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Quantitative zone-axis convergent-beam electron diffraction (CBED) studies of metals. II. Debye–Waller-factor measurements

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Abstract

Quantitative CBED techniques, such as the *ZAPMATCH* zone-axis pattern-matching method [Bird & Saunders (1992). *Ultramicroscopy*, **45**, 241–251], have been applied with great success to the accurate refinement of low-order structure factors. The major limitation on the accuracy of the structure-factor measurements is uncertainty in the Debye–Waller factors describing the temperature-dependent atomic vibrations. While X-ray and neutron diffraction techniques are both capable of accurate measurements of Debye–Waller factors, the frequent use of liquid-nitrogen-cooled samples in CBED experiments means that previous measurements are rarely available at the temperatures required. This has prompted attempts to determine Debye–Waller factors from electron diffraction data obtained under experimental conditions that match those used for the quantitative CBED work. In this paper, the possibility of extracting accurate Debye–Waller factors from the low-order reflections of a zone-axis CBED pattern is investigated. In this way, the Debye–Waller factors and structure factors could be obtained from the same data set. With this new approach, it is shown that errors lower than ± 0.02 Å^2 can be obtained for the measurement of Debye–Waller factors from room- and liquid-nitrogen-temperature nickel and copper $\langle 110 \rangle$ zone-axis data. The results obtained are compared with previous measurements and theoretical predictions.

1. Introduction

The technique of convergent-beam electron diffraction (CBED) has undergone a period of rapid development in the past 10–15 years. It has been transformed from a mainly qualitative tool, concentrating on the symmetry of or the positions of features in the diffraction patterns, into a truly quantitative technique with direct analysis of the diffracted intensities. Advances in microscope technology, such as the introduction of energy filters, coupled with the improved performance of modern workstations, have greatly enhanced the prospects for extracting more accurate and more complete information from CBED patterns. The increasingly quantitative nature of the electron diffraction experiments has spawned a multitude of new techniques for the analysis of the resulting data.

In principle, CBED patterns contain the same information as that available from X-ray and neutron diffraction experiments. Consequently, a complete analysis of a CBED pattern should allow for symmetry determination, lattice-parameter evaluation, and measurements of Debye–Waller and structure factors. Considerable progress towards the goal of full information retrieval has been made over the years. For example, symmetry analysis has long been a major application of CBED (Tanaka, 1989) and lattice parameters have been determined from the positions of higher-order Laue-zone (HOLZ) deficiency lines (Randle *et al.*, 1989). The past few years have seen the emergence of new quantitative CBED techniques aimed at a detailed study of the charge density in crystalline solids through high-accuracy measurements of low-order structure factors (Spence & Zuo, 1992; Holmestad *et al.*, 1995; Saunders *et al.*, 1995). The major limitation in the accuracy of these structure-factor refinements has proved to be uncertainty in the Debye–Waller factors used to describe atomic vibrations (Bird & Saunders, 1992).

There are established techniques for the determination of Debye–Waller factors based on X-ray and neutron diffraction (see, for example, Willis & Pryor, 1975). However, the majority of the measurements are made at room temperature whereas many electron diffraction experiments are performed at liquid-nitrogen temperatures to reduce the effects of thermal diffuse scattering (TDS). In addition, it is difficult to determine the true sample temperature accurately in transmission electron microscope (TEM) experiments. Thus, even when measured Debye–Waller factors are available across a range of temperatures, the selection of the appropriate value for the quantitative CBED analysis is

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not necessarily an obvious choice. To overcome this problem, Debye–Waller-factor measurement techniques based on electron diffraction have been proposed. In this way, the measurement could be performed under similar conditions to those used for the quantitative CBED structure-factor refinements.

A number of alternative techniques have been considered. Each has been demonstrated to produce Debye–Waller factors with reasonable accuracy though each has drawbacks associated with the experimental procedure. For example, the critical-voltage effect can be exploited to perform structure-factor measurements at two different temperatures and hence allow deduction of the Debye–Waller factor (Menon & Fox, 1998, and references therein). However, the low-order structure factors used for the analysis are often perturbed by the unknown effects of chemical bonding, which limits the accuracy of this technique for the determination of Debye–Waller factors. In addition, the measurement of the critical voltages requires a high-voltage microscope operating at up to 1 MV or higher.

Midgley *et al.* (1998) have shown that it is possible to apply standard X-ray diffraction analysis methods to electron precession data such that Debye–Waller factors can be obtained with relative ease. However, this technique requires the installation of additional electronics on a conventional transmission electron microscope to perform the precession. A more rigorous approach involving the fitting of theoretical calculations to line traces across HOLZ excess lines has been proposed by Holmestad *et al.* (1993). In this case, however, the difficulty lies in establishing the precise diffraction conditions for the simulations so that the correct incident-beam orientation and the appropriate diffracted beams are considered.

In a recent paper, Nüchter *et al.* (1998) described a new method for the determination of Debye–Waller factors based on the close-to systematics technique already used for low-order structure-factor measurements (Spence & Zuo, 1992). This approach has the advantage that the experiments are no more difficult to perform than those already required for the low-order structure-factor studies. The results obtained by Nüchter *et al.* (1998) for NiAl suggest that this should be a useful addition to the arsenal of quantitative diffraction techniques.

One disadvantage common to all of the techniques described above is that the measurements of the Debye–Waller factors and structure factors require *separate* experiments. Thus, it is never possible to guarantee that the experimental conditions, *e.g.* sample temperature, are consistent in the two experiments. This is important because uncertainty in the Debye–Waller factor has already been identified as the most significant source of error in the low-order structure-factor refinements (Bird & Saunders, 1992). In this paper, we describe another alternative method for refining Debye–Waller factors which is related to that described by Nüchter *et al.* (1998). In our case, we have chosen to adopt the zone-axis diffraction geometry used by Bird & Saunders for their structure-factor measurements (see, for example, Saunders *et al.*, 1995). Taking nickel and copper ⟨110⟩ zone-axis patterns as examples, we will investigate the feasibility of obtaining *both* structure factors and Debye–Waller factors from the same zone-axis data. The effects of different sample thicknesses and temperatures will also be considered.

2. Debye–Waller-factor measurements by quantitative CBED

Existing X-ray and neutron diffraction techniques for the measurement of Debye–Waller factors generally rely on the assumption that all structure factors are adequately described by their neutral-atom values (Willis & Pryor, 1975). For this reason, these methods usually restrict their analysis to mid- to high-order reflections where bonding effects are minimal. While these techniques have proven satisfactory in many cases, there are limitations resulting from the large volume of interaction with the sample and the necessity for various correction terms in the analysis (Menon & Fox, 1998).

The increased interest in electron diffraction techniques for the determination of Debye–Waller factors has a number of motivations. First, with the increasingly quantitative nature of electron diffraction experiments, the retrieval of accurate structural information from electron diffraction patterns is receiving considerably more attention. Second, because of the small probe sizes involved in electron diffraction experiments (of the order of a few nanometres), corrections for crystal imperfections can be ignored, which, at least in principle, offers the prospect of improved Debye–Waller-factor studies. Third, the introduction of other quantitative diffraction techniques in which accurate Debye–Waller factors are required for the analysis, such as those for bonding charge density determinations, means that Debye–Waller factors are now required under electron diffraction conditions, *i.e.* with a very thin sample under electron beam illumination and often cooled in a liquid-nitrogen stage.

The principal behind quantitative CBED is that a theoretical simulation is adjusted until the best fit is obtained between the simulation and a set of experimental diffracted intensities. The experimental data are usually elastic filtered to reduce the contributions of inelastic scattering which cannot be included with sufficient accuracy in the simulation. The goodness-of-fit is measured by the sum-of-squares difference between the theoretical and experimental intensities,

$$\chi^2 = (1/N_{\rm data})\sum_i (I_i^{\rm ex} - cI_i^{\rm th} - I^{\rm back})^2/\sigma_i^2, \qquad (1)$$

where the $I^{\rm ex}$ are the experimental intensities, the $I^{\rm th}$ are the calculated intensities, the $I^{\rm back}$ are a set of background intensity levels, c is a normalization constant, σ^2 is the statistical variance of the experimental data, and the sum is over all $N_{\rm data}$ intensities (see Saunders *et al.*, 1995, for more details).

The goodness of fit is minimized by adjusting the scattering potential, sample thickness and the normalization and background constants. The scattering potential is written as

$$V(\mathbf{r}) = \sum_{\mathbf{g}} V_g \exp(i2\pi\mathbf{g}\cdot\mathbf{r})\exp(-Bs^2), \qquad (2)$$

where the V_g are electron structure factors, $\mathbf{g}$ is a reciprocal-lattice vector ($s = g/2$), $\mathbf{r}$ is a real-space vector and B will be referred to here as the Debye–Waller factor (note that this name is often given to the whole of the final exponential term).

Two alternative diffraction geometries have been considered. Spence, Zuo and co-workers use a close-to systematics geometry which increases the sensitivity of the data to a specific structure factor (see Spence & Zuo, 1992, or Holmestad *et al.*, 1995, for details). Bird & Saunders opted to use a zone-axis geometry which takes advantage of the pattern symmetry and the ability to determine a number of structure factors from a single pattern (see Saunders *et al.*, 1995, 1999, for details). Both approaches have been demonstrated to yield low-order structure-factor measurements with sufficient accuracy to investigate bonding effects in crystalline materials. While these techniques were originally conceived as a means to determine accurate structure-factor values, it has been realised that it should be possible to use the same concept to measure accurate Debye–Waller factors. In fact, Nüchter *et al.* (1998) have already confirmed that such measurements are possible using the close-to systematics geometry.

In their work, Nüchter *et al.* (1998) chose to adjust their diffraction geometry by tilting the sample so that the data should be most sensitive to a medium-order reflection which is well approximated by a neutral-atom structure factor, *i.e.* they minimize the effects of the low-order structure factors which contain bonding information, enabling them to refine the Debye–Waller factor instead of the structure factor. The same Debye–Waller-factor information should also be available from zone-axis data, with the added bonus that the symmetry of the pattern at the zone axis gives a powerful means of evaluating the quality of the data, *i.e.* local strain or crystal imperfections which would reduce the accuracy of the results are immediately evident by a breakdown in the ideal symmetry of the pattern. However, the analysis is likely to be complicated by the fact that we cannot avoid the contributions of the bonding-modified low-order structure factors. Two approaches to quantitative zone-axis CBED Debye–Waller-factor determination have been investigated and are discussed in the next two sections.

3. Method I: sum-of-squares minimization

The first analysis procedure involves running a series of pattern-matching calculations (like those previously used for low-order structure-factor determination) with a range of Debye–Waller-factor values. In each fit, the Debye–Waller factor remains fixed and the fit converges to its best-fit chi-squared (χ^2) value (note that it is not possible to include the Debye–Waller factor as a fitting variable without a severe degradation in the performance of the refinement calculations). The aim is to find an optimum Debye–Waller factor at which a minimum in the best-fit χ^2 value is obtained. Plotting the best-fit χ^2 as a function of the Debye–Waller factor used for the fit produces a curve such as that shown in Fig. 1 (which was obtained for a ~1400 Å room-temperature nickel ⟨110⟩ zone-axis pattern with the {111}, {200}, {220} and {113} structure factors, thickness and normalization and background constants included as refinement parameters). This confirms that there is an optimum value of the Debye–Waller factor for this data set under these conditions. The solid curve represents a quadratic function fitted through the data points. The optimum Debye–Waller factor is obtained from the minimum in this fitted quadratic curve [in this case 0.34 (2) Å^2]. The question remains as to whether this optimum Debye–Waller factor corresponds to the true value or whether it

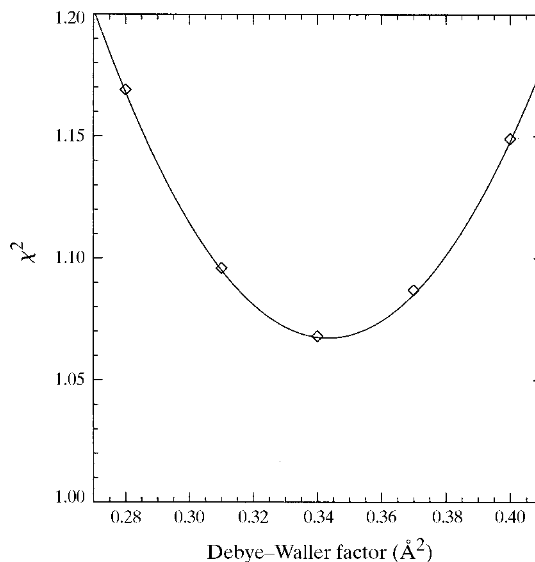

Fig. 1. Plot of the variation in the best-fit χ^2 [as defined by equation (1)] as a function of the fixed Debye–Waller factor for an ~1400 Å room-temperature nickel ⟨110⟩ zone-axis pattern. The solid line represents a quadratic function fitted through the data points. Note the low values of χ^2 (a perfect noise-limited fit being 1.0) which are typical of those obtained from the nickel and copper data.

is some compromise value which simply yields the lowest χ^2.

For example, the CBED pattern-matching calculations refine a small number of low-order structure factors while fixing a larger number of higher-order structure factors at their neutral-atom values. If too few low-order structure factors are allowed to vary during the fit, then the use of neutral-atom values is likely to introduce a systematic error resulting from the omission of bonding contributions. To investigate this error we repeat the analysis with different numbers of the bonding-modified structure-factor variables. In this way, we hope to introduce the bonding effects through the variable low-order structure factors while optimizing the Debye–Waller factor *via* its sensitivity to the fixed (neutral-atom) higher-order structure factors. Repeating the Debye–Waller-factor optimization for a range of variables from no structure factors (varying only the sample thickness, normalization and background constants) up to six structure factors ({111}, {200}, {220}, {113}, {222} and {400}) yields the optimum Debye–Waller factor as a function of the number of variables (as shown in Fig. 2 for the same nickel zone-axis pattern). It is clear that the total omission of bonding contributions from the low-order structure factors (no structure-factor variables) results in an overestimation of the Debye–Waller factor, *i.e.* the optimized Debye–Waller factor somehow compensates for the lost bonding information. When the fit is given the freedom to adjust the structure-factor values for the effects of bonding, there is a complimentary adjustment to the optimized Debye–Waller factor. The magnitude of the omitted structure-factor bonding modifications is lessened at higher scattering angles, leading to the convergence of the optimized Debye–Waller factor as more variables are introduced.

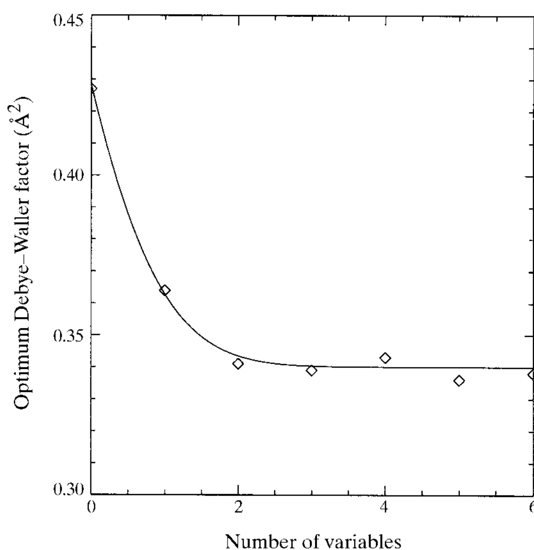

Fig. 2. Plot of the variation in the optimum Debye–Waller factor as a function of the number of structure-factor variables included in the refinement. The solid curve is interpolated from the data points.

These results indicate that the choice of the number of variables is crucial to the convergence of the fit at an acceptable solution. If too few structure factors are allowed to vary, the optimized Debye–Waller factor will be subject to errors arising from the omitted bonding contributions. However, it may not always be possible to include a sufficient number of variables to reach this converged result. As discussed by Saunders *et al.* (1999), the sensitivity of the data to the structure-factor variables is dependent on a combination of the diffraction geometry, the reflections from which we have experimental data, the incident-beam energy and the sample thickness. For any given sample thickness, there should be an optimum number of structure-factor variables (with thicker samples having greater sensitivity). If the sample is thin then the number of structure-factor variables to which the data is sensitive may not be sufficient to include all of the bonding effects. Thus, the best solution that can be obtained will still be influenced by systematic error. Adding more variables only succeeds in giving the fit too much freedom so that it converges to an incorrect (local) solution. The copper and nickel data studied here are less prone to these errors because significant bonding effects are only observed in the first two or three low-order structure factors, making it generally possible to find a sample thickness at which a sufficient number of variables can be included.

4. Method II: structure-factor intercepts

An alternative strategy for the determination of Debye–Waller factors is to analyse the best-fit structure-factor values obtained from the refinement calculations [an extension of a technique previously considered by W. G. Burgess, A. R. Preston, N. J. Zaluzec & C. J. Humphreys (unpublished)]. As with the sum-of-squares minimization method, fits are carried out with a range of (fixed) Debye–Waller-factor values. After conversion from electron to X-ray structure factors (using the Mott formula), the best-fit structure factors are plotted as a function of the Debye–Waller factor used for the fit. The refined values are then compared with their respective neutral-atom values (calculated according to Doyle & Turner, 1968). Where bonding modifications are small, the refined structure factor and its neutral-atom counterpart should be in agreement when the appropriate Debye–Waller factor is used.

An example of this analysis, applied to the same room-temperature nickel data as considered in §3, is shown in Fig. 3. The four plots show the variation of the best-fit {111}, {200}, {220} and {113} structure factors for Debye–Waller factors in the range 0.28–0.40 Å^2. In each case, the dashed line represents the equivalent neutral-

atom structure factor. It is known that the low-order structure factors are modified from their neutral-atom values by the effects of bonding (Saunders *et al.*, 1999). Thus, the intercept of the best-fit and neutral-atom lines for the lowest-order structure factors will not yield an accurate Debye–Waller factor. As higher-order structure factors are considered, however, bonding effects diminish and the Debye–Waller factor at which the intercept occurs should converge towards the correct value. This behaviour is demonstrated clearly by the four plots in Fig. 3, where the {111} and {200} intercepts occur well above 0.40 Å^2, while those obtained from the {220} and {113} structure factors (where bonding effects are minimal) occur at 0.34 and 0.33 Å^2, respectively. If the approximate magnitude of the bonding contribution to these structure factors is known, then this uncertainty in the neutral-atom value can be used to estimate the error arising from the omission of the bonding term when determining the intercept point. For the {220} and {113} intercepts shown in Fig. 3, this would result in errors of less than 0.01 Å^2 in each case.

Another source of uncertainty in the intercept point arises from errors in the refined structure-factor values. As shown in equation (2), the dependence of the structure factor on the Debye–Waller factor involves an exponential term in which the Debye–Waller factor is multiplied by s^2, where $s = \sin\theta/\lambda$, θ is the scattering angle and λ is the electron wavelength. Thus, the gradient of the structure factor *versus* Debye–Waller-factor line increases for higher-order structure factors. This effect is demonstrated in Fig. 3 where the gradient increases from the {111} structure-factor plot through to the {113} plot. Therefore, even if we allow for errors in the refined structure factors of up to 3%, the uncertainty

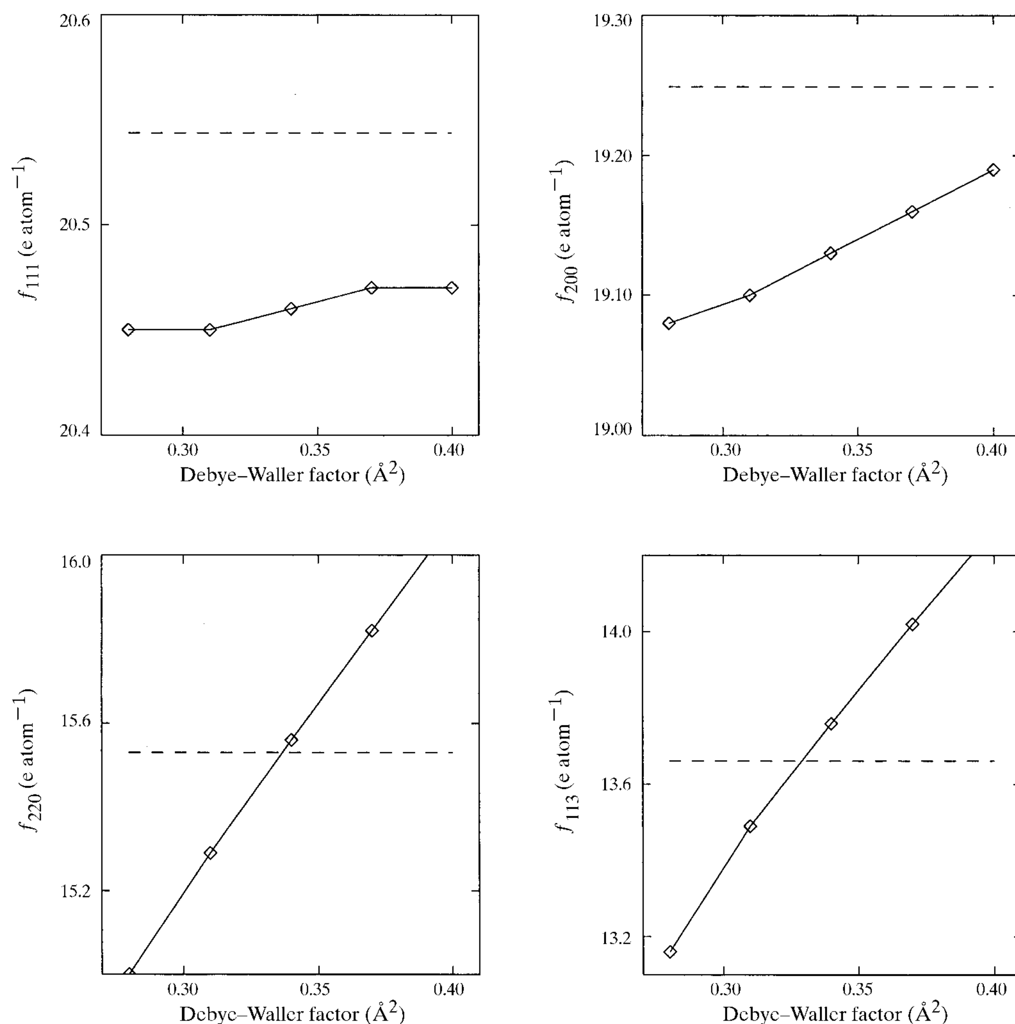

Fig. 3. Plots of the refined low-order structure factors for the ~1400 Å room-temperature nickel pattern as a function of the Debye–Waller factor used for the refinement (top row {111} and {200}, bottom row {220} and {113}). The dashed lines represent the neutral-atom values calculated according to Doyle & Turner (1968).

in the Debye–Waller factor determined from the {220} and {113} intercepts would be no more than 0.02 Å^2.

Once again, this technique is dependent on the sensitivity of the data to the different structure-factor variables. In order to determine an accurate Debye–Waller factor, the data must be sufficiently sensitive to refine structure factors for which the bonding contributions are small. In other words, if the data are only sensitive to structure factors that are significantly modified by bonding, then taking the intercept with the neutral-atom line will be grossly in error. For example, if we had been able only to determine the {111} and {200} structure factors for the nickel data considered in Fig. 3, then we would have obtained a Debye–Waller factor of 0.44 Å^2 from the {200} intercept with its neutral-atom line (whereas a value of 0.32 Å^2 would have been obtained by taking the intercept with a line representing a bonding-modified structure-factor value of 19.12 e atom^{-1} (as determined by Saunders *et al.*, 1999).

As discussed by Saunders *et al.* (1999), the sensitivity of the zone-axis pattern to the {220} and {113} structure factors in the reflections used for these pattern-matching calculations arises from multiple-scattering effects. Thus, the sensitivity of our measurements of the Debye–Waller factor is the result of a second-order effect, whereas the systematics method of Nüchter *et al.* (1998) is sensitive to the Debye–Waller factor through a first-order single-scattering effect. Thus, in principle, the systematics approach should have a higher sensitivity to the Debye–Waller-factor information. Unfortunately, this increased sensitivity is obtained at the expense of having to perform a separate experiment to determine the Debye–Waller factor.

5. Discussion

Both the χ^2-minimization and the neutral-atom line-intercept techniques have been applied to ⟨110⟩ zone-axis CBED data acquired from nickel (at room and liquid-nitrogen temperatures) and copper (at liquid-nitrogen temperatures). The data were acquired for sample thicknesses in the range 600–3000 Å, using a Hitachi HF2000 FEG-TEM at the University of Bristol equipped with a Gatan Imaging Filter. The data were elastic filtered to reduce the contributions of inelastic scattering to the diffraction contrast.

The results obtained for the different sample thicknesses and temperatures are shown in Table 1. All of the calculations allowed the four lowest-order structure factors, *i.e.* {111}, {200}, {220} and {113}, to vary during the refinement. The Debye–Waller factors obtained using the neutral-atom line-intercept method (§4) are shown for both the intercept of the best-fit {220} and {113} structure factors with their neutral-atom equivalents. The uncertainty arising from bonding contributions to these structure factors is minimal and results in errors of less than 0.01 Å^2 in all cases.

Table 1. *Debye–Waller factors (Å^2) determined from nickel and copper ⟨110⟩ zone-axis CBED patterns at a range of thicknesses and temperatures using both the χ^2-minimization and neutral-atom line-intercept methods*

Sample thickness (Å)	χ^2 minimization	Line intercept: {220} structure factor	Line intercept: {113} structure factor
Room-temperature nickel			
800	0.33 (2)	0.32 (2)	0.31 (2)
1150	0.35 (2)	0.36 (2)	0.35 (2)
1250	0.37 (2)	0.36 (2)	0.34 (2)
1400	0.34 (2)	0.34 (2)	0.33 (2)
Average	0.35	0.35	0.34
Liquid-nitrogen-temperature nickel			
650	0.15 (2)	0.14 (2)	0.13 (2)
1400	0.16 (2)	0.15 (2)	0.14 (2)
1450	0.15 (2)	0.15 (2)	0.14 (2)
2650	0.17 (2)	0.18 (2)	0.17 (2)
Average	0.16	0.16	0.15
Liquid-nitrogen-temperature copper			
900	0.23 (2)	0.21 (2)	0.21 (2)
950	0.24 (2)	0.21 (2)	0.21 (2)
3100	0.22 (2)	0.21 (2)	0.21 (2)
Average	0.23	0.21	0.21

A comparison of the results obtained from the two techniques shows that the neutral-atom intercept method generally gives a lower value for the Debye–Waller factor than the χ^2 minimization. Analysis of the refined low-order structure factors obtained using the different Debye–Waller-factor solutions suggests that the Debye–Waller factors obtained from the intercept method provide a more accurate solution for the bonding-modified scattering potential, *i.e.* they show better agreement with the results of other techniques (see Saunders *et al.*, 1999). This implies that the Debye–Waller factors obtained by minimizing the best-fit χ^2 are subject to systematic error. One possible explanation for this error can be found in the behaviour of the other fitting parameters when the fits are repeated with the different Debye–Waller factors. It has been observed that the best-fit background and normalization constants also change as a function of the chosen Debye–Waller factor. Thus, the Debye–Waller factor and the constant terms may not act as truly independent fitting parameters. The apparent systematic offset of the optimized Debye–Waller factor obtained from the χ^2 minimization may show that by fixing the Debye–Waller factor we are locating the minimum by adjusting the normalization and background constants. The χ^2 minimum may not be a true reflection of the quality of the fit as a function of the Debye–Waller factor alone. In the same way that omitting bonding effects leads to an erroneous Debye–Waller factor, it may also be true that fixing the Debye–Waller factor while adjusting the normalization and background terms may not yield an accurate solution. Therefore, any attempt to refine the Debye–Waller

Table 2. *Debye–Waller factors (Å²) determined previously from X-ray and neutron scattering experiments and from theoretical predictions*

Material	Debye–Waller factor	Technique	Source
Nickel (room temperature)	0.37 (1) (293 K)	X-ray diffraction	Inkinen & Suortti (1964)
	0.38 (1) (300 K)	Fit to inelastic neutron data	Barron & Smith (1966)
	0.43 (1) (293 K)	Neutron diffraction	Cooper & Taylor (1969)
	0.35 (293 K)†	Fit to inelastic neutron data	Peng *et al.* (1996)
Nickel (liquid-nitrogen cooled)	0.13 (110 K)	Fit to inelastic neutron data	Peng *et al.* (1996)
Copper (liquid-nitrogen cooled)	0.21 (110 K)	Fit to inelastic neutron data	Peng *et al.* (1996)

† Extrapolated from tabulated data

factor from the best-fit χ^2 values may be limited by our introduction of background and normalization constants into the definition of the χ^2 function [equation (1)].

The Debye–Waller factors determined from the intercepts of the {220} and {113} structure factors show how the omission of bonding effects can lead to errors in the position of the intercept point. The structure-factor measurements discussed by Saunders *et al.* (1999) indicate that the {113} structure factor of nickel is well represented by its neutral-atom value, whereas the {220} structure factor is slightly modified by the effects of bonding. This is reflected in the slightly higher Debye–Waller factors obtained from the intercept of the {220} structure factor with its neutral-atom equivalent. In the case of copper, however, both {220} and {113} are well described using neutral-atom structure factors. Hence, the intercept Debye–Waller factors for both structure factors are in better agreement. Table 2 lists previous measurements and theoretical predictions for the Debye–Waller factors of these materials. These include X-ray, neutron and theoretical results given by Willis & Pryor (1975, and references therein), and a theoretical fit to neutron inelastic scattering data by Sears & Shelley (1991), as republished by Peng *et al.* (1996). The results obtained from the {113} intercept method are in good agreement with those obtained from the data of Sears & Shelley (1991). There is less agreement, however, between our results and the other three room-temperature nickel values shown in Table 2. The neutron-scattering result of Cooper & Taylor (1969) is clearly an outlier, while the X-ray and theory values are slightly higher than our CBED measurements. If zone-axis CBED refinements are performed using these higher Debye–Waller-factor values, then the refined low-order structure factors demonstrate systematic deviations from the results obtained from other techniques and solid-state theory calculations (see Saunders *et al.*, 1999). This implies that the use of the accepted 'room-temperature' X-ray value of 0.37 Å² is not appropriate for our CBED analysis and demonstrates the importance, in this case, of making Debye–Waller-factor measurements directly from the CBED data.

It is apparent from the results shown in Table 1 that the various data sets acquired from different positions on the sample and at different sample thicknesses do not yield totally consistent results. This variation is observed using both the minimization and intercept methods. The scatter in the intercept results is larger than that expected from the uncertainty due to bonding effects in the neutral-atom reference value. It is possible that the scatter results from errors in the refined structure-factor values. However, to produce the variations observed in Table 1 would require errors in the fitted structure factor of between 3 and 5%. While this is not totally out of the question, we believe the errors arising from sources other than the uncertainty in the Debye–Waller factor to be much less significant (Bird & Saunders, 1992). In addition, the consistency of the values given from both the {220} and {113} intercepts implies that random error alone cannot explain the variation in the Debye–Waller factors measured from the different data sets.

If we rule out errors in both the neutral-atom reference structure-factor value and the refined structure factors then we are left with the conclusion that the variations in the Debye–Waller factors obtained from the different data sets are in fact a true reflection of the varying temperature of the material. One possible explanation for this could be variations in the beam heating effects for different sample thicknesses and probe positions. However, the approximate theory given by Reimer (1997) would appear to discount this option. Other possibilities are that the sample temperature varies as a result of fluctuations in the actual room temperature or, in the case of the cooled samples, through the liquid nitrogen boiling off. The magnitude of these effects estimated by Nüchter *et al.* (1998), *i.e.* around 10 K, could explain much of the variation observed in our experiments.

Whatever the cause, it is certainly true that the refined low-order structure factors obtained from different zone-axis CBED patterns are more consistent (both with each other and with the results of alternative experimental and theoretical techniques) when each data set is allowed to determine its own Debye–Waller factor using the intercept method (as shown by Saunders *et al.*, 1999). The use of a single averaged Debye–Waller factor leads to much less satisfactory results. For example, allowing each of the nickel room-temperature data sets to find its own Debye–Waller factor using the {113} intercept results in a 0.6% variation in the {220}

structure factors refined from the different patterns, whereas fixing the Debye–Waller factor at the Sears & Shelley (1991) value of 0.35 Å^2 gives a 1.9% variation. The comparable variations for the liquid-nitrogen-cooled data are 0.3% when the Debye–Waller factor is determined from the {113} intercept and 3.4% when the same Debye–Waller factor is used for all data sets. This leaves open the question as to whether it is better to use a more accurate measurement technique to perform a separate Debye–Waller-factor determination or to attempt to determine the Debye–Waller factor from the same data as the structure factors. In the former case, the improved accuracy of the measurement may be compromised by the introduction of a systematic error resulting from temperature differences between the Debye–Waller and structure-factor experiments. In the latter case, while this systematic error is avoided, the random error from uncertainty in the Debye–Waller-factor measurement is increased. While the data presented in this paper do not conclusively answer this question, they do show the need for further systematic investigations of the relative magnitudes of these systematic and random errors if the ultimate accuracy of CBED structure-factor refinements is to be realised.

6. Conclusions

Two alternative strategies have been considered for determining Debye–Waller factors from the diffracted intensities in the low-order reflections of an elastic filtered zone-axis CBED pattern. In the first, the goodness-of-fit between a theoretical simulation and the experimental data is adjusted by repeating the fit with a range of different fixed Debye–Waller factors. This analysis produces a clear optimum Debye–Waller factor for each data set at which the χ^2 measure of the goodness of fit is minimized. This optimized value will be subject to errors if bonding effects are ignored by fixing the low-order structure factors at their neutral-atom values. More accurate results are obtained by introducing the low-order structure factors as variables during the refinement in an attempt to include the bonding effects. However, there is evidence that the Debye–Waller factor and some of the other fitting parameters, *i.e.* a normalization constant and background terms, act in unison and that the optimized Debye–Waller factor may be influenced by the values of these other variables leading to a systematic overestimate of the Debye–Waller factor using this technique.

The second approach considers the refined low-order structure factors obtained from the fits run with the range of Debye–Waller-factor values. When bonding contributions to a specific structure factor are small, then the refined structure factor should coincide with its neutral-atom equivalent when the fit is performed with the correct Debye–Waller factor. Bonding effects are most pronounced for the lowest-order structure factors. Thus, each fit must include a sufficient number of structure-factor variables that the higher-order variables are well described by their neutral-atom values. We have shown, for example, how the {113} structure factor in nickel and copper can be used to determine an appropriate Debye–Waller factor for a given data set. Errors associated with uncertainties in the bonding contribution and random errors in the refined structure factor lead to Debye–Waller-factor measurements with an accuracy of around 0.02 Å^2. There is good agreement between these measurements and those obtained from neutron inelastic scattering measurements (Sears & Shelley, 1991).

The variation in the Debye–Waller factors determined from different patterns (acquired at different times and positions on the sample) is greater than our estimated error. Seemingly, this indicates that temperature fluctuations between successive experiments cannot be ignored. If this is the case, then the use of the same Debye–Waller factor for the analysis of CBED patterns acquired under different conditions would introduce systematic errors in the refined structure factors. This suggestion is supported by the nickel and copper data discussed here and by Saunders *et al.* (1999) where greater consistency between the results obtained from different CBED patterns (and with the results of other techniques) is obtained if a separate Debye–Waller-factor value is determined for each pattern. More work is required to resolve this issue if we are to achieve the ultimate accuracy in quantitative CBED experiments.

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