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# Multiple Elastic Scattering in Electron Diffraction by Crystals*

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In the case of electron diffraction by crystals containing heavy atoms, it is possible to improve the usual kinematical theory by formulating a pseudokinematical theory, which is expressed in terms of rigorous atomic scattering amplitudes rather than their Born-approximation values. A corresponding improvement can be made in the treatment of the problem by the dynamical theory, and consists in taking into account the coupling of a given diffracted beam with not only the incident beam (as is usually done in first approximation) but also with other diffracted beams. The pseudokinematical and dynamical theories are compared for very thin crystals and the conditions under which both give identical results are discussed. In particular, both predict a failure of Friedel's law in the case of acentric crystals.

## I. INTRODUCTION

In a previous paper,[1] elastic scattering of electrons by gas molecules has been described in terms of a pseudokinematical theory[2] (PKT), in which it is assumed that each atom in the molecule scatters under the influence of the incident beam only, contrary to the usual kinematical theory (KT), in which it is assumed that each infinitesimal volume element in the molecule scatters under the influence of the incident beam only. In other words, the Born approximation is made in the PKT to evaluate the total scattering from the contributions of the various atoms, but rigorous solutions to each single-atom scattering problem are used. The total scattering can be interpreted in terms of various paths taken by the incident electrons in the scatterer, every path involving a number of successive collisions. Whereas the KT takes into account only paths involving a single collision, the PKT also includes paths involving multiple collisions, provided that they all take place on the same atom. The paths neglected in both theories, involving multiple collisions on different atoms, are unimportant in the case of molecules or very small crystals. For larger crystals, however, they become predominant, since the number of such paths increases more rapidly than the number of atoms present. Use must then be made of the rigorous dynamical theory[3,4] (DT) where the full interaction between the various waves traveling in the crystal is taken into account.

It has usually been assumed in the past that the DT and KT results become identical for small enough crystals.[4] Since it has been recently established, however, that the scattering from molecules containing heavy atoms must be described in terms of the PKT, it is to be expected that the same will be true for very small crystals containing heavy atoms. Corresponding to the refinement of the KT into the PKT (obtained by replacing the Born-approximation values of the atomic scattering amplitudes by their rigorous values), an equivalent refinement must be made in the DT, so as to bring it into agreement with the PKT in the limiting case of very small crystals. It will be shown in the present paper that this can be done by taking into account in the study of a given diffracted beam not only the influence of the incident beam, but also interactions with other diffracted beams. The reason, however, why agreement between the DT and the PKT is not always reached will be discussed on the basis of several examples.

A short account of the three theories will first be presented. The diffraction from thin crystal plates of infinite lateral extent will be considered, as only then are calculations straightforward in the DT. Effects irrelevant to the comparisons of the various theories, namely absorption and thermal vibrations will be neglected.

## II. KINEMATICAL AND PSEUDOKINEMATICAL THEORIES

For simplicity, we consider a crystal where the three unit cell vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are orthogonal, and assume that the crystal is a parallelepiped of edges $N_1\mathbf{a}_1$, $N_2\mathbf{a}_2$, and $N_3\mathbf{a}_3$. In the KT the intensity scattered at distance $r$ by this crystal under the influence of the incident wave $\exp(i\mathbf{k}\cdot\mathbf{r})$ is

$$I=r^{-2}|F^B(\mathbf{b})|^2G_1(q_1)G_2(q_2)G_3(q_3), \tag{1}$$

where $\mathbf{b}=q_1\mathbf{b}_1+q_2\mathbf{b}_2+q_3\mathbf{b}_3$ is the reciprocal vector corresponding to the direction of observation and $G_i(q_i)=\sin^2\pi N_iq_i/\sin^2\pi q_i$; the unit reciprocal vectors $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ are defined by[5]

$$\mathbf{a}_i\cdot\mathbf{b}_k=2\pi\delta_{ik}(i,k=1,2,3).$$

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* This work was supported in part by the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the U. S. Government.

† Contribution No. 2056.

[1] J. A. Hoerni, preceding paper [Phys. Rev. **102**, 1530 (1956)].

[2] The elimination of the potential from the equations of scattering and its replacement by a function which characterizes the scattering properties of the individual scatterer is discussed by H. Ekstein, Phys. Rev. **83**, 721 (1951); **87**, 31 (1952); **89**, 490 (1953). Other recent discussions of multiple scattering in crystals, with special emphasis on neutron scattering problems, have been given by M. L. Goldberger and F. Seitz, Phys. Rev. **71**, 294 (1947); M. Lax, Revs. Modern Phys. **23**, 287 (1951); Phys. Rev. **85**, 621 (1952). See these papers for references to earlier work.

[3] H. Bethe, Ann. Physik **87**, 55 (1928).

[4] Z. G. Pinsker, *Electron Diffraction* (Butterworths Publications, London, 1953), Chap. 8.

[5] Our reciprocal vectors are $2\pi$ times as large as those commonly used in crystallography.

In (1), $F^B(\mathbf{b})$ is $\sum_{j=1}^J f_j^B \exp(-i\mathbf{b}\cdot\mathbf{r}_j)$, where the summation of the atomic scattering amplitudes $f_j^B$ is taken over the $J$ atoms contained in the unit cell. The main maxima of (1) occur when the $q_i$ take integral values $h_i$, namely, when $\mathbf{b}$ is a reciprocal lattice vector[5] $\mathbf{b}_h = h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3$. $F^B(\mathbf{b}_h)$ is then the structure factor:

$$F_h{}^B = \sum_{j=1}^{J} f_j{}^B \exp(-i\mathbf{b}_h\cdot\mathbf{r}_j). \qquad (2)$$

Equation (1) represents the intensity of a spherical wave and cannot be compared directly with the formulas of the DT, which refer to plane waves diffracted by a crystal of supposedly unlimited lateral extent ($N_1$ and $N_2 \to \infty$) and of thickness $D = N_3a_3$. In practice, the lateral extent is related to the cross section $\sigma$ of the incident beam by $N_1a_1N_2a_2 = \sigma/\cos\gamma$, where $\gamma$ is the angle between the direction of incidence and $\mathbf{a}_3$ (Fig. 1). The results of both theories can be compared if the integrated intensity or flux $J = \int I dS'$ of an observed diffracted spot is computed. In the KT, the spot corresponds to the intersection with the Ewald sphere of the extension of a reciprocal lattice point, as described by the functions $G_i$ in (1). To an area $dS'$ of a spot on a photograph, there corresponds on the Ewald sphere an area[6] $dS = b_1b_2dq_1dq_2/\cos\gamma = (k^2/r^2)dS'$. It follows that

$$J = (r^2b_1b_2/k^2\cos\gamma)\int\!\!\int_{\text{spot}} I dq_1dq_2, \qquad (3)$$

where $I$ is given by (1).

In the neighborhood of a reciprocal lattice point $\mathbf{b}_h$,

$$G(q_i) \cong N_i^2\left(\frac{\sin[\pi N_i(q_i-h_i)]}{\pi N_i(q_i-h_i)}\right)^2.$$

When this approximate expression is substituted in (3), the limits of integration can be taken as $\pm\infty$, so that $\int_{\text{spot}} G_i(q_i)dq_i$ $(i=1,2)$ reduces to $N_i$. For an incident beam of unit intensity and unit cross section the flux $J_h$ of a diffracted spot of indices $h_1h_2h_3$ is therefore

$$J_h = (2\pi/k\tau\cos\gamma)^2|F_h{}^B|^2D^2\left(\frac{\sin[\pi N_3(q_3-h_3)]}{\pi N_3(q_3-h_3)}\right)^2, \qquad (4)$$

where $\tau = a_1a_2a_3$ is the unit cell volume.

For equatorial reciprocal points ($h_3 = 0$), (4) reduces to

$$J_h = (2\pi/k\tau)^2|F_h{}^B|^2D^2\left(\frac{\sin\frac{1}{2}b_zD}{\frac{1}{2}b_zD}\right)^2, \qquad (5)$$

where $b_z = q_3b_3$ is the projection of $\mathbf{b}$ along $\mathbf{a}_3$. In the exact Bragg position, $q_3 = h_3$ and the last factor in (4) or (5) is unity. Formulas (4) and (5) are directly comparable with the intensities of the diffracted plane waves in the DT, since the intensity of a plane wave is numerically equal to the flux for an incident beam of unit cross section.

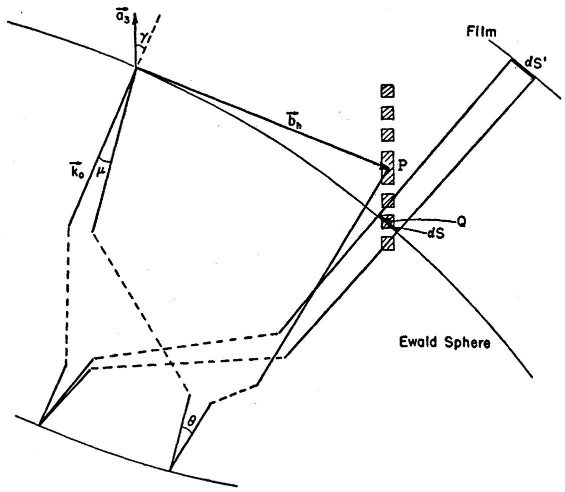

FIG. 1. Ewald construction in the kinematical theory. The intensity recorded in an area $dS'$ on the photographic film corresponds to the area $dS$ on the Ewald sphere in the region of intersection with the extension of the reciprocal lattice point $P$. The angle $\mu$ is the angular departure of the incident wave vector $\mathbf{k}_0$ from the Bragg position (for which the Ewald sphere would meet the point $P$). Note that $PQ = (q_3-h_3)b_3 \cong b_h\mu/\cos\gamma$.

In the PKT, multiple scattering within the atoms is taken into account by replacing the quantities $f_j^B$ by complex form factors[1] $f_j = |f_j|e^{i\eta_j}$. As before, the scattering from the whole crystal is obtained by adding the contributions of the various atoms. Formulas (4) and (5) are therefore unchanged except that $F_h{}^B$ has to be replaced by the structure factor

$$F_h = \sum f_j \exp(-i\mathbf{b}_h\cdot\mathbf{r}_j) = \sum|f_j|e^{i\eta_j}\exp(-i\mathbf{b}_h\cdot\mathbf{r}_j). \qquad (6)$$

The $F_h$ are in general complex even when the corresponding $F_h{}^B$ are real.

## III. DYNAMICAL THEORY

The DT is usually applied to the case of a semi-infinite crystal plate of thickness $D$ limited by two parallel faces. We shall consider here the transmission or Laue case, in which the incident beam is nearly normal to the front face and the diffracted beams emerge from the back face (Fig. 2). Solutions of the Schrödinger equation inside the crystal are Bloch functions[7]:

$$u(\mathbf{r}) = \sum u_h e^{i\mathbf{k}_h\cdot\mathbf{r}}, \quad (\mathbf{k}_h = \mathbf{k}_0 + \mathbf{b}_h). \qquad (7)$$

The $u_h$ satisfy the homogeneous equations

$$(k_h{}^2 - k^2)u_h - 2k\sum_{q\neq h}\omega_q u_{h-q} = 0, \qquad (8)$$

where $\omega_q = 2\pi F_q{}^B/k\tau$.

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[6] Since the scattering angle $\theta$ does not exceed a few degrees, $\cos(\gamma+\theta)$ can be taken as approximately equal to $\cos\gamma$.

[7] According to (7), $\mathbf{k}_0$ is undetermined to the amount of any reciprocal lattice vector. We shall define it as being closest in magnitude and direction to the vector $\mathbf{k}$ of the incident wave.

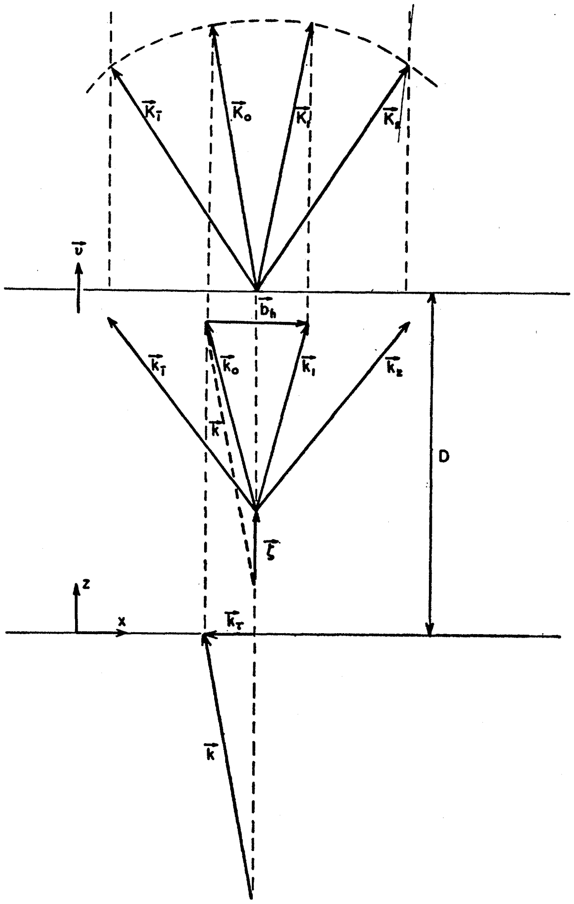

FIG. 2. Relations among wave vectors in the Laue case of the dynamical theory: $\mathbf{k}$, $\mathbf{K}_0$, and the $\mathbf{K}_h$ are the incident transmitted and diffracted wave vectors, respectively. Within the crystal only one of the solutions $u^j$, with wave vectors $\mathbf{k}_{\bar{1}}$, $\mathbf{k}_0$, $\mathbf{k}_1$, and $\mathbf{k}_2$, has been drawn. The orientation of $\mathbf{k}$ is such that the waves for $h=1$ are in the Bragg position. The boundary condition for vector tangential components is shown.

Equations (8) yield the eigenvalues of $|\mathbf{k}_0|$ (distinguished by an upper index $j$) and the corresponding amplitude ratios $\alpha_h{}^j = u_h{}^j/u_0{}^j$. The condition of continuity for the incident wave $\exp(i\mathbf{k}\cdot\mathbf{r})$ and the waves in the crystal determine the orientation of the $\mathbf{k}_0{}^j$ (in the way shown in Fig. 2) and the amplitudes $u_0{}^j$, namely

$$u_0{}^j = 1/\sum_h |\alpha_h{}^j|^2. \tag{9}$$

A superposition of diffracted plane waves, $\sum U_h \times \exp(i\mathbf{K}_h\cdot\mathbf{r})$, $(|\mathbf{K}_h| = k)$, emerges from the back face of the crystal. The intensity of a diffracted beam $h = h_1h_2h_3$ is

$$I_h = \sum_{jk} u_h{}^j u_h{}^{k*} \exp i(\zeta^k - \zeta^j)D. \tag{10}$$

Here $\zeta^j$ is the difference between the components of $\mathbf{k}$ and $\mathbf{k}_0{}^j$ in the direction of the normal $\mathbf{v}$ to the back face.

In practice, a small number of amplitudes $u_h$ are retained in (8). When only two amplitudes $u_0$ and $u_h$ for the incident and a single diffracted beam are retained, (10) reduces to the well-known expression

$$I_h = |\omega_h|^2 \frac{\sin^2[(\frac{1}{4}b_h{}^2\mu^2 + |\omega_h|^2)^{\frac{1}{2}} D/\cos\gamma]}{\frac{1}{4}b_h{}^2\mu^2 + |\omega_h|^2}, \tag{11}$$

$$I_0 = 1 - I_h.$$

Here $\mu$ is the angle (in a plane containing the vector $\mathbf{b}_h$) of departure from the Bragg position (the position for which $|\mathbf{k}_0{}^j| = |\mathbf{k}_h{}^j|$). For a given value of $\mu$, the diffracted intensity $I_h$ varies sinusoidally with the thickness $D$ whereas for a given value of $D$, it is an oscillating function of $\mu$. If a convergent beam is focused within the crystal,[8] the intensities corresponding to various values of $\mu$ can be observed simultaneously as a set of parallel fringes, the spacing of which permits an experimental determination[9,10] of $D$ and $|\omega_h|$. In the past, formula (11) has been applied to a number of problems, but, as will be made clear by the results of this paper, it cannot always be justified on theoretical grounds and might therefore lead to inconsistent results.

## IV. DYNAMICAL *vs* KINEMATICAL THEORY

The DT and KT are usually compared on the basis of formulas (11) and (4). To use a common notation, we rewrite (4) as

$$J_h = |\omega_h|^2 \frac{\sin^2(\frac{1}{2}b_h\mu D/\cos\gamma)}{\frac{1}{4}b_h{}^2\mu^2}, \tag{12}$$

since $2\pi F_h{}^B/k\tau = \omega_h$ and $q_3 - h_3 = a_3 b_h \mu / 2\pi \cos\gamma$ (see Fig. 1). In the case of thin enough crystals, (11) and (12) become identical, as the sine functions may be replaced by their arguments. Thus it appears that in the limit, the DT goes over into the KT. There is also another case, not restricted to small values of $D$, when both theories coincide, namely for a large angular departure from the Bragg position $(\frac{1}{4}b_h{}^2\mu^2 \gg |\omega_h|^2)$. In both cases $I_h$ is small relative to $I_0$ in (11), so that the basic condition of validity of the KT appears to be satisfied. As is well known, the comparison can also be made on the integrated reflections (obtained by integration of (11) over the angle $\mu$).[4] According to whether $(D/\cos\gamma)|\omega_h|$ is much larger or smaller than unity, the integral of (11) is proportional to $|\omega_h|$ or $|\omega_h|^2$ respectively, the latter value being again in agreement with the KT value.

The above considerations are unsatisfactory in two respects. First, work on electron scattering by molecules[11,12] has established that the KT has to be replaced by the PKT. Both theories yield similar results if only light atoms are present but differ significantly in the case of heavy atoms. Second, formula (11) in the DT

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[8] W. Kossel and G. Möllenstedt, Ann. Physik **36**, 113 (1939).
[9] C. H. MacGillavry, Physica **7**, 329 (1940).
[10] J. A. Hoerni, Helv. Phys. Acta **23**, 587 (1950).
[11] V. Schomaker and R. Glauber, Nature **170**, 290 (1952).
[12] J. A. Hoerni and J. A. Ibers, Phys. Rev. **91**, 1182 (1953).

is only valid when interactions among the diffracted beams are negligible, even for very thin crystals; these interactions again increase with the atomic number of the atoms present. We may therefore expect that whenever there is need to replace the KT by the PKT, at the same time it is necessary in the corresponding treatment by the DT to take into account the influence on a given diffracted beam of other diffracted beams. In the next paragraph, we shall discuss the two types of interactions which can take place among diffracted beams in the DT.

## V. INTERACTIONS BETWEEN DIFFRACTED WAVES IN THE DYNAMICAL THEORY

When the intensity of a given spot $h$ is computed from formula (10), diffracted waves $u_q \exp(i\mathbf{k}_q\cdot\mathbf{r})$ should be included in the calculations whenever $|\mathbf{k}_q|$ is close to $k$. Orientations of the crystal for which $\mathbf{k}_h$ remains in (or close to) the Bragg position are obtained by azimuthal rotations of the crystal around the direction of $\mathbf{b}_h$. The amplitudes of other waves will go through a sharp maximum whevever $|\mathbf{k}_q|=|\mathbf{k}_0|$ (or in the KT language whenever the points $\mathbf{b}_q$ traverse the Ewald sphere), except in the case of vectors that are multiples of $\mathbf{b}_h$ (namely $-\mathbf{b}_h$, $\pm\mathbf{b}_{2h}$, $\pm\mathbf{b}_{3h}$, $\cdots$, if $h_1$, $h_2$ and $h_3$ have no common integral factor). Thus some of the dynamical interactions expressed by Eq. (8) depend on a particular azimuthal orientation (accidental interactions), whereas the others do not (systematic interactions). In what follows, we shall assume that the azimuthal orientation is such that only systematic interactions have to be considered. In other words, we replace the tridimensional potential $V$ by a one-variable function $\bar{V}$ which clearly is the average value of $V$ over planes perpendicular to $\mathbf{b}_h$. This approximation has been shown to be satisfactory[13] when $h_1$, $h_2$, and $h_3$ are low indices which refer to strongly reflecting reticular planes. In this case, the average influence of the neglected waves, as given by the consideration of the average value of $I_h$ over all azimuthal orientations, is small, even though it might be important for a particular orientation. On the other hand, when the indices $h_1$, $h_2$, $h_3$ are high, this average influence may become greater than the interaction among the waves retained in the one-dimensional potential approximation.

In order to simplify the calculations, we further make the unessential assumptions that the faces of the crystal are parallel to $\mathbf{b}_h$, and that the three vectors $\mathbf{k}$, $\mathbf{b}_h$ and $\boldsymbol{\nu}$ are coplanar (Fig. 2). If $x$ and $z$ are coordinates in the directions of $\mathbf{b}_h$ and $\boldsymbol{\nu}$, respectively, we have

$$\bar{V}(x)=\textstyle\sum_{h'}V_{h'}\exp ih'\beta x,\quad (\beta=|\mathbf{b}_h|).$$

With these assumptions, the formulas given above keep the same form, although they now include waves relative to only one row of reciprocal lattice points. The Schrödinger equation is then separable, its solutions being of the type

$$u(\mathbf{r})=u(x,z)=\exp(ik_{0\nu}z)v(x),\tag{13}$$

where

$$v(x)=\textstyle\sum_h u_h \exp i(k_\tau+h\beta)x,\tag{14}$$

$\tau$ and $\nu$ referring to vector tangential and normal components, respectively. In the next paragraphs, a comparison of the DT results obtained in this way with the corresponding KT and PKT results will be made on the basis of several examples.

## VI. CASE OF A HARMONIC POTENTIAL

It is instructive to consider first the harmonic potential $\bar{V}=2V_1\cos\beta x$ since the Schrödinger equation can be solved directly in this case. Substitution of (13) in the Schrödinger equation yields Mathieu's equation

$$d^2v/dw^2+(a-\tfrac{1}{2}s\cos 2w)v=0,\tag{15}$$

with

$$w=\tfrac{1}{2}\beta x,\quad a=4(k^2-k_{0\nu}^2)/\beta^2\approx 4(k_\tau^2+2k\zeta)/\beta^2,$$
$$s=-32k|\omega_1|/\beta^2.$$

It is known that there exist sets of eigenvalues of $a$ for which the solutions of (15) are of period $\pi$, $2\pi$, $3\pi$, . . . Solutions of period $\pi$ and $2\pi$ and the corresponding eigenvalues $a^i$, have been tabulated[14] for a range of values of $s$ between $-100$ and $+100$. These solutions must then be normalized in the way suitable to our problem, namely by means of Eq. (9). Consideration of (14) shows that $v(w)$ is of period $\pi$ for $k_\tau/\beta=0$, $\pm 1$, $\pm 2$, . . . The same solution in reference 14 can be used for all these orientations of the incident wave, provided that the numbering of the waves in (14) is modified accordingly. (For instance, the case of $k_\tau=-\beta$ is deduced from the case $k_\tau=0$ by replacing every index $h$ in the former solution by $h+1$.) In every case, however, the normalization (9) is different. Similar considerations apply to solutions of period $2\pi$ and the values $k_\tau/\beta=\pm\frac{1}{2}$, $\pm\frac{3}{2}$, . . . For other values of $k_\tau/\beta$, interpolation has to be made.

Although $\bar{V}$ is never strictly harmonic in any actual crystal, it may be considered as approximately so when the coefficient $\omega$ for the second order of a strong reflection is zero. Such is the case for the reflection 111 in germanium ($\omega_{111}=0.0131$ A$^{-1}$ for 39.47-kev incident electrons ($k=103.75$ A$^{-1}$), $\omega_{222}=0$, $\beta=|\mathbf{b}_{111}|=1.936$ A$^{-1}$). The influence of couplings of higher orders involving $\omega_{333},\cdots$ is unimportant for at least the reflections 111 and 222 so that the use of Mathieu's solution is justified in computing these low-order reflections.

Table I shows the values of the $u^i$ and $\zeta^i$ for $h=000$, $\pm(111)$, $\pm(222)$, and 333 obtained from Mathieu's solutions in the case of $k_\tau=-\frac{1}{2}\beta$ (when the waves 111 are in Bragg position, see Fig. 2). The indexing in terms of

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[13] K. Artmann, Z. Physik **125**, 298 (1948).

[14] *Tables Relating to Mathieu Functions*, U. S. National Bureau of Standards (Columbia University Press, New York, 1951).

TABLE I. DT data for diffraction by germanium. Results given by the approximations (*a*) and (*b*) discussed in the text are shown in parentheses. The $\zeta^j$ are expressed in $A^{-1}$.

| $j$ | $10^4\zeta^j$ | $10^4u_{111}{}^j$ | $10^4u_{222}{}^j$ | $10^4u_{333}{}^j$ |
|---|---|---|---|---|
| 1 | $-165(-131,-164)$ | $4688(5000,4706)$ | $1202(0,1178)$ | $127(0,0)$ |
| 2 | $69(131,72)$ | $-4062(-5000,-4146)$ | $-1936(0,-1881)$ | $-250(0,0)$ |
| 3 | $371(0,394)$ | $310(0,294)$ | $-1185(0,-1178)$ | $-219(0,0)$ |
| 4 | $400(0,421)$ | $-935(0,-854)$ | $1915(0,1881)$ | $367(0,0)$ |
| 5 | $1092(0,0)$ | $2(0,0)$ | $-17(0,0)$ | $92(0,0)$ |
| 6 | $1092(0,0)$ | $-3(0,0)$ | $21(0,0)$ | $-117(0,0)$ |
| $10^4\bar{I}_h$ | | $3946(5000,4015)$ | $1026(0,985)$ | $28(0,0)$ |

$j$ is such that $a^1 < a^2 < \cdots$. Due to symmetry, the solutions $v^j(x)$ in (13) are alternately even and odd so that in our example $u_{1-h}{}^j = (-1)^j u_h{}^j$. The intensity of any diffracted beam can be computed from (10). Since it varies strongly with the crystal thickness, it has been found convenient to report in Table I a mean intensity

$$\bar{I}_h = \sum_j |u_h{}^j|^2, \qquad (16)$$

obtained by averaging (10) over all possible thicknesses. Whereas Table I refers to a given incidence angle ($k_\tau = -\frac{1}{2}\beta$), Fig. 3 shows the variation of $\bar{I}_{000}$, $\bar{I}_{111}$, and $\bar{I}_{222}$ with the incidence angle (or the tangential component $k_\tau$).

In order to test the reliability of the usual formulation of the DT (paragraph III), Eqs. (8) have been solved by successive approximations by retaining in these equations (a) two amplitudes $u_{000}$ and $u_{111}$, (b) four amplitudes $u_{\bar{1}\bar{1}\bar{1}}$ to $u_{222}$, (c) six amplitudes $u_{\bar{2}\bar{2}\bar{2}}$ to $u_{333}$. In Table I, values of the $u^j$ and $\zeta^j$, obtained from approximations (a) and (b), are listed in that order in the parentheses following the rigorous values. Results for approximation (c) have not been reported since they agree with the accurate results to within a few tenths of a percent. In approximation (a), an analytical expression for $\bar{I}_{111}$ can be deduced from (11), namely

$$\bar{I}_{111} = \tfrac{1}{2}[1 + (\tfrac{1}{4}\beta^2\mu^2/|\omega_1|^2)]^{-1},$$

where the angle of departure $\mu$ from the Bragg position for the waves 111 is $k^{-1}(\frac{1}{2}\beta - k_\tau)$. In Fig. 3, the dashed line shows the values of $\bar{I}_{111}$ obtained from approximation (a) ($\bar{I}_{222}$ vanishing in this approximation since $\omega_2$ is zero). Obviously, this approximation fails badly here, whereas approximation (b) (not shown on Fig. 3) is already in close agreement with the rigorous treatment, as may be directly inferred from Table I. The large intensity of the "forbidden" reflection 222 is entirely due to indirect coupling between the beams 000 and 222 through the beam 111.

Experimental evidence of a strong reflection 222 for germanium has been reported by Heidenreich.[15] According to Fig. 3, the integrated intensity of the 222 reflection should be about half of that of the 111 reflection. A powder photograph shown in Fig. 2(b) of reference 15 shows that the actual ratio is less. This is due to the fact that the assumption on which (16) is based is not satisfied. The powder is not made up of crystals of random thickness $D$, but the $D$ values range up to some upper limit, say 400 A. Over this limited range, the mean intensity does not reach the value indicated by (16). This can be seen from Fig. 4, where the expression (10) for the intensity of the 222 reflection is plotted against $D$ for the particular orientation $k_\tau = -\beta$ (when the waves 222 are in the Bragg position).

In his theoretical treatment of the reflection 222 from germanium, Heidenreich exclusively takes into account accidental interactions between the beam 222 and other beams 113, $33\bar{1}, \cdots$ in turn. Because the corresponding waves can be brought simultaneously into Bragg position, these interactions may exceed the systematic interactions discussed here. However, they take place only briefly during azimuthal rotations of the crystal, and, on the average, systematic interactions are predominant since they must be taken into account for any crystal orientation.[16]

The "anomalous" strong reflections 222 for $CuCl_2$ and $CaF_2$ observed by Germer[17] are associated with small coefficients $\omega_{222}$: again their increased intensity is due to a strong coupling with the reflection 111. The effect is most marked when $\omega_{222} \approx 0$, but should be generally observed for reflections of low indices. The case of germanium shows that it is important even for crystals composed of relatively light atoms. When the potential $\bar{V}$ is no longer harmonic, no rigorous solution analogous to the Mathieu solution is available and successive approximations of the type described above have to be made. The convergence is not as rapid as

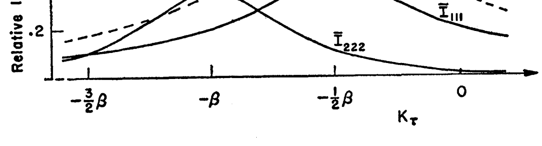

FIG. 3. Germanium: Graph of dependence of average intensities $\bar{I}_{000}$, $\bar{I}_{111}$, and $\bar{I}_{222}$ on direction of incident wave vector. The dashed line corresponds to approximation (*a*) discussed in text.

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[15] R. D. Heidenreich, Phys. Rev. **77**, 271 (1950).

[16] For this reason, the statement made in reference 15 that dynamical interactions only take place when the incident wave vector originates from corners or edges of Brillouin zones is incorrect.

[17] L. H. Germer, Phys. Rev. **56**, 58 (1939).

in the harmonic case since new coefficients $\omega_h$ are introduced at every successive stage.

Let us now compare our results for germanium with the formulas of the KT and PKT. If the beam $h$ is in the Bragg position, these formulas reduce respectively to

$$J_h=|\omega_h|^2D^2 \quad \text{or} \quad |\chi_h|^2D^2,$$

where $\chi_h=2\pi F_h/k\tau$ is obtained by replacing $F_h{}^B$ by $F_h$ in $\omega_h$. Using atomic scattering amplitudes $f$ and $f^B$ computed on the basis of the Thomas-Fermi field,[18] we have for the reflection 111, $J_{111}=(1.73\times10^{-4})D^2$ or $(1.53\times10^{-4})D^2$($D$ in A). Both expressions differ but little since the atomic number is relatively low. Figure 5 shows that the PKT result is somewhat closer to the accurate solution. On the other hand, no agreement will be reached in the case of the reflection 222, since $\omega_{222}=\chi_{222}=0$ and $I_{222}$ vanishes in the KT and PKT. Here the basic kinematical condition is not satisfied, even for small $D$ values when $I_{222}$ is much smaller than $I_{000}$, because there is another diffracted beam (111) of stronger intensity than $I_{222}$ and which acts in fact as the "primary beam" for the beam 222. In other words, this effect is due to successive collisions of the incident electron on different atoms and is therefore neglected in the PKT.[1] Similarly, the PKT will be inadequate to account for $I_{222}$ whenever $\omega_{222}$ is small relative to $\omega_{111}$ and $I_{222}$ is mainly due to indirect excitation through the beam 111. This is of course also the circumstance that causes Eq. (11) to fail in the DT.

Finally, we note that the phase factor $e^{i\eta}$ in $f$ was of no importance in the application of the PKT to germanium since the crystal was monatomic. We shall now study a case where phase factors are important, namely an acentric crystal.

### VII. FAILURE OF FRIEDEL'S LAW

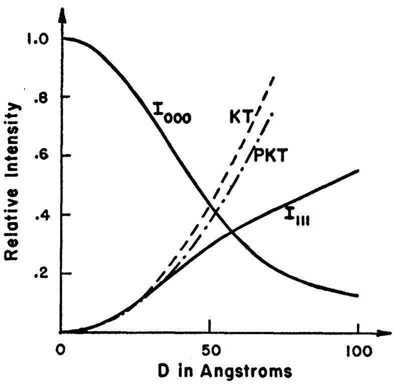

FIG. 5. Germanium: Graph of dependence of $I_{000}$ and $I_{111}$ on thickness $D$. DT results (solid lines) do not add up to unity since other diffracted beams have been included in the calculations. KT and PKT results for $I_{111}$ are shown for comparison.

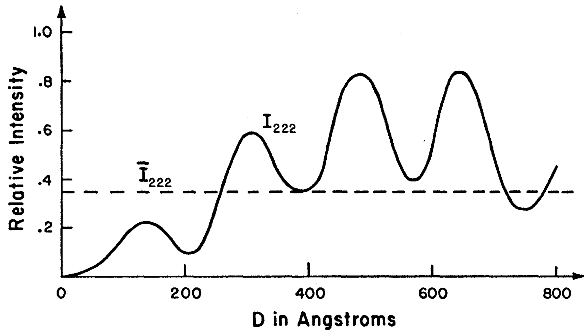

FIG. 4. Germanium: Graph of dependence of $I_{222}$ on thickness $D$. The value $\bar{I}_{222}$ results from the averaging of $I_{222}$ over a large range of $D$ values.

In an acentric crystal, it is not possible to find an origin of coordinates such that $V(\mathbf{r})=V(-\mathbf{r})$. In this case the structure factors $F_h{}^B$ in the KT are in general complex. Since $F_{-h}{}^B=F_h{}^{B*}$, however, Friedel's law—which states that the intensity of the diffracted beams $h$ and $-h$ should be equal—is verified. On the other hand, $|F_{-h}|$ may differ from $|F_h|$ in the PKT since $F_{-h}$ is deduced from $F_h$ by changing the sign of only the second phase factor in (6). (The only cases when $|F_{-h}|=|F_h|$ occur when $F_{-h}{}^B=\pm F_h{}^B$.) A failure of Friedel's law is therefore expected. We shall find it convenient to express this failure in the following alternative way: the intensity $I_h$ of the diffracted beam $h$ is not equal to the intensity $I_h'$ of the same beam obtained by replacing $V(\mathbf{r})$ by $V'(\mathbf{r})=V(-\mathbf{r})$, the shape and orientation of the crystal being unchanged.

Let us now describe the same effect in terms of the DT.[19] We again compare the intensity of a given diffracted beam $h$ for the potentials $V$ and $V'$, the direction of the incident beam and the crystal thickness being the same in both cases. If quantities relative to $V'$ are distinguished by an accent, we have $\omega_h'=\omega_h{}^*$ and, since the matrix formed by the coefficients of the $u$'s in (8) is Hermitian, $u_h'^j=u_h{}^{j*}$ and $\zeta'^j=\zeta^j$. $I_h$ and $I_h'$, as given by (10), are

$$I_h=\sum_{j,k}u_h{}^ju_h{}^{k*}\exp[i(\zeta^k-\zeta^j)D], \qquad (17)$$

$$I_h'=\sum_{j,k}u_h{}^{j*}u_h{}^k\exp[i(\zeta^k-\zeta^j)D]. \qquad (18)$$

These two expressions are different unless the $u_h{}^j$ are real (namely when the $\omega$'s are real and the crystal has a center of symmetry). The asymmetry is not brought out by solving the Schrödinger equation, but appears when boundary conditions are applied. It will be noted that the transmitted intensity $I_0'$ is always equal to $I_0$ since the $u_0{}^j$ as defined in (9) are real. Also the sum of the intensities of all diffracted beams is the same in both cases. Consequently when the intensity of a spot $h$ is computed from the two-waves formula (11), we have $I_h'=I_h$, this being physically obvious since (11) is equivalent to replacing the acentric potential by a function $V_h\exp(i\mathbf{b}_h\cdot\mathbf{r})+V_h{}^*$

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[18] J. A. Ibers and J. A. Hoerni, Acta Cryst. **7**, 405 (1954).

[19] See also a similar discussion by H. Niehrs, Z. Physik **140**, 106 (1955).

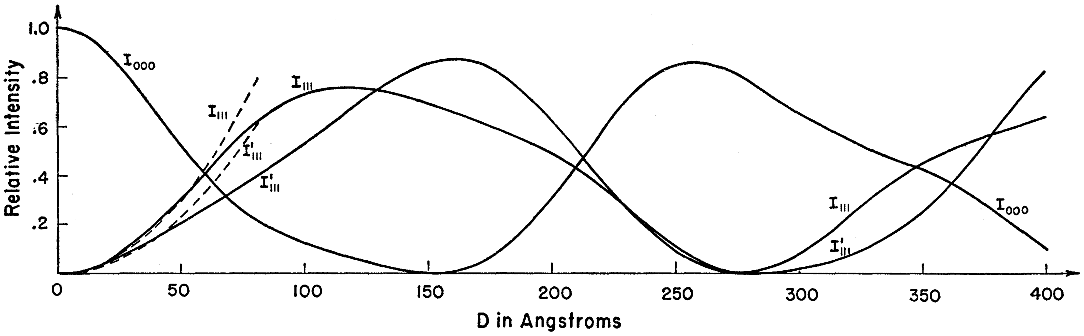

FIG. 6. Cadmium sulfide: Graph of dependence of $I_{000}$, $I_{111}$, and $I_{111}'$ on thickness $D$, the waves 111 being in Bragg position. Due to the failure of Friedel's law, the intensity $I_{111}'$ obtained by replacing the crystal potential $V(\mathbf{r})$ by $V(-\mathbf{r})$ is different from $I_{111}$. DT results are shown by solid lines, PKT results by dashed lines.

$\times\exp(-i\mathbf{b}_h\cdot\mathbf{r})$ which introduces a center of symmetry. In this connection, it is worth pointing out that Bethe's perturbation method[20] of taking into account the influence of additional weak diffracted beams in the two-wave problem does not yield the required asymmetry since the procedure leads essentially to the same final expression (11), the correction only modifying the numerical value of $|\omega_h|$ and $|\omega_h'|$ by an equal amount.

We shall now apply our equations to the numerical study of the reflection 111 from cadmium sulfide. The structure is polar and similar to that of zinc blende. Planes of cadmium and sulfur alternate parallel to the plane (111), the distance between the close pair of Cd and S planes being one quarter of the whole 111 spacing. We again assume that $\mathbf{b}_{111}$ is parallel to the crystal faces and locate the origin of coordinates in a Cd plane. Corresponding to the potentials $V$ and $V'$, we take the S plane nearest to the origin in the direction of $\mathbf{b}_{111}$, respectively $-\mathbf{b}_{111}$. Then $F_{111}=4(f_{\mathrm{Cd}}+if_{\mathrm{S}})$, whereas $F_{111}'=F_{\overline{111}}=4(f_{\mathrm{Cd}}-if_{\mathrm{S}})$. At the Bragg position the respective intensities given by the PKT are

$$J=1.22\times10^{-4}D^2,$$

$$J'=0.925\times10^{-4}D^2.$$

Here the numerical values $k=103.75$ A$^{-1}$, $b_{111}=1.870$ A$^{-1}$, $f_{\mathrm{Cd}}(111)$ (in A)$=6.91+2.30\,i$ and $f_{\mathrm{S}}(111)=4.19+0.69\,i$ have been used.[21]

In the corresponding dynamical treatment for the case where the waves 111 are in Bragg position, we make the approximation (b) already used for germanium by retaining in (8) the four amplitudes $u_{\overline{111}}$ to $u_{222}$. Because of symmetry, the equations can be transformed into four linear equations with real coefficients by considering suitable linear combinations of the unknowns. The final intensities $I_{111}$, $I_{111}'$, and $I_{000}$ $(=I_{000}')$, Eqs. (17) and (18), are plotted in Fig. 6 as functions of D. It will be seen that satisfactory agreement between the PKT and DT results is obtained for thicknesses up to 50 A, i.e., up to the point where the condition that the diffracted beam be small relative to the incident beam is no longer verified. For larger values of $D$, $I_{111}$ and $I_{111}'$ oscillate, their difference is alternatively positive and negative, showing that in that range the breakdown of Friedel's law cannot even qualitatively be interpreted in terms of the PKT. The intensities of the weaker beams 222 and $\overline{111}$ included in the calculations but not plotted in Fig. 6, show a similar failure of Friedel's law.

Other calculations for CdS have been made in the case where the waves 222 are in the Bragg position. For the reflection 222, the PKT does not predict any failure of Friedel's law since $F_{222}=F_{222}'=4(f_{\mathrm{Cd}}-f_{\mathrm{S}})$. From corresponding calculations in the DT (where five amplitudes $u_{\overline{111}}$ to $u_{333}$ have been taken into account), it turns out that such a failure actually occurs. In Fig. 7, the intensities $I_{222}$ and $I_{222}'$ are compared with the common PKT intensity. In spite of the fact that the waves 111 are not in the Bragg position, the (dynamical) intensities $I_{111}$ and $I_{111}'$—also shown on Fig. 7—are larger than $I_{222}$ and $I_{222}'$ in the range of thickness where the PKT should be valid. As has been shown previously, no agreement can therefore be expected in such a case between both theories since additional coupling between the beams 111 and 222 takes place, leading here to reinforcement of $I_{222}'$ and weakening of $I_{222}$.

In the case of a reflection of high order, systematic interactions with other diffracted beams become less

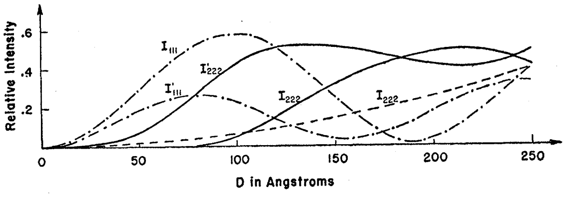

FIG. 7. Cadmium sulfide: Solid lines show the DT dependence of $I_{222}$ and $I_{222}'$ on thickness $D$, the waves 222 being in Bragg position. Here, no failure of Friedel's law is predicted by the PKT (dashed line), the lack of agreement between both theories being due to the simultaneously strong intensities $I_{111}$ or $I_{111}'$ (chain-dotted lines).

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[20] Reference 3, p. 77.

[21] The $f$ values given in reference 18 have been slightly adjusted so as to correspond to the DT calculations mentioned below, in which relativistic corrections were not taken into account and the $\omega_h$ were computed from different fits of the atomic potentials.

important than the accidental interactions which occur for any azimuthal orientation of the crystal (see paragraph V). Let us for instance consider the reflection 331 from CdS. According to the PKT, $I_{331}$ should be nearly twice as large as $I_{\overline{331}}$. In the dynamical treatment if the potential is averaged in the same way as before, namely over planes parallel to the planes 331, it is found that the systematic interactions of the beam 331 with the beams $\overline{331}$ and 662 are negligible so that $I_{331}$ is correctly given by the two-wave formula (11) and is therefore equal to $I_{331}'$. In this case any failure of Friedel's law is due to accidental interactions only, and will therefore vary with the azimuthal orientation of the crystal.

Experimental evidence of a failure of Friedel's law has been reported by Miyake and Uyeda.[22] The effect was observed on ZnS in the Bragg (reflection) case with the incident beam impinging on the cleavage face (110) in (or close to) the azimuthal plane $(\bar{1}10)$ so as to excite simultaneously the reflections $hhl$ and $hh\bar{l}$. In particular a large asymmetry between the beams 331 and $33\bar{1}$ has been observed. A satisfactory account of this effect has been given by Kohra,[23] who considered the accidental interactions occurring between the beams 000, 331 and $33\bar{1}$. Calculations were only performed in the case where the plane of incidence is strictly parallel to the plane $(\bar{1}10)$. Since the asymmetry seems to occur over at least a small range of azimuthal orientations, it would be desirable to extend the calculations to the cases where the waves 331 and $33\bar{1}$ do not reach the Bragg position simultaneously, in order to evaluate the possible importance of interactions with other diffracted beams. The same asymmetry can also be qualitatively explained by the PKT. A quantitative comparison of both theories can only be taken up in the Bragg case if absorption effects are included. For this reason, it would be preferable to investigate the failure of Friedel's law in the Laue (transmission) case.

## VIII. RELATION BETWEEN THE DYNAMICAL THEORY AND THE ENERGY BAND PROBLEM

The diffraction problem discussed in terms of the dynamical theory is only one aspect of the more general problem of electronic energy bands and wave functions in crystals. From Bloch's theorem any electron wave function is the product of an exponential factor $\exp(i\mathbf{k}\cdot\mathbf{r})$ and of a function having the lattice periodicity. Since there is an infinite set of discrete allowed energies $E$ corresponding to a given wave vector $\mathbf{k}$ the whole relationship can be described by an infinite set of surfaces in a four-dimensional space $E$, $\mathbf{k}$. If one assumes that an electron is but little perturbed by the periodic field, these surfaces can be calculated by a perturbation method (nearly free electron approximation). In the energy band problem, this method is applied to calculate the intersection of the energy surfaces by planes containing the $E$ axis and a given direction in $\mathbf{k}$ subspace, while in the diffraction problem it is applied to calculate intersections by planes of constant energy. In the latter case the Schrödinger equation yields eigenvalues for the normal component $k_{0\nu}$ of the wave vector $\mathbf{k}_0$, corresponding to the tangential component $k_{0\tau}$ fixed by the boundary conditions. Convergence of the method is very poor for atomic or valence electrons in a crystal, but our examples have shown that it can be slow even at the high energies met in the diffraction problem. This is the case when the incident electron travels nearly parallel to strong reflecting planes. In particle language, the electron zigzags between the walls of one of the potential valleys created by the reflecting planes, since its momentum component normal to the planes is too small to lift it over the walls. The behavior of the wave function in the direction normal to the walls is similar to that of a bound atomic electron and has to be expressed by the superposition of a necessarily large number of plane waves. It has been shown by Artmann[24] that this notion of laterally bound electrons leads to a simple qualitative interpretation of the intensity distribution in Kikuchi bands. In most cases, however, the electrons are not perfectly free nor perfectly laterally bound, and the numerical analysis is therefore involved. For the corresponding intermediary cases arising in the energy band problem, there exists several modified methods[25] (for instance the orthogonalized plane wave method[26]), which might equally prove useful in the diffraction problem.

The energy band problem corresponding to the diffraction problem for the harmonic one-dimensional potential, taken up in paragraph VI, has been discussed by Slater.[27] Since the Schrödinger equation reduces in this case to Mathieu's equation (15) (where the parameter $s$ has the same meaning as in the diffraction problem), it follows that Slater's discussion of the resulting wave functions can be directly applied to our function $v(x)$ in (13) or (14).

## IX. CONCLUSION

The present paper discusses the way in which the available kinematical and dynamical theories of electron diffraction have to be modified or amplified in the case of diffraction by crystals containing heavy atoms. Corresponding to the substitution in the KT of rigorous atomic scattering amplitudes for their Born-approximation values, mutual interactions of a number of diffracted waves are taken into account in the DT treatment. The PKT and the DT are compared in the

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[22] S. Miyake and R. Uyeda, Acta Cryst. **3**, 314 (1950).

[23] K. Kohra, J. Phys. Soc. Japan, **9**, 690 (1954).

[24] K. Artmann, Z. Physik, **125**, 225 (1948); **126**, 533 (1949).

[25] See for instance J. C. Slater, Technical Report No. 4, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, July 15, 1953 (unpublished).

[26] C. Herring, Phys. Rev. **57**, 1169 (1940).

[27] J. C. Slater, Phys. Rev. **87**, 807 (1952).

case of very thin crystals, where both should give identical results. Our examples have shown that such is indeed the case for reflections of the first order and of low indices, but that in general there is no agreement for other types of reflections. The discrepancy in the second case can be explained as follows: The diffracted beam under consideration is more strongly coupled with one or more other diffracted beams than it is with the incident beam; in other words, the contribution of electron paths with successive collisions on different atoms is predominant and is the cause of the discrepancy between both theories, since these paths are neglected in the PKT.

In the study of a given diffracted beam the number of other beams of equal or higher intensity is roughly the same as the order of the system of Eqs. (8); therefore DT calculations for weak beams of high indices would be very lengthy and, at the same time, strongly dependent on azimuthal orientation. No agreement with the PKT should then be expected in the limit of thin crystals. Furthermore, it will be clear from the previous discussion that the commonly accepted notion that integrated intensities are proportional to $|F_h^B|$ in the DT, in contrast to the values $|F_h^B|^2$ in the KT, is only correct insofar as the two-waves formula (11) is valid.

In weighting the relative merits of the PKT and the DT, it should be remembered that our comparison has been based on the scattering by a given potential field, and has therefore overlooked a main feature of the PKT, namely that, unlike the DT, it can take up in a straightforward way *all* single-atom scattering effects, including even those which cannot be strictly described by a potential (polarization, electron exchange for instance). There is yet no experimental evidence, however, that these effects are actually important.

Finally, it should be emphasized that the possibility of crystal structure determinations from Fourier inversion of diffraction data (a procedure which is based upon the validity of the KT, but can still be carried out if the PKT is valid[11]), is in fact brighter than it would appear from our discussion. Our calculations apply to perfect crystals of simple shape for which dynamical effects are most conspicuous. Since mosaic structure destroys the coherence between the waves scattered by the various mosaic blocks, the effective scatterer size may well correspond to the range of validity of the KT. This effect, combined with the small weight of the atoms present, is the probable reason of recent successful crystal structure determinations by electron diffraction.

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# Spin and Polarization Effects in the Annihilation of Triplet Positronium*

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The annihilation rate of triplet positronium has been calculated without summing at once over spin and polarization. The results, quoted without proof, apply to some recent measurements of spin and polarization effects.

## INTRODUCTION

THE calculation by Ore and Powell[1] and others[2,3] of the angular correlations and spectrum of the annihilation quanta from triplet positronium has been repeated without averaging over spin or summing over polarization. The results then apply to recent measurements of the relative polarization of a single annihilation quantum[4] and the effect of the $m=0$ spin state on the angular distribution of the annihilation quanta.[5,6]

The calculation follows readily from expressions given by Ore and Powell; the results will be quoted without proof.

## MATRIX ELEMENT

The transition probability for a positronium atom in the lowest triplet $S$-state to annihilate with the production of three quanta of energies $k_1$, $k_2$, $k_3$ and

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[*] Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Carnegie Institute of Technology.

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[1] A. Ore and J. Powell, Phys. Rev. **75**, 1696, 1963 (1948).

[2] J. Radcliffe, Phil. Mag. **42**, 1334 (1951).

[3] R. Ferrell, doctoral thesis, Princeton University, 1951 (unpublished).

[4] Leipuner, Siegel, and DeBenedetti, Phys. Rev. **91**, 198 (1953).

[5] J. Wheatley and D. Halliday, Phys. Rev. **88**, 424 (1952).

[6] Marder, Hughes, and Wu, Phys. Rev. **95**, 611 (1954), also **98**, 1840 (1955).