

Virtual Inelastic Scattering in High-Energy Electron Diffraction

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By the use of convergent-beam and critical-voltage measurements it has become possible to measure the crystal potential to an accuracy of about 10^{-3} . The possibility that the contribution from virtual inelastic scattering is greater than the errors in these experiments is examined and it is shown that only virtual scattering from single-electron excitations need be considered. Estimates are given for the Fourier coefficients of the virtual inelastic scattering potential for silicon, copper and germanium and these are compared with the errors in the critical-voltage experiments of Hewat & Humphreys [*High Voltage Electron Microscopy* (1974), edited by P. R. Swann, C. J. Humphreys & M. J. Goringe, pp. 52–56. London and New York: Academic Press]. It is concluded that the virtual inelastic scattering contribution is less than the experimental errors.

Introduction

It is now possible to measure the crystal potential to a high degree of accuracy ($\sim 10^{-3}$) by the critical-voltage effect (for example, Hewat & Humphreys, 1974; Hewat, 1975; Terasaki, Uchida & Watanabe, 1975), and convergent-beam methods (Goodman & Lempfuhl, 1967; Goodman, 1976), or a combination of the two methods (Shishido & Tanaka, 1976). Yoshioka (1957) has calculated the correction to the mean inner potential from virtual inelastic scattering due to single-electron excitations on a Fermi–Thomas model and concluded that it might be about the same magnitude as the imaginary part of the potential arising from real inelastic scattering. The plasmon and phonon virtual scattering contribution to the mean inner potential has been calculated by Ichikawa & Ohtsuki (1968) but there have been no calculations of the Fourier coefficients of the virtual inelastic scattering potential. If these are also similar in magnitude to the imaginary part of the potential it is possible that the virtual inelastic scattering contribution could be greater than the errors in accurate crystal potential measurements.

Correction to the potential from virtual inelastic scattering

According to Yoshioka (1957) the imaginary part of the crystal potential due to real inelastic scattering, leaving the crystal in an excited state n , is

$$C_{0g}^i = \frac{mV}{4\pi\hbar^2} \sum_n \iint \frac{H_0^{0n}(\mathbf{k}' - \mathbf{k}_0) H_{-g}^{n0}(\mathbf{k}_0 - \mathbf{k}') d^2\mathbf{k}'}{2k_z}$$

where $H_g^{0n}(\mathbf{k}' - \mathbf{k}_0)$ is a matrix element, V is the crystal volume, \mathbf{k}' is the wave vector of the inelastically scattered electron, \mathbf{k}_0 is the wave vector of

the initial fast-electron state and k_z is the z component of the fast-electron wave vector (parallel to the foil normal). The real part of the potential due to virtual inelastic scattering is given by

$$C_{0g}^r = \frac{1}{(2\pi)^3} \frac{mV}{\hbar^2 k_z} \sum_n \iint \frac{H_0^{0n}(\mathbf{k}' - \mathbf{k}_0) H_{-g}^{n0}(\mathbf{k}_0 - \mathbf{k}')}{(k'_z - k_z^n)} d^3\mathbf{k}' \quad (2)$$

where $k_z^n = k_z + \Delta k^n$ and

$$\Delta k^n = \frac{m\Delta E^n}{\hbar^2 k}, \quad (3)$$

ΔE^n being the energy of the n th excited state. Equation (2) can be rewritten as

$$\frac{V}{(2\pi)^2} \frac{m}{\hbar^2 k_z} \sum_n \iint \frac{H_0^{0n}(\mathbf{s}, z) H_{-g}^{n0}(\mathbf{s}, z)}{z - \Delta k^n} d^2\mathbf{s} dz \quad (4)$$

where $z = k'_z - k_z$. As $\Delta k^n \rightarrow 0$ the integral becomes antisymmetric and is therefore zero, so for inelastic scattering where there is a small energy loss, the real part of the potential becomes negligible. This means that phonon scattering does not contribute to the correction to the potential as the energy of a phonon is of the order $10^{-1} \sim 10^{-2}$ eV. As plasmon scattering gives no contribution to the Fourier coefficients of the absorption potential, it is also not going to affect the Fourier coefficients of the virtual inelastic potential.

This leaves only single-electron excitations and it is likely that those excitations from tightly bound core states (e.g. K and L shells) will contribute most, both because of their localization in the unit cell and the large energy contribution in the denominator. It is usual when calculating the single-electron contribution to absorption to use the closure relation between final states with an average energy loss. Clearly the value of the real part of the potential will depend on

whatever average energy loss is chosen. However, to calculate terms such as $H^{0n}(\mathbf{q})$ without making this approximation would require a knowledge of the excited states of the crystal for which a Hartree-Fock calculation is needed. Freeman (1959*a,b,c*, 1960*a,b*) tabulates matrix elements for various transitions and it might be a reasonable approximation to consider transitions between the fully occupied levels and the empty states of the lowest partially occupied state.

The correction to the potential can then be written as

$$\frac{\hbar^2 4}{2ma_0^2 k V_c \pi} \iint \sum_{\alpha} \exp(-i\mathbf{g} \cdot \mathbf{R}_{\alpha}) \frac{\sum_n f_{\alpha}^{n1} (s^2 + z^2)^{1/2} f_{\alpha}^{n1} [(s - \mathbf{g})^2 + z^2]^{1/2}}{(s^2 + z^2)[(s - \mathbf{g})^2 + z^2](z - \Delta k)} d^2\mathbf{s} dz. \quad (5)$$

The integration over the surface can be transformed into polar coordinates and, if $|\mathbf{g}| = 2a$, the integral becomes

$$\frac{\hbar^2 4}{2ma_0^2 k V_c \pi} \iiint \sum_{\alpha} \exp(-i\mathbf{g} \cdot \mathbf{R}_{\alpha}) \times \frac{\sum f_{\alpha}^{n1} [(a^2 + r^2 + z^2 - 2 \arccos \theta)^{1/2}] f_{\alpha}^{n1} [(a^2 + r^2 + z^2 + 2 \arccos \theta)^{1/2}]}{(a^2 + r^2 + 2 \arccos \theta)(a^2 + r^2 - 2 \arccos \theta)(z - \Delta k)} r dr d\theta dz. \quad (6)$$

If an average energy loss were used, the expression for the real part of the potential would be

$$\frac{\hbar^2 4}{2ma_0^2 k V_c \pi} \iiint \sum_{\alpha} \exp(-i\mathbf{g} \cdot \mathbf{R}_{\alpha}) \times \frac{f_{\alpha}^x(2a) - \sum_{nm} f_{\alpha}^{nm} [(a^2 + r^2 + z^2 + 2 \arccos \theta)^{1/2}] f_{\alpha}^{nm} [(a^2 + r^2 + z^2 - 2 \arccos \theta)^{1/2}]}{(a^2 + r^2 + z^2 + 2 \arccos \theta)(a^2 + r^2 + z^2 - 2 \arccos \theta)(z - \Delta k)} r dr dz \quad (7)$$

where $f_{\alpha}^x(2a)$ is the X-ray scattering factor.

The integral over θ can be performed by contour methods (Radi, 1970) to give

$$\frac{\hbar^2 8}{2ma_0^2 k V_c} \iint \sum_{\alpha} \exp(-i\mathbf{g} \cdot \mathbf{R}_{\alpha}) \times \frac{\sum_n f_{\alpha}^{n1} [(a^2 + r^2 + z^2 - 4a^2 r^2)^{1/2}] f_{\alpha}^{n1} (\{2(a^2 + r^2 + z^2) - [(a^2 + r^2 + z^2)^2 - 4a^2 r^2]^{1/2}\}^{1/2})}{(a^2 + r^2 + z^2)[(a^2 + r^2 + z^2)^2 - 4a^2 r^2]^{1/2}(z - \Delta k)} r dr dz \quad (8)$$

for equation (6), and

$$\frac{\hbar^2 8}{2ma_0^2 k V_c} \sum_{\alpha} \exp(-i\mathbf{g} \cdot \mathbf{R}_{\alpha}) \times \frac{f_{\alpha}^x(2a) - \sum_{nm} f_{\alpha}^{nm} [(a^2 + r^2 + z^2 - 4a^2 r^2)^{1/2}] f_{\alpha}^{nm} (\{2(a^2 + r^2 + z^2) - [(a^2 + r^2 + z^2)^2 - 4a^2 r^2]^{1/2}\}^{1/2})}{(a^2 + r^2 + z^2)[(a^2 + r^2 + z^2)^2 - 4a^2 r^2]^{1/2}(z - \Delta k)} r dr dz \quad (9)$$

for equation (7).

The multiple integral was performed by computer with Gaussian integration routines. To speed up the integration over z and avoid the singularity where $z = \Delta k$, a change of variables was used. In (7) and (9) the integral is written as

$$\int_{-z_a}^{z_a} \frac{G(z)}{z - \Delta k} dz \quad (10)$$

where $G(z)$ is a symmetric function of z . This can be transformed to

$$\int_0^{z_a - \Delta k} \frac{G(z' - \Delta k) - G(z' + \Delta k)}{z'} dz' + R$$

$$R = \int_{z_a - \Delta k}^{z_a + \Delta k} \frac{G(z' - \Delta k)}{z'} dz' \quad (11)$$

where $z' = z + \Delta k$.

It was found that $z_a = 2 \text{ \AA}^{-1}$ was equivalent to an integration over a larger range and the remainder, R , was negligible. As can be seen from (11) the expression for the real part will diverge if the expression for $G(z)$ diverges, as can happen when calculating the virtual scattering contribution to the mean inner potential assuming completeness of final states.

Table 1. *Estimates of the contribution to the potential from virtual inelastic scattering*

All values are in eV. Calculations for (a) columns assume completeness of final states; those for (b) columns assume transitions only to the lowest unoccupied states

Material and reflection	C_g^{i*}	C_g^i		C_g^r		C_g^r/V_g		Experimental relative error
	Radi	(a)	(b)	(a)	(b)	(a)	(b)	
Si 111		0.034	0.046	1.38×10^{-4}	2.2×10^{-4}	2.5×10^{-5}	4×10^{-5}	4×10^{-3}
Si 111	0.038	0.034	0.053	1.36×10^{-4}	7.6×10^{-5}	2.5×10^{-5}	1.2×10^{-5}	
Cu 111	0.131	0.138	0.0936	4.3×10^{-3}	2.7×10^{-4}	3.8×10^{-4}	2.5×10^{-5}	1.2×10^{-2}
Cu 200	0.101	0.103	0.0617	2.2×10^{-3}	1.7×10^{-4}	2.2×10^{-4}	1.6×10^{-5}	9×10^{-3}
Cu 311	0.029	0.026	0.0112	4.5×10^{-4}	5.5×10^{-5}	1.2×10^{-4}	1.0×10^{-5}	1.8×10^{-2}
Ge 111	0.087	0.074	0.062	2.6×10^{-3}	5.3×10^{-4}	3.8×10^{-4}	8.0×10^{-5}	1.0×10^{-3}
Ge 220	0.054	0.052	0.039	3.0×10^{-3}	7.9×10^{-4}	1.8×10^{-4}	1.27×10^{-4}	2.5×10^{-3}

* Radi (1970).

As the matrix elements given by Freeman used in the calculation are only tabulated over a limited range a function of the form $ax^b \exp(-cx^2)$ or $ax^b \exp(-cx)$ was fitted to the two points of highest scattering angle. There was not much difference between calculations with either of these asymptotic forms. Within the tabulated range, the function was determined with a cubic spline interpolation and, as a check on the program, the absorption part of the potential (no z) integration) was calculated and compared with the values given by Radi (1970).

Calculations of the contribution from virtual inelastic scattering

The contribution from virtual inelastic scattering to the crystal potential has been calculated for the 111 reflection in silicon, the 111, 200 and 311 reflections in copper and the 111 and 220 reflections in germanium; the results are given in eV in Table 1. In the calculations, the energies of the various atomic shells have been taken from Herman & Skillman (1963) and the accelerating voltage of the fast electron is assumed to be 100 kV. The results of those calculations, assuming completeness of final states and using (9) for the real part are given in columns marked (a); the results of those assuming transitions to the lowest unoccupied states and using (8) for the real part are given in columns marked (b). Where the second assumption had been made, transitions were assumed to take place to unoccupied $2p$ states in silicon, unoccupied $4s$ and $4p$ states in copper and unoccupied $4p$ states in germanium. In the case of silicon, the matrix elements for aluminium were used for the results given in the first row; in the second row the silicon matrix elements were used in those calculations where completeness of final states had been assumed; the Cl^- matrix elements were used in the other two calculations. Accurate measurements of

Table 2. *Estimates of the contribution of virtual inelastic scattering to the mean inner potential.*

All values are in eV. Calculations for (c) and (d) columns assume transitions to the lowest unoccupied state.

Material	(a) C_{00}^{i*}	(b) C_{00}^r †	(c) C_{00}^c	(d) C_{00}^d
Si	0.604	0.486	0.046	0.288
Cu	2.738	0.575	0.073	0.497
Ge	1.038	0.665	0.035	0.298

* Radi (1970).

† Yoshioka (1957).

the Fourier coefficients of the crystal potential considered have been made (Hewat, 1975; Hewat & Humphreys, 1974) using the critical voltage effect and the fractional errors in these measurements have been compared with the fractional change the virtual inelastic scattering makes to the potential.

The contribution of virtual inelastic scattering to the mean inner potential is given in Table 2. As the expression for the real part diverges if completeness of final states is assumed, only calculations with (6), (8) were performed and the results for real and imaginary parts are given in columns (c) and (d) respectively. The parts calculated with Yoshioka's (1957) formula, $(\lambda/2a_0)V_{00}$, where λ is the fast-electron wavelength, a_0 is the Bohr radius and V_{00} the mean inner potential, are given in column (b); in column (a) the corresponding values for the mean absorption calculated by Radi (1970) are given.

In the first three columns of Table 1 the imaginary part of the Fourier coefficients of the potential as calculated with the programs described is compared with that given by Radi (1970). There are small differences between the values calculated with completeness of final states assumed and Radi's values, probably because of the differences between Freeman's wave functions and those of Herman &

Skillman (1963) used by Radi. Another source of error is the procedure used to evaluate the matrix elements for arguments larger than those given by Freeman. The calculations with transitions to the lowest unoccupied states assumed give higher values for silicon than those calculated with completeness of final states assumed, whereas for copper and germanium they are lower. It is possible that the effect arises because the approximation of assuming transitions to the lowest unoccupied level overestimates the number of free-electron states for silicon and underestimates it for copper and germanium. For the mean potential, this approximation underestimates the imaginary part of the potential by about $\frac{1}{2}$ for Si, $\frac{1}{3}$ for Ge and $\frac{1}{5}$ for Cu.

Generally, the real parts of the potential are low and decrease for higher orders of reflection, except in the case of germanium where there is a slight increase. For silicon the estimates made by the two methods agree reasonably well but the results from calculations with (9) are greater than those with (8) by a factor of about 10 for copper and 5 for germanium. This must be partly because of the high value of the average energy in the denominator and so the calculations with (8) probably overestimate the contribution from virtual scattering. For the mean potential, estimates with transitions to the lowest unoccupied states assumed are about $\frac{1}{10}$ of the estimates from Yoshioka's (1957) formula. If the real part calculated with (8) is divided by the factor by which the corresponding imaginary part is less than that calculated by Radi, there is better agreement between the estimates for the virtual inelastic scattering correction to the mean inner potential. However, estimates given by Yoshioka's (1957) formula are still higher.

The most important point to note is that the estimates of the relative contribution of virtual inelastic scattering are less than the experimental errors given by Hewat (1975), which are typical of the sensitivity of the most accurate techniques currently available. This does not mean that virtual inelastic

scattering might not considerably affect values of the potential at lower energies (less than ~ 10 kV).

It seems that the correction to the crystal potential from virtual inelastic scattering is less than the experimental errors of accurate experiments where convergent-beam methods or the critical-voltage effect are used.

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