lungen von der festen Phase auf die Schmelze überträgt, letztlich nicht viel übrig bleibt für zusätzliche strukturelle Schwankungen.

Die bisher in (5) außer acht gelassenen Glieder führen zu einem unsymmetrischen Anteil in der Abstandsverteilung, der vom Gleichgewichtsabstand nach größeren Abständen hin abfällt. Unter der Annahme, daß X, Y und Z unabhängig voneinander sind, lassen sich die Momente von u errechnen:

$$\langle u \rangle = \frac{1}{2\,r} \left(\langle Y^2 \rangle + \langle Z^2 \rangle \right);$$

$$\langle u^2 \rangle = \langle X^2 \rangle + \frac{3}{4\,r^2} \left(\langle Y^2 \rangle + \langle Z^2 \rangle \right)^2.$$

$\langle u \rangle$ hat für nächste Nachbarn bei der Schmelztemperatur einen Wert in der Größenordnung von Hundertstel Å. Der Anteil der Y- und Z-Auslenkungen an $\langle u_1{}^2 \rangle$ beträgt bei dieser Temperatur einige Prozent. Die Unsymmetrie im ersten Maximum der Schmelzen ist viel größer und kann damit nur auf die besondere Struktur der Schmelzen zurückgeführt werden.

A Multiple Scattering Theory of Thermal-diffuse Scattering for Low-Energy Electrons

ANTHONY R. MOON *

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin-Dahlem, Germany **

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A perturbation theory of thermal diffuse scattering of low-energy electrons is developed along the lines of von Laue's "reciprocity theorem" approach successfully used by Kainuma in the consideration of diffuse scattering in high-energy electron diffraction. This theory takes into account the multiple scattering of the electrons within the crystal, and is so formulated that it may be used in conjunction with present LEED calculations for the elastic scattering from a perfect crystal. It is shown that by a pseudokinematical approximation for the perfect crystal wave functions, the normal pseudokinematical result for the diffuse intensity is obtained. Under certain conditions differences between the multiple scattering theory and the pseudokinematical theory are expected to occur. These deviations have their origin in resonance processes. Some numerical results comparing the two theories are presented.

1. Introduction

Electrons incident upon a crystal are scattered both elastically and inelastically within it. A study of those electrons which are inelastically scattered from phonons, that is the thermal diffuse scattered electrons, contributes to an understanding of the lattice dynamics of the crystal. Low-energy electrons penetrate the crystal only slightly and so a study of the thermal-diffuse-scattered electrons for these low incident energies would contribute to an understanding of the lattice dynamics near the crystal surface.

The most fruitful approach to this understanding is the proposal of a model of the lattice dynamics and then comparison of the theoretical predictions for this model with the experimentally measured results. In order to make this comparison, a knowledge of the scattering dynamics of the electron is needed. Some success in interpretation of experimental results has been achieved using pseudokinematical scattering ideas[1], in which the electron is assumed to undergo only *single* inter-atomic scatterings within the crystal. On the other hand, there exists a body of experimental evidence[2] emphasizing the dynamical (multiple scattering) nature of

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* Present address: School of Physics, University of Melbourne, Parkville, Victoria 3052, Australia.

** Abteilung Professor Dr. K. MOLIÈRE.

[1] E. R. JONES, J. T. MCKINNEY, and M. B. WEBB, Phys. Rev. **151**, 476 [1966]; **160**, 523 [1967]. — R. F. BARNES, M. G. LAGALLY, and M. B. WEBB, Phys. Rev. **171**, 627 [1968]. — M. G. LAGALLY, Ph. D. Thesis, University of Wisconsin 1968, unpublished.

[2] See for instance, Refs. [22, 24–26].

the electron scattering. To estimate the extent to which a pseudokinematical approach may lead to a correct description of the scattering, a multiple scattering theory for the thermal diffuse scattering from one-phonon processes was developed. The theory was so formulated that a direct comparison with the pseudokinematical theory was possible. It utilises present LEED calculations for elastic scattering from a perfect crystal, in particular the Kambe theory and calculations [3].

2. Theory

We assume that the diffuse scattering may be handled using perturbation theory methods. This is a rather large assumption and may not be at all justifiable even for *thermal* diffuse scattering, except perhaps at room temperatures or lower. Nonetheless the assumption is made. The perturbation approach is that used successfully by KAINUMA [4] in his explanation of Kikuchi lines in high-energy electron diffraction. This approach is based on a generalisation of the "reciprocity theorem" [4–6] the results of which may be carried over to the case of low-energy electrons. This reciprocity theorem states that for any two points in space, A and B, and a scatterer P (the crystal), the amplitude at B, $\overline{\Phi}(r_{\mathrm{B}})$, of a wave originating from a source at A and scattered by P is equal to the scattered amplitude at A, $\Phi(r_{\mathrm{A}})$, due to the same source placed at B; that is $\Phi(r_{\mathrm{A}}) = \overline{\Phi}(r_{\mathrm{B}})$. If the point A is very far from the crystal $\overline{\Phi}(r)$ can be assumed to be a plane wave when it falls on the crystal and thus $\Phi(r_{\mathrm{B}})$ may be calculated using a dynamical theory of diffraction suitable for low-energy electrons, in our case the Kambe theory [3]. For the situation where the source B in the crystal is no longer a point source we have [4, 5]

$$\Phi(r_{\mathrm{A}}) = \int_{\text{scatterer}} \overline{\Phi}(r)\, \varrho(r)\, \mathrm{d}^3 r \tag{2.1}$$

where $\varrho(r)$ is the source function. For a wave $\Phi_0(r)$ incident upon the crystal from outside, a perturbation calculation shows that this source function for inelastic waves is proportional to the amplitude of the incident wave, that is

$$\varrho_{n0}(r) = C_{n0}(r)\, \Phi_0(r) \tag{2.2}$$

and

$$\Phi_n(r_{\mathrm{A}}) = \int \overline{\Phi}_n(r)\, C_{n0}(r)\, \Phi_0(r)\, \mathrm{d}^3 r\,. \tag{2.3}$$

Here Φ_n is the wave diffusely scattered into state n and $\overline{\Phi}_n$ is the "reciprocal wave" [4]. The quantity $C_{n0}(r)$ is the interaction potential linking the state n with the initial state 0 and for one-phonon inelastic processes is given by

$$C_{n0}(r) = \langle n \,|\, \sum_l \boldsymbol{u}_l \cdot [\nabla_{\boldsymbol{R}_l} V(\boldsymbol{r}, \boldsymbol{R})]_{\boldsymbol{R}_l = \boldsymbol{R}_{l0}} \,|\, 0 \rangle\,. \tag{2.4}$$

This expression results from a Taylor's expansion of the crystal potential $V(\boldsymbol{r}, \boldsymbol{R})$. Here $\boldsymbol{R}$ represents the set of vectors $\boldsymbol{R}_l = \boldsymbol{R}_{l0} + \boldsymbol{u}_l$, where $\boldsymbol{R}_{l0}$ is the position vector of the equilibrium position of the l-th atom and $\boldsymbol{u}_l$ is its displacement from this equilibrium position. The state functions n and 0 signify the n-th excited state of the crystal and the initial state respectively.

Because the energy loss in one-phonon inelastic processes may be considered negligibly small compared with the initial energy of the incident electron, Φ_0 and $\overline{\Phi}_n$ are both solutions of the Schroedinger equation

$$(\nabla^2 + E)\, \Phi = V(\boldsymbol{r}, \boldsymbol{R}_0)\, \Phi$$

and satisfy the same type of boundary conditions. The symbol $\boldsymbol{R}_0$ represents the set of vectors $\boldsymbol{R}_{l0}$, and E is the electron energy. The potential function $V(\boldsymbol{r}, \boldsymbol{R}_0)$, the zeroth term in the Taylor's series expansion of the actual potential, is assumed in this theory to conform to the "muffin-tin" model [3] for a perfect crystal. In this model the crystal is divided into separate spherical regions, in each of which an atom is represented by a spherically symmetric potential. The space between these spherical regions is assumed to be one of constant potential. The boundary conditions are those for a wave incident on a crystal which is then scattered within the crystal leading to reflected and transmitted waves. The intensity diffusely scattered into direction $\boldsymbol{k}'$, resulting from inelastic scattering of the incident wave, wave vector $\boldsymbol{k}$, may thus be written

$$J_{\mathrm{TDS}}(\boldsymbol{k}', \boldsymbol{k}) \sim \langle |M(\boldsymbol{k}', \boldsymbol{k})|^2 \rangle\,. \tag{2.5}$$

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[3] K. KAMBE, Z. Naturforsch. **23 a**, 1280 [1968].

[4] Y. KAINUMA, Acta Cryst. **8**, 247 [1955].

[5] M. VON LAUE, Materiewellen und ihre Interferenzen, 2nd Edit., Akademische Verlagsgesellschaft, Leipzig 1948, p. 355.

[6] K. ARTMANN, Z. Phys. **124**, 80, 154 [1947/48]; **125**, 27, 298 [1948/49].

The brackets $\langle\ \rangle$ mean thermal average with respect to the motion of the atoms and the matrix element $M(\boldsymbol{k}', \boldsymbol{k})$ is defined by

$$M(\boldsymbol{k}', \boldsymbol{k}) = \sum_l \boldsymbol{u}_l \cdot \int \Phi_0^{-\boldsymbol{k}'}(r) \left[\nabla_{\boldsymbol{R}_l} V(\mathbf{r}, \mathbf{R}_l)\right]_{\boldsymbol{R}_l = \boldsymbol{R}_{l0}} \Phi_0^k \, \mathrm{d}^3 r \,. \tag{2.6}$$

The superscripts of Φ_0 indicate the boundary conditions appropriate for a wave incident on the crystal with wave vector $\boldsymbol{k}$ or $-\boldsymbol{k}'$. If the diffuse scattering is observed in a direction $\boldsymbol{k}'$ the "reciprocal-wave" is incident on the crystal with wave vector $-\boldsymbol{k}'$ (Fig. 1).

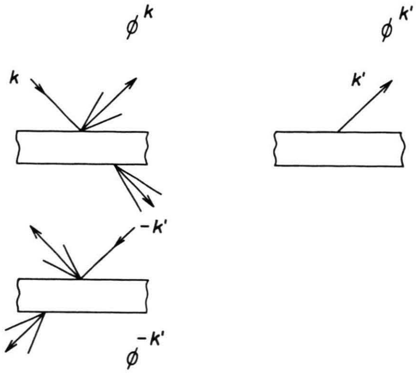

Fig. 1. The boundary conditions for the incident wave, the outgoing wave and the "reciprocal wave".

3. Evaluation of the Matrix Element $M(\boldsymbol{k}', \boldsymbol{k})$

If we write the potential function $V(\mathbf{r}, \mathbf{R})$ as $V(\mathbf{r}, \mathbf{R}) = \sum_l v(\mathbf{r} - \boldsymbol{R}_l)$ – the Nordheim model – then the interaction operator

$$\sum_l \boldsymbol{u}_l \cdot \left[\nabla_{\boldsymbol{R}_l} V(\mathbf{r}, \mathbf{R})\right]_{\boldsymbol{R}_l = \boldsymbol{R}_{l0}} \tag{3.1}$$

occurring in the expression (2.6) for the matrix element $M(\boldsymbol{k}', \boldsymbol{k})$ may be rewritten as

$$-\sum_l \boldsymbol{u}_l \cdot \nabla_r v(\mathbf{r} - \boldsymbol{R}_{l0}) \,. \tag{3.2}$$

The crystal, which is assumed infinite in the x, y-plane parallel to its surface and finite in the z-direction normal to this surface, is divided into "columns of reference"[3] – columns parallel to the z-axis, whose cross-section is a unit cell of the two-dimensional lattice. We define the vector $\boldsymbol{R}_{l0}$ as $\boldsymbol{R}_{l0} = \boldsymbol{R}_{L0} + \boldsymbol{R}_{c0}$, where the $\boldsymbol{R}_L$ (see Ref. [7]) are two-dimensional lattice vectors in the plane parallel to the crystal surface and as such refer to a particular column, and the $\boldsymbol{R}_c$ are the positions of the various atoms within such a column.

We may thus write the matrix element $M(\boldsymbol{k}', \boldsymbol{k})$ as

$$M(\boldsymbol{k}', \boldsymbol{k}) = -\sum_l \boldsymbol{u}_l \cdot \left(\int \Phi^{-\boldsymbol{k}'} \nabla v(\mathbf{r} - \mathbf{R}_\mathrm{c}) \Phi^{\boldsymbol{k}} \mathrm{d}^3 r\right) \exp\{i\,\mathbf{Q} \cdot \mathbf{R}_L\} \tag{3.3}$$

$$= -\sum_l \boldsymbol{u}_l \cdot \mathbf{S}^c \exp\{i\,\mathbf{Q} \cdot \mathbf{R}_L\} \,, \tag{3.4}$$

where the vector $\mathbf{Q}$ is given by $\mathbf{Q} = \boldsymbol{k} - \boldsymbol{k}'$ and $\mathbf{S}^c$ by

$$\mathbf{S}^c = \int \Phi^{-\boldsymbol{k}'} \nabla v(\mathbf{r} - \mathbf{R}_c) \, \Phi^{\boldsymbol{k}} \, \mathrm{d}^3 r \,. \tag{3.5}$$

The dependence of the matrix element on a particular column of reference is included in the phase factor $\exp\{i\,\mathbf{Q} \cdot \mathbf{R}_L\}$. This separation results from the translational symmetry of the wave functions and potential parallel to the crystal surface.

In order to use a result from group theory we define a special coordinate system in which the components (the so-called spherical components of a vector) are described in terms of their cartesian components in the following manner:

$$\mathbf{A} = (A_x, A_y, A_z) = (A_0, A_1, A_{-1}) \,,$$

where

$$A_0 = A_z \,, \quad A_1 = -(1/\sqrt{2})(A_x + i\,A_y) \,,$$

and

$$A_{-1} = (1/\sqrt{2})(A_x - i\,A_y) \,.$$

Thus we may write

$$M(\boldsymbol{k}', \boldsymbol{k}) = -\sum_l \sum_\mu^{\pm 1, 0} (-1)^\mu u_{l,-\mu} S_\mu^c \exp\{i\,\mathbf{Q} \cdot \mathbf{R}_L\} \,, \tag{3.6}$$

where

$$S_\mu^c = \int_{\text{sphere } c} \Phi^{-\boldsymbol{k}'} \nabla_\mu v(\boldsymbol{\rho}_c) \, \varphi \, \mathrm{d}^3 \varrho_c \, \Phi^{\boldsymbol{k}} \tag{3.7}$$

There is no contribution to the matrix element from the region outside the spheres since the potential is here constant and its gradient thus vanishes.

Multiplying the Schroedinger equation for the wave function $\Phi^{\boldsymbol{k}}$ from the left with the operator ∇_μ we obtain, after rearrangement, an expression for the quantity $\nabla_\mu v(\boldsymbol{\rho}_c) \, \Phi^{\boldsymbol{k}}$ occurring in the defining Eq. (3.7) for[8] S_μ^c. Thus we may write

$$\nabla_\mu v(\boldsymbol{\rho}_c) \, \Phi^{\boldsymbol{k}} = \left(\nabla^2 + \mathrm{E} - v(\boldsymbol{\rho}_c)\right) \nabla_\mu \Phi^{\boldsymbol{k}} \tag{3.8}$$

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[7] The subscript "0", indicating equilibrium values, will be omitted in subsequent proceedings.

[8] D. Golibersuch, Phys. Rev. **157**, 532 [1967].

By use of the vector algebra relationship for any two scalar quantities A, B

$$A \nabla^2 B = (\nabla^2 A)\, B + \nabla\big(A \nabla B - (\nabla A)\, B\big)$$

together with the expression for $\nabla_\mu v\, \Phi^{\boldsymbol{k}}$ we may rewrite[9] the expression (3.7) for the integral S^c_μ as

$$S^c_\mu = \int \nabla \big(\Phi^{-\boldsymbol{k}'} \nabla (\nabla_\mu \Phi^{\boldsymbol{k}'}) - (\nabla \Phi^{-\boldsymbol{k}'})\, \nabla_\mu \Phi^{\boldsymbol{k}}\big)\, \mathrm{d}^3 \varrho_c\,. \tag{3.9}$$

Using the divergence theorem this volume integral is reduced to a surface integral over the sphere c,

$$S^c_\mu = \int\limits_{\substack{\text{surface of}\\ \text{sphere } c}} \big(\Phi^{-\boldsymbol{k}'} \nabla (\nabla_\mu \Phi^{\boldsymbol{k}}) - (\nabla \Phi^{-\boldsymbol{k}'})\, \nabla_\mu \Phi^{\boldsymbol{k}}\big) \cdot \mathrm{d}\boldsymbol{s}_c\,. \tag{3.10}$$

Within and around the spherical region c the wave functions $\Phi^{\boldsymbol{k}}(\boldsymbol{r})$ and $\Phi^{-\boldsymbol{k}'}(\boldsymbol{r})$ may be expanded in spherical harmonic functions[3] $Y_{lm}(\hat{\boldsymbol{\rho}}_c)$. These spherical harmonics conform to the definition $Y^*_{lm} = Y_{l-m}$, the asterisk signifying the complex conjugate of the quantity indicated. Thus we may write

$$\Phi^{\boldsymbol{k}} = \sum_{l,m} X^{\boldsymbol{k}c}_{lm}\; Y_{lm}(\hat{\boldsymbol{\rho}}_c) \tag{3.11a}$$

and

$$\Phi^{-\boldsymbol{k}'} = \sum_{lm} X^{-\boldsymbol{k}'c}_{lm}\; (\varrho_c)\; Y_{lm}(\hat{\boldsymbol{\rho}}_c), \tag{3.11b}$$

where the vector $\boldsymbol{\rho}_c = (\varrho_c, \vartheta_c, \varphi_c) \equiv (\varrho_c, \hat{\boldsymbol{\rho}}_c)$ is the displacement of the electron from the centre of the c-th atom; that is, $\boldsymbol{\rho}_c = \boldsymbol{r} - \boldsymbol{R}_c$. The surface integral S^c_μ may now be rewritten as

$$S^c_\mu = \sum_{\substack{lm\\ l'm'}} R_s^2 \Big(X^{-\boldsymbol{k}'c}_{l'm'} \cdot \frac{\mathrm{d}}{\mathrm{d}\varrho_c} \big(\int \mathrm{d}\Omega_c\, Y_{l'm'}\, \nabla_\mu X^{\boldsymbol{k}c}_{lm}\, Y_{lm} \big) - \frac{\mathrm{d}}{\mathrm{d}\varrho_c} \big(X^{-\boldsymbol{k}'c}_{l'm'}\big) \int \mathrm{d}\Omega_c\, Y_{l'm'}\, \nabla_\mu X^{\boldsymbol{k}c}_{lm}\, Y_{lm} \Big)_{\varrho c = Rs}, \tag{3.12}$$

where R_s is the radius of the sphere c and $\mathrm{d}\Omega_c$ is the element of solid angle.

We may now evaluate the integral over solid angle in this expression (3.12) for S^c_μ by application of a result of the Wigner-Eckart theorem (factorisation of the matrix elements of Tensor operators). The immediate application of this theorem follows from the special form of the coordinate system used in these calculations[10, 11].

The result obtained is

$$\begin{aligned} \int \mathrm{d}\Omega_c\, Y_{l'm'}\, \nabla_\mu X^{\boldsymbol{k}c}_{lm}\, Y_{lm} &= \sqrt{4\pi/3} \Big[\delta_{l',\, l+1}\, \delta_{m',\, -(m+\mu)}\, C_{1\mu;\, l+1,\, m+\mu;\, lm} \cdot \Big(\frac{\mathrm{d}}{\mathrm{d}\varrho_c} - l/\varrho_c\Big) X^{\boldsymbol{k}c}_{lm} \Big] \\ &\quad + \Big[\delta_{l',\, l-1}\, \delta_{m',\, -(m+\mu)}\, C_{1\mu;\, l-1,\, m+\mu;\, lm} \cdot \Big(\frac{\mathrm{d}}{\mathrm{d}\varrho_c} + (l+1)/\varrho_c\Big) X^{\boldsymbol{k}c}_{lm} \Big]. \end{aligned} \tag{3.13}$$

Here δ is the Kronecker-delta symbol and the constant

$$C_{LM;\, lm;\, l'm'} \equiv \int Y_{LM}\, Y^*_{lm}\, Y_{l'm'}\, \mathrm{d}\Omega\,. \tag{3.14}$$

We wish now to find expressions for the X_{lm}. The solution of the wave equation in the space just outside the c-th spherical region, which in the muffin-tin model is a region of constant potential, consists of a sum of plane waves, each having the same energy. These plane waves may be considered to scatter from the spherical potential c. For a single plane wave incident upon atom c

$$X^{\boldsymbol{k}c}_{lm} = 4\pi\, i^l\, Y^*_{lm}(\boldsymbol{k})\, \big(j_l(k r) + i \cdot \exp\{i\, \delta^c_l\} \sin \delta^c_l\, h^1_l(k r)\big)\,. \tag{3.15}$$

For a sum of plane waves[12] incident upon atom c

$$X^{\boldsymbol{k}c}_{lm} = B^{\boldsymbol{k}c}_{lm}\, \big(j_l(k r) + i \cdot \exp\{i\, \delta^c_l\} \sin \delta^c_l\, h^1_l(k r)\big) \tag{3.16}$$

where the constant $B^{\boldsymbol{k}c}_{lm}$ depends on the boundary conditions and the scattering properties of the individual scatterers. The derivative $(\mathrm{d}/\mathrm{d}r)\, X^{\boldsymbol{k}c}_{lm}$ may be written as

$$\frac{\mathrm{d}}{\mathrm{d}r}\, X^{\boldsymbol{k}c}_{lm} = B^{\boldsymbol{k}c}_{lm} \Big(\Big[\frac{\mathrm{d}}{\mathrm{d}r}\, j_l(k r)\Big]_{r=R_s} + i \cdot \exp\{i\, \delta^c_l\} \sin \delta^c_l \Big[\frac{\mathrm{d}}{\mathrm{d}r}\, h^1_l\, (k r)\Big]_{r=R_s} \Big) \tag{3.17}$$

and similar expressions may be obtained for $X^{-\boldsymbol{k}'c}_{lm}$ and $[(\mathrm{d}/\mathrm{d}r)\, X^{-\boldsymbol{k}'c}_{lm}]_{r=R_s}$.

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[9] We write $A = \Phi^{-\boldsymbol{k}'}$ and $B = \nabla_\mu \Phi^{\boldsymbol{k}}$.

[10] E. MERZBACHER, Quantum Mechanics, J. Wiley & Sons, New York 1963, p. 519.

[11] The spherical harmonics used in this reference conform to the definition $Y^*_{lm} = (-1)^m\, Y_{l-m}$, but the results of the Wigner-Eckart theorem taken from this reference have been transformed so as to conform to our definition of the spherical harmonics and the spherical coordinate system. The required transformation is

$$Y_{lm}(\text{reference definition}) = (-1)^{(m+|m|)/2}\, Y_{lm}$$

(our definition).

[12] W. KOHN and N. ROSTOKER, Phys. Rev. **94**, 1111 [1954].

In these expressions the j_l are the spherical Bessel functions of l-th order and the first kind, the h_l^1 those of the l-th order and 3rd kind, and the δ_l^c are the reduced atomic phase shifts. These phase shifts[3], defined within the range $-\pi/2$ to $\pi/2$, characterise the scattering properties of the c-th atom. For low energy electrons only the first few δ_l are non-zero.

Use of these expressions for the X_{lm}, $(\mathrm{d}/\mathrm{d}r)\, X_{lm}$ in the expression (3.12) for S_μ^c gives us the result.

$$S_\mu^c = \sum_{lm} \sqrt{\frac{4\pi}{3}}\, [C_{1\mu;\, l+1,\, m+\mu;\, lm}\, B_{l+1,-(m+\mu)}^{-\boldsymbol{k}'c}\, B_{lm}^{\boldsymbol{k}c} \cdot (\exp\{2\, i\, \delta_l^c\} - \exp\{2\, i\, \delta_{l+1}^c\})/2\, i \\ + C_{1\mu;\, l-1,\, m+\mu;\, lm}\, B_{l-1,-(m+\mu)}^{-\boldsymbol{k}'c}\, B_{lm}^{\boldsymbol{k}c} \cdot (\exp\{2\, i\, \ddot{\delta}_{l-1}^c\} - \exp\{2\, i\, \delta^c\})/2\, i] \,. \tag{3.18}$$

This reduction follows from the special properties of the spherical Bessel functions (Appendix A).

In the approximation that the inter-atomic scattering processes are neglected (pseudokinematical approximation) the B_{lm} may be written as[3]

$$B_{lm}^{\boldsymbol{k}c} = \exp\{i\, \boldsymbol{k}\, \boldsymbol{R}_c\}\, 4\, \pi\, i^l\, Y_{lm}^*(\boldsymbol{k}) \,. \tag{3.19}$$

In this approximation the S_μ^c reduce to (Appendix B)

$$S_\mu^c = 4\, \pi\, i\, f^c \cdot \exp\{i\, \boldsymbol{Q}\, \boldsymbol{R}_c\} k\, (Y_{1\mu}(\boldsymbol{k}) + Y_{1\mu}(-\boldsymbol{k}')) \,.$$

where (3.20)

$$f^c = \sum_{lm} 4\, \pi\, \frac{(e^{2i\delta_l^c} - 1)}{2\, i\, k}\, Y_{lm}^*(\boldsymbol{k})\, Y_{lm}(\boldsymbol{k}') \tag{3.21}$$

is the exact atomic scattering factor.

Kambe in his theory of elastic scattering[3] for LEED defines a quantity x_{lm}, given by the relationship

$$x_{lm} = X_{lm} / (\sqrt{4\, \pi}\, i^l (j_l \cos \delta_l - y_l \sin \delta_l)) \tag{3.22}$$

where X_{lm} is as previously defined. In terms of the B_{lm} defined above we may then write[13]

$$x_{lm} = B_{lm} \exp\{i\, \delta_l\} (\sqrt{4\, \pi}\, i^l)^{-1}. \tag{3.23}$$

After rearrangement the expression (3.18) for S_μ^c may thus be written as[14]

$$S_\mu^c = 4\, \pi\, i \sqrt{\frac{4\, \pi}{3}} \sum_{lm} (-1)^l\, C_{1\mu;\, l+1,\, m+\mu;\, lm} \\ \cdot \sin(\delta_l^c - \delta_{l+1}^c)\, (x_{lm}^{\boldsymbol{k}c}\, x_{l+1,-(m+\mu)}^{-\boldsymbol{k}'c} \\ + x_{l+1,-(m+\mu)}^{\boldsymbol{k}c}\, x_{lm}^{-\boldsymbol{k}'c}) \,. \tag{3.24}$$

The vector components S_μ^c may now be referred to the normal cartesian components S_x^c etc. by means of the transformation

$$S_z = S_0; \\ S_x = (1/\sqrt{2})\, (S_{-1} - S_1); \\ S_y = (i/\sqrt{2})\, (S_{-1} + S_1) \,. \tag{3.25}$$

The quantities x_{lm}, and $C_{1\mu} \ldots$ are calculated in Kambe's[3] program for LEED elastic intensities.

4. The One-phonon Diffuse Intensity

The preceding calculations have enabled us to calculate the vector $\boldsymbol{S}^c$ occurring in the expression (3.4) for the matrix element $M(\boldsymbol{k}', \boldsymbol{k})$ in a form suitable for numerical calculation. The resultant expression for the inelastic intensity due to one-phonon processes is given by

$$J_{\mathrm{TDS}}(\boldsymbol{k}', \boldsymbol{k}) = \sum_{l,l'} \exp\{i\, \boldsymbol{Q} \cdot (\boldsymbol{R}_L - \boldsymbol{R}_{L'})\} \\ \cdot \langle \boldsymbol{u}_l \cdot \boldsymbol{S}^c\, \boldsymbol{u}_{l'} \cdot \boldsymbol{S}^{c'*} \rangle \,. \tag{4.1}$$

In the pseudokinematical approximation this reduces to

$$J_{\mathrm{TDS}}(\boldsymbol{k}', \boldsymbol{k}) = \sum_{l,l'} \exp\{i\, \boldsymbol{Q} \cdot (\boldsymbol{R}_l - \boldsymbol{R}_{l'})\} \\ \cdot |f|^2 \langle \boldsymbol{u}_l \cdot \boldsymbol{Q}\, \boldsymbol{u}_{l'} \cdot \boldsymbol{Q} \rangle \tag{4.2}$$

which is the well-known pseudokinematical result, normally obtained without explicit recourse to perturbation theory methods[1].

5. The Correlation Function

We may rewrite the expression for the thermal diffuse intensity as

$$J_{\mathrm{TDS}}(\boldsymbol{k}', \boldsymbol{k}) = \sum_{i,j} S_i\, S_j^*\, g_{ij} \,, \tag{5.1}$$

where the lattice correlation function g_{ij} is defined as

$$g_{ij} = \sum_{l,l'} \exp\{i\, \boldsymbol{Q} \cdot (\boldsymbol{R}_L - \boldsymbol{R}_{L'})\} \langle (\boldsymbol{u}_l)_i\, (\boldsymbol{u}_{l'})_j \rangle \,. \tag{5.2}$$

For purposes of simplicity in the numerical calculations we restrict ourselves now to the case in which scattering is assumed to take place only from the first atomic layer in the crystal (monolayer approximation). We further assume that the lattice itself contains only one atom per unit cell[15]. Under cer-

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[13] There is no inherent advantage in the choice of x_{lm} over B_{lm}. The substitution was made in order to facilitate use of Kambe's program for elastic scattering — which calculates the quantities x_{lm} — in computing values for the thermal diffuse scattering.

[14] This series converges after only a few terms for low energy electrons because of the δ_l-phase shift dependence.

[15] Under these assumptions the superscript "c" is dropped.

tain simplifying conditions[16] an explicit formula for this correlation function may be found, provided the difference between the incoming and outgoing wave-vectors of the electrons is near a reciprocal lattice rod. This expression is[16] $g_{ij} =$ constant.

$$\varDelta(Q_x+q_1)\,\varDelta(Q_y+q_2)(1/t)\{\delta_{ij}-(1/4)\,\delta_{i3}\,\delta_{j3} - (1/4)\,(1-\delta_{i3})\,(1-\delta_{j3})\,q_i\,q_j/t^2\} \tag{5.3}$$

where $t^2 = q_1^2 + q_2^2$, and q_1 and q_2 are defined [through $\varDelta(Q_x+q_1)$ and $\varDelta(Q_y+q_2)$][18] as the components of the displacement of the tip of the **Q**-vector away from the nearest reciprocal lattice rod in the x- and y-directions respectively. This expression contains contributions to the correlation from all phonons with $\boldsymbol{q}$-vector $\boldsymbol{q} = (q_1, q_2, q_z)$, with q_z being allowed all possible values (Fig. 2). The effects of surface modes of vibration are also included in this expression[19]. We assume that this expression is valid for temperatures low enough for the perturbation theory to be valid. This assumption is made purely for simplicity in the numerical calculations.

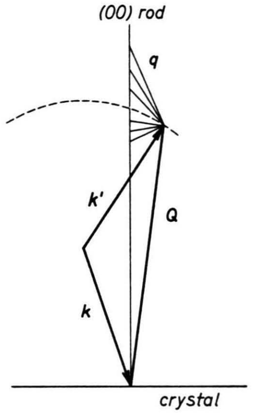

Fig. 2. The incident wave vector $\boldsymbol{k}$, the outgoing wave vector $-\boldsymbol{k}'$, the scattering vector $\boldsymbol{Q}$ and the phonon wave vector $\boldsymbol{q}$.

The expression for the thermal diffuse intensity may thus be written as

$$J_{\text{TDS}} \sim (1/t)\,(|S_x|^2+|S_y|^2 + (3/4)\,|S_z|^2 - |(S_x\,q_1 + S_y\,q_2)|^2/t^2) \tag{5.4}$$

with the corresponding expression in the pseudo-kinematical limit as

$$J_{\text{TDS}} \sim (|f|^2/t)\,(Q_x^2+Q_y^2+(3/4)\,Q_z^2 - (Q_x\,q_1+Q_y\,q_2)^2/t^2)\,. \tag{5.5}$$

6. Discussion and Numerical Results

On the basis of this reciprocity theorem approach to diffuse scattering resonances in the diffuse scattering are expected whenever the vectors $\boldsymbol{k}$ or $-\boldsymbol{k}'$ are such that the geometrical condition

$$(\boldsymbol{K}_t+\boldsymbol{B}_t)^2 = K^2$$

is fulfilled. Here the vector $\boldsymbol{K}$ represents either $\boldsymbol{k}$ or $-\boldsymbol{k}'$, and the subscript "t" signifies the tangential component of the vector (with respect to the crystal surface). Here K is simply the modulus of the vector $\boldsymbol{K}$, and $\boldsymbol{B}_t$ is a vector of the two-dimensional reciprocal lattice.

For the wave vector $\boldsymbol{k}$ this is the condition that a diffracted elastic wave $\boldsymbol{k}_t+\boldsymbol{B}_t$ is propagated parallel to the crystal surface. This is therefore the condition for a "surface-wave" resonance[3, 17, 20]. It results in a resonance in the source function for the inelastic waves. For the wave vector $-\boldsymbol{k}'$, this is the condition for a resonance in the reciprocal wave, of identical nature to that for the case of the wave vector $\boldsymbol{k}$. From the reciprocity theorem this means that there exist certain directions of the wave emitted by the internal source for which there appears a wave reflected parallel to the surface of the crystal. The appearance of this wave produces a modification in the emitted wave.

As the origin of these resonance phenomena is essentially due to the multiple scattering within the crystal we expect that multiple scattering expression value for the diffuse intensity to differ from its pseudokinematical value at and around the positions of resonance. The extent of the deviation will depend on the scattering properties of the individual atoms in the crystal. Some simple calculations for the (100) face of copper were carried out to investigate the effect of these resonance phenomena.

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[16] R. F. Wallis and A. A. Maradudin, Phys. Rev. **148**, 962 [1966]. — D. L. Huber, Phys. Rev. **153**, 772 [1967]; the results of this method differ from those of Wallis and Maradudin by approximately a factor of 2.

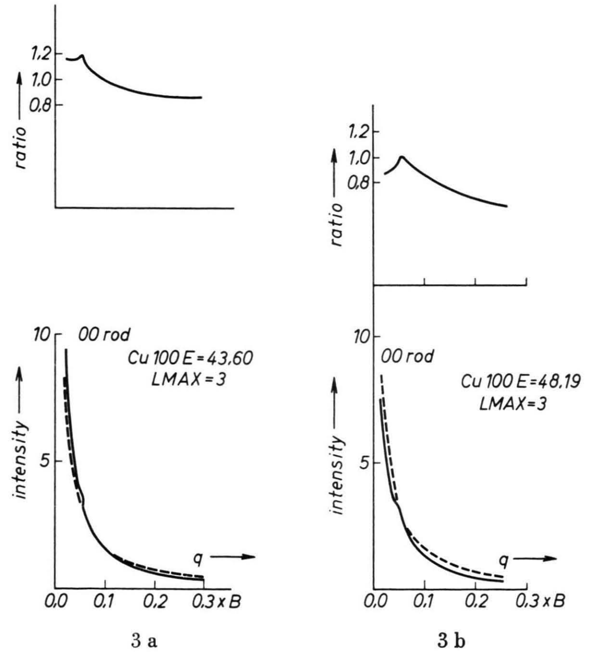
[18] $\varDelta(Q_x+q_1)$ [$\varDelta(Q_y+q_2)$] is unity if Q_x+q_1 [Q_y+q_2] is equal to the x-th [y-th] component of a reciprocal lattice vector and is zero otherwise.

[19] The corresponding expression where only volume modes of vibration are considered, that is, where the surface atoms are assumed to have the same vibrational properties as the bulk atoms, is $g_{ij} = \text{const}\cdot\varDelta(\boldsymbol{Q}+\boldsymbol{q})\,(1/q^2)\,(\delta_{ij}-\tfrac{2}{3}\,q_i\,q_j/q^2)$ where $q = |\boldsymbol{q}|$.

[17] E. G. McRae, J. Chem. Phys. **45**, 3258 [1966].

[20] D. S. Boudreaux and V. Heine, Surface Science **8**, 426 [1967].

We assume the validity of the monolayer approximation in these calculations (for simplicity). KAMBE[21] has shown for scattering from the Cu(100) face that the *elastic* intensity calculated for the two theories differ significantly only in the region of the resonances. This is because of the relatively small values of the phase shifts in the energy range chosen for his calculations. We should thus expect the deviations of the two theories only to be significant in our calculations in the regions around the resonances. The calculations correspond to the experimental situation where the incident beam ($\boldsymbol{k}$) is perpendicular to the 100-surface and the Faraday cage is rotated, enabling measurements to be made of the thermal-diffuse-scattered electrons at various scattering angles (various $-\boldsymbol{k}'$). Only rotations of the Faraday cage in the 010-plane are considered.



3 a 3 b

Fig. 3 a, b. The upper curve is the ratio of the thermal diffuse intensities as calculated by the multiple scattering theory (MST) to that calculated by the pseudokinematical theory (PKT). The lower curves show the intensities (in arbitrary units) for the MST (solid line) and for the PKT (dashed line) as a function of the distance of the tip of the scattering vector $\boldsymbol{Q}$ away from the (00)-reciprocal lattice rod (measured in units of the reciprocal lattice vector B). The peak is the position of the $-\boldsymbol{k}'$ resonance. Non-zero phases to LMAX=3 were included in the calculation. (a) $E=43.60$ eV; (b) $E=48.19$ eV. No inner potential correction is made.

In Fig. 3 we see the results of such a calculation. At least for Cu the pseudokinematic and exact theories give approximately the same value for the diffuse intensity. The local maximum in the diffuse intensity corresponds to a resonance for the $-\boldsymbol{k}'$ wave amplitude. The structure in the diffuse scattering observed by DE BERSUDER[22, 23] for scattering from the (001) face of Aluminium, and by GERMER and CHANG[24], and CHANG[25], for scattering from the (112) surface of Tungsten is probably due to such a $-\boldsymbol{k}'$ resonance. The geometry of this observed structure is as expected for such a resonance.

In Fig. 4 we see that an enhancement of the diffuse intensity occurs as the $\boldsymbol{k}$-resonance condition is approached (achieved experimentally by varying the energy of the incident electron, or its incident direction). Geometrically this condition is fulfilled

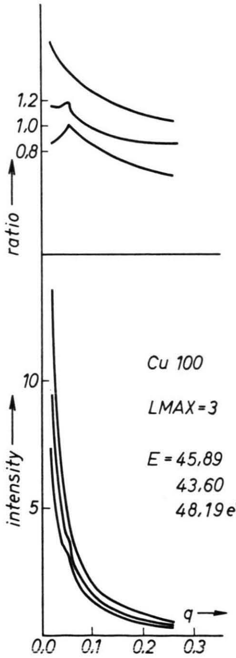


Fig. 4. Thermal diffuse intensity for a multiple scattering theory for energies at and around the position of a $\boldsymbol{k}$ resonance. The diffuse intensity is enhanced when this resonance condition is fulfilled. Non-zero phases to LMAX=3 were included in this calculation. The upper curve is for $E=45.89$ eV and the lower curve for $E=48.19$ eV (cf. Fig. 3).

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[21] K. KAMBE, Surface Science **20**, 213 [1970].

[22] L. DE BERSUDER, C. R. Acad. Sci. Paris **266** B, 1489 [1966].

[23] These $-\boldsymbol{k}'$ resonance effects are called K II by DE BERSUDER[22].

[24] L. H. GERMER and C. C. CHANG, Surface Science **4**, 498 [1966].

[25] C. C. CHANG, Ph. D. Thesis, Cornell University 1967, unpublished.

when the specular (elastic) diffraction spot coincides with the position of a resonance effect K II (see footnote [23]). Under such geometrical conditions the elastic scattering also exhibits this enhancement effect. This resonance phenomena for the **k**-vector explains the "strong interactions" observed by CHANG [25] and also explains the enhancement effect observed for the total reflected intensity, both diffuse and elastic, by MIYAKE and HAYAKAWA [26]. This effect is completely analogous to the case in reflection-high-energy-electron-diffraction where it is found that the intensity of the specular spot and the reflection pattern as a whole, including the diffuse scattering, is enhanced suddenly when the specular spot crosses a Kikuchi line which runs in a direction oblique with respect to horizontal Kikuchi lines [27].

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Appendix A

In the expression for the integral S_μ^c one needs to reduce terms of the form

$$X_{l+1,-(m+\mu)}^{-\boldsymbol{k}'c} \frac{\mathrm{d}}{\mathrm{d}r} \left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{l}{r} \right) X_{lm}^{\boldsymbol{k}c}$$

and

$$X_{l-1,-(m+\mu)}^{-\boldsymbol{k}'c} \frac{\mathrm{d}}{\mathrm{d}r} \left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{l+1}{r} \right) X_{lm}^{\boldsymbol{k}c},$$

where the X_{lm}'s are of the form

$$X_{lm} \sim (j_l(k\,r) + i \cdot \exp\{i\,\delta_l^c\} \sin \delta_l^c\, h_l^1(k\,r)) .$$

For this reduction the following properties of the spherical Bessel functions are needed:

$$\frac{\mathrm{d}}{\mathrm{d}r} f_l(k\,r) + \frac{(l+1)}{r} f_l(k\,r) = k\, f_{l-1}(k\,r) ;$$

$$\frac{\mathrm{d}}{\mathrm{d}r} f_l(k\,r) - \frac{l}{r} f_l(k\,r) = -k\, f_{l+1}(k\,r) ,$$

where f_l represents any of the Bessel functions j_l, $h_l^1, \ldots$;

Wronskian $(j_l(k\,r),\ y_l(k\,r))$

$$\equiv \frac{1}{k} \left(j_l \frac{\mathrm{d}}{\mathrm{d}r} y_l - \frac{\mathrm{d}}{\mathrm{d}r} j_l \cdot y_l \right) = \frac{1}{(k\,r)^2} ;$$

$$\text{Wronskian } (h_l^1, h_l^2) = \frac{-2\,i}{(k\,r)^2} ,$$

where y_l is a spherical Bessel function of the l-th order and the second kind; the different Bessel functions are related to each other by means of

$$h_l^1 = j_l + i\,y_l \quad \text{and} \quad h_l^2 = j_l - i\,y_l .$$

Appendix B

In finding a pseudokinematical expression for the integral S_μ^c we first rearrange the sum-expression for S_μ^c as follows:

$$\begin{aligned} S_\mu^c = \sqrt{4\,\pi/3} \sum_{lm} \{ & B_{lm}^{\boldsymbol{k}c} [\exp\{2\,i\,\delta_l^c\} - 1]/2\,i \cdot [C_{1\mu;\,l+1,\,m+\mu;\,lm}\, B_{l+1,-(m+\mu)}^{-\boldsymbol{k}'c} - C_{1\mu;\,l-1,\,m+\mu;\,lm}\, B_{l-1,-(m+\mu)}^{-\boldsymbol{k}'c}] \\ & + B_{l-1,-(m+\mu)}^{-\boldsymbol{k}'c}\, C_{1\mu;\,l+1,\,m+\mu;\,lm}\, B_{lm}^{\boldsymbol{k}c}\, [\exp\{2\,i\,\delta_{l-1}^c\} - 1]/2\,i - B_{l+1,-(m+\mu)}^{-\boldsymbol{k}'c}\, C_{1\mu;\,l+1,\,m+\mu;\,lm}\, B_{lm}^{\boldsymbol{k}c} \\ & \cdot [\exp\{2\,i\,\delta_{l+1}^c\} - 1]/2\,i \} . \end{aligned}$$

On substitution of the pseudokinematical value for the B_{lm} we obtain the result

$$\begin{aligned} S_\mu^c = i(4\,\pi)^2 \sqrt{4\,\pi/3} \exp\{i\,\mathbf{Q} \cdot \mathbf{R}_c\} [& \sum_{lm} [\exp\{2\,i\,\delta_l^c\} - 1]/2\,i \cdot (-1)^l\, Y_{lm}^*(\boldsymbol{k}) \\ & \cdot \{ C_{1\mu;\,l+1,\,m+\mu;\,lm}\, Y_{l+1,-(m+\mu)}^*(-\boldsymbol{k}') + C_{1\mu;\,l-1,\,m+\mu;\,lm}\, Y_{l-1,-(m+\mu)}^*(-\boldsymbol{k}') \} \\ & + \sum_{lm} [\exp\{2\,i\,\delta_l^c\} - 1]/2\,i \cdot (-1)^l\, Y_{lm}^*(-\boldsymbol{k}') \{ C_{1\mu;\,lm;\,l+1,\,-(m+\mu)}\, Y_{l+1,-(m+\mu)}^*(\boldsymbol{k}) \\ & + C_{1\mu;\,lm;\,l-1,\,-(m+\mu)}\, Y_{l-1,-(m+\mu)}^*(\boldsymbol{k}) \}] . \end{aligned}$$

Now it is a property of the spherical harmonics that

$$C_{1\mu;\,l+1,\,m+\mu;\,lm}\, Y_{l+1,\,m+\mu} + C_{1\mu;\,l-1,\,m+\mu;\,lm}\, Y_{l-1,\,m+\mu} = Y_{1\mu}\, Y_{lm}$$

and the coefficient $C_{LM;\,lm;\,l'm'}$ has the property (easily seen from their definition and the definition of the spherical harmonics) that

$$C_{LM;\,lm;\,l'-m'} = C_{LM;\,l'm';\,l-m} .$$

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[26] S. MIYAKE and K. HAYAKAWA, Acta Cryst., to be published; A **25** (supp. 3), 206 [1969].

[27] S. MIYAKE, K. KOHRA, and M. TAKAGI, Acta Cryst. **7**, 393 [1954]. — K. KOHRA, K. MOLIÈRE, S. NAKANO, and M. ARIYAMA, J. Phys. Soc. Japan **17** (supp. B II), 82 [1962].

Hence S^c_μ may be written as

$$S^c_\mu = (4\pi)^2\, i\sqrt{4\pi/3}\cdot\exp\{i\,\boldsymbol{Q}\cdot\boldsymbol{R}_c\}\sum_{lm}[\exp\{2\,i\,\delta^c_l\}-1)]/2\,i\cdot(-1)^l$$
$$\cdot\{Y^{*\prime}_{lm}(\boldsymbol{k})\,Y_{lm}(-\boldsymbol{k}')\,Y_{1\mu}(-\boldsymbol{k}')+Y^*_{lm}(-\boldsymbol{k}')\,Y_{lm}(\boldsymbol{k})\,Y_{1\mu}(\boldsymbol{k})\}\,.$$

Making use of the relationship for the spherical harmonics that

$$Y_{lm}(-\boldsymbol{k}') = (-1)^l\,Y_{lm}(\boldsymbol{k}')\,,$$

we may write the following expression for the S^c_μ in the pseudokinematical approximation:

$$S^c_\mu = 4\pi i\cdot\exp\{i\,\boldsymbol{Q}\cdot\boldsymbol{R}_c\}\sum_{l,m}[\exp\{2\,i\,\delta^c_l\}-1]/2\,i\,k\cdot 4\pi\,Y^*_{lm}(\boldsymbol{k})\,Y_{lm}(\boldsymbol{k}')\cdot k\cdot(Y_{1\mu}(\boldsymbol{k})+Y_{1\mu}(-\boldsymbol{k}'))\,,$$

whence follows the expression given in the text.

Der Einfluß einer streuenden Phasenplatte auf das elektronenmikroskopische Bild

H. G. Badde und L. Reimer

Physikalisches Institut der Universität Münster (Westf.), Elektronenmikroskopische Abteilung

(Z. Naturforsch. **25 a**, 760—765 [1970]; eingegangen am 16. März 1970)

Using carbon films for phase shifting in the focal plane of the objective one has to consider the decrease of the coherent part of the electron beam. Only the unscattered part contributes to the phase contrast. After passing a 90.8 nm carbon film with a phase shift of 2π the coherent amplitude decreases to 47%. But using a phase plate of different thickness for shifting all scattered electrons like a Zernike $\lambda/4$-plate, there will be a larger increase of contrast in images of platinum and carbon atoms than by optimal defocussing phase contrast. Calculations of phase shift and decrease of zero beam amplitude up to 1 MeV are reported. The use of Be-films with lower scattering cross section offers no large advantage.

Um das Prinzip der Zernikeschen $\lambda/4$-Platte auf die Elektronenmikroskopie zu übertragen, wurde die Verwendung von Kohleschichten geeigneter Dicke in der Brennebene des Objektivs vorgeschlagen[1–3]. Mit einem inneren Potential $U_\text{i} = 7{,}5$ Volt ist bei $U = 100$ kV eine $\lambda/4$-Kohleschicht 22,7 nm dick [s. u. Formel (5) für den relativistischen Brechungsindex]. Soll mit einer derartigen Schicht auch der Öffnungsfehler kompensiert werden, so sind Phasenplatten mit radialer Dickenverteilung erforderlich[3], welche stellenweise die 4-fache Dicke besitzen müssen. In der Elektronenmikroskopie ist die Annahme reiner Phasenobjekte jedoch illusorisch, da stets auch elastische und unelastische Elektronenstreuung auftritt. Dieser Einfluß wird zu oft unterschätzt. An Hand bekannter Streudaten[4, 5] und einigen weiteren Experimenten soll im folgenden der Einfluß einer Kohleschicht in der Brennebene des Objektivs dargelegt werden.

Einfluß der Streuung in große Winkel

Abb. 1 zeigt den schematischen Strahlengang. Das einfallende Elektronenbündel wird im Objekt gestreut. In der Brennebene des Objektivs werden in einem Punkt alle Elektronen vereinigt, die das Objekt in einer Richtung unter dem Streuwinkel ϑ verlassen. Betrachtet man einen Punkt in der Brennebene, so ist der Einfallswinkel in diesem Punkt eindeutig einem Objektpunkt zugeordnet. Findet in der Brennebene durch eine Kohleschicht eine Streuung um den Winkel ϑ' statt, so scheint hinter der Pha-

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[1] K. Kanaya, K. Ito u. H. Yotsumoto, J. Appl. Phys. **29**, 1046 [1958].

[2] M. Loquin, Z. Wiss. Mikr. **62**, 220 [1955].

[3] F. Thon, Vortrag Deutsche Gesellschaft für Elektronenmikroskopie, Wien 1969.

[4] L. Reimer u. K. H. Sommer, Z. Naturforsch. **23 a**, 1569 [1968].

[5] L. Reimer u. K. H. Sommer, Electron Microscopy 1968, **Vol. I**, 63, Rom 1968.