Diffraction models, dynamical structure tensors and electron–phonon interaction

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Abstract. A coherent exposition of the theory of scattering from a dynamic lattice, which applies to the scattering of Bloch-wave electrons as well as to the scattering of plane waves, is presented. This is achieved by developing a generalised diffraction model, along the lines conceived by Van Hove, appropriate for the scattering of Bloch waves. The resulting diffraction model provides a basis for treating processes controlled by electron–phonon interaction in general and subsumes the standard diffraction model results. The diffraction model origins of the standard approximate expressions used to describe electron–phonon interaction-controlled processes are also revealed.

1. Introduction

The diffraction model allows for a consistent treatment of diverse scattering phenomena. For example, when electron–phonon interaction is the scattering mechanism, the diffraction model provides for a unified treatment of electrical and thermal transport, phonon contributions to the electron effective mass, and acoustic attenuation in perfect and point- or line-defected crystalline alloys, and also in liquid, amorphous and disordered alloys.

The essence of diffraction model methods is factorisation of scattering rate matrix elements into terms such that the lattice vibrational properties are entirely contained in *dynamical structure factors*, which can be related to transforms of generalised pair distribution functions.

The most celebrated dynamical structure factor is that defined by Van Hove [1], viz.

$$S(K, \Omega) = \int_{-\infty}^{\infty} dt \exp(i\Omega t) \langle r(K, t) r^+(K, 0) \rangle_T \tag{1}$$

where $\langle O \rangle_T$ denotes thermal average in the equilibrium ensemble (i.e. $\langle O \rangle_T = \Sigma p_i \langle i | O | i \rangle$) and $r(K, t)$ is the spatial Fourier transform of the ion density operator. The Van Hove dynamical structure factor $S(K, \Omega)$ describes very general scattering phenomena in which the lattice absorbs pseudo-momentum K and energy Ω. It is directly measurable via neutron scattering experiments. It encompasses Debye–Waller factors, Umklapp processes, coupling to transverse phonons, multiphonon effects, etc. Thus, $S(K, \Omega)$ has been the object of intense theoretical interest.

Baym [2] elaborated a diffraction model approach to the treatment of electron–phonon interaction-controlled phenomena based upon the Van Hove dynamical structure factor. Baym's approach has proven to be extremely productive and has become standard. However, Baym's form of diffraction model, based on the Van Hove dynamical structure factor, is strictly correct only for the scattering of plane (or pseudo-plane) waves (PW). To apply diffraction model techniques to electron–phonon interaction-controlled processes in general, it is necessary to derive diffraction model expressions appropriate for treatment of the scattering of Bloch waves (BW).

Therefore, the principal objective of this paper is to present a coherent exposition of a generalised diffraction model, which applies to PW or BW in perfect, disordered, or defected crystalline alloys and to PW in liquid or amorphous alloys. This aim is realised through the introduction of a generalised diffraction model, which applies to BW electron–phonon interaction-controlled processes and reduces to the standard diffraction model in PW scattering cases.

An important secondary objective is to reveal the diffraction model origins of the approximate expressions appearing in the standard literature. In particular, the standard equations used to describe electron–phonon interaction-controlled processes are shown to be approximate diffraction model expressions.

This paper is organised as follows. The generalised diffraction model, which applies to Bloch-wave and plane-wave scattering, is presented in section 2. Generalised structure factors $S(k, k', \Omega)$ and $S'(k, k', \Omega)$ and structure tensors $\{I_n(K, \Omega)|n = 0, \infty\}$ are defined.

The special case of plane-wave scattering is discussed in section 3. The n-phonon structure tensors $\{\Phi_n(K, \Omega)|n = 0, \infty\}$ and the Debye–Waller tensor W are defined and the standard Van Hove dynamical structure factor form $S(K, \Omega)$ is deduced.

Explicit expressions for $\{I_n(K, \Omega), \Phi_n(K, \Omega)|n = 0, 2\}$ are given in section 4.

The experimental determination of the various structure tensors and factors is discussed in section 5.

The diffraction model origins of the 'standard expressions' are revealed in section 6. The plane-wave scattering expressions (i.e. the standard diffraction model results) are derived in section 6.1, the expressions describing nearly free-electron scattering in crystalline alloys (Baym's approximation) are derived in section 6.2, and in section 6.3 the standard approximate expression describing Bloch-wave scattering in perfect crystals is derived.

Electron–phonon spectral functions (usually denoted $\alpha^2(\Omega)F(\Omega)$), static structure factors (denoted $S(K)$), static structure tensors (which might be denoted $I_n(K)$, etc.), etc., are briefly discussed in section 7.

Concluding remarks are given in section 8.

2. The generalised diffraction model

The development of diffraction model factorisations for scattering of Bloch waves (BW) is demonstrated in this section. The essential diffraction model ideas are contained in [1]. The theoretical development follows that presented in chapters 19 and 20 of *Quantum Theory of Solids* by Kittel [3]. The methods employed here were also used by Van Hove [1]. The crucial step in either reference is the application of Bloch's theorem [4].

The notation will be streamlined: (i) Let q stand for (q, j) where q is a phonon wavevector and j is a phonon branch and polarisation index. (ii) Let k stand for (k, s)

where k is the scattered particle wavevector and s is an appropriate index. For example, for electron states, s might represent the spin. (iii) Consider pure materials—the generalisation required to treat alloys, via the introduction of partial structure factors, is straightforward and well known. (iv) The following shorthand notations are adopted:

$$K = k - k' \qquad A = K + G - H \qquad A' = K + G' - H'$$

where G, H, G' and H' are reciprocal lattice vectors (RLV).

Scattering from an initial state containing a BW of wavenumber–index k,

$$|k, i\rangle = \sum_G \alpha(G) \exp[i(k + G) \cdot x]|i\rangle \tag{2a}$$

into a final state containing a BW of wavenumber–index k',

$$|k', f\rangle = \sum_G \beta(G) \exp[i(k' + G) \cdot x]|f\rangle \tag{2b}$$

is treated. The sums are on RLV G.

The perturbation H' producing the scattering is assumed to be of the form

$$H' = \sum_l [V(x - x_l) - U(x - l)] \tag{3}$$

where x_l is the position of the ion, which, in the absence of the lattice vibration, would be at position l, $V(x)$ is the ionic potential and $U(x)$ is the unperturbed potential. We think of these potentials as fully screened, etc., and use the same letters to denote the Fourier transforms,

$$\{U(A), V(A)\} = \int dx \exp(iA \cdot x)\{U(x), V(x)\}. \tag{4a}$$

The origin is chosen in such a way that

$$A \cdot l = K \cdot l + (\text{integer}) \, 2\pi.$$

We also denote the difference in the transformed potentials (i.e. the transform of the undisplaced potentials) by

$$W(A) = V(A) - U(A). \tag{4b}$$

Thus, using equations (2) to (4),

$$\langle k', f|H'|k, i\rangle = \sum_{l, G, H} \beta(G)^* \alpha(H)$$
$$\times [V(A)\langle f|\exp(iA \cdot x_l)|i\rangle - U(A) \exp(iK \cdot l)\langle f|i\rangle] \tag{5}$$

and

$$\langle k', f|H'|k, i\rangle \exp[i(\varepsilon_i - \varepsilon_f)t] = \sum_{l, G, H} \beta(G)^* \alpha(H)$$
$$\times \{V(A)\langle f|\exp[iA \cdot x_l(t)]|i\rangle - U(A) \exp(iK \cdot l)\langle f|i\rangle\} \tag{6a}$$

where $x_l(t)$ is in Heisenberg representation and we have used

$$H_0|i\rangle = \varepsilon_i|i\rangle \tag{6b}$$

$$H_0|f\rangle = \varepsilon_f|f\rangle. \tag{6c}$$

It then follows that the scattering rate, *neglecting factors accounting for occupation of the states k, k', etc.*, is given by

$$X(k, k', \Omega) = \sum_{i,f} p_i |\langle k', f|H'|k, i\rangle|^2 \delta(\varepsilon_i - \varepsilon_f - \Omega)$$

$$= \sum_{i,f} \int \frac{\mathrm{d}t}{2\pi} p_i |\langle k', f|H'|k, i\rangle|^2 \exp[i(\varepsilon_i - \varepsilon_f - \Omega)t]$$

$$= \sum_{G,H,G',H'} \beta(G)^* \alpha(H) [\beta(G')^* \alpha(H')]^* [V(A)V(A')^* S'(A, A', \Omega)$$

$$+ W(A)W(A')^* a(K)\delta(\Omega)]. \tag{7}$$

Here the geometrical structure factor $a(K)$ is defined in the usual way, i.e.

$$a(K) = \sum_{l,l'} \exp[iK \cdot (l - l')] = N \sum_{d} \exp(iK \cdot d) \tag{8}$$

the dynamical structure factor $S'(A, A', \Omega)$ is defined as

$$S'(A, A', \Omega) = S(A, A', \Omega) - a(K)\delta(\Omega) \tag{9a}$$

where the dynamical structure factor $S(A, A', \Omega)$ is defined as

$$S(A, A', \Omega) = \sum_{l,l'} \exp[iK \cdot (l - l')]$$

$$\times \int \frac{\mathrm{d}t}{2\pi} \exp(-i\Omega t)\langle \exp[-iA' \cdot u_{l'}(0)]\exp[iA \cdot u_l(t)]\rangle_T \tag{9b}$$

and $u_l(t)$ is the displacement of the ion at l due to the lattice vibrations, i.e. $x_l(t) = l + u_1((t)$. Note that equation (7) allows for arbitrary combinations of disorder and defect scattering; for example, equation (7) allows for straightforward application to scattering in impure and/or point-defect-containing crystalline solids at finite temperature.

$S(A, A', \Omega)$ is a generalisation of the Van Hove dynamical structure factor [1], i.e.

$$S(K, K, \Omega) = S(K, \Omega) \tag{9c}$$

and $S'(A, A', \Omega)$ is a generalisation of the modified Van Hove dynamical structure factor, defined by Baym [2], i.e.

$$S'(K, K, \Omega) = S'(K, \Omega). \tag{9d}$$

Generalising the development in [3], one obtains

$$\langle \exp[-iA' \cdot u_{l'}(0)] \exp[iA \cdot u_l(t)]\rangle_T = \exp[A' \cdot Z(l - l', t) \cdot A) \tag{10a}$$

where we have expanded u_l and invoked the theorem of Bloch [4] to obtain

$$Z(d, t) = -\sum_{q} w_q [\langle 2n_q + 1\rangle - \langle n_q + 1\rangle \exp(i\theta_{d,t}) - \langle n_q\rangle \exp(-i\theta_{d,t})]. \tag{10b}$$

Here

$$w_q = e_q e_q / 2NM\Omega_q \tag{10c}$$

$d = l - l'$ is an ion spacing in the absence of thermal vibrations, N is the number of ions,

M is the ion mass, Ω_q, n_q and e_q are respectively the phonon frequency, number density and polarisation vector at q, and

$$\theta_{d,t} = q \cdot d + \Omega_q t. \tag{10d}$$

Note that $Z(d, t)$ is a symmetric second-rank tensor that is independent of K, A and A'.

Thus, we can express the dynamical structure factor $S(A, A', \Omega)$ in the form

$$S(A, A', \Omega) = N \sum_d \exp(\mathrm{i} K \cdot d) \int \frac{\mathrm{d}t}{2\pi} \exp(-\mathrm{i}\Omega t) \exp[A \cdot Z(d, t) \cdot A'] \tag{11a}$$

$$= \sum_{n=0} [A \ldots A] \ldots I_n(K, \Omega) \ldots [A' \ldots A']/n! \tag{11b}$$

where $[A \ldots A]$ is an n-fold open product of the vector A. Equation (11b) defines the structure tensor $I_n(K, \Omega)$ of rank $2n$ and is obtained by expanding the exponential in equation (11a) and performing the sum over d and the t integration. (Note that the tensor $I_n(K, \Omega)$ is not uniquely defined by equation (11b): however the most symmetric forms with respect to the left and right inner products are the obvious choice and are intended.)

Combining equations (7) and (11),

$$X(k, k', \Omega) = \sum_{G,H,G',H'} \beta(G)^* \alpha(H)[\beta(G')^* \alpha(H')]^* [V(A)V(A')^* S'(A, A', \Omega)$$

$$+ W(A)W(A')^* a(k)\delta(\Omega)]$$

$$= \sum_{n=1}^{\infty} V_n(k, k')^* \ldots I_n(K, \Omega) \ldots V_n(k, k')/n! + |W_0(k, k')|^2 I_0(K, \Omega) \tag{12}$$

where we have defined the scalar

$$W_0(k, k') = \langle k' | W(x) | k \rangle \tag{13a}$$

and for $n = 1$ to ∞, the rank-n tensor

$$V_n(k, k') = \langle k' | \{[(\mathrm{i}\nabla) \ldots (\mathrm{i}\nabla)]V(x)\} | k \rangle \tag{13b}$$

and we have used the relation

$$\sum_{G,H} \beta(G)^* \alpha(H)[A \ldots A]V(A) = \int \mathrm{d}x \left(\sum_H \beta(H) \exp[\mathrm{i}(k' + H) \cdot x] \right)^*$$

$$\times \{[(\mathrm{i}\nabla) \ldots (\mathrm{i}\nabla)]V(x)\} \left(\sum_G \alpha(G) \exp[\mathrm{i}(k' + G) \cdot x] \right)$$

$$= \langle k' | \{[(\mathrm{i}\nabla) \ldots (\mathrm{i}\nabla)]V(x)\} | k \rangle = V_n(K). \tag{13c}$$

All the dynamical properties of the lattice are contained in the structure tensors $\{I_n(K, \Omega) | n = 0, \infty\}$.

Equation (12) with $\{I_n(K, \Omega) | n = 0, \infty\}$ defined in equations (10) and (11), $W_0(k, k')$ defined in equation (13a) and the $\{V_n(k, k') | n = 1, \infty\}$ defined in equation (13b) constitute the generalised diffraction model expression and are the principal results of this paper. Note that to obtain actual scattering rates one must include appropriate factors (e.g. $(2\pi/h)f(k)[1 - f(k')]$) in equation (12).

3. Plane-wave scattering, n-phonon structure tensor $\Phi_n(K, \Omega)$, Debye–Waller tensor W and the Van Hove dynamical structure factor $S(K, \Omega)$

Since the first term in equation (10b) is independent of d and t, it is useful to define the tensor

$$Z'(d, t) = \sum_q w_a[\langle n_q + 1\rangle \exp(i\theta_{d,t}) + \langle n_q\rangle \exp(-i\theta_{d,t})] \qquad (14a)$$

and

$$W = \sum_q w_q \langle 2n_q + 1\rangle. \qquad (14b)$$

Thus, equation (10b) can be rewritten in the form

$$Z(d, t) = -W + Z'(d, t) \qquad (14c)$$

and since the Debye–Waller exponent $2W(K)$ is simply related to W, viz.

$$2W(K) = K \cdot W \cdot K \qquad (14d)$$

we designate W the (second-rank) Debye–Waller tensor.

Equations (14) suggest that a different factorisation of the scattering rate will be particularly appropriate in the PW case. The treatment of PW scattering leads in a natural way to the introduction of the n-phonon structure tensor $\Phi_n(K, \Omega)$, which is also useful in expressing limiting BW expressions. Thus, equation (2a) becomes

$$|k, i\rangle = \exp(ik \cdot x) |i\rangle \qquad \text{etc.} \qquad (15a)$$

and

$$A, A' \rightarrow K. \qquad (15b)$$

Thus, recalling equation (9), equation (11) yields

$$S(K, \Omega) = N \sum_d \exp(iK \cdot d) \int \frac{dt}{2\pi} \exp(-i\Omega t) \exp[K \cdot Z(d, t) \cdot K] \qquad (16a)$$

$$= \sum_{n=0} [K \ldots K] \ldots I_n(K, \Omega) \ldots [K \ldots K]/n!. \qquad (16b)$$

Employing equations (14c) and (16a), equation (16a) yields

$$S(K, \Omega) = \exp[-2W(K)]\, N \sum_d \exp(iK \cdot d) \int \frac{dt}{2\pi} \exp(-i\Omega t) \exp[K \cdot Z'(d, t) \cdot K]$$

$$= \exp[-2W(K)] \sum_{n=0} [K \ldots K] \ldots \Phi_n(K, \Omega) \ldots [K \ldots K]/n!. \qquad (16c)$$

Equations (14a) and (16c) serve to define the $\Phi_n(K, \Omega)$, which is designated as the n-phonon structure tensor, and $\exp[-2W(K)]$ ($=\exp(-K \cdot W \cdot K)$) is the Debye–Waller factor. (We can also relate the $\{I_n(K, \Omega)\}$ to the $\{\Phi_n(K, \Omega)\}$ by expanding $\exp[-2W(K)]$, forming the product and identifying the tensor coefficients.)

4. The low-order structure tensors

Since the structure tensors play a central role in diffraction models, it is worth while to display the expressions for the first few in some detail. The expressions are deduced by examination of expansions in equations (16).

4.1. The zero-rank structure tensor $I_0(K, \Omega)$ and zero-phonon structure tensor $\Phi_0(K, \Omega)$

$$\Phi_0(K, \Omega) = I_0(K, \Omega) = N \sum_d \exp(iK \cdot d) \int \frac{dt}{2\pi} \exp(-i\Omega t) = a(K)\delta(\Omega) \tag{17}$$

defines the zero-rank structure tensor $I_0(K, \Omega)$ and zero-rank zero-phonon structure tensor $\Phi_0(K, \Omega)$.

4.2. Second-rank structure tensor $I_1(K, \Omega)$ and one-phonon structure tensor $\Phi_1(K, \Omega)$

$$I_1(K, \Omega) = N \sum_d \exp(iK \cdot d) \int \frac{dt}{2\pi} \exp(-i\Omega t) Z(d, t)$$

$$= N \sum_d \exp(iK \cdot d) \int \frac{dt}{2\pi} \exp(-i\Omega t)$$

$$\times \sum_q w_q[-\langle 2n_q + 1\rangle + \langle n_q + 1\rangle \exp(i\theta_{d,t}) + \langle n_q\rangle \exp(-i\theta_{d,t})]$$

$$= -a(K)\delta(\Omega)W + \Phi_1(K, \Omega)$$

$$= I_0(K, \Omega)(-W) + \Phi_1(K, \Omega) \tag{18a}$$

where

$$\Phi_1(K, \Omega) = \sum_q w_q[\langle n_q + 1\rangle a(K + q)\delta(\Omega - \Omega_q) + \langle n_q\rangle a(K - q)\delta(\Omega + \Omega_q)] \tag{18b}$$

is the one-phonon scattering structure tensor, equation (14b) defines the (second-rank) Debye–Waller tensor W and we have used

$$a(K \pm q)\delta(-\Omega \pm \Omega_q) = \sum_d \exp(iK \cdot d) \int \frac{dt}{2\pi} \exp(-i\Omega t) \exp(\pm i\theta_{d,t}). \tag{18c}$$

4.3. Fourth-rank structure tensor $I_2(K, \Omega)$ and the two-phonon structure tensor $\Phi_2(K, \Omega)$

$$I_2(K, \Omega)_{i,i',h',h} = N \sum_d \exp(iK \cdot d) \int \frac{dt}{2\pi} \exp(-i\Omega t) Z(d, t)_{i,h} Z(d, t)_{i',h'}$$

$$= N \sum_d \exp(iK \cdot d) \int \frac{dt}{2\pi} \exp(-i\Omega t)$$

$$\times \sum_{q'} [w_{q'}]_{i',h'}[\langle 2n_{q'} + 1\rangle - \langle n_{q'} + 1\rangle \exp(i\theta'_{d,t}) - \langle n_{q'}\rangle \exp(-i\theta'_{d,t})]$$

$$\times \sum_q [w_q]_{i,h}[\langle 2n_q + 1\rangle - \langle n_q + 1\rangle \exp(i\theta_{d,t}) - \langle n_q\rangle \exp(-i\theta_{d,t})]$$

$$= a(K)\delta(\Omega)[W_2]_{i,i',h',h} - [W]_{i,h}[\Phi_1(K, \Omega)]_{i',h'}$$

$$- [\Phi_1(K, \Omega)]_{i,h}[W]_{i',h'} + [\Phi_2(K, \Omega)]_{i,i',h',h} \qquad (19a)$$

where

$$\Phi_2(K, \Omega) = \sum_{q,q'} \Gamma_{q,q'}[\langle n_q + 1\rangle\langle n_{q'} + 1\rangle a(K + q + q')\delta(\Omega - \Omega_q - \Omega_{q'})$$

$$+ \langle n_q + 1\rangle\langle n_{q'}\rangle a(K + q - q')\delta(\Omega - \Omega_q + \Omega_{q'})$$

$$+ \langle n_q\rangle\langle n_{q'} + 1\rangle a(K - q + q')\delta(\Omega + \Omega_q - \Omega_{q'})$$

$$+ \langle n_q\rangle\langle n_{q'}\rangle a(K - q - q')\delta(\Omega + \Omega_q + \Omega_{q'})] \qquad (19b)$$

is designated as the two-phonon scattering structure tensor,

$$\Gamma_{q,q'} = e_{q'}e_q e_q e_{q'}/[(2NM)^2\Omega_q\Omega_{q'}] \qquad (19c)$$

and

$$[W_2]_{i,i',h',h} = W_{i,h}W_{i'h'} \qquad (19d)$$

where $W_{i,h}$ is the i, h component of the Debye–Waller tensor. (One might designate $[W_2]_{i,i',h',h}$ as the fourth-rank Debye–Waller tensor.)

5. Experimental evaluation of $S(K, \Omega)$, $I_n(K, \Omega)$, W and $\Phi_n(K, \Omega)$

As is well known, $S(K, \Omega)$ may be directly determined by neutron scattering experiments. It is also clear that, in principle, one may deduce the tensor $I_n(K, \Omega)$ from analysis of the expression for $S(K, \Omega)$ contained in equation (16b). Similarly one could deduce W and the $\Phi_n(K, \Omega)$ from analysis of the expression for $S(K, \Omega)$ contained in equation (16c) or from the $I_n(K, \Omega)$. Of course, in practice, the experimental determination of $S(K, \Omega)$ is exacting and the experimental evaluation of $I_n(K, \Omega)$ or $\Phi_n(K, \Omega)$ for $n > 1$ may be impracticable. Nevertheless, it is important to note that the same tensor $I_n(K, \Omega)$ or W and $\Phi_n(K, \Omega)$ appear in the BW expression as in the PW expression and that, in principle, one can deduce the tensor appropriate for treating the BW case from the analysis of PW scattering experiments.

6. The standard expressions

6.1. Plane-wave cases

6.1.1. The standard form: electron scattering in liquid and amorphous metals and neutron scattering

When PW are appropriate basis functions, equations (15) are appropriate and the two forms of equations (16b) and (16c) define the appropriate structure factor, i.e. the

Van Hove dynamical structure factor [1]. Furthermore, when a PW basis is employed, vanishing unperturbed potential ($U(x) = 0$) is appropriate, and thus

$$W_0(k, k') = V_0(k, k') \rightarrow V(K).$$ (20a)

Also, recalling equation (13)

$$V_n(k, k') = [AA \dots A]V(k, k') \rightarrow [KK \dots K]V(K) = V_n(K)$$ (20b)

so that, employing equations (20) and (16b), equation (12) becomes

$$X(K, \Omega) = X(k, k', \Omega)$$

$$= \sum_{n=1} V_n(k, k')^* \dots I_n(K, \Omega) \dots V_n(k, k')/n! + |W_0(k, k')|^2 I_0(K, \Omega)$$

$$= |V(K)|^2 \left(\sum_{n=1}^{\infty} [KK \dots K] \dots I_n(K, \Omega) \dots [KK \dots K]/n! + I_0(K, \Omega) \right)$$

$$= |V(K)|^2 S(K, \Omega).$$ (21)

Equation (21) is immediately recognised as the standard form for electron scattering in liquid and amorphous metals and neutron scattering; i.e. as they must, the BW expressions reduce to the standard forms in the special case of PW.

6.1.2. *Approximate forms*

The approximate forms are based on equation (16c) for PW.

 (a) *Markowitz's approximation.* Markowitz [5] observed that the temperature variation of the electrical resistivity of relatively high-resistivity amorphous metals could be reasonably represented by neglecting all but the elastic scattering term in the expression for $S(K, \Omega)$, i.e.

$$S(K, \Omega) \simeq \exp[-2W(K)]\Phi_0(K, \Omega)$$ (22)

where $\Phi_0(K, \Omega)$ is defined in equation (17). (Generalisation for anisotropic materials is obvious.) The fact that such a drastic approximation yields reasonable agreement with experiment suggests a breakdown of conventional theory of electrical transport in the relatively high-resistivity amorphous metals studied.

 (b) *Sham–Ziman approximation.* The Sham–Ziman [6] approach to approximating the multiphonon contributions to the scattering rate is the most popular. Arguments are presented in [6] to support this procedure, but the simplicity of the resulting forms and their relatively good performance is at the core of their wide acceptance. One assumes that the effect of the multiphonon series is to cancel the effect of the Debye–Waller factor in the one-phonon term in equation (16c), i.e.

$$S(K, \Omega) \simeq \exp[-2W(K)]\Phi_0(K, \Omega) + K \cdot \Phi_1(K, \Omega) \cdot K$$ (23a)

where $\Phi_0(K, \Omega)$ and $\Phi_1(K, \Omega)$ are defined in equations (17) and (18b). For isotropic materials (e.g. amorphous metals), equation (23a) becomes

$$S(K, \Omega) \simeq \exp[-2W(K)]\Phi_0(K, \Omega) + \Phi_1(K, \Omega)K^2.$$ (23b)

 (c) *Other approximations.* Other approximations are employed. Sometimes the multiphonon contributions are simply ignored. Cote and Meisel [7] have compared an

approximation proposed by Hernandez–Calderone *et al* [8] with Sham–Ziman approximation [6]. Little basis for selection of one over the other could be found in fitting experimental data.

6.2. Baym's form: the nearly free-electron (NFE) case

Here we consider an important special case of PW scattering. Strictly speaking PW are not appropriate electron basis functions for the treatment of crystalline materials. Nevertheless PW are frequently a reasonable approximation. We shall refer to such instances as NFE cases.

The NFE procedure for treating scattering of electrons due to lattice vibrations in perfectly crystalline solids is to use PW as approximate basis functions of the unperturbed Hamiltonian H_0, which has a potential of the form

$$\sum_l U(x - l) \qquad \text{where } V(x) = U(x). \tag{24}$$

Thus, $W(K) = 0$, and equation (13) becomes

$$X(k, k', \Omega) = \sum_{n=1}^{\infty} V_n(k, k')^* \dots I_n(K, \Omega) \dots V_n(k, k')/n! \tag{25a}$$

$$= |V(K)|^2 \left(\sum_{n=1}^{\infty} [KK \dots K] \dots I_n(K, \Omega) \dots [KK \dots K]/n! \right) \tag{25b}$$

$$= |V(K)|^2 S'(K, \Omega) \tag{25c}$$

where one uses

$$V_n(k, k') \simeq V_n(K) = [K \dots K]V(K) \tag{25d}$$

which holds for PW. Note that the elastic term $(n = 0)$ is absent from equation (25). Equation (25) is frequently applied in crystalline metals (e.g. [2]); we refer to this form as Baym's approximation or the NFE approximation.

6.3. Bloch-wave scattering in perfect crystals

6.3.1. The standard form.
The procedure for treating scattering of electrons due to lattice vibrations in perfectly crystalline solids (for which a NFE model is inadequate) is to use (approximate) BW solutions of the unperturbed Hamiltonian H_0 as basis functions, where H_0 has a potential of the form

$$\sum_l U(x - l) \qquad \text{where } V(x) = U(x). \tag{26}$$

Thus, $W(K) = 0$, and equation (13) becomes

$$X(k, k', \Omega) = \sum_{n=1}^{\infty} V_n(k, k')^* \dots I_n(K, \Omega) \dots V_n(k, k')/n!. \tag{27}$$

Note that equations (26) and (27) are identical to equations (24) and (25a); however, since equation (25d) does not obtain for BW, the forms in equation (25b) and (25c) do not obtain for BW. As in Baym's approximation, the elastic term $(n = 0)$ is absent from

equation (27), i.e. the 'natural' Bloch electrons are not elastically scattered in perfect crystals. Equation (23) is the appropriate form to substitute for $a(\boldsymbol{K})$ in the expressions for $I_n(\boldsymbol{K}, \Omega)$ in the perfect crystal case.

6.3.2. Approximate forms: Sham–Ziman approximation. The Sham–Ziman approximation [6] was originally introduced in the context of perfect crystals. The Sham–Ziman approximation for BW scattering yields

$$X(k, k', \Omega) \simeq V_1(k, k')^* \cdot \Phi_1(\boldsymbol{K}, \Omega) \cdot V_1(k, k'). \tag{28}$$

Thus, substituting equation (23) for $a(\boldsymbol{K})$, one finds

$$X(k, k', \Omega) = \frac{(2\pi)^3}{V_c} \sum_{G,q} \frac{|e_q \cdot V_1(k, k')|^2}{2M\Omega_q} [\langle n_q + 1 \rangle \delta(\boldsymbol{K} + \boldsymbol{G} + \boldsymbol{q}) \delta(\Omega - \Omega_q)$$

$$- \langle n_q \rangle \delta(\boldsymbol{K} + \boldsymbol{G} - \boldsymbol{q}) \delta(\Omega + \Omega_q)] \tag{29a}$$

$$= \frac{(2\pi)^3}{V_c} \sum_{G,q} |g(k, k')|^2 [\langle n_q + 1 \rangle \delta (\boldsymbol{K} + \boldsymbol{G} + \boldsymbol{g}) \delta(\Omega - \Omega_q)$$

$$- \langle n_q \rangle \delta(\boldsymbol{K} + \boldsymbol{G} - \boldsymbol{q}) \delta(\Omega + \Omega_q)]. \tag{29b}$$

Equation (29) is in the form usually employed to treat electron–phonon interaction-controlled scattering of Bloch electrons in crystalline metals; i.e. the typical study of electron–phonon interaction-controlled processes employing BW electrons implicitly assumes perfect crystallinity and invokes the Sham–Ziman approximation. For example, equation (29) gives the 'first-principles' form† used in the work of Butler *et al* [9]. (One assumes that in [9], $\delta(\boldsymbol{K} - \boldsymbol{q})$ stands for a summation over RLV $\boldsymbol{G}$ on $\delta(\boldsymbol{K} + \boldsymbol{G} - \boldsymbol{q})$.) Thus, the diffraction model origin and the nature of the multiphonon scattering approximation implicitly adopted in standard treatments of electron–phonon interaction-controlled processes are revealed.

7. Electron–phonon spectral functions and static structure factors

When dealing with electron–phonon interaction-controlled phenomena it is customary to define various electron–phonon spectral functions, denoted $\alpha^2(\Omega)F(\Omega)$. For example, the Eliashberg function [10] is an electron–phonon spectral function. The $\alpha^2(\Omega)F(\Omega)$ may be defined by integrating appropriately weighted diffraction model scattering rates over $\boldsymbol{K}$. These electron–phonon spectral functions are of theoretical importance; however, the procedures followed in applying them often obscure the diffraction model origins of the analyses.

On the other hand, when dealing with electron–phonon interaction-controlled phenomena it is also possible to define static structure factors, which would be denoted $S(\boldsymbol{K})$, $I_m(\boldsymbol{K})$, or $\Phi_m(\boldsymbol{K})$. The various static structures factors (or tensor) may be defined by integrating appropriately weighted diffraction model scattering rates over Ω. The x-ray and resistivity static structure factors for amorphous metals, as discussed by Meisel and Cote [11], are examples. The static structure factors, which are wholly determined by the lattice dynamics, are also of theoretical interest and emphasise the diffraction model origins of the analysis being performed.

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† These authors employ this form in a number of papers, of which [9] is typical.

8. Concluding remarks

A generalised diffraction model appropriate for BW electron as well as PW scattering from a dynamic lattice has been presented. It is shown that the resulting model reduces to the standard diffraction model in the case of PW scattering. These findings have the virtue of unifying the treatment of diverse phenomena. For example, neutron scattering in amorphous solids and electron–phonon interaction contributions to electrical transport in perfect crystals are conveniently treated in the context of the generalised diffraction model.

Furthermore, it has been explicitly demonstrated that many important standard expressions appearing in the literature are obtained as approximations to the diffraction model. Thus, the diffraction model origins of the standard expressions is revealed and the nature of the implicit approximations in the standard forms is clarified.

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