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The Role of Debye–Waller-Factor Measurement in the Analysis of Diffuse-Scattering Data

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Abstract

The cumulant expression for the diffuse intensity scattered from disordered crystals shows that the often-observed anomalies in total diffuse scattering also extend to the total displacement scattering. Comparison of experimental data on displacement scattering with Debye–Waller factors for Cu_3Au shows the anomaly to be due primarily to inaccurate extrapolation in the vicinity of fundamental reflections. It is suggested that Debye–Waller-factor measurements are a necessary adjunct to diffuse-scattering measurements if the errors incurred in extrapolation are to be reduced.

Measurements of diffuse X-ray scattering from disordered, binary-alloy single crystals are analysed using the separation procedure devised by Borie & Sparks (1971) or by least-squares fitting of a moment expression for the diffuse intensity (Williams, 1974);

$$I_o(\mathbf{h}) = \Delta F^* \Delta F A(\mathbf{h}) + \bar{F}^* \Delta F \mathbf{h}.\mathbf{Q}(\mathbf{h}) + \bar{F}^* \bar{F} \mathbf{h}.\mathbf{R}(\mathbf{h}).\mathbf{h},$$

where $\bar{F} = c_A F_A + c_B F_B$, $\Delta F = F_A - F_B$ and $F_X = f_X \exp[-B_X(\sin^2\theta)/\lambda^2]$, f_X being the scattering factor or scattering length for atom X and B_X its Debye–Waller factor (DWF). The alloy AB has the composition $c_A{:}c_B$ and for cubic ordering systems the indices $\mathbf{h}$ are chosen so that $\sin^2\theta/\lambda^2 = (4a_0)^{-2}(h_1^2 + h_2^2 + h_3^2)$.

The completeness of the separation is generally assessed by comparing the zeroth Fourier coefficient, α_{000}, of the order function $A(\mathbf{h})$ with its theoretical value of unity. Table 1 shows that agreement even in careful studies is seldom better than 20%.

It is the purpose of this communication to show how a second check, on the total-displacement diffuse scattering, may aid the analysis. The matrix product $\mathbf{h}.\mathbf{R}(\mathbf{h}).\mathbf{h}$ describes the intensity lost from both fundamental and superlattice Bragg reflections, and from short-range-order diffuse scattering which peaks near the corresponding reflection position. The zeroth Fourier coefficient δ^x_{000} of $[\mathbf{R}(\mathbf{h})]_{xx}$ is a measure of the mean-square displacement (Bardhan & Cohen, 1976). The average diffuse intensity due to displacements is

$$\bar{I}_{\text{disp}} = |\Delta f|^2 c_A c_B \delta^x_{000}(h_1^2 + h_2^2 + h_3^2) \qquad (1)$$

in the Borie & Sparks (1971) notation. The cumulant approach (March, Wilkins & Tibballs, 1976) gives this average as the redistribution of the intensity removed from the fundamental, superlattice and/or short-range-order peaks by the presence of mean-square displacements, *viz*

$$\begin{aligned}\bar{I}_{\text{disp}} &= |\bar{f}|^2 - |\bar{F}|^2 + |\Delta f|^2 - |\Delta \bar{F}|^2 \\ &= c_A(|f_A|^2 - |F_A|^2) + c_B(|f_B|^2 - |F_B|^2). \qquad (2)\end{aligned}$$

Writing the structure factors in terms of the DWF's for fundamental and superlattice peaks

$$\bar{F} = \bar{f} \exp[-(B_F \sin^2\theta)/\lambda^2] \qquad (3a)$$

$$\Delta F = \Delta f \exp[-(B_s \sin^2\theta)/\lambda^2] \qquad (3b)$$

$$\bar{I}_{\text{disp}} = 2(\bar{f}^2 B_F + \Delta f^2 B_s)\sin^2\theta/\lambda^2, \qquad (4)$$

and equating (2) and (4) it is found that

$$\delta^x_{000} \approx \frac{\eta^{-2} B_F + B_s}{6 c_A c_B a_0}, \qquad (5)$$

where $\eta = \langle \Delta f/\bar{f} \rangle$ is an estimate of the scattering-factor ratio (Tibballs, 1975).

Table 1. *Total diffuse intensity due to displacements and disorder*

Alloy	α_{000}	δ^x_{000} (obs)	δ^x_{000} (calc)
Al–0·05Ag[a]	1·547	0·178	0·12*
Cu_3Au (396 °C)[b]	1·641	0·237	0·17†
(420 °C)[b]	1·107	0·139	0·11
(475 °C)[b]	1·239	0·228	0·12
(685 °C)[b]	1·369	0·288	0·16
(750 °C)[b]	1·442	0·428	0·17
(930 °C)[b]	0·898	0·568	0·20

References: (*a*) Gragg & Cohen (1971). (*b*) Bardhan & Cohen (1976).

* $B_s = 0$ for a clustering alloy. The B_{Al} value used will underestimate B_F for the alloy.

† B_s from Bardhan, Chen & Cohen (1977).

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In Table 1, values of δ^x_{000} from experimental diffuse-scattering analyses are compared with those derived from measured DWF's *via* (5). Both α_{000} and δ^x_{000} are greater for the experimental analyses and the difference between the results increases with the total displacement scattering. Since the greatest uncertainty in the experimental analysis lies in extrapolating the behaviour of the diffuse scattering into the region of the fundamental Bragg position (Hayakawa, Gragg & Cohen, 1973), any means of improving the extrapolation should improve the accuracy of the analysis.

The effect of poor extrapolation is not confined to δ^x_{000} as may be seen from Fig. 1 where the displacement diffuse intensity along $(h_1 00)$ in reciprocal space is reconstructed from the Fourier coefficients of Bardhan & Cohen's (1976) analysis of Cu_3Au at T_c + 2°C (T_c = 391·1°C; Hashimoto, Miyoshi & Ohtsuka, 1976) and the average values given by (1) and (4). The DWF's are from a neutron determination (Tibballs, Towers & Barnea, 1978). Clearly, the large average obtained from (1) arises from the contribution under the Bragg peak which is inconsistent with the approximately equal values of ΔF and $\bar{F}$ and the ratio of B_{Cu} and B_{Au} found by Tibballs *et al.* (1978). Further, the higher order Fourier coefficients required to reproduce the apparently large modulation of the average intensity derived from (1) do not represent the modulation with respect to the average derived from (4) or equation (1) using δ^x_{000} from (5). This modulation is given in the cumulant approach by

$$\sum_{X,Y} F^*_X F_Y \sum_{l\neq 0} P^{XY}_l [\exp(-2\pi^2 \mathbf{h}.\mathbf{L}^{XY}_l.\mathbf{h}) \times \cos(2\pi \mathbf{h}.\mathbf{K}^{XY}_l) - 1] \cos|(\pi \mathbf{h}.\mathbf{l}),$$

where

$$[\mathbf{L}^{XY}_l]_{xy} = \langle x^{XY}_l y^{XY}_l \rangle - \langle x^{XY}_l \rangle \langle y^{XY}_l \rangle - \frac{\delta_{xy}(B_X + B_Y)}{8\pi^2}$$

and $[\mathbf{K}^{XY}_l]_x = \langle x^{XY}_l \rangle$ in the notation of Bardhan & Cohen (1976). This reduces to the moment expression $c_A c_B |\bar{F}|^2 \mathbf{h}.\mathbf{B}(\mathbf{h}).\mathbf{h}$ when truncated at second order in $|h|$ and the elements of $P^{XY}_l.\mathbf{L}^{XY}_l$ are assumed constant for all X,Y. Similarly $c_A c_B \Delta F^* \bar{F} \mathbf{h}.\mathbf{Q}(\mathbf{h})$ is a useful approximation to

$$\sum_{X,Y} F^*_X F_Y \sum_{l\neq 0} P^{XY}_l \exp(-2\pi^2 \mathbf{h}.\mathbf{L}^{XY}_l \mathbf{h}) \sin(2\pi \mathbf{h}.\mathbf{K}^{XY}_l) \times \sin(\pi \mathbf{h}.\mathbf{l})$$

out to $(B \sin^2\theta)/\lambda^2 \approx 0{\cdot}25$.

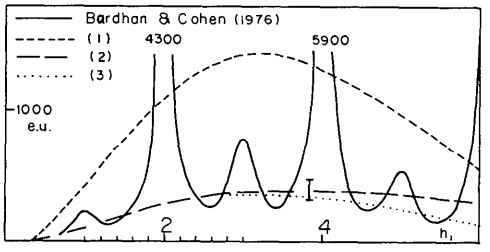

Fig. 1. Displacement diffuse scattering for Cu_3Au at 396°C (Bardhan & Cohen, 1976). —— Observed modulated intensity; (1) average intensity from the Borie & Sparks analysis; (2) average intensity from DWF (cumulant expression); (3) average intensity from DWF (moment expression). The divisions on the h_1 axis indicate the range and spatial frequency of diffuse-scattering measurements.

Conclusions

Accuracy in analysis of diffuse displacement scattering has been shown to depend on the separation of Bragg scattering from the scattering due to statistical disorder. It is especially important to remove the effects of line shape (due to domain broadening or wavelength spread) from that intensity for which the analysis is to be based on a statistical theory of ordering. This restraint is achieved by restricting the values of the zeroth-order coefficients, α_{000} and δ^x_{000}, to the values required by statistical considerations and Debye–Waller-factor measurements as indicated above, rather than allowing them to remain free parameters. Certainly, future studies of alloy systems would benefit from careful Debye–Waller-factor determination carried out in conjunction with the diffuse-scattering measurement whether the ultimate subject of the experiment be the disorder, displacement or vibrational properties of the system.

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References

BARDHAN, P., CHEN, H. & COHEN, J. B. (1977). *Philos. Mag.* **35**, 1653–1666.

BARDHAN, P. & COHEN, J. B. (1976). *Acta Cryst.* A**32**, 597–614.

BORIE, B. & SPARKS, C. J. (1971). *Acta Cryst.* A**27**, 198–201.

GRAGG, J. E. & COHEN, J. B. (1971). *Acta Metall.* **19**, 507–519.

HASHIMOTO, T., MIYOSHI, T. & OHTSUKA, H. (1976). *Phys. Rev. B*, **13**, 1119–1122.

HAYAKAWA, M., GRAGG, J. E. JR & COHEN, J. B. (1973). *J. Appl. Cryst.* **6**, 59.

MARCH, N. G., WILKINS, S. W. & TIBBALLS, J. E. (1976). *J. Cryst. Lattice Defects*, **6**, 253–270.

TIBBALLS, J. E. (1975). *J. Appl. Cryst.* **8**, 111–114.

TIBBALLS, J. E., TOWERS, G. R. & BARNEA, Z. (1978). Submitted for publication.

WILLIAMS, R. O. (1974). *Metall. Trans.* **5**, 1843–1850.