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Modeling Thermal Diffuse Scattering in Electron Diffraction Involving Higher-Order Laue Zones

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Abstract

The importance of thermal diffuse scattering (TDS) in electron diffraction contrast is well known. Experiments involving higher-order Laue-zone (HOLZ) reflections are highly sensitive to variations in the TDS form factors. The Einstein model for TDS gives excellent agreement with experimental convergent-beam electron diffraction (CBED) patterns containing HOLZ lines provided that the absorption coefficients are not calculated using perturbative methods but instead are evaluated exactly. This is in contrast to absorption potentials determined from experiments sensitive to beams in the zero-order Laue zone (ZOLZ) only, the use of which can be inconsistent with data sensitive to HOLZ beams. Here the features of the Einstein model important for the correct interpretation of the experimental data are analyzed and why it is inadequate to treat HOLZ beams perturbatively is discussed.

1. Introduction

Even at low temperatures, the effects of thermal diffuse scattering (TDS) on electron diffraction contrast are significant. Quantitative analytical work, such as accurate crystal structure-factor determination and microanalytical techniques require accurate modeling of TDS. TDS is well understood from a theoretical point of view and has been discussed in detail elsewhere (Yoshioka & Kainuma, 1962; Hall, 1965; Whelan, 1965; Hall & Hirsch, 1968; Humphreys & Hirsch, 1968; Allen & Rossouw, 1989; Bird & King, 1990; Wang, 1995). In particular, the Einstein model for TDS, which assumes independently oscillating atoms and takes into account phonon modes for which the frequency is independent of wave vector, is well known to result in form factors that have been used to model TDS and diffraction contrast successfully (Allen & Rossouw, 1990; Rossouw, Miller, Drennan & Allen, 1990; Allen, Rossouw & Wright, 1992). The effect of TDS can be well simulated by the Einstein model for both low and high scattering angles (Rossouw & Hampikian, 1993; Rossouw & Miller, 1993), where multiphonon contributions are important. The Einstein model provides a good average description of the TDS intensity as a function of scattering angle (Hall, 1965; Hall & Hirsch, 1965; Wang, 1995).

Recently, Lehmpfuhl, Krahl & Uchida (1995) have taken experimental energy-filtered convergent-beam electron diffraction (CBED) patterns near the [111], [110] and [100] zone axes for Si at room temperature. Use of the Voss, Lehmpfuhl & Smith (1980) absorption model for TDS to simulate these zero-beam experimental patterns results in the appearance of anomalous effects in the first-order Laue-zone (FOLZ) lines occurring in the theoretical CBED pattern. To eliminate these anomalies, different Debye–Waller factors were used for different zone axes and the experimental results were then interpreted as possible evidence for anisotropy in the Debye–Waller factor for Si.

However, a subsequent calculation (Allen & Josefsson, 1996) using the Einstein model showed that the intensity distribution in higher-order Laue-zone (HOLZ) patterns can be well simulated when using the Einstein model for TDS as a basis for the absorption potential. This potential must be used in an exact solution of the fundamental equations of the dynamical diffraction theory, which involves the solution of an eigenvalue problem for a non-Hermitian matrix (Allen & Rossouw, 1989). Here, we want to describe and to analyze the subtle but important issues that are essential for a correct interpretation of the experimental HOLZ patterns, since their simulation is very sensitive to variations in the TDS form factors.

2. TDS in HOLZ patterns

An absorption potential for TDS in silicon (for 100 keV electrons and room temperature) was determined by Voss, Lehmpfuhl & Smith (1980). Low-indexed structure factors $V_g^{\rm real}$ and TDS absorption form factors $V_g^{\rm im}$ were determined for Si by fitting to an energy-unfiltered CBED pattern for {111} systematic-row interactions in the ZOLZ up to a magnitude of about $g = 6$ [in units of the beam index numbers $g = (h^2 + k^2 + l^2)^{1/2}$]. We note that HOLZ reflections have magnitude roughly twice this value. The crystal was oriented so that ($1\bar{1}\bar{1}$) was in the exact Bragg orientation. A densitometer line scan was taken along the length of the systematic

row CBED discs. After a background subtraction had been performed to remove inelastic plasmon scattered electrons, the resulting line scan was used to fit a theoretical calculated intensity distribution. The TDS scattering form factors $V_g^{\rm im}$ were expressed in parametrized parabolic form for convenience,

$$V_g^{\rm im} = V_g^{\rm real}(Ag - Bg^2). \quad (1)$$

The experimentally determined densitometer trace was reproduced accurately for certain values of the elastic structure factors and for the values $A = 0.004$ and $B = 0.0003$ in (1).

In Fig. 1(*a*), we compare the ratio $V_g^{\rm im}/V_g^{\rm real}$ obtained by Voss, Lehmpfuhl & Smith (1980) for Si at room temperature and at 100 keV with those calculated from the Einstein model using the elastic scattering factors of Waasmaier & Kirfel (1995). This parametrization is only valid for $g > 0$. The mean absorption potential $V_0^{\rm im}$ is introduced separately into the calculations, as described by Voss, Lehmpfuhl & Smith (1980). We note that less-accurate elastic form-factor parametrizations (Doyle & Turner, 1968; Rez, Rez & Grant, 1994) give almost identical results to those obtained using the Waasmaier & Kirfel (1995) parametrization. The particular absorption parameters A and B obtained by Voss, Lehmpfuhl & Smith (1980) are significantly different from those obtained from a parabolic fit to the Einstein model, *i.e.* $A = 0.0146$ and $B = 0.00061$ (see Fig. 1*a* also). Reducing $V_g^{\rm im}$ calculated from the Einstein model by a factor of 0.25 gives approximate agreement with the Voss *et al.* absorptive potential for small g but not for large g. This can be seen in Fig. 1(*b*) where we show the ratio $V_g^{\rm im}/V_g^{\rm real}$ using exactly 0.25 × Einstein TDS scattering factors (solid line), the Voss *et al.* model [the same as shown in Fig. 1(*a*), dotted line] and a parabolic fit to 0.25 × Einstein model with $A = 0.003\,65$ and $B = 0.000\,152\,5$ (broken line). It is important to note that these parametrizations are only valid for this particular temperature and incident energy. Furthermore, simple parametrizations, such as a parabolic form, are not always justified – see Figs. 3 and 8 in Allen & Rossouw (1990). However, the absorptive potential in the Einstein model is easily calculated from first principles for any temperature and accelerating voltage (Allen & Rossouw, 1989; Bird & King, 1990).

It was noted by Lehmpfuhl, Krahl & Uchida (1995) that, in their simulation of the experimental CBED patterns (including HOLZ lines), no discernible difference was obtained whether commonly employed perturbative techniques or an exact scheme (Allen & Rossouw, 1989) was used to calculate the absorption coefficients. This is not the case when using the Einstein model. In Fig. 2, we show one quarter of the zero-beam CBED pattern, calculated using various assumptions, near the [100] zone axis for 99.177 keV electrons incident on an Si crystal of thickness 2720 Å with a Debye–Waller factor of $D = 0.46$ Å^2. All the results were obtained using a 93-beam Bloch-wave calculation, with different models for the absorption potential and with the resulting absorption coefficients calculated either using the exact scheme or in the perturbative approximation. The results in Figs. 2(*a*) and (*b*) were obtained with Einstein model TDS form factors, as discussed in Allen & Josefsson (1996). In Fig. 2(*a*), the absorption coefficients were calculated using the exact scheme, and in Fig. 2(*b*) in the perturbative approximation. The intensity in the HOLZ lines is substantially different in the two cases. The exact scheme results agree very well with experiment

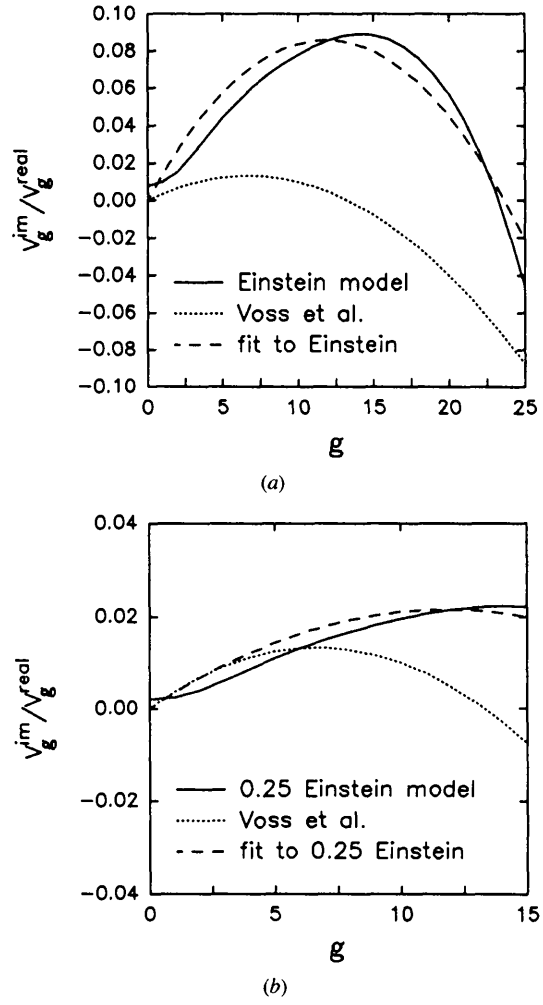

Fig. 1. The ratio of TDS to elastic scattering form factors $V_g^{\rm im}/V_g^{\rm real}$. (*a*) The results obtained by Voss, Lehmpfuhl & Smith (1980) for Si at room temperature and at 100 keV (dotted line) calculated from equation (1) with $A = 0.004$ and $B = 0.0003$. The same ratio calculated from the Einstein model using the elastic scattering factors of Waasmaier & Kirfel (1995) (solid line). A parabolic fit to the Einstein model with $A = 0.0146$ and $B = 0.00061$ (dashed line). (*b*) The Voss *et al.* model (dotted line) compared to the 0.25 Einstein model (solid line) and a parabolic fit to the 0.25 Einstein model with $A = 0.00365$ and $B = 0.000152$ (dashed line).

[see Fig. 2(*a*) of Lehmpfuhl, Krahl & Uchida (1995)] while the perturbative method shows anomalous effects similar to those obtained using the Voss, Lehmpfuhl & Smith (1980) TDS potential [see Figs. 5(*b*) and (*c*) in Lehmpfuhl, Krahl & Uchida (1995)]. Similar results are obtained when using the parabolic fit (see Fig. 1*a*) to the Einstein model. This can be seen in Figs. 2(*c*) and (*d*), where the absorption coefficients are calculated in the exact scheme and in the perturbative approximation, respectively. The effect of using a perturbative approach is to underestimate the contribution of the FOLZ beams. The Voss, Lehmpfuhl & Smith (1980) TDS potential severely underestimates the absorption relative to the Einstein model at large reflection angles (see Fig. 1).

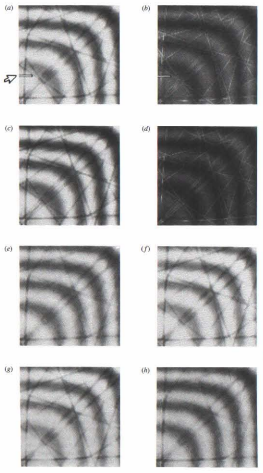

Fig. 2. The zero-beam CBED pattern near the [100] zone axis for 99.177 keV electrons incident on an Si crystal of thickness 2720 Å. The results were obtained from a 93-beam Bloch-wave calculation, with TDS absorption included by: (*a*) an exact calculation using the Einstein model; (*b*) a perturbative calculation using the Einstein model; (*c*) an exact calculation using the parametrized Einstein model; (*d*) a perturbative calculation using the parametrized Einstein model; (*e*) an exact calculation using the 0.25 Einstein model; (*f*) a perturbative calculation using the 0.25 Einstein model; (*g*) an exact calculation using the parametrized 0.25 Einstein model; (*h*) a perturbative calculation using the parametrized 0.25 Einstein model.

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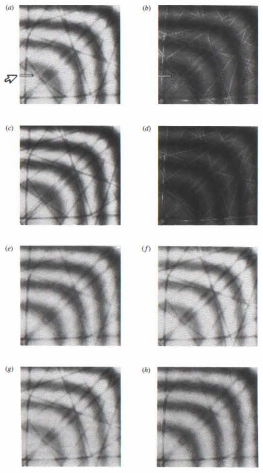

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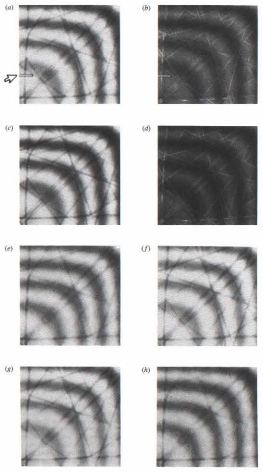

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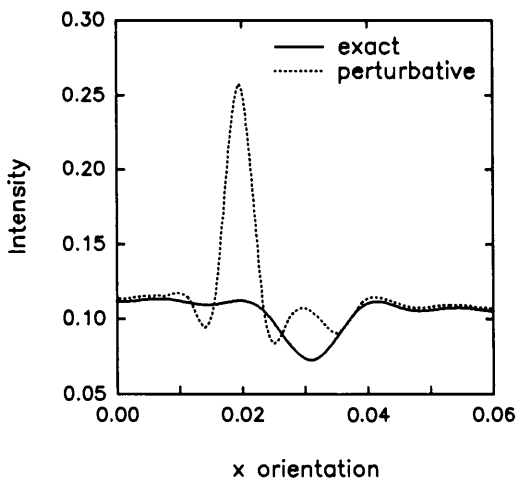
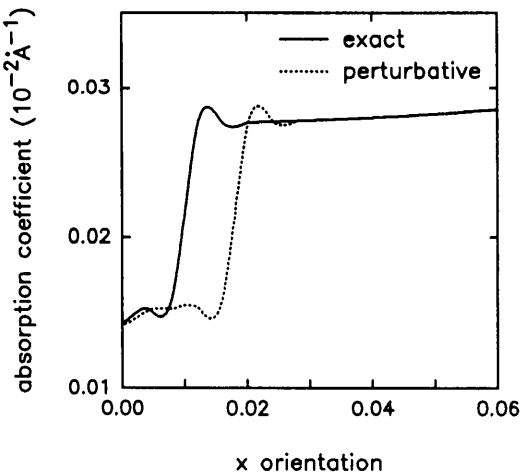
This is why, as pointed out by Lehmpfuhl, Krahl & Uchida (1995), the use of a perturbative or exact scheme had very little effect on their simulated CBED patterns.

Because reducing the Einstein potential by a factor of 0.25 gives approximate agreement with the Voss *et al.* absorptive potential for small g, in Fig. 2(*e*) we show the CBED intensity obtained using exactly one quarter of the Einstein potential (with the absorption coefficients calculated exactly) and in Fig. 2(*f*) with the absorption coefficients calculated perturbatively. Similar results are obtained using the parabolic fit to the 0.25 Einstein model shown in Fig. 1(*b*). This can be seen in Figs. 2(*g*) and (*h*) where the parabolic fit to the 0.25 Einstein model is used in an exact [Fig. 2(*g*)] and perturbative [Fig. 2(*h*)] calculation of the absorption coefficients. It is interesting that in using this reduced potential a similar diffraction contrast is obtained to the full Einstein model [*cf.* Figs. 2(*a*) and (*e*)]. Although the 0.25 Einstein model does not change diffraction contrast greatly in this case (when compared to the actual Einstein model), this will not in general be true, and in any case the absolute intensity will be very different. The CBED intensity patterns shown in Fig. 2 are not absolute intensities but are instead normalized to their own individual maximum intensity.

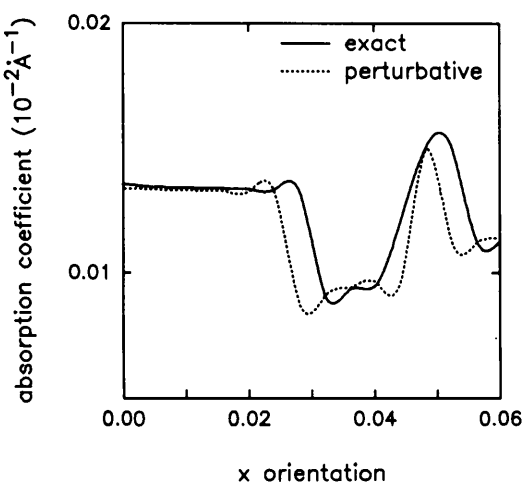
In order to avoid intensity artefacts in the simulation of a HOLZ pattern, the functional dependence of the absorption potential on g is more important than the magnitude, at least in this case. Using the reduced Einstein model in a perturbative calculation also gives artefacts in the intensity [see Fig. 2(*f*)] but not as pronounced as those for the full Einstein model shown in Fig. 2(*b*) (a perturbative treatment is expected to be better for the weaker potential). However, this is consistent with the fact that in this case a reasonable agreement with the experimental results could be ob-



(*a*)



(*b*)



(*c*)

Fig. 3. (*a*) The CBED intensity calculated in the exact scheme (solid line) and perturbatively (dashed line) along the line crossing the HOLZ line shown in Figs. 2(*a*) (indicated by the arrow) and (*b*). This line corresponds to the tangential component k_t of the incident beam varying as $k_t = x(011) + 0.125(01\bar{1})$ with x varying from 0 to 0.06. Examples of two significant absorption coefficients belonging to excited Bloch waves are shown in (*b*) and (*c*) for the same orientations as in (*a*). The results are calculated using the exact scheme (solid line) and in the often used perturbative approximation (dashed line).

tained by assuming that the absorption due to TDS is zero (Lehmpfuhl, Krahl & Uchida, 1995). Therefore, one cannot say that, in general, agreement with experimental HOLZ patterns will be maintained by reducing the strength of the Einstein model, particularly if TDS substantially changes diffraction contrast (Rossouw, Miller, Drennan & Allen, 1990). Anomalous absorption due to TDS and the associated modification of diffraction contrast is an essential part of the physics, especially for thick crystals (thousands of ångströms). While in the case considered here the diffraction contrast does not change substantially, there are subtle changes in contrast. Careful comparison of [100] calculations with experimental results [see Fig. 2(*a*) of Lehmpfuhl, Krahl & Uchida (1995)] shows better agreement with the inclusion of TDS.

If one considers effects only due to the ZOLZ (as in Voss, Lehmpfuhl & Smith 1980), then one cannot discriminate between the 0.25 Einstein and the Voss *et al.* model, since both are in reasonable agreement for all values of g in the ZOLZ (*i.e.* $g < 7$). Only when simulating HOLZ patterns (where values with $g > 7$ are included) is the absorption model crucial, and here the Voss *et al.* model fails to reproduce the experimental intensity while the Einstein model is successful.

In Fig. 3(*a*), we show the CBED intensity calculated in the exact scheme (using the Einstein model for absorption) along the line indicated by the arrow in Fig. 2(*a*). The results are compared with the intensity calculated in the perturbative approximation [*i.e.* along the line shown in Fig. 2(*b*)]. This line corresponds to the tangential component k_t of the incident beam varying as $k_t = x(011) + 0.125(01\bar{1})$ with x varying from 0 to 0.06. The increase in intensity observed as a peak near the orientation $x = 0.02$ (close to the HOLZ line at approximately $x = 0.03$) in the perturbative approximation is due to an underestimation of the TDS absorption coefficients calculated perturbatively at these orientations. The standard perturbative techniques result in incorrect absorption coefficients and Bloch-wave excitation amplitudes while the elastic coefficients remain almost unchanged. Of the 93 Bloch waves used in this calculation, approximately 15 had non-zero excitation amplitudes and absorption coefficients that differed at times by up to 200% when calculated perturbatively or exactly. In Figs. 3(*b*) and (*c*), we show two of these absorption coefficients (both belonging to excited Bloch waves) calculated in the exact scheme (solid line) and in the perturbative approximation (dashed line) for the same orientations as the intensity pattern in Fig. 3(*a*). The increase in intensity of the perturbative *versus* the exact calculations near the HOLZ lines in Fig. 3(*a*) (at orientations of $x = 0.02$ and $x = 0.03$) is due in part to the decrease of the absorption coefficients calculated in the perturbative approximation at these orientations, as seen in Figs. 3(*b*) and (*c*). Clearly, for certain orientations, the perturbative approximation is entirely inadequate in calculating the absorption coefficients.

3. Conclusions

We reiterate that the effects of even relatively small variations in absorption can be significant, particularly where HOLZ reflections are involved. The Einstein model has repeatedly been shown to be highly successful and atomic TDS form factors calculated in the Einstein model are readily available either in simple Doyle–Turner (Gaussian) parametrized form (Dudarev, Peng & Whelan 1995), or in the form of computer subroutines (*i.e.* Bird & King 1990). We caution that care must be taken when making use of TDS form factors (whether experimentally determined or otherwise) that are substantially at variance with the readily available or easily calculated Einstein model. Furthermore, an exact (not perturbative) treatment of TDS absorption coefficients is required to avoid artificial anomalous HOLZ intensity effects.

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