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On the scattering of Bloch-waves at a surface

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Résumé. — On établit quelques propriétés générales de la diffusion des ondes de Bloch par une surface. On énonce tout d'abord une condition nécessaire pour l'apparition d'un état de surface dans une bande interdite : elle stipule que le groupe d'espace doit contenir la rotation de 180° autour de la direction normale à la surface ou que le substrat doit avoir un centre de symétrie. On établit ensuite une loi de conservation de la matrice de diffusion des ondes de Bloch par la surface. On discute sa signification physique en relation avec celle du théorème optique. Finalement on montre que le champ d'onde diffusé au voisinage de la surface dépend d'une condition initiale portant sur l'onde de Bloch incidente. On compare, sur un exemple spécifique, la signification physique de trois conditions différentes, utilisées couramment dans les calculs.

Abstract. — Some general properties of three-dimensional Bloch-waves scattered by a surface are derived. An existence condition, for a surface two-dimensional Bloch state to arise in a forbidden gap, is first given : it requires either the space group to contain the rotation by π around the surface normal direction or the substrate to have an inversion centre. A conservation law of the scattering matrix of bulk Bloch-waves at the surface is then worked out. Its physical significance is discussed together with that of the optical theorem. Finally the scattered wave-field in the neighbourhood of the surface is shown to depend upon an initial condition bearing on the incident Bloch-wave. The physical relevances of three different conditions, used in current calculations, are compared for a specific example.

1. Introduction.

The eigenstates of a crystal, owing to the three dimensional (3D) periodicity of the lattice, can be expressed as Bloch functions [1]. This statement holds equally for electrons, phonons, plasmons, magnons and so on. A Bloch-wave is characterised by an energy E and a wave-vector \mathbf{q} . This latter is confined inside the 3D Brillouin zone. The dispersion law $E(\mathbf{q})$, defined for any \mathbf{q} within the Brillouin zone, is a characteristic property of the crystal. The spectrum of E -values consists of bulk bands separated by forbidden gaps. The energy E varies continuously within a band, whereas there is no real \mathbf{q} for a bulk excitation at any E value inside a gap. However a Bloch function with complex \mathbf{q} can be associated with any E in the gap.

By cutting a 3D crystal along a plane, a semi-infinite crystal, limited on the vacuum side by a surface plane, is produced. This semi-infinite crystal has still 2D periodicity along the surface. However the loss of periodicity in the direction, not contained in the surface plane,

has two consequences [2, 3], both being of paramount importance as regards chemical and physical processes taking place at a surface :

- i) surface states may arise in the gaps ;
- ii) the bulk 3D Bloch-waves are scattered by the surface. The purpose of this work is to present and to discuss several new properties of the surface states and bulk Bloch wave scattering at the surface.

The surface does not necessarily sustain surface states. Little effort has so far been made to go beyond the conclusions of Gurman and Pendry [4]. Nevertheless Stonely's discussion [5] of the possible occurrence of a Rayleigh branch within the framework of elasticity theory is worth mentioning. A necessary requirement for the existence of a surface state will be presented here.

The properties of the scattering matrix which describes the shape of the scattered wavefunction far away from the scattering region have been studied in detail for the scattering by a localised potential [6]. A celebrated conservation law, known as the optical theorem, has even been worked out for this case. We shall extend here this discussion to the case of 3D Bloch-waves scattered at a surface.

Whenever a 3D Bloch-wave is scattered at a surface, the scattering wave-function in the vicinity of the surface has been shown elsewhere [7] to depend on the incoming partial wave. This was called the initial condition of scattering in reference [7]. Here we resume this discussion by clearly identifying the relevant initial condition in the cases of Green's function and slab calculation. Furthermore we introduce a third initial condition and we calculate the scattering solutions corresponding to these three initial conditions of scattering in a specific case. As the result, as expected, is found to depend on the choice of the initial condition, a discussion is given of which condition among the three ones is likely to account at best for the scattering of thermally excited 3D Bloch-waves at the surface of a real semi-infinite crystal.

The article is organised as follows : in section 2, 2D Bloch-waves are defined with respect to 3D Bloch-waves and useful properties for our purpose are recalled ; section 3 presents a necessary condition for the existence of a surface state ; section 4 deals with the properties of the scattering matrix of 3D Bloch-waves ; in section 5 three different initial conditions of scattering are compared and their physical implications are analysed.

All properties to be shown here result merely from the Bloch-like character of the eigenstates of the 3D periodic crystal, and are consequently valid generally for any type of Bloch-like excitation. However for the sake of specificity it has proven to be convenient to consider electrons in sections 2, 3 and 4, and phonons in section 5.

2. General properties of 2D Bloch functions.

The interface between vacuum and bulk matter is made up of an arbitrarily large number of relaxed, reconstructed or adsorbed layers, all of which should have a 2D periodicity commensurate with that of the 2D lattice. These layers are hereafter referred to as the surface slab. Beyond this surface slab in bulk matter the crystal is 3D periodic and is characterised by the unit cell spanned by the vectors \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 . Any position vector \mathbf{r} is defined by its three components x_1 , x_2 , x_3 taken in an orthogonal coordinate frame. The surface plane is spanned by the \mathbf{a}_1 , \mathbf{a}_2 vectors whereas the x_3 direction along \mathbf{a}_3 is normal to the surface.

Any electronic eigenstate $|E, \mathbf{q}\rangle$ of the 3D crystal can be regarded [1] as a Bloch wave of energy E and wavevector \mathbf{q} , defined itself by its projections q_s , q_3 , onto the surface and normal to it respectively. The vector \mathbf{q}_s remains confined inside the 2D Brillouin zone. The wave function $|E, \mathbf{q}\rangle$ is equal to $e^{i\mathbf{q}\cdot\mathbf{r}} u(\mathbf{r})$ where the function $u(\mathbf{r})$ has the periodicity of the 3D lattice.

The eigenstates of the semi-infinite crystal are 2D Bloch functions, equal to $e^{i\mathbf{q}_s \cdot \mathbf{r}} f(\mathbf{r})$ where f has the periodicity of the 2D lattice. The function $f(\mathbf{r})$ is obtained by solving the Bloch equation [1] :

$$\frac{\Delta f}{2} + i\mathbf{q}_s \cdot \Delta \mathbf{f} + (E - q_s^2 - V(\mathbf{r})) f = 0 \quad (2.1)$$

where Δf and $\Delta \mathbf{f}$ denote respectively the Laplacian and gradient operators acting on $f(\mathbf{r})$, \hbar and the electron mass are taken equal to unity and $V(\mathbf{r})$ is the real 2D periodic potential of the semi-infinite crystal. Equation (2.1) can be rewritten as :

$$D(E, \mathbf{q}_s) f(\mathbf{r}) = 0 \quad (2.2)$$

where $D(E, \mathbf{q}_s)$ is a linear operator. It is inferred from equation (2.1) to have the property :

$$D(E, -\mathbf{q}_s) = D^+(E, \mathbf{q}_s) \quad (2.3)$$

where the superscript + means complex conjugate.

Let us now recall from reference [8] the properties of $f(\mathbf{r})$, if the space-group of the semi-infinite crystal is assumed to contain the surface inversion c defined by :

$$c \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = \begin{bmatrix} -x_1 \\ -x_2 \\ x_3 \end{bmatrix}. \quad (2.4)$$

Letting c act on equation (2.2), while taking advantage of equation (2.3), implies :

$$D(E, \mathbf{q}_s) f^+(\mathbf{c}\mathbf{r}) = 0. \quad (2.5)$$

By comparing equations (2.2) and (2.5), it is inferred that $f^+(\mathbf{c}\mathbf{r})$ is solution of equation (2.1) too. Consequently if f_i is a solution of equation (2.1), there is another solution f_j , so that :

$$f_i^+(\mathbf{c}\mathbf{r}) = f_j(\mathbf{r}). \quad (2.6)$$

As the function $e^{iq_3 \cdot x_3} u(\mathbf{r})$ originating from the Bloch-function $|E, \mathbf{q}\rangle$ is a solution of equation (2.1) in bulk matter, equation (2.6) entails that there is in general a pair of functions $u_i(\mathbf{r})$ and $u_j(\mathbf{r})$ with the same E and \mathbf{q}_s , but with $q_{3i} = -q_{3j}^+$ and $u_i^+(\mathbf{c}\mathbf{r}) = u_j(\mathbf{r})$.

Finally let us consider the \mathbf{g} component of the 2D Fourier transform of $f(\mathbf{r})$:

$$f(\mathbf{g}) = \iint f(\mathbf{r}) e^{i\mathbf{g} \cdot \mathbf{r}} dx_1 dx_2 \quad (2.7)$$

where \mathbf{g} is a vector of the 2D reciprocal lattice and the integration in equation (2.7) is performed over the 2D unit cell ($\mathbf{a}_1, \mathbf{a}_2$). It is deduced from equation (2.6) that $f_i(\mathbf{g}) = f_j^+(\mathbf{g})$ for any \mathbf{g} . This property underlies the following section.

3. Existence condition for the surface state.

We consider here the solution f of equation (2.1) at an energy E falling in a forbidden gap. As 3D periodicity is retrieved on the bulk matter side $x_3 > 0$, f in this region consists of a linear combination of an infinite [9, 10] number of evanescent 3D Bloch-waves :

$$f(E, \mathbf{q}_s, \mathbf{r}) = \sum_{m=0}^{\infty} e^{iq_{3m} \cdot x_3} u_m R_m^c \quad (3.1)$$

where the complex component q_{3m} of the 3D wavevector \mathbf{q}_m is such that $|e^{iq_{3m} \cdot x_3}| < 1$ for $x_3 > 0$, and R_m^c is the weighting coefficient attached to the m -th partial evanescent wave $e^{iq_{3m} \cdot x_3} u_m(\mathbf{r})$. The dispersion relation $q_{3m}(E)$ is a property of the complex bulk band structure and is henceforth assumed to be known as well as the 3D periodic functions $u_m(\mathbf{r})$. These latter are degenerate, in so far as they have the same energy E and same projection \mathbf{q}_s . Thus they differ only by their component q_{3m} .

On the vacuum side $x_3 < 0$ which includes also the surface slab, the solution f of equation (2.1) can be written [11] as a linear combination :

$$f(E, \mathbf{q}_s, \mathbf{r}) = \sum_{n=0}^{\infty} \alpha_n v_n(E, \mathbf{q}_s, \mathbf{r}) \quad (3.2)$$

where the function v_n are degenerate in the same way as the functions $u_m(\mathbf{r})$ hereabove and the α_n are weighting coefficients. The functions v_n are uniquely determined [11] by the requirements that they be 2D periodic along the surface and vanish exponentially far from the surface in vacuum.

As both functions $u_m(\mathbf{r})$ and $v_n(\mathbf{r})$ are assumed to be known, the only unknowns are the coefficients R_m^c and α_n . They can be found by requiring that f and $\partial f / \partial x_3$ be continuous at $x_3 = 0$ where the interface separating the bulk matter from the surface slab is located. It proves to be convenient [11] to express these two conditions on the 2D Fourier transforms of the u_m and v_n functions, as defined in equation (2.7) :

$$\sum_{n=0}^{\infty} (R_n^c u_n(\mathbf{g}) - \alpha_n v_n(\mathbf{g})) = 0$$

$$\sum_{n=0}^{\infty} \left(R_n^c \left(i q_{3n} u_n(\mathbf{g}) + \frac{\partial u_n}{\partial x_3}(\mathbf{g}) \right) - \alpha_n \frac{\partial v_n}{\partial x_3}(\mathbf{g}) \right) = 0. \quad (3.3)$$

Once written for every \mathbf{g} of the 2D reciprocal lattice, equations (3.3) make up a linear homogeneous system of equations :

$$D_s(E, \mathbf{q}_s) \mathbf{x} = \mathbf{0} \quad (3.4)$$

where the unknown components of \mathbf{x} are the R_n^c and α_n coefficients. Equation (3.4) is equivalent to finding the real E roots of the determinant of D_s . As the matrix elements of D_s are in general complex, equation (3.4) amounts to equating to zero both the real and imaginary parts of its determinant. This system of two equations with only one unknown, the real energy E , has thus in general no solution, except when the determinant of D_s is real or purely imaginary. This will happen in general only if the space-group contain the c operation, so that equation (2.6) holds. Indeed this leads to a D_s matrix consisting of pairs of columns, corresponding to $f_i(\mathbf{g})$ and $f_j(\mathbf{g})$ and hence complex conjugate of each other. As a consequence the determinant of D_s is either real or purely imaginary. Hence the property of the semi-infinite crystal that its space group contains the c operation is our desired prerequisite for the surface to sustain a surface state. As shown in reference [8], if the space-group of the semi-infinite crystal does not contain c but rather a mirror plane, surface states may arise only for those \mathbf{q}_s normal to the mirror plane. Consequently if the space group does not contain either the c operation or any mirror plane, a surface state cannot arise except for $\mathbf{q}_s = \mathbf{0}$, that is at the centre of the 2D Brillouin zone, because the solution f of equation (2.1) is real there.

Nevertheless if we consider a finite slab rather than a semi-infinite crystal, surface inversion is not necessary for the occurrence of surface states. An inversion centre in the middle of the slab actually suffices. As a proof of this statement, we apply first the inversion to equation (2.1) which leads to the result that, if $f(\mathbf{r})$ is a solution, $f^+(-\mathbf{r})$ is a solution too, since the eigenstates of a slab are non-degenerate. Now the matching equations (3.3) must be written twice, that is at the two boundaries of the slab. Once this is done, the D_s matrix turns out again to consist of pairs of columns, complex conjugate of each other, which was seen above to be required for a surface state to arise. Since the expansion in equation (3.1) contains only evanescent components, it makes no difference while solving equation (2.1), whether we consider a semi-infinite crystal or a finite slab, provided the slab is thick enough (note that this argument is not valid for travelling waves which do not vanish even at infinite distances). Then our desired prerequisite is equivalent to the statement that the substrate (but not necessarily the surface slab) has an inversion centre, which includes in particular all Bravais lattices.

In summary, it has been shown that a semi-infinite crystal generally cannot have a surface state, except at the 2D Brillouin zone centre, unless either it has the surface inversion symmetry defined by equation (2.4), or its substrate has an inversion centre.

4. Properties of the scattering matrix.

Since the surface breaks the periodicity along \mathbf{a}_3 , it also scatters every incident Bloch-wave $|E, \mathbf{q}_i\rangle$ with $\mathbf{q}_i = (\mathbf{q}_s, q_{3i})$. The scattered field in the $x_3 < 0$ region is still given by equation (3.2), as for the surface state. Conversely on the $x_3 > 0$ side, it reads

$$f_i = e^{iq_{3i} \cdot x_3} u_i + \sum_{j=1}^{n_t} e^{-iq_{3j} \cdot x_3} u_j R_{ji}^t + \sum_{m=1}^{\infty} e^{iq_{3m} x_3} u_m R_{mi}^c. \tag{4.1}$$

The q_{3m} , u_m and R_{mi}^c are defined as in equation (3.1). The functions u_i and u_j correspond respectively to the incident 3D Bloch-wave $|E, \mathbf{q}_s, q_{3i}\rangle$ and the outgoing ones $|E, \mathbf{q}_s, -q_{3j}\rangle$, each of them having the weight R_{ji}^t . Incoming 3D Bloch-waves are distinguished, in this work, from outgoing ones by their respective group velocities $\partial E / \partial q_3$ displaying opposite signs. The integer $n_t(E, \mathbf{q}_s)$ is the number of pairs of degenerate 3D travelling Bloch-waves $|E, \mathbf{q}_s, \pm q_{3j}\rangle$. Expressions in equation (3.1) and equation (4.1) differ in two respects :

i) there is an incoming partial wave $|E, \mathbf{q}_s, q_{3i}\rangle$ in equation (4.1) while there is none for the surface state in equation (3.1) ;

ii) the initial condition of scattering [7] is defined by the choice of q_{3i} . As there are n_t possible values for q_{3i} , the f_i defined by equation (4.1) make up a n_t -degenerate manifold, whereas the surface state of equation (3.1) is non-degenerate.

The $(n_t \times n_t)$ matrix R^t of element R_{ji}^t is realised to be a scattering matrix, as it maps the incoming asymptote of f_i , $|E, \mathbf{q}_s, q_{3i}\rangle$, onto n_t of its outgoing ones $|E, \mathbf{q}_s, -q_{3j}\rangle$. Moreover if the 2D space group contains the surface inversion, defined by equation (2.4), R^t has the following property, as shown in reference [7] :

$$R^t(R^t)^+ = \mathbf{1} \tag{4.2}$$

where $\mathbf{1}$ is the $(n_t \times n_t)$ unit matrix, and the subscript + means complex conjugate.

We present now a new property of R^t which is valid in general [12] :

$$R^t \frac{\partial E}{\partial q_3} (R^t)^* = \frac{\partial E}{\partial q_3} \tag{4.3}$$

where $(R^t)_{ij}^* = (R_{ji}^t)^+$, and $\partial E/\partial q_3$ is a diagonal ($n_t \times n_t$) matrix, defined by $(\partial E/\partial q_3)_{jj} = \partial E/\partial q_{3j}$. The demonstration of the identity (4.3) is given in the appendix. An application of equation (4.3) leads to the conservation law, the meaning of which is discussed elsewhere [13]:

$$\sum_{j=1}^{n_t} |R_{ji}^t|^2 \frac{\partial E}{\partial q_{3j}} = \frac{\partial E}{\partial q_{3i}}. \quad (4.4)$$

As working out equation (4.3) requires only that the potential of the Schrödinger equation be real, equation (4.3) is also valid for the scattering of spherical waves by a finite range potential embedded in vacuum. In this latter case $\partial E/\partial q$ is proportional to the unit matrix, which entails, according to equation (4.3), that R^t is a unitary matrix and the statement in equation (4.4) is merely equivalent to the optical theorem. The fact that equation (4.2) also holds for this case, combined with R^t being unitary enables us to retrieve the result [6] that R^t is also symmetric. It is noteworthy that R^t is unitary and symmetric only if the Hamiltonian, outside the scattering region, is diagonal in a basis of spherical waves and the scattered field is indeed expanded in spherical waves (but not in planes waves!). However in contrast to the proofs of equations (4.2) and (4.3) given in textbooks [6], our demonstration does not resort at all to such arguments as the conservation of the total flux of particles and the time-inversion symmetry. Moreover we recall [7] in a compact form a by-product of equation (4.2) which has been apparently overlooked in the textbooks:

$$\begin{aligned} \alpha^+ &= \bar{\alpha} (R^t)^+ \\ (R^e)^+ &= \bar{R}^e (R^t)^+ \end{aligned} \quad (4.5)$$

where the matrices α and R^e are defined by their elements α_{ji} and R_{ji}^e ; the matrices $\bar{\alpha}$ and \bar{R}^e are defined with respect to α and R^e by their elements equal to $\bar{\alpha}_{ji} = \alpha_{mi}$ and $\bar{R}_{ji}^e = R_{mi}^e$ respectively; the indices j and m are related by $v_j(\mathbf{r}) = (v_m(\mathbf{cr}))^+$ and $u_j(\mathbf{r}) = (u_m(\mathbf{cr}))^+$. Finally it should be noticed that, at the surface of a semi-infinite crystal, $\partial E/\partial q_3$ is not proportional to the unit matrix, which entails that n_t of the f_i defined by equation (4.1) are not orthogonal.

5. Significance of the initial condition of scattering.

We want now to point out how influential the initial condition of scattering is in assessing the value of the 2D Bloch function inside the surface slab. To this purpose, we consider unrelaxed Ni(100) with a lattice dynamical model assumed to consist of central forces between nearest neighbours everywhere including the surface slab. We first recall [14] the definition of the partial spectral density ρ_w :

$$\rho_w(\omega) = \sum_i |w(\omega_i)|^2 \delta(\omega - \omega_i) \quad (5.1)$$

where w designates here the vibrational amplitude parallel to the surface in the first layer, ω is the bulk phonon frequency and the i -sum is carried out over all 2D phonons of frequency ω_i , i.e. the vibrational eigenstates of the semi-infinite crystal. We focus on the even modes in the (010) direction at a point Q of the 2D Brillouin zone distant by $\pi/(2\sqrt{2}a)$ from the centre ($a = 2.49 \text{ \AA}$ stands for the Ni lattice parameter). The 3D phonon dispersion normal to the surface at Q is given in figure 1.

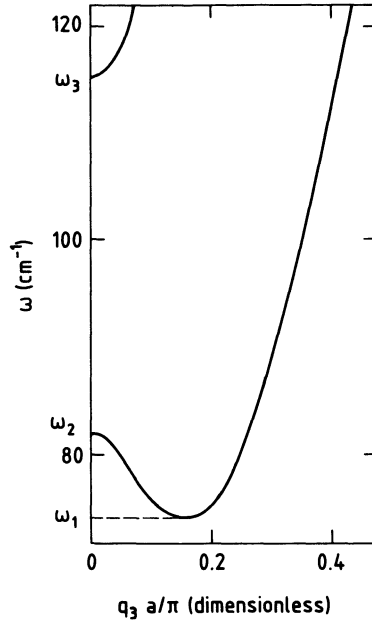


Fig. 1. — Bulk phonon dispersion law $\omega(q_3)$ in Ni for $\mathbf{q} = (\pi/4 a, \pi/4 a, q_3)$. The phonons are even with respect to the mirror plane (010). Only that part of the dispersion curves useful for the discussion of the results in figure 3 has been represented. The Van Hove singularities are denoted ω_1 , ω_2 and ω_3 .

Within the forbidden gaps ($n_t = 0$) and the $n_t = 1$ bulk frequency domains, the initial condition of scattering is unique because there is either no incoming 3D Bloch-wave ($n_t = 0$) or a single one ($n_t = 1$). In both cases the corresponding scattered 2D Bloch state is not degenerate. Inversely there are two of them in the $n_t = 2$ regions. We shall calculate the spectral density ρ_w with three different initial conditions of scattering :

i) condition I has been discussed in the previous section. The 2D phonon comprises a single incoming 3D wave. Incoming and outgoing 3D phonons are distinguished by the opposite signs of their respective group velocity $\partial\omega/\partial q_3$. A typical scattered field is depicted in figure 2a ;

ii) condition II differs from condition I by the criterion used to distinguish incoming from outgoing 3D phonons. Here the sign of the phase velocity q_3 is taken instead of that of $\partial\omega/\partial q_3$. If q_3 and $\partial\omega/\partial q_3$ have the same sign, the scattered field looks as in figure 2a. However if they are opposite, it looks as in figure 2b. Each set of eigenstates of the kind depicted in either figure 2a or figure 2b makes up a basis for the n_t -manifold. Both sets are related to each other through a linear transformation which is however not unitary, since none of the two sets is orthogonal, as noticed in the previous section ;

iii) condition III corresponds to the case of the slab calculation (a thickness of 21 layers is taken here). The scattered field then includes n_t of the degenerate pairs $|\omega, \mathbf{q}_s, \pm q_{3i}\rangle$. Thus the eigenstates are seen to consist of stationary waves rather than travelling ones as in conditions I and II. For each pair, the respective weights of the incoming and outgoing partial waves are in general of unequal modulus. Hence the scattered field looks as pictured in figure 2c. It is of importance for the following discussion to note that there is a definite phase

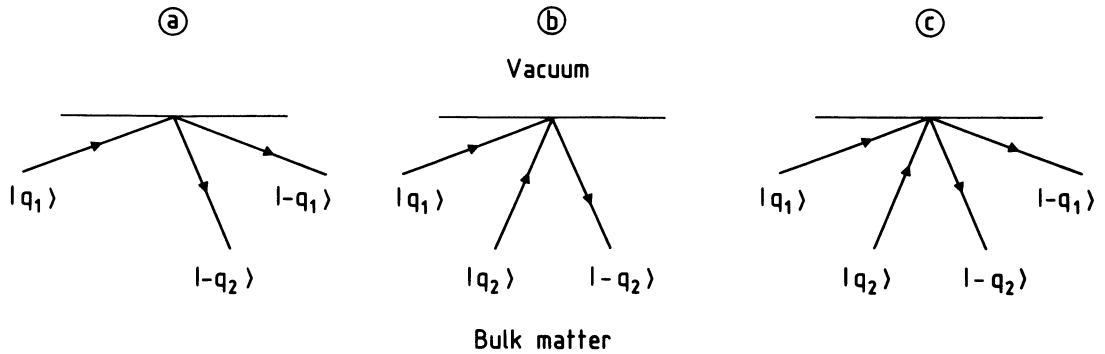


Fig. 2. — Sketch of the asymptotic shape of the 2D Bloch-wave with $n_t = 2$ for three different scattering conditions I, II and III. Incoming and outgoing 3D Bloch-waves, according to the definition of section 4, are denoted $|q_i\rangle$ and $|-q_i\rangle$ respectively.

shift between the two incoming beams in figure 2c. As the scattered state for condition III is not degenerate, this means that the n_t -fold degeneracy is completely lifted between n_t orthogonal eigenstates of slightly different frequencies. All n_t of the corresponding eigenstates look as in figure 2c. Consequently, even though the thickness of the slab is increased to infinity, they still will merge into a non-degenerate eigenstate of the same type as in figure 2c. Thus the n_t -fold degeneracy is completely overlooked, if condition III is assumed to calculate the partial spectral density.

In most calculations of the spectral density with Green's function [15], the orthonormal basis of non-degenerate eigenstates corresponding to condition III in figure 2c is assumed. At the outset the crystal is taken to be a finite slab, the thickness of which is subsequently increased to infinity. The partial density, obtained in the limiting case of infinite thickness, is accordingly found to agree well with that calculated with the slab method [16]. Nevertheless there is another procedure to calculate the spectral density with Green's function [17]: it takes advantage of the property that the equations of motion can be solved with the unknowns being the desired partial spectral densities [14]. The initial condition of scattering is determined by the form assumed for the bulk spectral densities. In principle all conditions, outlined in figure 2, can be taken with this method. However it is not explicitly stated in reference [17] which one has been actually chosen.

The calculated results are represented in figure 3. The bulk phonon density of states at fixed \mathbf{q}_s

$$\rho(\omega) = \sum_{i=1}^{n_t} |\partial q_{3i} / \partial \omega|$$

is plotted in the upper part. As expected, it diverges like $|\omega - \omega_i|^{-1/2}$ at each Van Hove singularity ω_i . The spectral density ρ_w is given in the lower part of figure 3 for the three initial conditions mentioned above. In the $n_t = 0$ and 1 domains, all three conditions lead to the same result since the 2D scattering state is not degenerate, which is equivalent to the statement that the initial condition of scattering is unique in the $n_t = 0, 1$ regions. Inversely in the $n_t = 2$ regions, the ρ_w associated with conditions I and II are equal or are not according to whether the phase and group velocities have the same sign, as for $\omega > \omega_3$, or have opposite signs, as for $\omega_1 < \omega < \omega_2$. As condition III never coincides with conditions I and II in

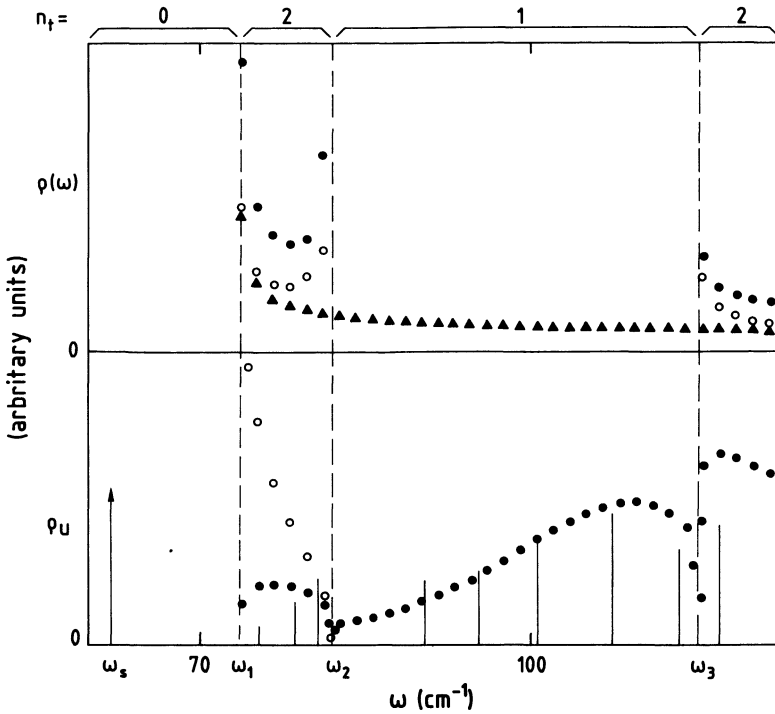


Fig. 3. — Plots of the bulk phonon density of states $\rho(\omega)$ and the partial spectral density $\rho_w(\omega)$ for three different conditions. The value of n_t is recalled at the top. Vertical dashed lines denote the Van Hove singularities ω_1 , ω_2 and ω_3 . In the upper part, for $n_t = 2$ regions, black triangles and white circles on the one hand and black circles on the other hand represent respectively the partial densities $|\partial q_{3i}/\partial \omega|$ and the total one $\rho(\omega) = \sum_{i=1}^{n_t} |\partial q_{3i}/\partial \omega|$. In the lower part, the spectral density $\rho_w(\omega)$ has been plotted in black circles, white circles and vertical solid lines for conditions I, II and III, respectively. The vertical arrow at ω_s represents the contribution of a surface state.

$n_t > 1$ regions (see Fig. 2) the spectral density ρ_w attached with condition III differs also markedly from those obtained with conditions I and II.

To decide which condition among I, II and III best describes the situation in a real semi-infinite crystal, a physical picture of the scattering of thermal phonons at a surface is needed. To that end we first define a surface selvedge, extending from the surface into bulk matter over a thickness equal to the mean free path of bulk phonons. Whenever any pair of 3D phonons are created by thermal scattering inside the surface selvedge, there can be no definite phase relationship on average between them. Such thermal phonons, propagating subsequently towards the surface, are scattered according to the picture in figure 2a. The well defined phase-shifts between the various incoming and outgoing beams are not lost, until the outgoing waves have travelled out of the surface selvedge over several mean free paths, so that thermal equilibrium of the phonon bath is recovered in bulk matter.

The scattering condition III, because of the definite phase shifts between the incoming beams in figure 2c, is hence seen to be at odds with a basic property of thermal 3D phonons and can be discarded except for a slab for which the bulk phonon mean free path is equal to the thickness. Selecting further the relevant physical picture out of conditions I and II will

await a careful and accurate comparison of the calculated ρ_w within conditions I and II with a measured one. As the measured data always involve an ill-known matrix element, describing the interaction between the experimental probe and phonons, a meaningful comparison must take advantage of sharp resonances. As a matter of fact, conditions I and II, in $n_i > 1$ regions where the corresponding scattering states do not coincide, will give rise to resonances occurring at different frequencies [7].

6. Conclusion.

Several properties of the scattering of 3D Bloch-waves at a surface have been borne out :

- i) surface states may arise only if the 2D space group contains the rotation by π around the surface normal or if the substrate has the point inversion symmetry ;
- ii) a new property of the scattering matrix describing the scattered Bloch-wave field far from the surface has been worked out. It has enabled us to point out the general significance of the optical theorem ;
- iii) ample light has been shed on the role of the initial condition of scattering. In energy regions where the number of degenerate pairs n_i of travelling bulk Bloch-waves $|E, \mathbf{q}_s, \pm q_{3i}\rangle$ is equal to 0 (forbidden gap) or 1, the 2D eigenstates are uniquely defined so that all types of calculation yield the same results as for the surface states and the resonances. On the contrary in $n_i > 1$ regions, the partial spectral densities and the resonances, if any, will depend upon the form of the 2D eigenstates, taken to do the calculation.

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Appendix.

Let us consider two degenerate 2D Bloch-functions ψ_i and ψ_j which are solutions of the same Schrödinger equation :

$$\Delta\psi_i + (E - V).\psi_i = 0 \quad (\text{A1})$$

$$\Delta\psi_j^+ + (E - V) \psi_j^+ = 0 \quad (\text{A2})$$

where the potential V is real. Multiplying equation (A1) and equation (A2) by ψ_j^+ and ψ_i , respectively, and applying Green's theorem to the difference results into :

$$\iint_{S(\Omega)} (\psi_j^+ \Delta\psi_i - \psi_i \Delta\psi_j^+) \mathbf{n} \, dS = 0 \quad (\text{A3})$$

where \mathbf{n} is a unit vector normal to the surface $S(\Omega)$ of any closed volume Ω .

The volume Ω is taken so as to cross the surface according to the 2D unit cell $(\mathbf{a}_1, \mathbf{a}_2)$ and to extend along \mathbf{a}_3 in both $x_3 < 0$ and $x_3 > 0$ regions up to $\pm x_\infty$. The value $x_\infty > 0$ is chosen large enough, so that $\psi_k(-x_\infty) = 0$ with $k = i, j$ in vacuum, and the evanescent $u_m(\mathbf{r})$ in equation (4.1) also vanish at x_∞ in the bulk region for both ψ_i and ψ_j .

As ψ_i and ψ_j are degenerate 2D Bloch functions, they have in particular the same \mathbf{q}_s . Consequently the contributions to the integral in equation (A3) calculated on the faces of

$S(\Omega)$ parallel to \mathbf{a}_3 vanish strictly. Furthermore since $\psi_i(-x_\infty) = \psi_j(-x_\infty) = 0$, the integral of equation (A3) finally reduces to :

$$\iint_{S'(\Omega)} \left(y_j^+ \frac{\partial y_i}{\partial x_3} - y_i \frac{\partial y_j^+}{\partial x_3} \right) dx_1 dx_2 = 0 \tag{A4}$$

where $S'(\Omega)$ is a 2D unit cell located in the $x_3 = x_\infty$ plane and y_i and y_j are deduced from equation (4.1) to read :

$$\begin{aligned} y_i &= e^{iq_{3i}x_3} u_i + \sum_{\ell=1}^{n_i} e^{-iq_{3\ell}x_3} u_\ell R_{\ell i}^t \\ y_j &= e^{iq_{3j}x_3} u_j + \sum_{m=1}^{n_j} e^{-iq_{3m}x_3} u_m R_{mj}^t \end{aligned} \tag{A5}$$

Then we integrate expression (A4) along \mathbf{a}_3 over the 3D unit cell, which leads to :

$$\iiint \left(y_j^+ \frac{\partial y_i}{\partial x_3} - y_i \frac{\partial y_j^+}{\partial x_3} \right) dx_1 dx_2 dx_3 = 0 . \tag{A6}$$

Integral (A6) consists of a sum of integrals of cross-products, proportional to $e^{i(\pm q_{3\ell} \mp q_{3m})} u_\ell^+ \partial u_m / \partial x_3$. The integral over x_3 of any such term is nothing but the Fourier transform of $u_\ell^+ \partial u_m / \partial x_3$ at $(\pm q_{3\ell} \mp q_{3m})$. Since $|E, \mathbf{q}_s, q_{3\ell}\rangle$ and $|E, \mathbf{q}_s, q_{3m}\rangle$ are 3D Bloch-functions, u_ℓ^+ and $\partial u_m / \partial x_3$ are 3D periodic. Hence the Fourier transform of $u_\ell^+ \partial u_m / \partial x_3$ vanishes unless $(\pm q_{3m} \mp q_{3\ell})$ belongs to the reciprocal lattice. This happens only for $q_{3m} = q_{3\ell}$, because both are confined inside the 3D Brillouin zone. Consequently equation (A6) reads :

$$\text{Im} \left(\iiint \left(\delta_{ij} u_i \frac{\partial u_i^+}{\partial x_3} + \sum_{\ell=1}^{n_i} R_{i\ell}^t (R_{j\ell}^t)^+ u_\ell \frac{\partial u_\ell^+}{\partial x_3} \right) dx_1 dx_2 dx_3 \right) = 0 \tag{A7}$$

where Im means imaginary part and δ_{ij} is a Kronecker symbol. By noticing [1] that

$$\text{Im} \left(\iiint u_\ell \frac{\partial u_\ell^+}{\partial x_3} dx_1 dx_2 dx_3 \right) = \partial E / \partial q_{3\ell} ,$$

equation (A7) is finally cast into :

$$\sum_{\ell=1}^{n_i} R_{i\ell}^t (R_{j\ell}^t)^+ \partial E / \partial q_{3\ell} = \delta_{ij} \partial E / \partial q_{3i} \tag{A8}$$

which is rewritten in a closed form in equation (4.3).

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