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Theoretical Consideration of the Thermal-Vibration Effect on X-ray Integrated Intensities from a Noncentrosymmetric Crystal near an Absorption Edge

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Abstract

The intensities of Bragg reflexions generally show a large change in the energy region near an absorption edge of the constituent atoms. The integrated reflecting powers, $R_{\mathbf{h}}(\omega)$ and $R_{\bar{\mathbf{h}}}(\omega)$, measured in the energy-dispersive mode, have been calculated for a Friedel pair of reflexions from a noncentrosymmetric crystal. In order to investigate the effect of thermal vibrations, both perfect and mosaic cases are considered. It has been found that the values of the isotropic temperature factors strongly affect the shapes of the curves for $R_{\mathbf{h}}(\omega)$ and $R_{\bar{\mathbf{h}}}(\omega)$. It is shown, for CuI, that the intensity ratio $r_{\mathbf{h}}(\omega)$ between the Friedel pair tends to the limit value, unity, when the relevant B_j factors become large: *i.e.* large thermal vibrations screen the effects due to the polarity.

Introduction

For several years, there has been considerable interest in the energy dependence of X-ray diffraction intensity in the energy range near an absorption edge. The change of diffraction intensity owing to energy was studied by Cole & Stemple (1962) in the symmetric Bragg case. They derived theoretical relations for the integrated intensities, based on the dynamical theory of Zachariasen (1945), for a perfect crystal without a centre of symmetry, taking absorption into account. According to their results, it seems possible that the values of integrated intensities from opposite reflexions **h** and $\bar{\mathbf{h}}$ near the absorption edge enable us to determine the degree of perfection qualitatively. Furthermore, the ratio of the integrated intensities for this pair is given by

$$r_{\mathbf{h}}(\omega) = |F_{\mathbf{h}}|^2/|F_{\bar{\mathbf{h}}}|^2, \qquad (1)$$

when the crystal is either perfect or ideally mosaic. It was thus suggested that the value of this ratio might not be affected by the degree of perfection. Experimental confirmation of the validity of relation (1) was reported by Holloway (1969) for nearly perfect crystals (GaSb and InAs) in the symmetric Bragg case by conventional angle-dispersive diffractometry.

In the present energy-dispersive diffractometry, theoretical expressions of integrated intensities and experimental verifications were worked out in detail for a GaAs crystal, with a large improvement in energy resolution, both in the symmetric Bragg case and the symmetric Laue case (Fukamachi, Hosoya & Okunuki, 1976*a*,*b*). However, as far as we know, only a few papers deal with the effect of thermal vibrations on the integrated intensities, $I_{\mathbf{h}}(\omega)$ and $I_{\bar{\mathbf{h}}}(\omega)$, and their ratio $r_{\mathbf{h}}(\omega)$ near the absorption edge. This point is discussed within the framework of the dynamical theory with absorption taken into account in the case of a diatomic crystal by Kawamura & Fukamachi (1979), assuming the same temperature-factor value B for both atoms. Under such conditions, the shape of the integrated intensities as a function of ω is affected by the B values only in the case of a perfect crystal. It is evident that the intensity for a mosaic crystal is reduced by the constant factor $\exp(-Bs_{\mathbf{h}}^2)$ over the whole energy range.

In the present paper, we attempt to give a more general analysis of the influence of B_j factors. The changes in B_j values strongly affect the shape of the curves $R_{\mathbf{h}}(\omega)$ and $R_{\bar{\mathbf{h}}}(\omega)$ for both perfect and mosaic crystals. The integrated reflexion powers $R_{\mathbf{h}}(\omega)$ and $R_{\bar{\mathbf{h}}}(\omega)$ have been numerically calculated for a CuI crystal (in its γ phase with the zinc blende structure) for which, as is well known, large thermal vibrations occur even at room temperature (Miyake & Hoshino, 1958).

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Formulation

The notation and relations necessary for numerical calculations are summarized here. The structure factor $F_{\mathbf{h}}$ for the $\mathbf{h}$ reflexion is given by

$$F_{\mathbf{h}}(\omega)=\sum_j \{f_j^0(\mathbf{h})+f_j'(\omega)+if_j''(\omega)\} \times \exp(2\pi i\mathbf{h}\mathbf{r}_j)\exp(-B_j s_{\mathbf{h}}^2), \quad (2)$$

where the f_j^0 ($\mathbf{h}$) are normal atomic scattering factors, and $f_j'(\omega)+if_j''(\omega)$ is the anomalous-scattering factor.

In the X-ray region, the polarizability χ and the electric susceptibility are nearly equal if the international units are used, or related by the factor 4π with atomic units. The Fourier components $\chi_{\mathbf{h}}$ of the lattice function χ, over the reciprocal lattice, are related to the structure factors $F_{\mathbf{h}}$ through the relation

$$\chi_{\mathbf{h}}(\omega)=-\{4\pi F_{\mathbf{h}}(\omega)\}/(v\omega^2), \quad (3)$$

where v is the volume of a unit cell. It is convenient to write this as

$$\chi_{\mathbf{h}}(\omega)=\chi_{\mathbf{h}}'(\omega)+i\chi_{\mathbf{h}}''(\omega), \quad (4)$$

$$\chi_{\mathbf{h}}'(\omega)=-(4\pi/v\omega^2)\left[\sum_j\{f_j^0(\omega)+f_j'(\omega)\}\exp(2\pi i\mathbf{h}\mathbf{r}_j) \times \exp(-B_j s_{\mathbf{h}}^2)\right]=|\chi_{\mathbf{h}}'|\exp(i\alpha_{\mathbf{h}}'), \quad (5)$$

and

$$\chi_{\mathbf{h}}''(\omega)=-(4\pi/v\omega^2)\left\{\sum_j f_j''(\omega)\exp(2\pi i\mathbf{h}\mathbf{r}_j) \times \exp(-B_j s_{\mathbf{h}}^2)\right\}=|\chi_{\mathbf{h}}''|\exp(i\alpha_{\mathbf{h}}''), \quad (6)$$

where $\chi_{\mathbf{h}}'$ and $\chi_{\mathbf{h}}''$ are complex quantities for a noncentrosymmetric crystal.

For a symmetric Bragg case, in the energy-dispersive mode, the integrated reflecting power for a perfect crystal is given by (Fukamachi *et al.*, 1976*a*)

$$R_{\mathbf{h}}=\{C\omega_B|\chi_{\mathbf{h}}'|/(2\sin^2\theta_B)\}\int P_{\mathbf{h}}(w,C)\,\mathrm{d}w, \quad (7)$$

with

$$P_{\mathbf{h}}(w,C)=\frac{1+k^2-2k\sin\delta}{\{(1-k^2)^2+4k^2\cos^2\delta\}^{1/2}} \times\frac{1}{L(w)+\{L^2(w)-1\}^{1/2}} \quad (8)$$

and

$$L(w)=\frac{\{(w^2-1-g^2+k^2)^2+4(gw-k\cos\delta)^2\}^{1/2}+w^2+g^2}{\{(1-k^2)^2+4k^2\cos^2\delta\}^{1/2}}, \quad (9)$$

where the parameters g, k and δ are given by

$$g_{\mathbf{h}}=g_{\mathbf{h}}(\omega,B_j)=\chi_0''/(C|\chi_{\mathbf{h}}'|), \quad (10)$$

$$k=|\chi_{\mathbf{h}}''|/|\chi_{\mathbf{h}}'|, \quad (11)$$

$$\delta=\alpha_{\mathbf{h}}''-\alpha_{\mathbf{h}}', \quad (12)$$

and the parameter w is the *Selektionsfehler*. The intensity ratio between opposite reflexions is given by

$$r_{\mathbf{h}}(\omega)=\frac{1-2k\sin\delta/(1+k^2)}{1+2k\sin\delta/(1+k^2)}=|F_{\mathbf{h}}|^2/|F_{\bar{\mathbf{h}}}|^2 \quad (13)$$

for both perfect and mosaic crystals. In (7), C is unity for normal polarization, and $|\cos 2\theta_B|$ for parallel polarization, where ω_B and θ_B are the energy and Bragg angle at the Bragg condition.

In the case of a mosaic crystal, the integrated intensity is proportional to $|F_{\mathbf{h}}|^2$. For a symmetric Bragg reflexion in energy-dispersive mode, the integrated reflecting power is given by

$$R_{\mathbf{h}}=Q_{\mathbf{h}}/\{2\mu(\omega_B)\} \quad (14)$$

and

$$Q_{\mathbf{h}}=(2\pi c)^3 r_e^2 p(\theta_B)|F_{\mathbf{h}}|^2/(2v^2\omega_B\sin^2\theta_B), \quad (15)$$

where r_e is the radius of a classical electron, c is the velocity of light and $p(\theta_B)$ is the polarization factor.

The above expressions of the integrated reflecting power [(7) and (14)] contain no restrictive conditions with respect to both centrosymmetry and absorption, and thus can be applied to the most general case.

Calculation and discussion

The effect of the B_j factors on the integrated reflecting power $R_{\mathbf{h}}(\omega)$ and $R_{\bar{\mathbf{h}}}(\omega)$ near the absorption edge is investigated through numerical calculations of relations (7) and (14), with B_j taken as parameters. In the case of a monoatomic absorbing mosaic crystal, or a polyatomic crystal with all B values equal, no change in the shape of $R_{\mathbf{h}}(\omega)$ and $R_{\bar{\mathbf{h}}}(\omega)$ can be expected when B is varied, as the intensities are multiplied by the constant factor $\exp(-Bs_{\mathbf{h}}^2)$. Moreover, for a perfect crystal, large changes may occur, as the most important parameter $g_{\mathbf{h}}(\omega,B)$ depends on B according to the relation

$$g_{\mathbf{h}}(\omega,B)=g_{\mathbf{h}}(\omega,0)\exp(-Bs_{\mathbf{h}}^2), \quad (16)$$

where $g_{\mathbf{h}}(\omega,0)$ is the value of $g_{\mathbf{h}}$ with thermal vibrations neglected. This case has been worked out for a perfect GaAs crystal, the same B factor being assumed for the Ga and As atoms (Kawamura & Fukamachi, 1979).

For a polyatomic crystal with different B_j factors, relations (7) and (14) can be applied to a zinc blende-type crystal, CuI, for which it is well known that the thermal vibrations are large. At room temperature, both B_{I} and B_{Cu} were estimated to be about 2 Å^2 (Miyake & Hoshino, 1958). Therefore, in the results reported here, the value $B_{\mathrm{I}}=2$ Å^2 was adopted, while B_{Cu} was taken as a parameter varying from 0 to 5·0 Å^2.

The anomalous-scattering factors $f'(\omega)$ and $f''(\omega)$ for Cu and I atoms are calculated in an energy range near the Cu absorption edge, using the relations of Parratt & Hempstead (1954) and Cromer's (1965) parameters (see Fig. 1). The crystal structure factors $|F_{555}|$ and $|F_{\bar{5}\bar{5}\bar{5}}|$ of CuI near the Cu absorption edge are calculated from relations (17) and (18), on the assumption that Cu is at (0,0,0) and I is at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$.

$$|F_{555}| = 4[\{T_{\rm Cu}[f^0_{\rm Cu} + f'_{\rm Cu}(\omega)] + T_{\rm I}\, f''_{\rm I}\}^2 + \{T_{\rm Cu}\, f''_{\rm Cu}(\omega) - T_{\rm I}(f^0_{\rm I} + f'_{\rm I})\}^2]^{1/2} \quad (17)$$

and

$$|F_{\bar{5}\bar{5}\bar{5}}| = 4[\{T_{\rm Cu}[f^0_{\rm Cu} + f'_{\rm Cu}(\omega)] - T_{\rm I}\, f''_{\rm I}\}^2 + \{T_{\rm Cu}\, f''_{\rm Cu}(\omega) + T_{\rm I}(f^0_{\rm I} + f'_{\rm I})\}^2]^{1/2}, \quad (18)$$

where $T_{\rm Cu} = \exp(-B_{\rm Cu}\, s_5^2)$ and $T_{\rm I} = \exp(-B_{\rm I}\, s_5^2)$.

Fig. 2 shows that $|F_{555}|$ increases regularly, whereas $|F_{\bar{5}\bar{5}\bar{5}}|$ decreases as the thermal vibrations of the metal atom increase. For a reflexion with high indices, $f^0_{\rm Cu} + f'_{\rm Cu}(\omega)$ is small near the Cu absorption edge; if, in addition, $B_{\rm Cu}$ is large, the factor $T_{\rm Cu} f''_{\rm Cu}(\omega)$ is also small, and finally $|F_{555}|$ and $|F_{\bar{5}\bar{5}\bar{5}}|$ tend to the common limit

$$4T_{\rm I}\{f''^2_{\rm I} + (f^0_{\rm I} + f'_{\rm I})^2\}^{1/2}. \quad (19)$$

The variations of the relative integrated reflecting powers $R_{555}(\omega)$ and $R_{\bar{5}\bar{5}\bar{5}}(\omega)$ are shown in Figs. 3 and 4 for perfect and mosaic crystals respectively. For the perfect crystal, and with unpolarized X-rays, $R_{\mathbf{h}}(\omega)$ is obtained as $(\frac{1}{2})[R^{\perp}_{\mathbf{h}}(\omega) + R^{\parallel}_{\mathbf{h}}(\omega)]$, which is an average of the $R_{\mathbf{h}}(\omega)$ values for polarized X-rays with $C = 1$ and $C = |\cos 2\theta_B|$.

The general features of the integrated reflecting power are similar in the perfect and mosaic cases; moreover, when $B_{\rm Cu}$ changes, the behaviours of opposite reflexions are different: $R_{\bar{5}\bar{5}\bar{5}}$ is more strongly affected by $B_{\rm Cu}$ variations than is R_{555}. It is well known that the opposite faces (111) and $(\bar{1}\bar{1}\bar{1})$ of the zinc blende structure behave differently with regard to properties such as etching and oxidation. This asymmetry also appears with regard to the effect of thermal vibrations on the integrated intensities near the absorption edge.

From relations (14) and (15),

$$R_{\mathbf{h}}(\omega) \propto |F_{\mathbf{h}}(\omega)|^2/\mu(\omega) \propto |F_{\mathbf{h}}(\omega)|^2/\{f''_{\rm Cu}(\omega) + f''_{\rm I}\} \quad (20)$$

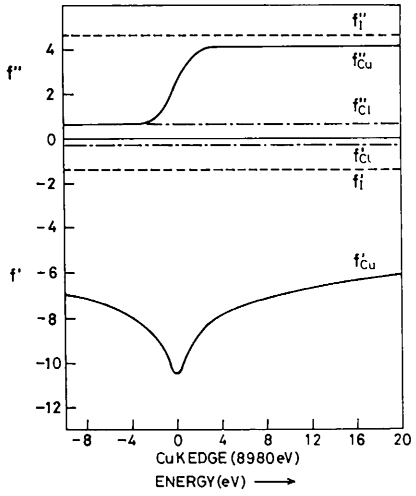

Fig. 1. Calculated anomalous-scattering factors of Cu, I and Cl near the Cu K absorption edge (8980 eV).

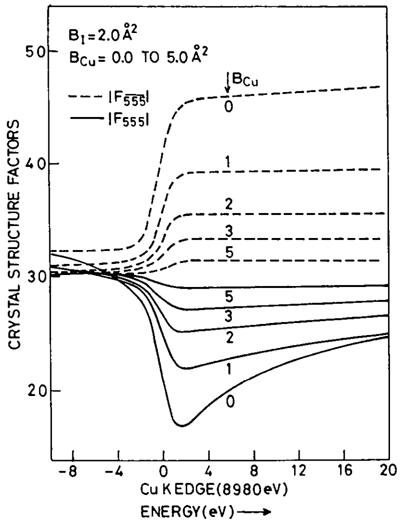

Fig. 2. Variations of the crystal structure factors calculated for the 555 and $\bar{5}\bar{5}\bar{5}$ reflexions of CuI near the Cu edge, with different $B_{\rm Cu}$ values but with $B_{\rm I} = 2{\cdot}0$ Å^2.

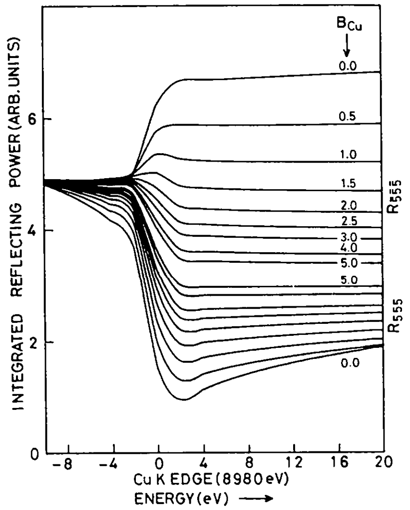

Fig. 3. The case of a perfect crystal. Calculated curves for the integrated reflecting powers $R_{555}(\omega)$ and $R_{\bar{5}\bar{5}\bar{5}}(\omega)$ for CuI, near the Cu edge, and the thermal parameters: $B_{\rm Cu} = 0{\cdot}0$ to $5{\cdot}0$ Å^2 and $B_{\rm I} = 2{\cdot}0$ Å^2 are used.

is obtained if the other parameters are assumed to be nearly constant in the narrow energy range of present interest.

The sharp change in $f''_{\mathrm{Cu}}(\omega)$ across the edge causes the difference in the shapes of $F_{\bar{5}\bar{5}\bar{5}}(\omega)$ and $R_{\bar{5}\bar{5}\bar{5}}(\omega)$. When B_{Cu} increases, the change in the shape of $R_{\bar{5}\bar{5}\bar{5}}(\omega)$ would be more pronounced in the case of CuCl, as f''_{Cl} is much smaller than f''_{I} for energies near the Cu edge (Fig. 1).

The effect of the the thermal vibrations on the Friedel ratio $r_{555}(\omega)$ can be clearly seen in Fig. 5: the value of $r_{555}(\omega)$ tends to unity when B_{Cu} is large. It seems that large thermal vibrations of the anomalous scatterer decrease the polarity effect. In many papers, the B_j factors are not taken into account in the calculations of $F_{\mathbf{h}}$ and $F_{\bar{\mathbf{h}}}$, and it is then assumed that the thermal motion does not much affect the intensity ratio $r_{\mathbf{h}}$ because the Debye factor cancels out in the ratio $|F_{\mathbf{h}}|^2/|F_{\bar{\mathbf{h}}}|^2$ (Holloway, 1969). This statement only holds if the B_j factors are the same for the different atoms in the crystal, but is no longer valid in the general case, as numerically proved in the present paper (Fig. 5).

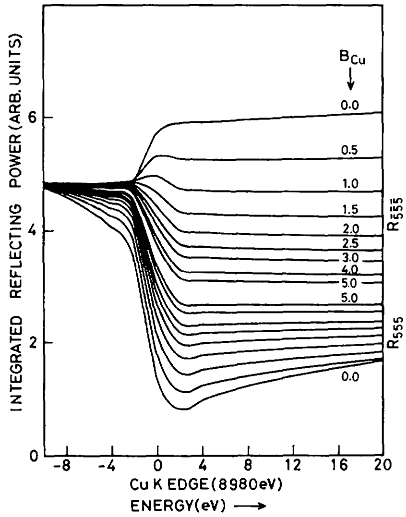

Fig. 4. The case of a mosaic crystal. Conditions are identical with those of Fig. 3.

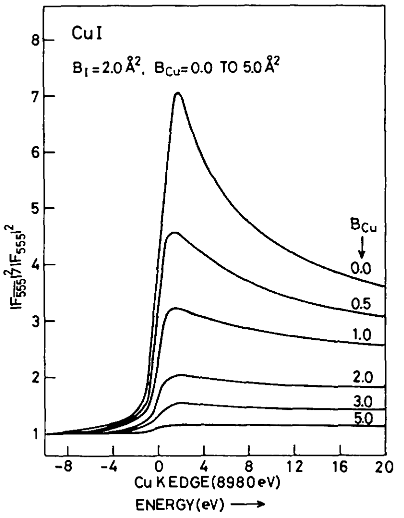

Fig. 5. Energy variations of the calculated Friedel ratio $r_{555}(\omega)$ of CuI near the Cu edge for different B_{Cu} values.

From Figs. 3 and 4, it appears that the integrated intensities near the Cu edge are very sensitive to the B values, and nearly independent of the crystal texture. It follows that an experimental study of the integrated intensities of a pair of reflexions **h** and $\bar{\mathbf{h}}$ in a noncentrosymmetric crystal, together with a precise determination of the anomalous-scattering factors $f'(\omega)$ and $f''(\omega)$ in the exact vicinity of the absorption edge, can provide a tool for obtaining knowledge of the thermal parameters B_j (Fukamachi & Hosoya, 1975); the B_j values can be determined by fitting the experimental values to the calculated curves $R_{\mathbf{h}}(\omega)$ and $R_{\bar{\mathbf{h}}}(\omega)$, where the latter includes B_j as variable parameters. An application to the determination of the B_j factors in CuI will be reported in another paper, together with the fine structure of f'_{Cu} and $f''_{\mathrm{Cu}}(\omega)$ near the Cu edge.

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