

## Validity of the Structure Factor Formalism\*

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### *Abstract*

Where density fluctuations in a crystal are very large as a result of proximity to a structural phase transition, contributions to the diffraction data associated with critical scattering (CRS) can make it difficult to determine the average structure with any great precision. This matter is discussed on the basis of the structure factor formalism.

### 1. Introduction

In general, the X-ray or neutron diffuse scattering observed from a crystal is a reciprocal space representation of the density fluctuation in the crystal, whether its origin is static or dynamical, as is seen from the simple Fourier theory of kinematical diffraction. Thus, the dynamical properties of a crystal near a structural phase transition have been widely investigated by the measurement and analysis of the diffuse scattering which is usually enhanced near a phase transition point. This is already a well-known technique used to obtain directly the dynamical mechanism of a structural phase transition.

To understand the physical nature of a phase transition on a microscopic basis it is, however, essential to know the exact structure below and above the phase transition, since knowledge of the initial and final structures can tell us what happens when a transformation takes place. As techniques in structure refinement by X-ray and neutron diffraction have been improved, refinement of the structures of some typical ferroelectric substances has been repeated on several occasions. The following study corresponds to a new attempt to follow up the gradual change of structure during a phase transition, especially for the second kind, by analysing the structure successively at several distinct temperatures close to the transition point (Sakata *et al.* 1980; Itoh *et al.* 1980; Itoh 1984; Nelmes *et al.* 1985).

However, it should be noted that such a structure analysis has been attempted for a crystal in which the density fluctuation is extremely large, since the experiment is carried out near a phase transition. The question arises as to whether the average structure is well defined by a diffraction experiment for such a critical point. In other words, this is equivalent to asking whether the Bragg reflection responsible for

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the determination of the average structure is separated out from the critical diffuse scattering. This situation has similarities to the case of thermal diffuse scattering (TDS) and the problem of applying an appropriate correction.

In discussing this problem on the validity of the structure factor formalism, we point out that there is a case in which the average structure is certainly difficult to define in the light of the present level of structure analysis by diffraction experiments.

## 2. Average Structure and Density Modulation

Within the framework of kinematical diffraction theory, the scattered intensity is proportional to the space-time Fourier transform of a density correlation function:

$$I(\mathbf{K}, \omega) = \int \int \langle \rho(-\mathbf{r}, -t) \otimes \rho(\mathbf{r}, t) \rangle \exp\{i(\mathbf{K} \cdot \mathbf{r} - \omega t)\} d\mathbf{r} dt, \quad (1)$$

where  $\rho(-\mathbf{r}, -t) \otimes \rho(\mathbf{r}, t)$  represents the convolution of the density distribution and  $\langle \dots \rangle$  denotes the thermal average of the system at temperature  $T$ . If an average periodic lattice is defined for a given crystal, the density distribution of the crystal  $\rho(\mathbf{r}, t)$  may be given by the sum of the average periodic lattice  $\langle \rho(\mathbf{r}) \rangle$  which should be time independent, with a deviation from it of  $\Delta\rho(\mathbf{r}, t)$ :

$$\rho(\mathbf{r}, t) = \langle \rho(\mathbf{r}) \rangle + \Delta\rho(\mathbf{r}, t). \quad (2)$$

The Fourier transform of (1) for the density distribution (2) gives two terms:

$$I(\mathbf{K}, \omega) = \left| \int \langle \rho(\mathbf{r}) \rangle \exp(i\mathbf{K} \cdot \mathbf{r}) d\mathbf{r} \right| \delta(\omega) + \int \int \langle \Delta\rho \otimes \Delta\rho \rangle \exp\{i(\mathbf{K} \cdot \mathbf{r} - \omega t)\} d\mathbf{r} dt, \quad (3)$$

where  $\langle \Delta\rho \rangle = 0$  by definition. The first term represents the sharp Bragg reflection at the reciprocal lattice points for pure elastic scattering because of the term  $\delta(\omega)$ . The second term shows diffuse scattering consisting of a continuous intensity distribution in the reciprocal lattice, instead of sharp peaks, due to the lack of the long range periodicity in  $\Delta\rho$ . This term is essentially inelastic scattering. In this paper we confine ourselves to the intensity integrated over energy, corresponding to the X-ray scattering case, but the argument is valid for neutron scattering as far as quasi-elastic scattering is concerned, such as the critical scattering.

It should be noted that the average lattice structure of a crystal, such as the position and mean square displacement of the atoms in a unit cell, is obtained from the analysis of the Bragg reflections. Therefore, it is essential to eliminate other scattering contributions from the observed Bragg intensity. The information about deviation from the average structure or density modulation is, on the other hand, obtained from the analysis of the second term of the diffuse scattering. As the origin of diffuse scattering is due to lattice vibrations, the strain distribution, which is usually accompanied by some types of lattice defect, and the structural fluctuation in connection with a phase transition could be considered. The diffuse scattering corresponding to those density modulations are thermal diffuse scattering, Huang scattering and critical scattering (CRS) respectively.

### 3. TDS Contribution

Among the different types of diffuse scattering, it is well known that first order TDS due to the acoustic lattice vibrations of small wave number produces sharp maxima at reciprocal lattice points so that, in the course of the measurement of the integrated Bragg intensity, a certain amount of TDS is included. In general, the contribution of TDS to the Bragg intensity increases with an increase in the scattering vector  $K$ , and this may often amount to over 35% for higher order Bragg reflections. Accurate studies of the average structure by utilising a shorter wavelength necessarily require a correction for the TDS contribution to the Bragg peaks. There is no experimental way, however, to separate out the TDS contribution from the observed Bragg intensities. Thus, this correction is carried out at present on the basis of theoretical predictions (see e.g. Harada and Sakata 1974; Sakata and Harada 1976).

As the TDS at a reciprocal lattice point is proportional to the Bragg intensity at that point, the observed integrated intensity is given by

$$J_{\text{obs}}(B) = J_{\text{Bragg}}(B)(1 + \alpha_{\text{TDS}}). \quad (4)$$

Since the TDS is proportional to the square of the scalar product of the scattering vector  $K$  and the phonon displacement vector  $\xi$ ,  $\alpha_{\text{TDS}}$  is given in the quadratic form

$$\alpha_{\text{TDS}} = \tilde{h}\Delta\beta h, \quad (5)$$

where  $h$  represents the Miller indices  $h, k, l$  and  $\Delta\beta$  is the tensor characterising the anisotropy of the TDS in the reciprocal lattice.

### 4. CRS Contribution

A problem similar to the TDS correction encountered in the usual structure analysis may arise when the structure refinement of a ferroelectric-like crystal is attempted at a temperature very close to the phase transition point. Then, the critical diffuse scattering due to the enhancement of a long range density fluctuation associated with the phase transition also produces peaks at the reciprocal lattice points.

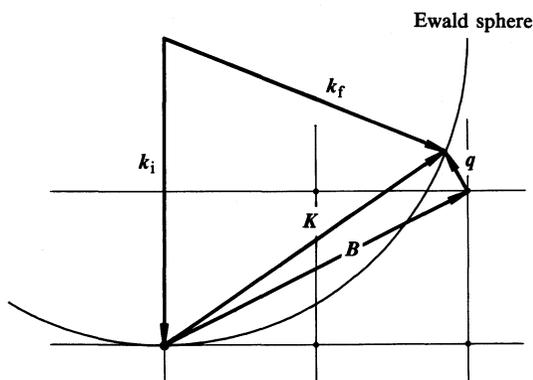


Fig. 1. Ewald construction representing the scattering vector  $K$ , the reciprocal lattice point  $B$  and the deviation  $q$ .

According to the Landau (1937) theory of critical scattering due to a second order phase transition, the scattered intensity from a crystal above the Curie point is written in the form

$$I_{\text{CRS}}(\mathbf{K}) \approx \left\{ |\Delta F|^2 k_{\text{B}} T / \left( B(T - T_0) + \sum_{ij} A_{ij} q_i q_j \right) \right\} \times \delta(\mathbf{K} + \mathbf{q} - \mathbf{B}), \quad (6)$$

where  $T_0$  is the Curie temperature,  $q_i$  is the  $i$ th component of the wave number vector  $\mathbf{q}$  with respect to the density fluctuation of which the anisotropy is characterised by a tensor  $A_{ij}$ , and  $\Delta F$  is the difference of the structure factors between the two phases, one above and one below the phase transition point. The wave number vector  $\mathbf{q}$  represents the deviation of the scattering vector  $\mathbf{K}$  from the nearest neighbour reciprocal lattice point  $\mathbf{B}$ , as illustrated in Fig. 1. From (6) we see that  $I_{\text{CRS}}(\mathbf{K})$  is enhanced when  $T$  is close to  $T_0$ , and peaks are also produced at the reciprocal lattice points where  $\mathbf{q}$  corresponds to zero. The intensity modulation in the reciprocal lattice is given by  $|\Delta F|^2$  which is usually not proportional to the Bragg intensity.

In the course of a scan for measurement of the Bragg intensity, we see that some of the CRS may contribute to the integrated Bragg intensity in a manner similar to TDS. The contribution of the CRS is given by the integral of (6) for the volume swept out around the reciprocal lattice point  $\mathbf{B}$  by a detector:

$$J_{\text{CRS}}(\mathbf{B}) \approx \int I_{\text{CRS}}(\mathbf{K}) d^3 K = |\Delta F|^2 \gamma_{\text{CRS}}. \quad (7)$$

There is a case in which the phase transition results from the instability of one of the optical phonon branches, as is often seen in the phase transition of perovskite-type crystals. In such a case,  $\Delta F$  in (6) is rewritten as the structure factor for such phonons which is proportional to the scalar product of the scattering vector  $\mathbf{K}$  and atomic displacement vector  $\xi_j$ :

$$\Delta F(\mathbf{K}) = \sum_j (\mathbf{K} \cdot \xi_j) f'_j \exp\{i(\mathbf{K} \cdot \mathbf{r}_j)\}, \quad (8)$$

where  $f'_j$  is the atomic scattering factor in which the Debye-Waller factor  $\exp(-M_j)$  is corrected. In general, some of the atoms are moved relative to others in the unit cell for the optical phonon mode, so that  $\xi_j$  depends very much on the mode. The modulation of  $|\Delta F|^2$  in reciprocal space is, therefore, not simply proportional but even opposite to that of the Bragg scattering; i.e.  $|\Delta F|^2$  is large at the reciprocal lattice point at which the Bragg intensity is weak.

Nevertheless, it is also possible to represent equation (7) in a quadratic form by using (8):

$$J_{\text{CRS}}(\mathbf{B}) = J_{\text{Bragg}}(\mathbf{B})(\hbar \Delta \gamma \mathbf{h}), \quad (9)$$

$$\Delta \gamma_{lm} = (F_l F_m) \tau / J_{\text{Bragg}}(\mathbf{B}), \quad (10)$$

$$\tau = (2\pi)^{-3} \int k_{\text{B}} T / \left( B(T - T_0) + \sum_{ij} A_{ij} q_i q_j \right) d^3 q, \quad (11)$$

where  $\tilde{h}$  and  $h$  represent the Miller indices  $h, k, l$ ,  $\Delta\gamma$  is the  $3 \times 3$  tensor characterising the intensity modulation of the CRS,  $F_l$  is the  $l$ th component of the phonon structure factor along one of the principal reciprocal axes, and  $\tau$  is the integral for the volume swept out around a reciprocal lattice point  $B$  by a detector.

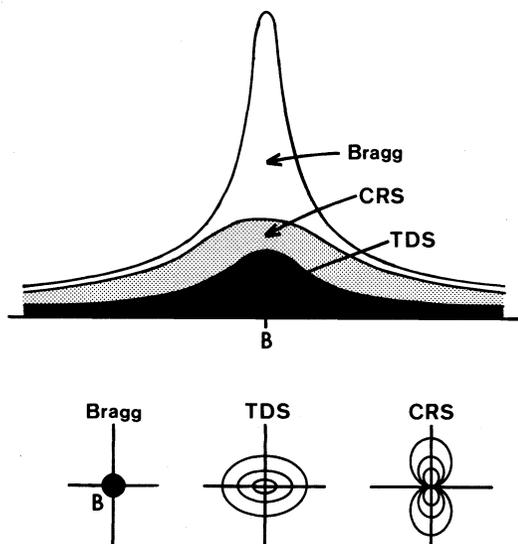


Fig. 2. Illustration of a Bragg peak where the integrated Bragg intensity consists of three components: Bragg scattering, thermal diffuse scattering (TDS) and critical scattering (CRS). Their two-dimensional distributions in the diffraction plane are illustrated in the lower part of the figure.

## 5. Integrated Bragg Intensity

In an attempt to determine the average structure of a crystal as accurately as possible at a temperature very close to its phase transition point by analysing the diffraction data, we must pay attention to the fact that the integrated Bragg intensity which is measured by scanning around a reciprocal lattice point consists of three parts; that is, the TDS and CRS contributions are included as well as the true Bragg intensity. Such a situation is illustrated in Fig. 2. On the basis of equations (4), (5) and (7), the integrated Bragg intensity is given by

$$J_{\text{obs}}(\mathbf{B}) = J_{\text{Bragg}}(\mathbf{B})(1 + \tilde{h}\Delta\beta h) + |\Delta F|\gamma_{\text{CRS}}. \quad (12)$$

If the CRS originates from the soft phonon mode, the observed intensity is written on the basis of (9) as

$$J_{\text{obs}}(\mathbf{B}) = J_{\text{Bragg}}(\mathbf{B})\{1 + \tilde{h}(\Delta\beta + \Delta\gamma)h\}. \quad (13)$$

In these expressions the TDS tensor  $\Delta\beta$  is well represented in terms of a set of elastic constants for the crystal and the experimental conditions under which the Bragg intensities have been measured. There is, therefore, no particular difficulty at present in estimating  $\Delta\beta$  in equations (12) and (13). However, it is rather difficult to evaluate

$\gamma_{\text{CRS}}$  or  $\Delta\gamma$ , as all the parameters (see equation 6) which are necessary to evaluate them are only obtained by a full understanding of the critical scattering of (6). But we see qualitatively from (13) that the additional correction term  $\Delta\gamma$  modulates  $\Delta\beta$  in a different manner. In the case of expression (12), we notice that the TDS correction  $(1 + \hbar\Delta\beta h)$  should always be made after correcting the CRS contribution  $|\Delta F|^2 \gamma_{\text{CRS}}$  to the observed intensity  $J_{\text{obs}}(\mathbf{B})$ , if that is possible.

## 6. Discussion and Conclusions

The consequences of neglecting the TDS correction for structure analysis have been discussed by Harada and Sakata (1974) and Stevenson and Harada (1983) on the basis of the general formalism of TDS correction. According to their predictions, the thermal parameters are modified in such a way that the principal axes of the thermal ellipsoids change their directions, while the position parameters are little affected. Presumably this conclusion continues to be valid as a general tendency even in the case where the CRS correction is necessary, because  $J_{\text{CRS}}(\mathbf{B})$  itself is a small correction term for the strong Bragg intensity.

It is very interesting to obtain even a rough idea about the CRS contribution to the Bragg intensity, although a theoretical estimation is extremely difficult, as mentioned in Section 5. According to the experimentally observed value of the CRS for  $\text{NaNO}_2$ , at a temperature about two degrees above the phase transition point (Hoshino and Motegi 1967), the phase transition is of antiferroelectric type, and it is estimated to be 25% of the weak Bragg intensity. Similar estimations for  $\text{KD}_2\text{PO}_4$  and  $\text{CsD}_2\text{PO}_4$  have been obtained from neutron scattering experiments (Skalyo *et al.* 1970; Semmingsen *et al.* 1977). However, we note that the CRS is stronger than TDS near a weak Bragg reflection, but not at the reciprocal lattice point at which the Bragg reflection is strong (Shibuya and Mitsui 1961). Such a tendency has also been observed in the X-ray photograph of  $\text{BaTiO}_3$  above the phase transition point in which the soft optical phonon mode is known to contribute to the diffuse scattering (Harada and Honjo 1967). This is a characteristic of CRS and these experimental results are in good agreement with the theoretical prediction.

Such a characteristic of the CRS modulation can be understood as resulting from the density modulation which arises from the displacement of specific atoms, or the change of the orientation of particular molecules in the unit cell, in connection with the phase transformation. Therefore, it is easily understood that the thermal parameters of the atoms or molecules involved directly in the density fluctuation are largely modulated as the consequence of the neglect of the CRS correction to the Bragg intensity. Since no standard method to correct this CRS has yet been established, this should be kept in mind for structures determined especially near a phase transition point. It should also be noted that the CRS intensity and its modulation in reciprocal space depends very much on the phase transition which changes from crystal to crystal.

In this paper we have confined ourselves to the influence of the CRS, but it is also conceivable that Huang scattering can influence diffraction data if a strain distribution exists in a sample crystal. An example can be seen in the X-ray study of the electron-density distribution of  $\text{K}_2(\text{PtCl}_4)$  by Ohba *et al.* (1983). They noticed that spurious peaks are produced in the difference Fourier maps if diffraction data including Huang scattering are used and they identified them as due to the existence

of strain in the crystal. Therefore, we may say that there is a crystalline state for which an average structure is difficult to define by diffraction experiments, as a result of large density fluctuations.

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