + \delta u_{c,4}(\mathbf{r}), \quad (7)$$

where

$$u_{a,3}(\mathbf{r}) = F_3(r) \{xyz/r^3\} \quad (8)$$

and

$$\delta u_{c,4}(\mathbf{r}) = G_4(r) \left\{ \frac{x^4 + y^4 + z^4}{r^4} - \frac{3}{5} \right\}. \quad (9)$$

$\bar{u}_c(r)$, $F_3(r)$ and $G_4(r)$ are spherically symmetrical functions of r which become zero at $r = 0$.

Substituting for $\cos \mathbf{H}\mathbf{r}$ and $\mathbf{u}(\mathbf{r})$ from expressions (6) to (9) in (5), we get

$$G(\mathbf{k}) = i \int \left[\left\{ \bar{u}_c(r) + F_3(r) \left(\frac{xyz}{r^3} \right) + G_4(r) \left(\frac{x^4 + y^4 + z^4}{r^4} - \frac{3}{5} \right) \right\} \times \{ l_1 \sin \theta \cos \varphi + l_2 \sin \theta \sin \varphi + l_3 \cos \theta \} \right] e^{i\mathbf{k} \cdot \mathbf{r}} dv. \quad (10)$$

The expansion of $e^{i\mathbf{k} \cdot \mathbf{r}}$ in spherical harmonics is (Powell & Craseman, 1961)

$$e^{i\mathbf{k} \cdot \mathbf{r}} = 4\pi \sum_{l,m} i^l Y_l^{*m}(\theta^*, \varphi^*) Y_l^m(\theta, \varphi) j_l(kr). \quad (11)$$

θ, φ and θ^*, φ^* are the spherical angular coordinates of \mathbf{r} and \mathbf{k} , respectively. In order to evaluate the integral in (10), the expression within square brackets was expressed as a linear combination of tesseral harmonics. Expression (11) was substituted for $e^{i\mathbf{k} \cdot \mathbf{r}}$, and the integral evaluated by making use of the orthogonal property of spherical harmonics. The final expression for $T(\mathbf{S})$ is

$$T(\mathbf{S}) = \frac{8\pi f(\mathbf{S})|\mathbf{S}|}{v} [\bar{G}_c(\mathbf{S}) + G_{a,3}(\mathbf{S}) + G_{c,4}(\mathbf{S})],$$

where

$$\begin{aligned} \bar{G}_c(\mathbf{S}) = & - \left[l_1 \left(2\sqrt{\frac{\pi}{3}} \right) \langle \bar{u}_c \rangle C_1^1 + l_2 \left(2\sqrt{\frac{\pi}{3}} \right) \langle \bar{u}_c \rangle S_1^1 \right. \\ & \left. + l_3 \left(2\sqrt{\frac{\pi}{3}} \right) \langle \bar{u}_c \rangle C_0^0 \right]; \\ G_{a,3}(\mathbf{S}) = & i \left[l_1 \left\{ \frac{1}{3\sqrt{35}} \sqrt{\frac{2\pi}{5}} \langle F_4 \rangle S_4^3 - \frac{1}{21\sqrt{5}} \sqrt{\frac{2\pi}{5}} \langle F_4 \rangle S_4^1 \right. \right. \\ & \left. \left. - \frac{2}{7\sqrt{15}} \sqrt{\frac{\pi}{5}} \langle F_2 \rangle S_2^1 \right\} + l_2 \left\{ -\frac{1}{3\sqrt{35}} \sqrt{\frac{2\pi}{5}} \langle F_4 \rangle C_4^3 \right. \right. \\ & \left. \left. - \frac{1}{21\sqrt{5}} \sqrt{\frac{2\pi}{5}} \langle F_4 \rangle C_4^1 - \frac{2}{7\sqrt{15}} \sqrt{\frac{\pi}{5}} \langle F_2 \rangle C_2^1 \right\} \right. \\ & \left. + l_3 \left\{ \frac{4}{21\sqrt{5}} \sqrt{\frac{\pi}{5}} \langle F_4 \rangle S_4^2 - \frac{2}{7\sqrt{15}} \sqrt{\frac{\pi}{5}} \langle F_2 \rangle S_2^2 \right\} \right]; \\ G_{c,4}(\mathbf{S}) = & - \left[l_1 \left\{ \frac{4}{15\sqrt{33}} \sqrt{\frac{5\pi}{3}} \langle G_5 \rangle C_5^3 + \frac{4}{15\sqrt{21}} \sqrt{\frac{2\pi}{21}} \langle G_3 \rangle C_3^3 \right. \right. \\ & \left. \left. + \frac{4}{3\sqrt{154}} \sqrt{\frac{\pi}{154}} \langle G_5 \rangle C_5^5 - \frac{4}{9\sqrt{770}} \sqrt{\frac{\pi}{770}} \langle G_5 \rangle C_5^3 \right. \right. \\ & \left. \left. - \frac{4}{9\sqrt{35}} \sqrt{\frac{2\pi}{35}} \langle G_3 \rangle C_3^3 \right\} + l_2 \left\{ \frac{4}{15\sqrt{33}} \sqrt{\frac{5\pi}{3}} \langle G_5 \rangle S_5^3 \right. \right. \\ & \left. \left. + \frac{4}{15\sqrt{21}} \sqrt{\frac{2\pi}{21}} \langle G_3 \rangle S_3^3 + \frac{4}{3\sqrt{154}} \sqrt{\frac{\pi}{154}} \langle G_5 \rangle S_5^5 \right. \right. \end{aligned}$$

$$\begin{aligned}
& + \frac{4}{9\sqrt{N}} \sqrt{\frac{\pi}{770}} \langle G_5 \rangle S_3^3 + \frac{4}{9\sqrt{N}} \sqrt{\frac{2\pi}{35}} \langle G_3 \rangle S_3^3 \Big\} \\
& + l_3 \left\{ \frac{4}{9\sqrt{N}} \sqrt{\frac{\pi}{11}} \langle G_5 \rangle C_3^0 - \frac{16}{45\sqrt{N}} \sqrt{\frac{\pi}{7}} \langle G_3 \rangle C_3^0 \right. \\
& \left. + \frac{4}{15\sqrt{N}} \sqrt{\frac{5\pi}{77}} \langle G_5 \rangle C_3^4 \right\}. \quad (12)
\end{aligned}$$

In the above,

$$\langle \bar{u}_c \rangle = \int 4\pi r^2 \bar{u}_c(r) j_1(kr) dr,$$

$$\langle F_n \rangle = \int 4\pi r^2 F_n(r) j_n(kr) dr$$

and

$$\langle G_n \rangle = \int 4\pi r^2 G_n(r) j_n(kr) dr,$$

and the tesseral harmonics are as defined in Prather (1961) and refer to \mathbf{k} space. A convenient form for the functions $\bar{u}_c(r)$, $F_3(r)$ and $G_4(r)$ is, as used by Dawson (1967, *a,b,c*) in the study of covalent bonds in diamond structures, $\{ar^2 \exp(-br^2)\}$, where a and b are constants to be adjusted with experimental data. For $\bar{u}_c(r)$, Cochran (1956) has used a function following the inverse square law; this function becomes infinite at $r = 0$. Cochran's expression for intensity and the one obtained in this paper for the isotropic term give a similar shape for the diffuse spot.

Discussion

The expression for $T(\mathbf{S})$ simplifies if diffuse scattering is studied around a reciprocal point $(0,0,l)$, because then l_1 and l_2 become zero and l_3 becomes unity, and we get

$$\begin{aligned}
T(\mathbf{S}) = \frac{8\pi f(\mathbf{S})|S|}{v} & \left\{ \left(-2 \sqrt{\frac{\pi}{3}} \langle \bar{u}_c \rangle C_1^0 - \frac{4}{9\sqrt{N}} \sqrt{\frac{\pi}{11}} \langle G_5 \rangle C_3^0 \right. \right. \\
& + \frac{16}{45\sqrt{N}} \sqrt{\frac{\pi}{7}} \langle G_3 \rangle C_3^0 - \frac{4}{15\sqrt{N}} \sqrt{\frac{5\pi}{77}} \langle G_5 \rangle C_3^4 \Big) \\
& \left. + i \left(\frac{4}{21\sqrt{N}} \sqrt{\frac{\pi}{5}} \langle F_4 \rangle S_4^2 - \frac{2}{7\sqrt{N}} \sqrt{\frac{\pi}{15}} \langle F_2 \rangle S_2^2 \right) \right\}. \quad (13)
\end{aligned}$$

In the absence of anisotropic terms, we get

$$T(\mathbf{S}) = \frac{8\pi f(\mathbf{S})|S|}{v} \left(-2 \sqrt{\frac{\pi}{3}} \langle \bar{u}_c \rangle C_1^0 \right). \quad (14)$$

The diffuse spot for isotropic distortion, shown in Fig. 1(a), is dumb-bell shaped (roughly like the p_z atomic orbitals for hydrogen); the exact intensity distribution will of course depend on the function $\bar{u}_c(r)$. There is

cylindrical symmetry about the \mathbf{H} vector, and the diffuse spot is centrosymmetrical about $(0,0,l)$; however, the sign of $T(\mathbf{S})$ is different on the two sides of the reciprocal lattice point. It may be mentioned that the centrosymmetry of the diffuse spot is approximate because of the factors $|S|$ and $f(\mathbf{S})$ in $T(\mathbf{S})$; these factors change slightly for different regions of the diffuse spot. There is no intensity in the reciprocal plane passing through $(0,0,l)$ and normal to \mathbf{H} .

The influence of the centrosymmetrical anisotropic term $\delta u_{c,4}(\mathbf{r})$ in $u(\mathbf{r})$ is to add terms containing C_3^0 , C_3^4 and C_5^0 in the expression for $T(\mathbf{S})$. These terms leave the diffuse spot centrosymmetrical and do not give any intensity in the reciprocal plane through $(0,0,l)$ normal to \mathbf{H} . Terms with C_3^0 and C_3^4 leave the spot cylindrically symmetrical, but the term with C_3^4 gives it fourfold symmetry.

The influence of the anti-symmetrical term $u_{a,3}(\mathbf{r})$ in $u(\mathbf{r})$ is to add the imaginary part containing terms with S_2^2 and S_4^2 in $T(\mathbf{S})$. These terms reinforce each other and give maximum intensity with fourfold symmetry in the reciprocal plane through $(0,0,l)$ and normal to \mathbf{H} (Jahnke & Emde, 1945); the regions of diffuse intensity, shown in the broken line in Fig. 1(b), are present midway between the x^* and y^* reciprocal axes through $(0,0,l)$. The exact intensity distribution will, however, depend on the function $F_3(r)$. This intensity comes in the reciprocal plane where other terms [including the dominant term $\bar{u}_c(r)$] give zero intensity, and hence has the brightest chance of being seen experimentally. The estimated intensity in this plane should also be reasonably free from series truncation errors, since the next anti-symmetrical term in the KH series is only $u_{a,7}(\mathbf{r})$.

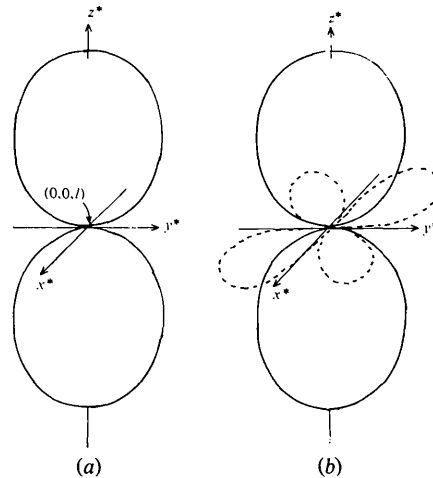


Fig. 1. Diffuse spot around $(00l)$ reciprocal lattice point for (a) isotropic distortion and (b) anisotropic distortion. The lobes shown by broken lines in (b) have maximum intensity in the reciprocal plane through $(00l)$ and normal to z^* . The diagrams are merely illustrative; the change in shape of the lobes along z^* due to anisotropy is not shown.

The diffuse spot around $(h,0,0)$ and $(0,k,0)$ will of course be similar; the coefficients of l_1 and l_2 in (12) acquire the same form as that of the coefficient of l_3 on appropriate transformation of axes.

In order to observe these diffuse spots, single crystals of cubic ZnS doped with, say, Se must be grown. Se is expected to replace S and form distortion centres of T_d symmetry. The difficulties in these experiments are the faintness of the diffuse scattering due to low strength of the substitutional distortion centres, and the presence of thermal diffuse scattering. However, by working at low temperatures, it may be possible to observe the anisotropic effect in the reciprocal plane (normal to H) through some strong axial reflexion.

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Macromolecular Structure Refinement by Restrained Least-Squares and Interactive Graphics as Applied to Sickling Deer Type III Hemoglobin

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Abstract

A restrained least-squares (RLS) computer program and two interactive graphics (IG) systems have been used in combination to refine the structure of deer type III hemoglobin. By alternating applications of RLS with examinations and corrections of the atomic model superposed on electron density maps (IG), the residual has been reduced from ~ 0.42 to ~ 0.25 and the sites of dubious fit between model and map reduced to $\sim 6\%$ of the residues or $\sim 3\%$ of the atoms. It was possible to fit routinely ~ 4600 atoms to X-ray intensity data sets ranging from less than 6000 (9.0 – 4.0 Å resolution) to $\sim 21\,500$ points (6.0 – 1.98 Å resolution) employing RLS, which uses interatomic distances to retain structural integrity. Convergence was rapid and many shifts greater than 1 Å were recorded. An in-house graphics display allowed the placement of atoms not in the original atomic model and GRIP, a fast-response interactive graphics system, was used to correct any gross conformational misfit of the atomic model to the electron density maps. The man hours needed to run both GRIP and RLS is less than previously reported

real-space methods. The strategy of how RLS and IG can be best applied and how the molecular structure changed during refinement are discussed.

Introduction

A key factor in an X-ray protein structural refinement is the improvement in the interpretability of the electron density maps so that structural features are more readily perceived. The use of high-resolution X-ray data to improve the atomic coordinates of a macromolecule whose basic structure is 'solved' at low resolution has followed diverse paths (Blundell & Johnson, 1976). Until recently, the refinement methods reported were: real-space fitting by visual fit in a Richards Box (Richards, 1968) or its present equivalent, the electronic optical comparator (Collins, Cotton, Hazen, Meyer & Morimoto, 1975); automated real-space fitting (e.g. Diamond, 1966, 1974; Huber, Kukla, Bode, Schwager, Bartels, Deisenhofer & Steigemann, 1974; Freer, Alden, Carter & Kraut, 1975; Ladner, Heidner & Perutz, 1977; Moews & Kretsinger, 1975);