is known, functions of scattering by other simple geometrical bodies which are widely used for modelling different structures (oblate and prolate ellipsoids of revolution, discs and other short cylinders) have not been given a proper representation and, therefore, the development of an analogous technique for them is apparently impossible.

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Bloch Wave Notation in Many-Beam Electron Diffraction Theory

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There are a number of different Bloch wave labelling systems currently in use in the theory of the diffraction of electrons by crystals. It is suggested that the Bloch wave labelling scheme for electron diffraction which is the simplest and the most logical is an ordered labelling scheme in which the top branch of the dispersion surface corresponds to wave 1, the second branch to wave 2, the third branch to wave 3, and so on. Such a scheme would be consistent with accepted notations in other forms of Bloch wave propagation. The essential mathematical unity of all forms of wave propagation in crystals is discussed, and the use of the proposed notation in describing the critical voltage effect is briefly considered.

1. Introduction

In recent years it has become increasingly clear that the use of a many-beam theory of electron diffraction is essential for the quantitative interpretation of electron micrographs of crystals taken using conventional 100 kV microscopes, and for both qualitative and quantitative interpretation of micrographs taken using higher voltage instruments. However, no satisfactory labelling scheme has been established for identifying the various Bloch waves which represent the fast electron within the crystal. A variety of such schemes exist in the literature, and the purpose of this paper is to examine the situation and to propose a simple but unambiguous method of referring to the individual Bloch waves which it is suggested might be generally adopted. It is also unfortunately the case that the theory of electron diffraction has developed largely independently from that of, for example, lattice vibrations and band theory. In this paper the essential unity of all forms of Bloch wave propagation in crystals will be emphasized, and the proposed notation will be chosen to be consistent with standard notations in related fields.

2. Definition of the problem

Consider an electron incident upon a perfect crystal. The wave function of the electron within the crystal

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may, by Bloch's theorem, be represented by a Bloch wave of the form

$$b(\mathbf{k},\mathbf{r})=\sum_{g} C_g(\mathbf{k})\exp\{2\pi i(\mathbf{k}+\mathbf{g})\cdot\mathbf{r}\} \qquad (1)$$

where the Bloch wave has been expanded in terms of the reciprocal-lattice vectors g of the crystal. In general, if n terms of the expansion are considered, the total electron wave function, $\Phi(\mathbf{r})$, will be a linear superposition of n such Bloch waves:

$$\Phi(\mathbf{r})=\sum_{j=1}^{n} A^{(j)}\sum_{g} C_g^{(j)}\exp\{2\pi i(\mathbf{k}^{(j)}+\mathbf{g})\cdot\mathbf{r}\} \qquad (2)$$

where the excitation amplitude, $A^{(j)}$, of the jth Bloch wave is determined by the boundary conditions at the crystal surface. The values of the Bloch wave coefficients $C_g^{(j)}$ and wave vectors $\mathbf{k}^{(j)}$ are determined in the usual manner (Bethe, 1928) by substitution of equation (2) into the Schrödinger equation:

$$\nabla^2\Psi(\mathbf{r})+\frac{8\pi^2 m}{h^2}[E+eV(\mathbf{r})]\Psi(\mathbf{r})=0 \qquad (3)$$

where E is the total electron energy and $V(\mathbf{r})$ is the periodic lattice potential.

Owing to the continuity of Ψ and grad Ψ at the crystal surface, the wave vectors $\mathbf{k}^{(j)}$ can differ only in their component normal to the crystal surface; this component will be denoted by $k_{\perp}^{(j)}$. A plot in reciprocal space of the values of $k_{\perp}^{(j)}$ as a function of the incident electron orientation for a fixed incident electron energy is known as a dispersion surface; the plot for a particular value of j is known as the jth branch (or sheet) of the dispersion surface.

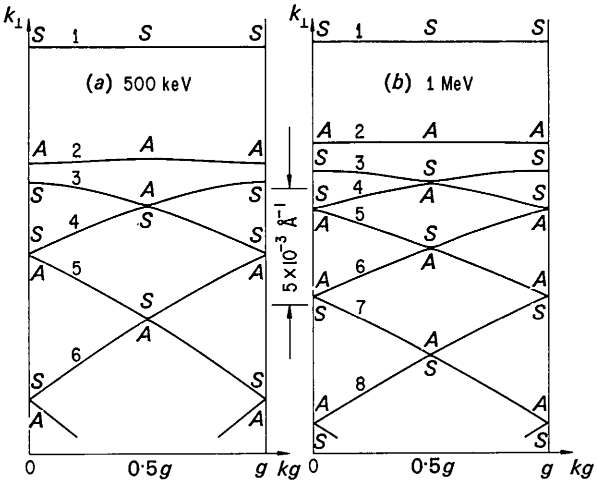

Fig. 1. Dispersion surfaces for gold at 300°K for incident electron energies of (*a*) 500 keV and (*b*) 1 MeV. The many-beam calculations took into account 20 systematic 111 reflections. The position $k_g=0{\cdot}5g$ corresponds to the 111 Bragg reflecting position; $k_g=g$ corresponds to the 222 Bragg position. S and A refer to symmetry points in the zone at which the Bloch waves are symmetric and antisymmetric respectively. The branches are numbered according to the scheme suggested in this paper.

In developing the theory of dynamical electron diffraction, Bethe (1928) introduced the approximation of considering only the two most important Bloch waves. This 'two-beam' approximation has been widely used in the interpretation of electron micrographs, and in this approximation it is conventional to label the Bloch wave with the larger value of $k_{\perp}^{(j)}$ as wave 2 (*i.e.* j is assigned the index 2) and the Bloch wave having the smaller wave vector is labelled wave 1. However, as mentioned in § 1, the two-beam approximation is often a very poor approximation, and for the quantitative and frequently also the qualitative interpretation of electron micrographs it is necessary to take into account a number of diffracted beams using a many-beam theory.

Various labelling systems have been suggested for identifying the Bloch waves in a many-beam theory, as the following examples show. Fujimoto (1959) suggested labelling as g and g' those dispersion surface branches having as asymptotes the spheres centred on reciprocal-lattice points g and h–g respectively. Howie & Whelan (1960) labelled the branch with the largest $k_{\perp}^{(j)}$ value as branch 2, that with the second largest as branch 1, the third largest as branch 3, the fourth largest as branch 4. Howie (1966) implicitly defined the Bloch waves in terms of their symmetry rather than their wave vectors: the scheme given in that paper implied that in terms of dispersion surfaces for 100 keV electrons, in order of decreasing $k_{\perp}$ values the branch numbers are 2, 1, 4 and 3. Finally, it has been suggested (Humphreys, 1967) that the dispersion surface branches be numbered from the upper to the lower, *i.e.* 1, 2, 3, 4, etc. in order of decreasing $k_{\perp}$. An example of this system is shown in Fig. 1.

The various different Bloch wave labelling schemes currently in use in electron diffraction can only lead to confusion and a standard notation is highly desirable. Before discussing the relative merits of possible schemes for labelling Bloch waves in the specific field of electron diffraction, the general theory of Bloch wave propagation will be briefly examined.

3. Wave propagation in crystalline materials

By Bloch's theorem, any wave propagating in a periodic medium may be represented by a Bloch wave. Hence equations (1) and (2) apply to any type of wave motion in crystals. The particular wave equation which these Bloch wave solutions must satisfy depends on the particular form of the wave. For example the wave equation for 'quantum particles' is the Schrödinger equation [equation (3)], for electromagnetic radiation is Maxwell's equations and for 'classical particles' is the usual classical wave equation. The mathematical solution to all these problems is basically the same, and hence there is an essential unity in the theory of the thermal vibrations of crystals, the energy bands of conduction electrons, the diffraction of electromagnetic radiation, the diffraction and channelling of fast particles, *etc.*

Equations (1),(2) and (3) apply to both the energy bands of crystals and to the diffraction of fast electrons, for example. In the former case $E<0$, and the possible solutions of the Schrödinger equation are conventionally expressed in the familar *E versus k* curves of band theory. In electron diffraction theory, on the other hand, E is positive and the possible solutions are represented by the dispersion surface, as described in § 2. Thermal waves in crystals may be represented by the usual classical wave equation

$$\nabla^2\varphi - \frac{1}{v^2}\frac{\partial^2\varphi}{\partial t^2} = 0\,. \tag{4}$$

Assuming the separable solution

$$\varphi(\mathbf{r},t) = \Psi(\mathbf{r}) \exp\,(iwt)$$

yields the following time-independent wave equation, which is equivalent to the Schrödinger equation (3):

$$\nabla^2\Psi(\mathbf{r}) + \frac{w^2}{v^2}\Psi(\mathbf{r}) = 0 \tag{5}$$

where v is the (periodic) phase velocity of the wave and $\Phi(\mathbf{r})$ has the form of equation (2), except that it is conventional to call the phonon wave vector $\mathbf{q}$ instead of $\mathbf{k}$. Solution of equation (5) gives the usual *w versus q* dispersion curves for lattice vibrations.

These examples illustrate the fact that any wave propagating in a periodic medium may be described by a linear combination of Bloch waves and that allowed solutions of the wave equation are conventionally represented by dispersion surfaces. The essential unity of all wave propagation in periodic structures suggests that the choice of a Bloch wave labelling scheme for one particular form of wave propagation, in particular for electron diffraction theory, must be compatible with accepted notations for other forms of Bloch wave propagation.

Excluding electron diffraction theory, two related labelling schemes have been generally adopted in the theory of Bloch wave propagation. If Bloch wave solutions to the wave equation are determined at symmetry points in the Brillouin zone, then the Bloch waves are usually labelled according to the group representation scheme proposed by Bouckaert, Smoluchowski & Wigner (1936). Such a scheme is widely used in band theory in which the vast majority of calculations refer to symmetry points in the zone. However, when calculations are made which do not refer to symmetry points, the Bloch wave solutions have no particular symmetry and the above labelling scheme cannot be used. In this case it is standard practice to label the Bloch waves in terms of their eigenvalues, that is with reference to *E versus k* curves in band theory, *w versus q* curves in phonon theory, *etc.*, and to simply label the bands 1,2,3,4, *etc.*, in order. Such a scheme has been used in band theory for many years for referring to Bloch waves which have no particular symmetry. Similarly this scheme is widely used in the theory of lattice vibrations (see, *e.g.*, Van Hove, 1953), and Phillips (1956) has proposed that it be called the ordered labelling scheme.

4. The critical voltage effect

The existence of this effect in electron diffraction has considerable relevance to a discussion of Bloch wave labelling schemes and hence the effect will be briefly outlined. Nagata & Fukuhara (1967) found that at a certain value of the incident electron accelerating voltage (*i.e.* for a certain incident electron energy) the intensity of a second order Bragg reflection may exhibit a sharp minimum. This effect can be explained in terms of a contact between two dispersion surface branches at a symmetry point, that is the two Bloch waves become degenerate at this particular electron energy (Nagata & Fukuhara, 1967; Metherell & Fisher, 1969). The existence of contact points between branches is in fact a general effect and may lead to minima in reflexions other than second order (Lally, Humphreys, Metherell & Fisher, 1970). It should be pointed out that points of contact between dispersion surface branches are well known in other forms of Bloch wave propagation, as might be expected due to the essential unity of the theory outlined in § 3. For example, Herring (1937) has considered points of contact in the *E versus k* curves of energy band theory; Van Hove (1953) and Phillips (1956) have studied similar points of contact in *w versus q* phonon dispersion curves.

If, using the ordered labelling scheme, the point of contact occurs between the jth and $(j+1)$th dispersion surface branches, then at the critical voltage the jth and $(j+1)$th Bloch waves interchange their eigenvectors (*i.e.* the Fourier coefficients $C_g^{(j)}$ and $C_g^{(j+1)}$ in equation (2) are interchanged), and hence the Bloch waves interchange their symmetries. Two such symmetry interchanges between branches are shown in Fig. 1 to have occurred between 500 keV and 1 MeV. (Fig. 1 was computed using mean values of the data recently given by Doyle & Turner (1968) and Radi (1970), the Fourier coefficients of lattice potential were Debye–Waller corrected.) The application of the ordered labelling scheme to identifying the Bloch waves both above and below the critical voltage is both simple and unambiguous. A notation based on the symmetry of the Bloch waves could only be used at symmetry points in the zone and would be considerably complicated by the critical voltage effect.

5. Bloch wave notation in electron diffraction theory

Of the various labelling schemes used in electron diffraction theory which are described in § 2, the only two which are consistent with accepted systems in other forms of Bloch wave propagation are the one based on the symmetry of the Bloch waves and the one which uses an 'ordered' labelling scheme, as shown in Fig. 1.

Whereas in band theory the majority of calculations are performed at symmetry points in the Brillouin zone, in electron diffraction theory this is not the case. For example, in conventional 100 keV electron microscopy the crystal orientation normally used, because this provides the best electron transmission in bright field (Hashimoto, Howie & Whelan, 1962) is with the crystal set slightly positive of a Bragg reflecting position; the corresponding Bloch waves usually have no particular symmetry at such a setting. With 1 MeV incident electrons the situation is different and although the crystal orientation which maximizes the electron transmission is often a point of symmetry (Humphreys & Lally, 1970), in many cases it is a point of no symmetry (Humphreys, Lally, Thomas & Fisher, 1970).

It is possible that in electron diffraction calculations for points of very high symmetry a group representation system may be desirable. However these points have in the past been of little interest to experimental electron microscopists and only a few theoretical calculations have been made. The authors feel that in general the labelling scheme for electron diffraction theory which is the most logical, simple and consistent with schemes in related fields is the system which labels the Bloch waves in terms of the dispersion surface in order of the magnitude of their $k_\perp$ component wave vectors, as shown in Fig. 1. Following Phillips (1956) it is suggested that this system be called the ordered labelling scheme. The use of such a scheme is entirely straightforward, and the authors suggest that this scheme be generally adopted in electron diffraction theory.

Summary and conclusions

(1) The essential mathematical unity of all wave propagation in periodic structures is illustrated and emphasized.

(2) A brief discussion of the critical voltage effect is given and equivalent effects in other forms of wave propagation are stated.

(3) It is suggested that the Bloch wave labelling scheme for electron diffraction which is the simplest and most logical, and which is consistent with accepted notations in other forms of Bloch wave propagation, is an ordered labelling scheme in which the top branch of the dispersion surface corresponds to wave 1, the second branch to wave 2, the third branch to wave 3, and so on.

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A Note on the Correlation of the Heavy-Atom Positions in Different Isomorphous Protein Crystals Using Both Isomorphous-Replacement and Anomalous-Dispersion Data

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In this note more accurate expressions are obtained for the Fourier coefficients of the iso-ano correlation function and the origin correlation function of Kartha & Parthasarathy.

Introduction

After obtaining the intensity data from the native protein and its isomorphous heavy atom derivatives the first stage involved in the determination of the protein structure is the location of the heavy atoms in the derivative crystals. This is usually carried out in two steps, namely, (i) to obtain the coordinates of the heavy atoms in each derivative crystal and (ii) to correlate the positions of the heavy atoms in the different derivatives to a common origin. Kartha & Par-

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