Aaltonen Foundation, Finland, for financial assistance. Support of this work by the National Science Foundation, USA (grant CHE 790587) is gratefully acknowledged.

References

BROWN, P. J. (1957). *Acta Cryst.* **10**, 133–135.
CAPLIN, A. D. & NICHOLSON, L. K. (1978). *J. Phys. F*, **8**, 51–73.
CAVA, R. J., REIDINGER, F. & WUENSCH, B. J. (1977). *Solid State Commun.* **24**, 411–416.
COOPER, M. J., ROUSE, K. D. & FUESS, H. (1973). *Acta Cryst.* A**29**, 49–56.
COPPENS, P. (1980). *Electronic and Magnetic Distributions in Molecules and Crystals*, edited by P. BECKER. New York: Plenum.
HARADA, J., SUZUKI, H. & HOSHINO, S. (1976). *J. Phys. Soc. Jpn*, **41**, 1707–1715.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
JOHNSON, C. K. (1969). *Acta Cryst.* A**25**, 187–194.
KONTIO, A. & COPPENS, P. (1981). *Acta Cryst.* B**37**, 433–435.
KONTIO, A., STEVENS, E. D., BOEHME, R. F. & COPPENS, P. (1982). In preparation.
KONTIO, A., STEVENS, E. D., COPPENS, P., BROWN, R. D., DWIGHT, A. E. & WILLIAMS, J. M. (1980). *Acta Cryst.* B**36**, 435–436.
MCINTYRE, G. J., MOSS, G. & BARNEA, Z. (1980). *Acta Cryst.* A**36**, 482–490.
MAIR, S. L. (1980). *J. Phys. C*, **13**, 1419–1425.
MAIR, S. L. (1982). *J. Phys. C*, **15**, 25–36.
MAIR, S. L. & WILKINS, S. W. (1976). *J. Phys. C*, **9**, 1145–1158.
MOSS, B. K. (1979). Thesis. Univ. of Melbourne.
MOSS, B. K., MCMULLAN, R. K. & KOETZLE, T. F. (1980). *J. Chem. Phys.* **73**, 495–508.
RAY, A. E. & SMITH, J. F. (1957). *Acta Cryst.* **10**, 604–605.
STEVENS, E. D. (1979). *Mol. Phys.* **37**, 27–45.
STEVENS, E. D., DELUCIA, M. L. & COPPENS, P. (1980). *Inorg. Chem.* **19**, 813–820.
STEVENS, E. D. & KONTIO, A. (1982). In preparation.
WILLIS, B. T. M. (1969). *Acta Cryst.* A**25**, 277–300.

Acta Cryst. (1982). A**38**, 629–631

Intensity Formula for Single Bragg Reflection, Including Corrections for the Effects of Extinction and Thermal Diffuse Scattering

BY JIMPEI HARADA*

School of Physics, University of Melbourne, Parkville, Victoria 3052, *Australia*

(*Received* 19 *February* 1982; *accepted* 24 *March* 1982)

Abstract

Two existing intensity formulae of a single Bragg reflection which include corrections for the effects of extinction and thermal diffuse scattering are discussed on the basis of energy-transfer equations for secondary extinction. It is shown that one of them, which has been recommended by Cooper & Rouse [In *Thermal Neutron Diffraction* (1970), edited by B. T. M. Willis, Oxford Univ. Press], is not valid.

1. Introduction

In the accurate analysis of density distribution by means of X-ray and neutron diffraction from single crystals, the most remarkable progress made in the last decade comes from the fact that the observed integrated intensities can now be corrected for extinction and thermal diffuse scattering. In the actual analysis, at present, the integrated Bragg intensity is represented by two slightly different formulae in which corrections for the effects of absorption, polarization, extinction and thermal diffuse scattering are included. However, there has been no discussion about the difference between these two formulae, except for a comment given by Cooper & Rouse (1970). Consequently the choice seems to have depended upon the convenience to the analyst. The purpose of this paper is to reconsider what sort of scattering process is really represented by each formula and to recommend that one of them be used for the refinement as representing more plausibly the scattering process.

2. Expressions for the integrated Bragg intensity

In corrections for the effect of extinction as well as thermal diffuse scattering to the observed integrated

* On leave from the Department of Applied Physics, Nagoya University, Nagoya 464, Japan.

0567-7394/82/050629-03$01.00

Bragg intensity, I_{hkl}(obs), the following two formulae are widely used:

$$I_{hkl}(\text{obs}) = sA_{\mu}\,(Y_{hkl} + \alpha_{hkl})|F_{hkl}(\text{calc})|^2\text{Lp}\,\lambda^3, \quad (1)$$

$$I_{hkl}(\text{obs}) = sA_{\mu}\,Y_{hkl}\,(1 + \alpha_{hkl})|F_{hkl}|^2\text{Lp}\,\lambda^3; \quad (2)$$

where the notation used is as follows: s is the scale factor, A_{μ} is the transmission factor (for absorption), Y_{hkl} is the extinction factor, α_{hkl} is the thermal diffuse scattering correction factor, F_{hkl} is the structure factor of the hkl reflection, Lp is the Lorentz–polarization correction factor, and λ is the X-ray wavelength. Formula (1) is recommended by Cooper & Rouse (1970) on the basis of the following argument. The observed integrated intensities are given by the sum of two independent scattering components; the normal Bragg scattering component and the thermal diffuse scattering, TDS, component. TDS arises from the scattering by long-wavelength phonons which are incoherent.

The scattering cross section for the TDS is usually very small in comparison with that of Bragg scattering, although the TDS can amount to more than 20% of the observed Bragg intensity for higher-order reflections, if all the scattering under the Bragg reflection is integrated. Cooper & Rouse (1970) then suggested that the kinematical diffraction theory could be applied to the TDS component, whilst the Bragg reflection is subject to extinction. Such a scattering process is illustrated in Fig. 1(*a*). On the other hand, the scattering process corresponding to (2) is given in Fig. 1(*b*), where the TDS, *i.e.* the X-rays scattered forward along the direction of the Bragg reflection by a long-wavelength phonon, are not treated separately from the X-rays scattered by the Bragg reflection. The repetition of energy transfer between the incident and Bragg beam directions is, therefore, included as not negligible even for this weak and incoherent component, TDS.

The differences between the scattering process represented by the two formulae will be clearly understood by comparing Figs. 1(*a*) and (*b*) with formulae (1) and (2). The point is therefore whether the weak and incoherent X-rays created by phonon scattering can be diffracted again by Bragg scattering. An answer to this question can be easily obtained if one considers the meaning of the scattering process in terms of the Darwin energy-transfer equation, which is valid for an incoherent X-ray beam.

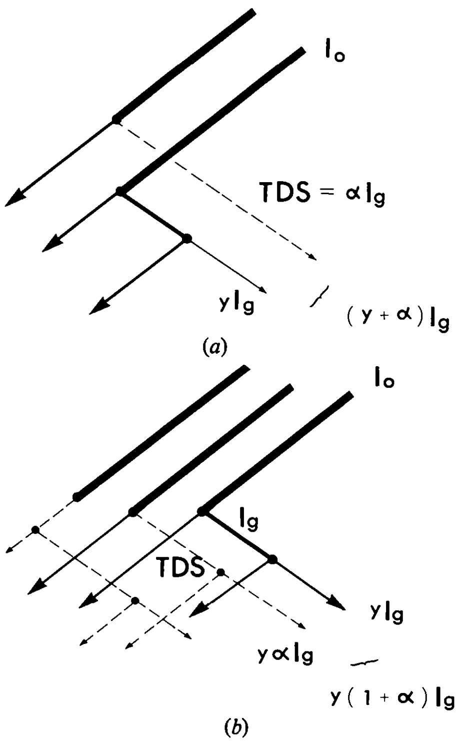

Fig. 1. (*a*) Case where the TDS of a single phonon in the direction of a Bragg beam is not scattered. (*b*) Case where the TDS is also subject to Bragg scattering.

3. Energy-transfer relationship

If the energy transfer between the incident and diffracted beams at various points is considered on the basis of Hamilton's (1957) formalism for the secondary extinction effect, the well known energy-transfer equations can be obtained:

$$\frac{\partial I_0}{\partial x_1} = -\bar{\sigma}(I_0 - I_g) \quad (3a)$$

$$\frac{\partial I_g}{\partial x_2} = -\bar{\sigma}(I_g - I_0) \quad (3b)$$

where the absorption effect is neglected for simplicity and I_0, I_g are the incident and the diffracted beam intensities, respectively, at a point $M(x_1, x_2)$ as shown in Fig. 2, and $\bar{\sigma}$ is the quantity proportional to the

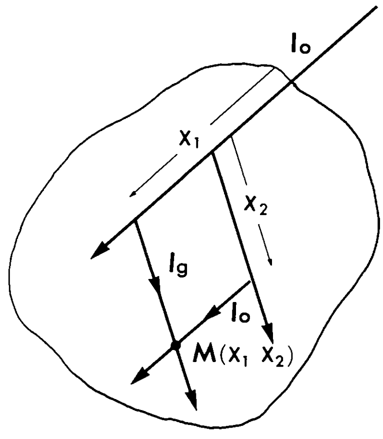

Fig. 2. Illustration of incident and diffracted beam intensities at point $M(x_1, x_2)$.

scattering cross section at that point, *i.e.* proportional to the square of the structure factor and orientation of mosaic block at that part of crystal. In (3*a*) and (3*b*) the first terms represent the decrease of intensities due to a single Bragg reflection, while the second terms show the increase of intensities due to repeated Bragg reflection. We see from the equations how the X-ray energy or intensity is transferred from the incident beam direction to the Bragg direction and *vice versa* at any point $M(x_1, x_2)$, where x_1 and x_2 are coordinates along the two propagation directions from the surface of the crystal. Since the change of intensities with path x_i depends linearly on the primary and diffracted beam intensity, we see that the energy transfer between the beams depends only on the scattering cross section $\bar{\sigma}$ and is independent of the strength of the primary beam or the diffracted beam intensities. This means that even for a very weak X-ray beam, such as only one photon, energy transfer would be repeated between the primary and the diffracted beams if the scattering cross section is large. This is a very important point in considering the scattering process for X-rays either weak or strong.

Therefore we see that once the X-ray is scattered along the direction of a Bragg reflection, for example by single scattering with a long-wavelength phonon, it must follow the same scattering process as that for the Bragg reflection case.

4. Conclusion

It is clear from the above argument that between the two formulae representing the integrated Bragg intensity in which both the TDS and the extinction corrections are included (2) represents the correct scattering process in a real crystal.

It should also be emphasized here that the extinction effect is not due to the strength of the X-ray beam but rather to the magnitude of the scattering cross section. By saying that the extinction is not severe for a weak beam we understand that the weak beam in a crystal is created from the scattering due to small scattering cross section and has not the chance of being repeatedly scattered.

Although Cooper & Rouse (1970) recommend that structure refinement should be made on the basis of (1) by correcting not individually but simultaneously the TDS and the extinction effect, it is concluded that it is unnecessary to do so. After correction of the observed intensity for TDS and Lorentz–polarization, analysis can be made by refinement of the structure parameters and the extinction parameters, using available programs.

We also consider here the problem of whether the structure parameters and the extinction parameters determined on the basis of (1) are acceptable. Since the TDS cross section is proportional to the square of the scattering vector, *i.e.* $(\sin\theta/\lambda)^2$, the TDS is usually not large for the lower-order Bragg reflection of large structure factors which are subjected severely to extinction. The senses of the corrections for TDS and extinction are opposite. Therefore, we can see that the parameters determined on the basis of the two formulae are very much the same within the experimental errors, except for some extreme cases where the extinction is not negligible even for higher-order reflections, as seen sometimes in neutron diffraction data.

The argument made in this paper is based on the energy-transfer equations which are valid only for correction for secondary extinction; however the same argument may be extended to the primary extinction case. For the validity of energy-transfer equations (3*a*) and (3*b*) on the basis of more fundamental Takagi–Taupin equations for a distorted crystal a series of papers by Kato (1976, 1980) should be referred to.

The author would like to thank Dr Z. Barnea and Mr A. Stevenson for their interest in this work and also gratefully acknowledges a Sir Thomas Lyle Fellowship, which enabled him to stay at the School of Physics, University of Melbourne. Special thanks also go to Dr J. V. Sanders, Materials Science Division, CSIRO, University of Melbourne, for his valuable comments during the preparation of this paper.

References

Cooper, M. J. & Rouse, K. D. (1970). *Thermal Neutron Diffraction*, edited by B. T. M. Willis, pp. 1–13. Oxford Univ. Press.
Hamilton, W. C. (1957). *Acta Cryst.* **10**, 629–634.
Kato, N. (1976). *Acta Cryst.* A**32**, 458–466.
Kato, N. (1980). *Acta Cryst.* A**36**, 171–177.