the simplified model is indeed only an approximation. If it were exact, larger pyrolusite concentrations $p$ than that of pattern $D(p = 0{\cdot}25)$ would yield patterns converging to that of an $ab'c$-lattice (for which $p = 0{\cdot}50$), with the shifted lines gradually sharpening to normal powder lines. Now the continuous series of $\gamma$-$MnO_2$ patterns, which is generally supposed to exist, does nothing of the sort. Instead it shows an increasing deterioration, down to stages such as Fig. 1 *C*. According to Delano (1950), a further continuous series exists between that stage and pyrolusite.

By heat treatment of $\gamma$-$MnO_2$, Brenet *et al.* (1957) have indeed obtained a continuous transition from a pattern not unlike our Fig. 1 *D*, to something close to the pyrolusite pattern. Comparison of the latter stages in this series with pure pyrolusite again shows anomalous shift and broadening of certain lines. Rather than attaching specific significance to one of those (as Brenet *et al.* (1957) do to (110), $d = 3{\cdot}11$ Å), we find that these phenomena are in qualitative agreement with another simplification of our model, valid for $p$ near unity (viz., pyrolusite with $b'$ stacking faults, corresponding to isolated ramsdellite layers).*

Recently, an explanation in terms of atomic parameters has been given by Kedesdy *et al.* (1957) for the relation between $\gamma$-$MnO_2$ and ramsdellite. However, this hypothesis cannot possibly account for the anomalous diffraction phenomena shown by $\gamma$-$MnO_2$. Probably a similar argument holds for their interpretation of what they call $\varrho$-$MnO_2$, since neither the definition of that phase nor the reasons for distinguishing it from $\gamma$-$MnO_2$ have been made clear.

Finally, the author wishes to express his gratitude to Prof. Brenet (Institut de Chimie, Université de Strasbourg, France) for providing helpful samples and documentation; to Mrs van Damme-van Weele (Central Lab. T.N.O., Delft) for stimulating discussions; and to the Governing Board of the T.P.D. for their permission to publish.

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* In this connection a curious detail of many pyrolusite patterns may be mentioned. Fig. 1 *A*, a pattern of a synthetic sample obtained by treating $\gamma$-$MnO_2$ at 160° with concentrated $HNO_3$, is shown here to represent a pure, well-crystallized $\beta$-$MnO_2$. Fig. 1 *B* is a pattern of a mineral sample with preferred orientation, the ($hk0$) reflections being enhanced on $B'$ and suppressed on $B''$. Since $B'$ was obtained by vertical, and $B''$ by horizontal flow of the specimen paste, this sample obviously has the fibrous habitus$||c$ mentioned by Vaux & Bennet (1937).

The broadening shown by several lines in Fig. 1 *B* (notably (200), (210), (310) and (400)) cannot, however, be explained as particle-size broadening. The latter would make (400) hardly broader than (200), whereas it is actually twice as broad. It turns out that the line width is equal to the distance between doublet components which would be obtained from an orthorhombic lattice slightly departing from the alleged tetragonal lattice of pyrolusite. Indeed the broadened lines have the profile of a hardly resolved doublet.

Such patterns do not fit in the series found by Brenet *et al.* (1957), nor can they be interpreted in terms of the above model for $\gamma$-$MnO_2$. On the other hand, they appear to shed new light on the much-debated existence of an orthorhombic, pseudotetragonal form of pyrolusite (Vaux & Bennett (1937); Strunz (1943)).

## Short Communications

*Contributions intended for publication under this heading should be expressly so marked; they should not exceed about* 500 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.*

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### Group velocity and energy (or particle) flow density of waves in a periodic medium.

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For the propagation of electromagnetic waves (X-rays or light) in crystals, the direction of the averaged Poynting vector is normal to the surface of dispersion in the point representing the wave field. This has been pointed out by N. Kato (1958) recently, and the same relation holds for the current density vector of electron waves.

P. P. Ewald (1958) in a subsequent paper uses the group velocity vector, which is normal to the dispersion surface too, for studying the propagation of energy through crystals. Both authors considered monochromatic wave packets only (explicitly by Ewald, tacitly assumed by Kato). The results quoted, however, are more definite and more familiar, if one considers polychromatic wave packets right from the beginning.

For an electron moving in a periodic potential, R. Peierls (1929) has shown the validity of the de Broglie relation between phase and group velocity. If one uses non-normalized Bloch functions $\psi(\mathbf{x}, \mathbf{k})$ for the electron and takes into account the Hermitian property of the momentum operator, the result of Peierls reads

$$(1/m)\mathbf{p}\overline{\psi^*\psi} = \overline{\mathbf{s}} = (1/h)\overline{\psi^*\psi}\,\mathrm{grad}_{\mathbf{k}}E(\mathbf{k})\,, \tag{1}$$

$\mathbf{p}$ expectation value of momentum, $\overline{\mathbf{s}}$ probability current density, $m$ electron mass, $h$ Planck's constant; the bar denotes averaging over one unit cell. $E(\mathbf{k})$, the energy of the electron, is a manyvalued (one value in each energy band) periodic function of the electron wave vector $\mathbf{k}$

$$E(\mathbf{k}+\mathbf{b}_m) = E(\mathbf{k})\,, \tag{2}$$

$\mathrm{grad}_{\mathbf{k}}$ denotes differentiation with respect to $\mathbf{k}$. For electron diffraction problems, all electrons being independent and having the same energy $E_0$, the equation

$$E(\mathbf{k}) = E_0 = \text{const.} \tag{3}$$

describes the surface of dispersion, a two-dimensional surface in three-dimensional $\mathbf{k}$-space given in implicit form. This statement is immediately evident, because we calculate $E(\mathbf{k})$ (for problems of electron states in crystals) from the same determinantal equation, from which we calculate the surface of dispersion (by solving it for one component of $\mathbf{k}$ for example). As a consequence of equation (2), the dispersion surface is periodic in $\mathbf{k}$-space too, it has a finite number of real branches. Now, $E(\mathbf{k})/h$ gives the frequency of the electron waves, the vector $\mathrm{grad}_{\mathbf{k}}\, E(\mathbf{k})/h$, being normal to the dispersion surface, is the group velocity vector. Equation (1), due to Peierls (1929), not only contains the result quoted by N. Kato for electron waves, but it gives the link between the papers of N. Kato and P. P. Ewald.*

[Actually, there is a slight difference in the definition (2) of the surface of dispersion and Ewald's original definition: The $\mathbf{k}$-vectors describing the dispersion surface in our definition have to be drawn from the origin of $\mathbf{k}$-space to the dispersion surface; this treatment is due to E. Fues (1939), the surface was called by him 'Ausbreitungsfläche', i.e., the dispersion surface defined by (2) differs from Ewald's by an inversion at the origin of $\mathbf{k}$-space.]

A relation completely analogous to equation (1) holds for electromagnetic waves, if no absorption and no total reflection take place; i.e. the wave vector $\mathbf{k}$ and the dielectric tensor $\boldsymbol{\varepsilon}$ being assumed to be real, $\boldsymbol{\varepsilon}(\mathbf{x}, \nu)$ is a periodic function of space with the periodicity of the crystal lattice, which may depend on the frequency as well. Particularly, there is no assumption involved concerning the magnitude of the polarizability $\boldsymbol{\varepsilon}-\mathbf{1}$ as in the dynamical theory of X-rays. A straightforward calculation, applying Peierls' method to Maxwell's equations, gives the Poynting vector corresponding to one single branch of the dispersion surface*

$$\overline{\overline{\mathbf{S}}} = \overline{\overline{W}}\,\mathrm{grad}_{\mathbf{k}}\,\nu(\mathbf{k})\,. \tag{4}$$

The double bar denotes the average over time and one unit cell of the crystal, the dispersion surface is given by the frequency function

$$\nu(\mathbf{k}) = \nu_0 = \text{const.}\,, \tag{5}$$

$\nu_0$ is the frequency of the incident wave. The definitions of $\overline{\overline{\mathbf{S}}}$ and $\overline{\overline{W}}$ are

$$\left.\begin{aligned} \overline{\overline{\mathbf{S}}} &= (c/16\pi)\,[\overline{\mathbf{E}^*\times\mathbf{H}}+\overline{\mathbf{E}\times\mathbf{H}^*}] \\ \overline{\overline{W}} &= (1/16\pi)\left[\overline{\mathbf{E}^*\cdot\frac{\partial}{\partial\nu}(\nu\boldsymbol{\varepsilon})\cdot\mathbf{E}}+\overline{\mathbf{H}^*\cdot\mathbf{H}}\right] \\ &= (1/16\pi)\left[\overline{\mathbf{E}^*\cdot\left(2\boldsymbol{\varepsilon}+\nu\frac{\partial\boldsymbol{\varepsilon}}{\partial\nu}\right)\cdot\mathbf{E}}\right] \end{aligned}\right\} \tag{6}$$

$\mathbf{E}(\mathbf{x}, \mathbf{k})$ and $\mathbf{H}(\mathbf{x}, \mathbf{k})$ are time-independent, complex solutions of the Maxwell equations (Bloch functions), the single bar again denotes the average over one unit cell. $\overline{\overline{W}}$ is the averaged energy density of the electromagnetic field, strictly speaking of an infinitely small wave packet with mean wave vector $\mathbf{k}$. $\overline{\overline{W}}$ differs from the 'naive' expression by the term $(1/16\pi)\mathbf{E}^*.\nu(\partial\boldsymbol{\varepsilon}/\partial\nu).\mathbf{E}$ as a consequence of the assumed frequency dependence of the dielectric tensor. For a special type dependence $\boldsymbol{\varepsilon}(\nu)$ the existence of this term has already been pointed out by H. Peltzer (1951).

The interpretation of equation (4) is exactly the same as in the electron wave case. Equation (4) modifies the proportionality between $\overline{\overline{\mathbf{S}}}$ and $\overline{\overline{W}}$, well-known from elementary optics, for the case of dispersion and for non-parallel vectors of phase and group velocity.

The author sincerely thanks Prof. M. von Laue and Dr H. Niehrs for many stimulating discussions.

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* With N. Kato's (1958) method, H. Niehrs (*Phys. Verhandl.* 7, 212, 1956) has given a general proof (for an arbitrary number of reflected beams) that the current density vector of electron waves is normal to the dispersion surface.

* Details will be published by the author in *Z. Phys.* The calculations were done two years ago for an appendix to the forthcoming 3rd edition of Prof. v. Laue's book 'Röntgenstrahlinterferenzen', which has been delayed in print. A lecture on this topic was given in March, 1958, by the author in Hamburg (unpublished).