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# The Effect of Plasmon Production on Phase Determination *via* the Unitarity Equation

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Phase determination of electron scattering from thin crystals *via* the unitarity equation including inelasticity due to plasmons is considered. It is concluded that the uniqueness properties of the solution are unlikely to be affected by plasmon production.

## Introduction

In a previous publication (Boyce & Roberts, 1974) (hereinafter referred to as I) we have applied the unitarity equation to the determination of the phases of electron scattering from thin crystals. The present work considers the effect of plasmon excitation and concludes that the uniqueness properties of the elastic case are unlikely to be affected by plasmon production.

The principal change in the analysis is the introduction of a new term into the unitarity relation. This represents the effect of an intermediate plasmon state on the elastic scattering amplitude. Although the proof of phase uniqueness used in I is no longer directly applicable, the form of the change is such that the property of uniqueness is likely to be unaffected. This has been confirmed by a numerical test case.

In the first section we restate the main results of I. In § 2 the free and interaction Hamiltonians for inelastic scattering from a crystal of finite width are obtained, while in § 3 the corresponding unitarity relation is derived and reduced to a form similar to that of I. The results of a numerical test case are given in § 4.

## 1. Resumé of elastic scattering

In I we considered the elastic scattering from a crystal of finite width. Using time-independent transition matrix formalism it was shown that the scattering amplitude, $f(\mathbf{p}',\mathbf{p})$, for an electron of initial momentum $\mathbf{p}$ scattering to a final momentum $\mathbf{p}'$, could be expanded as

$$f(\mathbf{p}',\mathbf{p})=-\pi\sum_{\mathbf{M}} f(p^2,\mathbf{M})\delta^2(\mathbf{p}'-\mathbf{p})^{\perp c}+\mathbf{M}) \,. \quad (1.1)$$

The lattice vectors are $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$; their reciprocals are defined by $\tilde{\mathbf{a}}=2\pi v^{-1}\,(\mathbf{b}\times\mathbf{c})$, with $v=\mathbf{a}\,.\,(\mathbf{b}\times\mathbf{c})$. The lattice is finite in the $\mathbf{c}$ direction while

$$\mathbf{M}=l\tilde{\mathbf{a}}+m\tilde{\mathbf{b}} \,,$$

summation over $\mathbf{M}$ implying summation over the integer pair $(l,m)$.

Conservation of probability imposes the non-linear unitarity equation

$$2vp\tilde{\mathbf{c}}\,\mathrm{Im}\,f(p^2,\mathbf{L})=(2\pi)^3\sum_{\mathbf{M}} f(p^2,\mathbf{M})^* f(p^2,\mathbf{L}-\mathbf{M}) \,. \quad (1.2)$$

Subject to a constraint condition on the moduli, equation (3.12) of I, the above equation defines a contraction mapping on the principal values of the phases of the amplitudes; consequently it may be iterated to yield a unique set of phases for any set of intensities which satisfy the constraint. We wish to establish the equivalent equation in the presence of plasmon excitation. In order to do so we consider the form of the total Hamiltonian in the next section.

## 2. The Hamiltonian and completeness relation

As we shall be concerned with the creation and annihilation of plasmons it will be convenient to adopt a second-quantized formalism. We define the creation operator, $C^\dagger(\mathbf{p})$, and the annihilation operator, $C(\mathbf{p})$, of an electron of momentum $\mathbf{p}$ to satisfy the anti-commutation relations

$$\{C(\mathbf{p}),C^\dagger(\mathbf{p})\}=\delta^3(\mathbf{p}-\mathbf{p}') \,. \quad (2.1)$$

The Hamiltonian of a free electron of mass $m_0$ may be expressed in terms of them as*

$$H(\text{electron})=\int \mathrm{d}^3p\varepsilon(\mathbf{p})C^\dagger(\mathbf{p})C(\mathbf{p}) \quad (2.2)$$

where

$$\varepsilon(\mathbf{p})=(2m_0)^{-1}p^2. \quad (2.3)$$

The electron-lattice interaction Hamiltonian, $V$, may be expressed as *

$$V=\int \mathrm{d}^3p'\int \mathrm{d}^3pC^\dagger(\mathbf{p}')\mathscr{V}(\mathbf{p}'-\mathbf{p})C(\mathbf{p}) \,, \quad (2.4)$$

where $\mathscr{V}(\mathbf{q})$ is the Fourier transform of the total lattice potential,

$$\mathscr{V}(\mathbf{x})=\sum_{\mathbf{A}}\mathscr{V}(\mathbf{x}-\mathbf{x}_A) \quad (2.5)$$

where

$$X_A=l\mathbf{a}+m\mathbf{b}+n\mathbf{c} \,, \quad (2.6)$$

the summation being over the integer triple $(l,m,n)$. We shall suppose that the lattice is rectangular, with $|l|\le L, |m|\le M, |n|\le N$, the volume of the specimen being

$$\Omega=(2L+1)\,(2M+1)\,(2N+1)abc \,. \quad (2.7)$$

* We employ the same notation as in I.

It is shown in Appendix *A* that for large $L$, $M$ and $N$ the potential appearing in equation (2.3) takes the form

$$\mathscr{V}(\mathbf{q}) = V(\mathbf{q})\Psi_L(\mathbf{q}\,.\,\mathbf{a})\Psi_M(\mathbf{q}\,.\,\mathbf{b})\Psi_N(\mathbf{q}\,.\,\mathbf{c}) \quad (2.8)$$

where

$$\Psi_L(\alpha) \simeq \sum_l 2L \exp\{-L^2\pi^{-1}(\alpha - 2\pi l)^2\}\,. \quad (2.9)$$

Bohm and Pines (Pines, 1963; Shevchik, 1974) have shown that given a collection of $\mathscr{N}$ free electrons confined to a volume $\Omega$ the collective excitations caused by the long-range part of the Coulomb interaction may be represented, to a good approximation, in terms of plasmon annihilation and creation operators, $b(\mathbf{k})$ and $b^\dagger(\mathbf{k})$, respectively, by the Hamiltonian

$$H = \sum_{\mathbf{k}} \{b^\dagger(\mathbf{k})b(\mathbf{k}) + \tfrac{1}{2}\}\hbar\omega\,. \quad (2.10)$$

If periodic boundary conditions are imposed then

$$\mathbf{k} = 2\pi\{l(2L+1)^{-1}a^{-1}\mathbf{\hat{i}} + m(2M+1)^{-1}b^{-1}\mathbf{\hat{j}} + n(2N+1)^{-1}c^{-1}\mathbf{\hat{k}}\} \quad (2.11)$$

while the plasmon operators satisfy the commutation relations

$$[b(\mathbf{k}), b^\dagger(\mathbf{k}')] = \delta_{\mathbf{k},\mathbf{k}'}\,. \quad (2.12)$$

The plasmon frequency is determined by

$$\omega = (4\pi\mathscr{N} e^2 m_0^{-1})^{1/2}. \quad (2.13)$$

while the range of $\mathbf{k}$ summation is restricted by $|\mathbf{k}| \leq k_c$, $k_c$ being chosen so that only the long-range part of the Coulomb interaction is represented; $k_c$ is approximately half the momentum of the Fermi level.

It is convenient to neutralize the overall charge of the specimen by adding a constant background charge of total $\mathscr{N}e$. This modifies the Hamiltonian to

$$H(\text{plasmon}) = \sum_{\mathbf{k}}{}' [\{b^\dagger(\mathbf{k})b(\mathbf{k}) + \tfrac{1}{2}\}\hbar\omega - \tfrac{1}{2}\mathscr{N}M^2(\mathbf{k})] \quad (2.14)$$

with

$$M(\mathbf{k})^2 = 4\pi e^2 (\mathbf{k}^2 + i\epsilon)^{-1} \quad (2.15)$$

the $\mathbf{k} = \mathbf{0}$ term being omitted from the summation.

The matrix element of the interaction Hamiltonian between a fast electron at $\mathbf{x}$ and $\mathscr{N}$ conduction electrons at $\mathbf{x}_1, \ldots, \mathbf{x}_{\mathscr{N}}$ is

$$\langle \mathbf{x}'; \mathbf{x}_1', \ldots, \mathbf{x}_{\mathscr{N}}' | U | \mathbf{x}; \mathbf{x}_1, \ldots, \mathbf{x}_{\mathscr{N}} \rangle = \delta(\mathbf{x}' - \mathbf{x})\delta(\mathbf{x}_1' - \mathbf{x}_1)\ldots\delta(\mathbf{x}_{\mathscr{N}}' - \mathbf{x}_{\mathscr{N}})U(\mathbf{x}; \mathbf{x}_1, \ldots, \mathbf{x}_{\mathscr{N}}) \quad (2.16)$$

where

$$U(\mathbf{x}; \mathbf{x}_1, \ldots, \mathbf{x}_{\mathscr{N}}) = \sum_{i=1}^{\mathscr{N}} e^2 |\mathbf{x} - \mathbf{x}_i|^{-1}. \quad (2.17)$$

Within the specimen *i.e.* $\mathbf{x} \in \Omega$

$$e^2 |\mathbf{x}|^{-1} = \Omega^{-1} \sum_{\mathbf{k}} M(\mathbf{k})^2 \exp(i\mathbf{k}\,.\,\mathbf{x}) \quad (2.18)$$

and consequently we may express the long-range part of the interaction matrix element, including a constant background, as

$$U(\mathbf{x}, \mathbf{x}_1, \ldots, \mathbf{x}_{\mathscr{N}}) = \Omega^{-1} \sum_{\mathbf{k}}{}' \varrho(\mathbf{k})M^2(\mathbf{k}) \exp(i\mathbf{k}\,.\,\mathbf{x}) \quad \mathbf{x} \in \Omega \quad (2.19)$$
$$= 0 \quad \mathbf{x} \notin \Omega$$

where

$$\varrho(\mathbf{k}) = \sum_{i=1}^{\mathscr{N}} \exp(i\mathbf{k}\,.\,\mathbf{x}_i) \quad (2.20)$$

is the Fourier transform of the number density of conduction electrons, and $|\mathbf{k}| \leq k_c$, with $\mathbf{k} = \mathbf{0}$ omitted.

The Bohm–Pines subsidiary condition (Shevchik, 1974) for physical states enables $\varrho(\mathbf{k})$ to be related to the plasmon collective momentum operator, $\Pi(\mathbf{k})$ by

$$\{\Pi(\mathbf{k}) - M(\mathbf{k})\varrho(\mathbf{k})\} \mid \text{phys}\rangle = 0 \quad (2.21)$$

while $\Pi(\mathbf{k})$ may be represented in terms of plasmon operators as

$$\Pi(\mathbf{k}) = i(\tfrac{1}{2}\hbar\omega)^{1/2}\{b^\dagger(\mathbf{k}) - (b - \mathbf{k})\}\,. \quad (2.22)$$

As a result the interaction Hamiltonian between a fast electron and the plasmons may be expressed as

$$U = i\Omega^{-1}(\tfrac{1}{2}\hbar\omega)^{1/2} \sum_{\mathbf{k}}{}' \int \mathrm{d}^3p' \int \mathrm{d}^2p M(\mathbf{k}) \times \{b^\dagger(\mathbf{k}) - b(-\mathbf{k})C^\dagger(\mathbf{p}')C(\mathbf{p})\Phi(\mathbf{p}' + \mathbf{k} - \mathbf{p}) \quad (2.23)$$

where

$$\Phi(\mathbf{p}) = \int_2 \mathrm{d}^3x \exp(i\mathbf{p}\,.\,\mathbf{x}) \quad (2.24)$$

and it is shown in Appendix *B* that

$$\Phi(\mathbf{p}) = v\phi_L(\mathbf{q}\,.\,\mathbf{a})\phi_M(\mathbf{q}\,.\,\mathbf{b})\phi_N(\mathbf{q}\,.\,\mathbf{c}) \quad (2.25)$$

with

$$\phi_L(\alpha) \simeq 2L \exp\{-\pi^{-1}L^2\alpha^2\}\,. \quad (2.26)$$

The free Hamiltonian is

$$H_0 = H(\text{electron}) + H(\text{plasmon}) \quad (2.27)$$

where the right-hand side is defined by equations (2.2) and (2.13). The ground state, $|0\rangle$, is defined to be an eigenstate of the free Hamiltonian which has no plasmons, and all of the electron states occupied up to the Fermi level, *i.e.*

$$b(\mathbf{k})\,|0\rangle = 0; \quad C(\mathbf{p})\,|0\rangle = 0,\ p > p_F; \quad C^\dagger(\mathbf{p})\,|0\rangle = 0,\ p < p_F\,. \quad (2.28)$$

Electron and plasmon states may be formed by applying appropriate creation operators to $|0\rangle$. In particular, the state containing a fast electron of momentum $\mathbf{p}$ and a plasmon of momentum $\mathbf{k}$ is defined by

$$|\mathbf{p};\ \mathbf{k}\rangle = C^\dagger(\mathbf{p})b^\dagger(\mathbf{k})\,|0\rangle\,. \quad (2.29)$$

This is an eigenstate of the free Hamiltonian, $H_0$, with eigenvalue

$$E=E_0+\varepsilon(\mathbf{p})+\hbar\omega \tag{2.30}$$

where $E_0$ is the energy of the ground state.

If we make the approximation of considering only single plasmon intermediate states then the completeness relation for states involving a single fast electron is

$$1=\int \mathrm{d}^2p\,|\mathbf{p}\rangle\langle\mathbf{p}|+\int \mathrm{d}^3p\sum_{\mathbf{k}}{}'|\mathbf{p};\mathbf{k}\rangle\langle\mathbf{p};\mathbf{k}|\,. \tag{2.31}$$

We shall make use of this relation when we consider the unitarity relation in the following section.

### 3. The unitarity relation

As shown in I, the unitarity relation may be expressed in terms of the transition matrix, $T$, as

$$i(T-T^\dagger)=T^\dagger T\,. \tag{3.1}$$

If we consider scattering between single-electron states and make use of the completeness relation, equation (2.31), assuming single plasmon production, this becomes

$$i\{\langle\mathbf{p}'|T|\mathbf{p}\rangle-\langle\mathbf{p}'|T^\dagger|\mathbf{p}\rangle\}=\int \mathrm{d}^3q\langle\mathbf{p}'|T^\dagger|\mathbf{q}\rangle\langle\mathbf{q}|T|\mathbf{p}\rangle + \int \mathrm{d}^3q\sum_{\mathbf{k}}\langle\mathbf{p}'|T^\dagger|\mathbf{q};\mathbf{k}\rangle\langle\mathbf{q};\mathbf{k}|T|\mathbf{p}\rangle\,. \tag{3.2}$$

For potentials which fall off sufficiently rapidly at large distances the transition matrix, $T$, is related to the Lippmann–Schwinger transition operator, $T(z)$, by

$$\langle\mathbf{p}'|T|\mathbf{p}\rangle=\delta[\varepsilon(\mathbf{p})-\varepsilon(\mathbf{p}')]\lim_{\epsilon\downarrow 0}\langle\mathbf{p}'|T[\varepsilon(\mathbf{p})+i\epsilon]\,|\mathbf{p}\rangle$$
$$\langle\mathbf{p}|T|\mathbf{q};\mathbf{k}\rangle=\delta[\varepsilon(\mathbf{p})-\varepsilon(\mathbf{q})-\hbar\omega]\lim_{\epsilon\downarrow 0}\langle\mathbf{p}|T[\varepsilon(\mathbf{p})+i\epsilon]\,|\mathbf{q},\mathbf{k}\rangle\,. \tag{3.3}$$

Therefore the unitarity relation becomes the limit as $z\to\varepsilon(\mathbf{p})$ from above of

$$i\{\langle\mathbf{p}|T(z)\,|\mathbf{p}'\rangle-\langle\mathbf{p}'|T(z)\,|\mathbf{p}\rangle\} =\int \mathrm{d}^3q\langle\mathbf{p}'|T^\dagger(z)\,|\mathbf{q}\rangle\delta[\varepsilon(\mathbf{q})-\varepsilon(\mathbf{p})]\langle\mathbf{q}|T(z)\,|\mathbf{p}'\rangle + \int \mathrm{d}^3\mathbf{q}\int\sum_{\mathbf{k}}\langle\mathbf{p}'|T^\dagger(z)\,|\mathbf{q};\mathbf{k}\rangle\delta[\varepsilon(\mathbf{q})+\hbar\omega-\varepsilon(\mathbf{p})] \times\langle\mathbf{q};\mathbf{k}|T(z)\,|\mathbf{p}\rangle \tag{3.4}$$

with

$$\varepsilon(\mathbf{p}')=\varepsilon(\mathbf{p})\,.$$

In the absence of plasmon production the second sum of equation (3.4), which represents scattering *via* an intermediate plasmon state, disappears; the relation then yields the elastic constraint, equation (1.2), which was utilised in I. In the general case, however, it is necessary to relate the amplitude for plasmon production, $\langle\mathbf{q};\mathbf{k}|T|\mathbf{p}\rangle$ to that for elastic scattering, $\langle\mathbf{p}'|T|\mathbf{p}\rangle$. Of course a unitarity equation also applies to the plasmon production amplitude. However, the sum over states on its right-hand side will involve the amplitude for elastic scattering between single-electron, single-plasmon states. Thus an open hierarchy of unitarity equations is obtained which can be closed only by some approximation.

A suitable approximation may be obtained more directly by considering the Lippmann–Schwinger equation. This defines the transition operator, $T(Z)$, in terms of the free, $H_0$, and interaction, $H_I$, Hamiltonians, by

$$T(Z)=H_I+H_I(Z-H_0-H_I)^{-1}H_I\,. \tag{3.5}$$

For the present situation $H_0$ is defined by equation (2.27), while $H_I$ is the sum of the lattice, $V$, and plasmon, $U$, interaction Hamiltonians, equations (2.4) and (2.23) respectively:

$$H_I=U+V\,. \tag{3.6}$$

As shown in I, as a result of the lattice invariance, we may expand

$$\langle\mathbf{p}'|T[\varepsilon(\mathbf{p})+i\epsilon]\,|\mathbf{p}\rangle=-2pm_0^{-1}\sum_{\mathbf{k}}f(p^2,\mathbf{K})\delta^2(\mathbf{p}'-\mathbf{p}+\mathbf{K}) \tag{3.7}$$

where the summation is over the two-dimensional inverse lattice vectors

$$\mathbf{K}=la^{-1}\hat{\mathbf{i}}+mb^{-1}\mathbf{j}\,. \tag{3.8}$$

Now we may also define an elastic transition operator, $\hat{T}(Z)$, by

$$\hat{T}(Z)=V+V(Z-H_0-V)^{-1}V\,. \tag{3.9}$$

Although $\hat{T}$ contains the free-plasmon Hamiltonian *via* $H_0$ it is independent of $U$ and therefore cannot alter the number of plasmons of a state. From the definitions we may express $T$ in terms of $\hat{T}$ as

$$T(Z)=\hat{T}(Z)+U+U\Delta\hat{T}(Z)+\hat{T}(Z)\Delta U +\hat{T}(Z)\Delta U\Delta\hat{T}(Z)+\mathrm{O}(U^2) \tag{3.10}$$

where

$$\Delta=(Z-H_0)^{-1}. \tag{3.11}$$

Upon substituting this expansion into the contribution to the unitarity equation which involves an intermediate plasmon, we obtain a set of terms which may be written symbolically as

$$U^\dagger\delta U+U^\dagger\delta U\Delta\hat{T}+\hat{T}^\dagger\Delta^\dagger U^\dagger\delta U+U^\dagger\delta\hat{T}\Delta U +U^\dagger\Delta^\dagger\hat{T}^\dagger\delta U+\text{higher orders}\,, \tag{3.12}$$

where $\delta$ implies an energy-conservation delta function.

The last two terms involve elastic scattering between single-electron, single-plasmon states. If we may assume that to first order the elastic scattering from the lattice is independent of the presence of plasmons, *viz.*

$$\langle\mathbf{p};\mathbf{k}'|\hat{T}(Z)\,|\mathbf{p},\mathbf{k}\rangle=\delta_{\mathbf{k}',\mathbf{k}}\langle\mathbf{p}'|\hat{T}(Z)\,|\mathbf{p}\rangle+\mathrm{O}(U^2) \tag{3.13}$$

then since it follows from equation (3.10) that

$$\langle \mathbf{p}'|T(Z)\,|\mathbf{p}\rangle = \langle \mathbf{p}'|\hat{T}(Z)\,|\mathbf{p}\rangle + \mathrm{O}(U^2)\,, \quad (3.14)$$

we may re-express $\hat{T}$ in terms of $T$ within the unitarity sum, thereby obtaining an equation correct to order $U^4$, since the terms to which the approximations of equations (3.13) and (3.14) have been applied are of order $U^2$.

The various contributions to the unitarity relation are explicitly evaluated in Appendix *C*, where it is shown that

$$\begin{aligned}
\langle \mathbf{p}'|U^\dagger \delta U|\mathbf{p}\rangle &= 2pm_0^{-1}A(p)\delta^2(\mathbf{p}'-\mathbf{p}) \\
\langle \mathbf{p}'|U^\dagger \delta U \Delta \hat{T}|\mathbf{p}\rangle &= -iA(p)\langle \mathbf{p}'|T|\mathbf{p}\rangle \\
\langle \mathbf{p}'|\hat{T}^\dagger \Delta^\dagger U^\dagger \delta U|\mathbf{p}\rangle &= iA(p)\langle \mathbf{p}'|T^\dagger|\mathbf{p}\rangle \\
\langle \mathbf{p}'|U^\dagger \delta \hat{T} \Delta U|\mathbf{p}\rangle &= i2pm_0^{-1}A(p)f(p^2-2m_0\hbar\omega,\mathbf{0}) \\
&\quad \times \delta^2(\mathbf{p}'-\mathbf{p}) \\
&\quad + i2pm_0^{-1}B \sum_{\mathbf{K}}{}' \mathrm{K}^{-1} f(p^2-2m_0\hbar\omega,\mathbf{K}) \\
&\quad \times \delta^2(\mathbf{p}'-\mathbf{p}+\mathbf{K}) \\
&= (\langle \mathbf{p}'|U^\dagger \Delta^\dagger \hat{T}^\dagger \delta U|\mathbf{p}\rangle)^* \qquad (3.15)
\end{aligned}$$

with

$$\begin{aligned}
A(p) &= \hbar e^2\, \omega p^{-2} m_0^2 Nc \log\{pk_c(\hbar m_0\omega)^{-1}\} \\
B &= \tfrac{1}{2}\pi\hbar e^2\, \omega m_0^2\{(\hbar\omega m_0)^2 + \hbar\omega m_0 K^2\}^{-1/2} \qquad (3.16)
\end{aligned}$$

and the transition operator matrix element has been expanded as in (3.7).

When these contributions are substituted into (3.12) and use is made of the above expansion the unitarity relation, equation (3.4) becomes

$$\begin{aligned}
\{1+A(p)\}\,\mathrm{Im}\, f(p^2,\mathbf{K}) + BK^{-1}\,\mathrm{Im}\, f(p^2-2m_0\hbar\omega,\mathbf{K}) \\
= \sum_{\mathbf{L}} f^*(p^2,\mathbf{L}) f(p^2,\mathbf{K}-\mathbf{L}) \quad \mathbf{K}\neq\mathbf{0} \qquad (3.17)
\end{aligned}$$

and

$$\begin{aligned}
\{1-A(p)\}\,\mathrm{Im}\, f(p^2,\mathbf{0}) + A(p)\,\mathrm{Im}\, f(p^2-2m_0\hbar\omega,\mathbf{0}) \\
= \sum_{\mathbf{L}} |f(p^2,\mathbf{L})|^2 + \tfrac{1}{2}A(p)\,. \qquad (3.18)
\end{aligned}$$

As inelastic scattering is involved the amplitudes corresponding to two energies, $\varepsilon(\mathbf{p})$ and $\varepsilon(\mathbf{p})-\hbar\omega$, appear. If we may assume that the energy dependence is weak, *viz.*

$$f(p^2-2m_0\hbar\omega,\mathbf{K}) = f(p^2,\mathbf{K}) + \mathrm{O}(U^2)\,, \quad (3.19)$$

then the structure of the equation becomes similar to that of the elastic case, treated in I.

With the definitions,

$$G(\mathbf{K}) = |f(p^2,\mathbf{K})| \quad (3.20)$$

and

$$f(p^2,\mathbf{K}) = G(\mathbf{K})\exp\{i\varphi(\mathbf{K})\}\,, \quad (3.21)$$

equation (3.17) becomes

$$\begin{aligned}
RG(\mathbf{K})\sin\{\varphi(\mathbf{K})-\zeta\} \\
= \sum_{\mathbf{L}}{}' G(\mathbf{L})G(\mathbf{K}-\mathbf{L})\cos\{\varphi(\mathbf{L})-\varphi(\mathbf{K}-\mathbf{L})\}\,, \qquad (3.22)
\end{aligned}$$

where the prime on the summation indicates that $\mathbf{L}=\mathbf{0}$ and $\mathbf{L}=\mathbf{K}$ are to be omitted while

$$\begin{aligned}
R\sin\zeta &= 2G(\mathbf{0})\cos\varphi(\mathbf{0}) \\
R\cos\zeta &= 1+A(p)+BK^{-1}-2G(\mathbf{0})\sin\varphi(\mathbf{0})\,. \qquad (3.23)
\end{aligned}$$

The phase of the centre spot follows from expressing equation (3.18) as

$$\{1+2A(p)\}G(\mathbf{0})\sin\varphi(\mathbf{0}) = \sum_{\mathbf{L}} |G(\mathbf{L})|^2 + \tfrac{1}{2}A(p)\,. \quad (3.24)$$

The above equations may be compared with the equivalent ones for the purely elastic case, equations (3.5), (3.6) and (3.7) of I. They would be structurally the same were it not for the $K$ dependence of $R$ and $\zeta$ in the inelastic case. Since they differ it follows that the ambiguity analysis of I does not apply directly to the inelastic case; however, the $K$ dependence is weak, and consequently it is unlikely that the uniqueness of a solution is affected. We examine this by means of a specific test case in the next section.

## 4. A numerical example

In order to compare our results with the elastic case, we chose to test the above analysis by using the theoretical data employed in I, namely amplitudes corresponding to the elastic scattering of 500 keV electrons by a layer of crystalline sodium nine unit cells thick. The moduli of the amplitudes (shown in Table 1 of I) were used to generate a set of unitary phases by iterating equation (3.22), assuming the density of conduction electrons to be $10^{23}$ cm$^{-3}$. The resulting phases were found to be independent of the initial values em-

Table 1. *Phases* ($\times 10^3$) *obtained by iterating the unitarity equation, effects of plasmon production not included*

| $h$ \ $k$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 104 | | 288 | | 429 | | 542 | | 597 | | 583 |
| 1 | | 224 | | 373 | | 488 | | 572 | | 614 | |
| 2 | 288 | | 353 | | 457 | | 556 | | 602 | | 564 |
| 3 | | 373 | | 444 | | 533 | | 588 | | 609 | |
| 4 | 429 | | 457 | | 523 | | 576 | | 614 | | |
| 5 | | 488 | | 533 | | 572 | | 611 | | 555 | |
| 6 | 542 | | 556 | | 576 | | 609 | | 589 | | |
| 7 | | 572 | | 588 | | 611 | | 597 | | | |
| 8 | 597 | | 602 | | 614 | | 589 | | | | |
| 9 | | 614 | | 609 | | 555 | | | | | |
| 10 | 583 | | 564 | | | | | | | | |

ployed in the iteration and are shown in Table 2. The set of unitary phases which does not include effects of plasmon production is shown in Table 1.

## 5. Conclusions

A method for obtaining the phases of electron scattering amplitudes from thin crystals has been successfully modified to include effects of plasmon excitation. It is considered unlikely that the uniqueness properties of the solution are affected. This has been confirmed by computing the phases corresponding to 500 keV electrons scattered from sodium.

Comparison of Tables 1 and 2 shows that plasmon excitation in sodium has a significant effect on the phases, leading to changes in the phases of up to 37%. This is expected as sodium has a large density of conduction electrons. The increase in the phase of the centre spot in contrast with the decrease of all other phases, is due to the purely inelastic term in the unitarity equation contributing only to the forward-scattered beam.

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## APPENDIX *A*

From equations (2.5) and (2.6)

$$\mathscr{V}(q)=V(q)\sum_{\mathbf{A}}\exp(-i\mathbf{q}\cdot\mathbf{X}_{\mathbf{A}})\,. \qquad (A.1)$$

But

$$\sum_{\mathbf{A}}\exp(-i\mathbf{q}\cdot\mathbf{X}_{\mathbf{A}})=\Psi_L(\mathbf{q}\cdot\mathbf{a})\Psi_M(\mathbf{q}\cdot\mathbf{b})\Psi_N(\mathbf{q}\cdot\mathbf{c}) \qquad (A.2)$$

where

$$\Psi_L(\alpha)=\sum_{l=-L}^{L}\exp(-i\alpha l)=\lim_{\epsilon\downarrow 0}\frac{\sin(L+\frac{1}{2})(\alpha+\epsilon)}{\sin\frac{1}{2}(\alpha+\epsilon)}\,. \qquad (A.3)$$

Now $\Psi_L(\alpha)$ has maxima at $\alpha=2l\pi$ of height $(2L+1)$ while

$$\lim_{L\to\infty}\frac{\sin L\alpha}{\sin\frac{1}{2}\alpha}=2\pi\sum_{l}\delta(\alpha-2l\pi)\,. \qquad (A.4)$$

Thus

$$\Psi_L(\alpha)\simeq\sum_{l}2L\exp\left\{-\frac{L^2}{\pi}(\alpha-2l\pi)^2\right\} \qquad (A.5)$$

and consequently equations (2.8) and (2.9) follow.

## APPENDIX *B*

$$\int_{\Omega}\mathrm{d}^3x\exp(-i\mathbf{q}\cdot\mathbf{x})=v\Phi_L(\mathbf{q}\cdot\mathbf{a})\Phi_M(\mathbf{q}\cdot\mathbf{b})\Phi_N(\mathbf{q}\cdot\mathbf{c}) \qquad (B.1)$$

where, since we have assumed a rectangular lattice,

$$\Phi_L(\alpha)=\int_{-L}^{L}\mathrm{d}x\exp(-i\alpha x)=\lim_{\epsilon\to 0}\frac{2\sin L(\alpha+\epsilon)}{(\alpha+\epsilon)}\,. \qquad (B.2)$$

By an argument similar to that of Appendix *A*

$$\frac{2\sin L(\alpha+\epsilon)}{(\alpha+\epsilon)}\simeq 2L\exp\left\{-\frac{L^2\alpha^2}{\pi}\right\} \qquad (B.3)$$

and thus equations (2.25) and (2.26) follow.

## APPENDIX *C*

In the calculation of the inelastic contributions to the unitarity sum we shall assume that the crystal is effectively infinite in the **a** and **b** directions, the incident electron being in the **c** direction, along the $z$ axis. This means that

$$\Psi_L(\mathbf{q}\cdot\mathbf{a})\Psi_M(\mathbf{q}\cdot\mathbf{b})=(ab)^{-1}\delta^2(\mathbf{q})^{\perp} \qquad (C.1)$$

where $\mathbf{q}^{\perp}$ are the components of $\mathbf{q}$ perpendicular to the $z$ axis.

Using the definition of $U$ given by equation (2.23) the contribution of the first term of (3.12) becomes

$$\begin{aligned}\langle\mathbf{p}'|U^{\dagger}\delta U|\mathbf{p}\rangle&=\int\mathrm{đ}^3\mathbf{q}\sum_{\mathbf{k}}{}'\langle\mathbf{p}'|U^{\dagger}|\mathbf{q}\,;\mathbf{k}\rangle\\&\quad\times\delta[\varepsilon(\mathbf{p})-\varepsilon(\mathbf{q})-\hbar\omega]\langle\mathbf{q};\mathbf{k}|U|\mathbf{p}\rangle\\&=\tfrac{1}{2}\hbar\omega\Omega^{-1}\sum_{\mathbf{k}}{}'M(\mathbf{k})^2\\&\quad\times\int\mathrm{đ}^3\mathbf{q}\delta^2(\mathbf{p}'-\mathbf{q}-\mathbf{k})^{\perp}\Phi_N(\mathbf{p}'-\mathbf{q}-\mathbf{k})_z)\\&\quad\times\delta[\varepsilon(\mathbf{p}')-\varepsilon(\mathbf{q})-\hbar\omega]\delta^2(\mathbf{q}+\mathbf{k}-\mathbf{p})^{\perp}\Phi_N[(\mathbf{q}+\mathbf{k}-\mathbf{p})_z]\\&=2\pi\,e^2\,\hbar\omega\delta^2(\mathbf{p}')^{\perp}\Phi_N(\mathbf{p}'-\mathbf{p})_z)\\&\quad\times\int\mathrm{đ}^3k\,k^{-2}\delta[\varepsilon(\mathbf{p})-\varepsilon(\mathbf{p}-\mathbf{k})-\hbar\omega]\end{aligned} \qquad (C.2)$$

Table 2. *Phases* ($\times 10^3$) *obtained by iterating the unitarity equation, including the effects of plasmon production*

| $h$ | $k$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | | 119 | | 219 | | 393 | | 517 | | 577 | | 568 |
| 1 | | | 141 | | 329 | | 461 | | 550 | | 559 | |
| 2 | | 219 | | 303 | | 426 | | 532 | | 617 | | 549 |
| 3 | | | 329 | | 411 | | 508 | | 567 | | 592 | |
| 4 | | 393 | | 426 | | 497 | | 555 | | 596 | | |
| 5 | | | 461 | | 508 | | 551 | | 592 | | 542 | |
| 6 | | 517 | | 532 | | 555 | | 590 | | 574 | | |
| 7 | | | 550 | | 567 | | 592 | | 582 | | | |
| 8 | | 577 | | 617 | | 596 | | 574 | | | | |
| 9 | | | 595 | | 592 | | 542 | | | | | |
| 10 | | 568 | | 549 | | | | | | | | |

where we have used

$$\Phi_N[(\mathbf{p}-\mathbf{q}-\mathbf{k})_z] \simeq \delta[(\mathbf{p}-\mathbf{q}-\mathbf{k})_z] \qquad (C.3)$$

within the integral, and made the replacement

$$\sum_{\mathbf{k}}{}' \to \Omega \int \mathrm{d}^3k \,.$$

In polar coordinates

$$\int \mathrm{d}^3k k^{-2}\delta[\varepsilon(\mathbf{p})-\varepsilon(\mathbf{p}-\mathbf{k})-\hbar\omega]$$
$$= m_0(2\pi p)^{-1}\int_0^{k_c} \mathrm{d}k k^{-1}\int_{-1}^{1}\mathrm{d}(\cos\theta)$$
$$\times\delta[\cos\theta-(2pk)^{-1}\{k^2+2m_0\hbar\omega\})] = m_0(2\pi p)^{-1}\int_{k_0}^{k_c}\mathrm{d}k k^{-1} \qquad (C.4)$$

where

$$k_0 = p-(p^2-2m_0\hbar\omega)^{1/2}. \qquad (C.5)$$

Hence, for $p$ large,

$$\langle \mathbf{p}'|U^\dagger\delta U|\mathbf{p}\rangle$$
$$= 2\, e^2\,\hbar\omega p^{-1}m_0 Nc \log\,[pk_c(m_0\hbar\omega)^{-1}]\delta^2(\mathbf{p}')^\perp$$
$$= 2pm_0^{-1}A(p)\delta^2(\mathbf{p}'-\mathbf{p})^\perp \qquad (C.6)$$

as $\mathbf{p}$ is along the $z$ axis.

The calculation of the unitarity contribution from $\hat{T}^\dagger\Delta^\dagger U^\dagger\delta U$ is simplified by writing it as

$$\langle \mathbf{p}'|\hat{T}^\dagger\Delta^\dagger U^\dagger\delta U|\mathbf{p}\rangle$$
$$= \int \mathrm{d}^3q\langle \mathbf{p}'|\hat{T}^\dagger|\mathbf{q}\rangle\,[\varepsilon(\mathbf{p})-\varepsilon(\mathbf{q})-i\epsilon]^{-1}\langle \mathbf{q}|U^\dagger\delta U|\mathbf{p}\rangle$$
$$= (2Nc)^{-1}A(p)\int \mathrm{d}^3q\langle \mathbf{p}'|\hat{T}^\dagger|\mathbf{q}\rangle$$
$$\times[\varepsilon(\mathbf{p})-\varepsilon(\mathbf{q})-i\epsilon]^{-1}\delta^2(\mathbf{p}-\mathbf{q})^\perp\Phi_N[(\mathbf{q}-\mathbf{p})_z]$$
$$= (2Nc)^{-1}A(p)\int \mathrm{d}q_z\,\frac{2\sin[(p-q_z)c]}{(p-q_z)}$$
$$\times[\varepsilon(\mathbf{p})-\varepsilon(\mathbf{q})-i\epsilon]^{-1}\langle \mathbf{p}'|\hat{T}^\dagger|\mathbf{q}\rangle \simeq iA(\mathbf{p})\langle \mathbf{p}'|\hat{T}^\dagger|\mathbf{p}\rangle \qquad (C.7)$$

for $p$ large, where we have ignored the contribution from backward elastic scattering. Thus the second equation of (3.15) follows. The third is obtained by a similar analysis.

In the calculation of the fourth and fifth terms of (3.12) it is necessary to utilize the lattice symmetry expressed by equation (3.7) and also to treat forward scattering, $\mathbf{p}'=\mathbf{p}$, separately. Utilising equation (3.13) yields

$$\langle \mathbf{p}'|U^\dagger\delta\hat{T}\Delta U|\mathbf{p}\rangle$$
$$= \int \mathrm{d}^3q\sum_{\mathbf{k}}\int \mathrm{d}^3q'\langle \mathbf{p}'|U|\mathbf{q};\mathbf{k}\rangle\delta[\varepsilon(\mathbf{p})-\varepsilon(\mathbf{q})-\hbar\omega]\langle \mathbf{q}|\hat{T}|\mathbf{q}'\rangle$$
$$\times[\varepsilon(\mathbf{p})-\varepsilon(\mathbf{q}')-\hbar\omega-i\epsilon]^{-1}\langle \mathbf{q}';\mathbf{k}'|U|\mathbf{p}\rangle\,, \qquad (C.8)$$

but

$$\delta[\varepsilon(\mathbf{p}')-\varepsilon(\mathbf{q})-\hbar\omega] = m\bar{q}^{-1}\{\delta(q_z-\bar{q})+\delta(q_z+\bar{q})\} \qquad (C.9)$$

with

$$\bar{q} = \{p_3'^2-k_\perp^2+2\mathbf{p}'.\mathbf{k}_\perp-2m_0\hbar\omega\}^{1/2}, \qquad (C.10)$$

where $\mathbf{k}_\perp$ are the components of $\mathbf{k}$ perpendicular to the $z$ direction. Also we may approximate the $\Phi_N$ within the integrand by delta functions, and consequently

$$\langle \mathbf{p}'|U^\dagger\delta\hat{T}\Delta U|\mathbf{p}\rangle$$
$$= 2m_0\pi e^2\hbar\omega\int \mathrm{d}^2k_\perp[k^2\bar{q}\{\varepsilon(\mathbf{p})-\varepsilon(\mathbf{p}-\mathbf{k})-\hbar\omega+i\varepsilon\}]^{-1}$$
$$\times\langle \mathbf{p}'-\mathbf{k}|\hat{T}|\mathbf{p}-\mathbf{k}\rangle \qquad (C.11)$$

in which

$$k^2 = k_\perp^2+k_3^2 \qquad (C.12)$$

with

$$k_3 = p_3'-\bar{q}\,. \qquad (C.13)$$

When the elastic matrix element is expanded by means of equation (3.7) the expression becomes

$$\langle \mathbf{p}'|U^\dagger\delta\hat{T}\Delta U|\mathbf{p}\rangle$$
$$= -4\pi e^2\,\hbar\omega p\sum_{\mathbf{K}}{}' f(p^2-2m_0\hbar\omega,\mathbf{K})\delta^2(\mathbf{p}'-\mathbf{p}+\mathbf{K})W(p)\,, \qquad (C.14)$$

where

$$W(p) = \int \mathrm{d}^2k[k^2\bar{q}\{\varepsilon(\mathbf{p})-\varepsilon(\mathbf{p}-\mathbf{k})-\hbar\omega+i\epsilon\}]^{-1} \qquad (C.15)$$

and we have approximated the expansion amplitude by its value on the physical energy shell. It then follows from a straightforward, though tedious, calculation, that for $p$ large

$$W(p) \simeq -4iK^{-1}\{(m_0\hbar\omega)^2+m_0\hbar\omega K\}^{-1/2}\,. \qquad (C.16)$$

Hence

$$\langle \mathbf{p}'|U^\dagger\delta\hat{T}\Delta U|\mathbf{p}\rangle$$
$$= iB\sum_{\mathbf{K}}{}' K^{-1}f(p^2-2m_0\hbar\omega,\mathbf{K})\delta^2(\mathbf{p}'-\mathbf{p}+K) \quad \mathbf{p}'\neq\mathbf{p}\,. \qquad (C.17)$$

For forward scattering,

$$\langle \mathbf{p}'|U^\dagger\delta\hat{T}U|\mathbf{p}\rangle = 2\pi\, e^2\,\hbar\omega\int \mathrm{d}^3k k^{-2}\delta[\varepsilon(\mathbf{p})-\varepsilon(\mathbf{p}-\mathbf{k})-\hbar\omega]$$
$$\times\int \mathrm{d}q_z\Phi_N[(\mathbf{q}+\mathbf{k}-\mathbf{p})_z]\,\{\varepsilon(\mathbf{p})-\varepsilon(\mathbf{q})-\hbar\omega+i\epsilon\}$$
$$\times\langle \mathbf{p}-\mathbf{k}|\hat{T}|\mathbf{q}\rangle\,. \qquad (C.18)$$

By an analysis similar to that which led to equation (C.7),

$$\int \mathrm{d}^3q_z\Phi_N[(\mathbf{q}+\mathbf{k}-\mathbf{p})_z]\,\{\varepsilon(\mathbf{p})-\varepsilon(\mathbf{q})-\hbar\omega+i\epsilon\}^{-1}\langle \mathbf{p}-\mathbf{k}|\hat{T}|\mathbf{q}\rangle$$
$$\simeq -iq(2Nc)\,(p-k_z)^{-1}f(p^2-2m_0\hbar\omega,\mathbf{0})\delta^2(\mathbf{p}'-\mathbf{p})\,. \qquad (C.19)$$

Thus, for $\mathbf{K}=\mathbf{0}$,

$$\langle \mathbf{p}'|U^{\dagger}\delta\hat{T}U|\mathbf{p}\rangle = -i4\pi\, e^2\, p\hbar\omega c I(p) \times f(p^2-2m_0\hbar\omega,\mathbf{0})\delta(\mathbf{p}'-\mathbf{p}), \quad (C.20)$$

where

$$I(\mathbf{p})=\int \mathrm{d}^3k k^{-2}(p-k_z)^{-1}\delta[\varepsilon(\mathbf{p})-\varepsilon(\mathbf{p}-\mathbf{k})-\hbar\omega]$$

$$=m_0(4\pi p^2)^{-1}\int_{k_0}^{k_c}\mathrm{d}k k^{-1}(2p^2-k^2-2m_0\hbar\omega)^{-1} \quad (C.21)$$

with

$$k_0=p-(p^2-2m_0\hbar\omega)^{1/2} \quad (C.22)$$

and, for $p$ large,

$$I(p)\simeq m_0(2\pi p^2)^{-1}\log\{k_c p(m_0\hbar\omega)^{-1}\}, \quad (C.23)$$

it following that

$$\langle \mathbf{p}'|U^{\dagger}\delta\hat{T}U|\mathbf{p}\rangle = iA(p)f(p^2-2m_0\hbar\omega,\mathbf{0})\delta(\mathbf{p}'-\mathbf{p}) \quad (C.24)$$

for $\mathbf{K}=\mathbf{0}$.

The contribution from $U^{\dagger}\Delta^{\dagger}\hat{T}^{\dagger}\delta U$ may be computed similarly.

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# A Probable Crystallographic Path for Phase Transformations in Single Crystals of Ammonium Nitrate


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Assuming that the shuffles of a solid-state single-crystal phase transformation are least-motion processes consistent with the symmetry of the phases and with the accepted interatomic distances, it follows that the structure of the higher-symmetry phase will be predictable solely from its space-group symmetry and unit-cell dimensions if the complete crystal structure of the low-symmetry phase has already been determined [Swaminathan & Srinivasan, *Acta Cryst.* (1975). A**31**, 628–634]. The possibility has been here verified successfully in the sequence V → IV → II of the phase transformations in ammonium nitrate.


## Introduction

At the end of a paper on the thermal cycle of phase transformations in potassium nitrate (Swaminathan & Srinivasan, 1975) is the following statement: 'Crystallographically an important point also emerges. If the crystal structure of the lower-symmetry phase is known, the crystal structure of the higher-symmetry phase may be predicted from only a knowledge of the unit-cell dimensions and the space-group symmetry of the higher-symmetry phase'.

Many transformations in crystals of inorganic substances show the important characteristics of martensitic transformations in metals and alloys. The underlying idea of the paper on the $KNO_3$ transformations is that the 'shuffles' of solid-state phase transformations must be least-motion processes consistent with the symmetry of the phases and subject to acceptable interatomic van der Waals contact distances between chemically non-bonded atoms, and that therefore the structure of the higher-symmetry phase of a transformation must be predictable from the structure of the low-symmetry phase.

## Martensitic transformations

Martensitic transformations generally involve lattice deformations which lead to macroscopic shape changes in crystals undergoing transitions from one phase to another. Between the phases of a transformation exists a strong orientation relationship. Often the lattice deformations will not produce the correct atomic or molecular positions within the unit-cell, and additional displacements (shuffles) which produce no macroscopic effects are then required. They may arise, for example, if the atomic positions in the parent deformed cell do not have the observed space-group symmetry of the daughter phase (Christian, 1965; Wayman, 1964).

## The polymorphs of ammonium nitrate

Below its fusion temperature of 165°C ammonium nitrate exists in five distinct phases with reversible transitions between them in the sequence V → IV → III → II → I (Hendricks, Posnjak & Kracek, 1932; Cleaver, Rhodes & Ubbelohde, 1963). In dry crystals without occluded water phase IV goes directly over to phase II