Generalized theory of neutron scattering from hydrogen in metals

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A recent analysis by the author of inelastic scattering of neutrons from dilute hydrogen in metals in terms of coherent itinerant-proton energy bands is generalized to include incoherent processes such as the spontaneous decay of the proton from excited-oscillator states to the ground state, as well as incoherent hopping among excited local-oscillator states centered at neighboring interstitial occupancy sites. Similarly, the analysis of Chudley and Elliott of quasielastic neutron scattering and its extension by Rowe, Sköld, Flowtow, and Rush are generalized to include coherent hopping (band transport) in the self-correlation function describing motion of the proton among neighboring oscillator ground states (and, when applicable, among excited states). The general formalism developed here encompasses quasielastic and inelastic scattering and allows for the coexistence of coherent and incoherent processes. At each level of complexity, the expressions obtained for the cross sections are shown to reduce to earlier results in the limits when either the coherent or the incoherent contributions to the neutron bandwidths can be ignored.

I. INTRODUCTION

Recently the structure of excited-state itinerant hydrogen bands in bcc metals has been derived and their relevance to inelastic neutron scatttering experiments discussed.[1] These bands describe the coherent transport of dilute hydrogen (in the α phase) among excited local-oscillator states centered about tetrahedrally coordinated interstitial occupancy sites. In this theory, the elementary excitations for inelastic neutron scattering from hydrogen initially in the oscillator ground state are Bloch states which are taken to be linear combinations of the excited local-oscillator wave functions. The overlap between these excited-state local wave functions leads to energy bands of small but finite width, much as the overlap between neighboring atomic orbitals produces electronic energy bands in semiconductors. It has also been demonstrated in Ref. 1 that these bands allow for a width of the absorption bands in inelastic neutron scattering. The latter stems from the width of the density of states associated with the itinerant hydrogen band, and exists even in the absence of other width-producing processes such as the finite lifetime of the excited-state proton due to decay to the oscillator ground-state emitting phonons, or, in a local description, incoherent hopping of the proton between excited oscillator states centered at different interstitial occupancy sites. Experimentally, the widths of the excited-state hydrogen bands in the bcc metals Nb, Ta, and V are typically $O(10$ meV), as compared with quasielastic peak widths which are less than $O(1$ meV).[2-4] The latter are usually associated with transport of the proton among oscillator ground states at neighboring sites.

The importance of *coherent* transport has been demonstrated experimentally by the direct observation via neutron scattering of tunnel splitting of the ground state of hydrogen in niobium in the presence of defects which produce a two-well trap.[5] This experimental finding together with the observed magnitude of the excited-state bandwidths motivated the analysis in Ref. 1. The theory of neutron-induced transitions to coherent excited states within a two-well system has also been investigated.[6] On the other hand, *incoherent* transport among what are here referred to as the oscillator ground states centered at nearby sites is conventionally associated with the width of the quasielastic neutron scattering peak, following the theory first developed by Chudley and Elliott.[7] There need be no conflict between these ideas. It is entirely possible for the excited-state transport to be dominated by the coherent band process while the (reduced) overlap-induced width of the ground-state band is sufficiently small that incoherent hopping dominates the contribution to quasielastic scattering, at least for temperatures such that the excited-state bands are unoccupied in equilibrium. [Since the excited bands typically lie $O(100$ meV) above the ground state for H in the bcc metals, Nb, Ta, and V, this condition applies over much, but not all, of the temperature range experimentally investigated.[4]] Which process dominates the contributions to the widths of the excited states of hydrogen in these metals, when describing inelastic neutron scattering inducing transitions thereto, devolves on quantitative issues which must be settled for each case. In any event, to be able even to frame the relevant questions requires a more general theory which allows for *both* coherent and incoherent transport of the (electronically shielded) proton while in the excited state, as well as allowing for its decay to the ground state. Conversely, a generalization of the Chudley-Elliott (CE) theory to include coherent as well as incoherent transport processes in the description of quasielastic neutron scattering seems worthwhile.

I develop such a general theory here for both quasielastic and inelastic neutron scattering and show how the results of the earlier theories are recovered in the relevant limits. For simplicity, the analysis is given in detail for the special case when the hydrogen occupancy sites form a Bravais lattice and the degeneracy of the excited oscillator states is ignored. This case suffices to illustrate the main physical points without introducing the complication of

the additional structure present where there is more than one occupancy site in the primitive cell and/or account is taken of the degeneracy of the excited local-oscillator levels. Then a brief outline is given of the analysis required when, in addition to the simultaneous presence of coherent and incoherent processes, these structural effects are taken into account. (For the case when only incoherent hopping contributes to the quasielastic peak width, this nontrivial structural generalization of the CE theory was first given by Rowe *et al.*[3] Similarly, when only band transport contributes to the width of the excitation bands observed by inelastic neutron scattering, the effects of added structure have been treated by this author in Ref. 1.)

To achieve the synthesis required when both coherent and incoherent processes play a role in either quasielastic or inelastic scattering of neutrons from hydrogen in metals, it is convenient to develop each problem in terms of two somewhat distinct, albeit equivalent, formal approaches. The analysis of intraband and interband transitions is readily carried out by straightforward calculation of the scattering matrix using the band states and Fermi pseudopotential (and taking a thermal average over the initial proton states), without first making the standard Van Hove transformation,[8] i.e., without first expressing the neutron cross section in terms of the self-correlation function for the proton. (Of course, since the two formalisms are equivalent, the band problem can always be recast in the language of correlation functions.) On the other hand, in the CE theory one directly obtains the proton self-correlation function $G(\vec{x},t)$ by solving a master equation and then Fourier transforms to obtain the scattering function, $S(\vec{q},\omega)=(1/2\pi)G(\vec{q},\omega)$. To include both band and incoherent-hopping contributions to the widths of the neutron cross section, it is convenient to invoke both formalisms, using as a link between them, the well-known result that *coherent* hopping between local sites leads to a band description.

To introduce notation, I shall conclude this section by recalling the result, obtained in Ref. 1, for the differential cross section $d^2\sigma/d\Omega\, d\epsilon$ for inelastic scattering of neutrons from hydrogen in metals, inducing interband transitions of the shielded proton to the excited-oscillator bands. The quoted result applies for temperatures such that only the oscillator ground-state band is occupied in equilibrium. Equation (1) is also restricted to the special case, discussed earlier, of a Bravais occupancy-site lattice, and oscillator degeneracy is ignored. Then

$$\frac{d^2\sigma}{d\Omega\, d\epsilon}=\frac{k_F}{k_I}\,|\bar{a}|^2\,|\tilde{F}(\vec{q})|^2 g(\omega)\,, \tag{1}$$

where

$$g(\omega)=(1/N)\sum_{\vec{k}}\delta(E_{ex}(\vec{k})-E_0+\omega) \tag{2}$$

and

$$\tilde{F}(\vec{q})=\int d^3x\, e^{-i\vec{q}\cdot\vec{x}} f^*_{ex}(\vec{x}) f_0(\vec{x})\,. \tag{3}$$

Here $g(\omega)$ is the density-of-states function (normalized to unity) that is associated with the dispersion of the itinerant hydrogen excited-state band $E_{ex}(\vec{k})$ when the ground-state band E_0 is assumed flat,[9] ω and $\vec{q}$ denote the energy and momentum transfer to the neutron, and $\tilde{F}(\vec{q})$ is the form factor associated with the neutron-induced transition of the proton from an isolated local oscillator in its ground state $f_0(\vec{x})$ to its excited state $f_{ex}(\vec{x})$. (The lattice Debye-Waller factor is, by definition, included in the renormalized scattered length $\bar{a}$.) The product $|\tilde{F}(\vec{q})|^2 g(\omega)$ is equal to the unrenormalized scattering function $S(\vec{q},\omega)$. The shape and width of the inelastic neutron scattering band at fixed $\vec{q}$ are clearly determined by the (normalized) density-of-states function $g(\omega)$, given by Eq. (2).[1]

In Sec. II, I shall derive a similar expression for the *intra*band transitions induced by the scattered neutrons on protons among states within the ground-state band. In the hypothetical absence of incoherent processes, these intraband transitions determine the width of the quasielastic peak. Next, the CE analysis, which assumes incoherent hopping is reviewed (partly, to establish notation), then repeated under the assumption of *coherent* hopping. The latter result is then compared with the intraband result, allowing identification of the Fourier transform of the coherent self-correlation function of the proton with the normalized intraband-transition density-of-states function $g(\vec{q},\omega)$. Finally, the formalism is developed which includes the presence of both coherent and incoherent processes and the resulting expression for the quasielastic neutron scattering cross section is shown to reduce to the earlier results, when either the incoherent or coherent process dominates. [It is perhaps worth remarking that because of differences in scale, there need be no inconsistency in neglecting the width of the ground-state band entirely when computing the neutron cross section for interband transitions to the much wider excited-state band, as was done to obtain Eq. (2), while allowing that the ground-state band has finite width when dealing with quasielastic scattering of the proton among states within it.] The inclusion of incoherent processes when treating inelastic neutron scattering inducing *inter*band transitions of the proton to an excited band is discussed in Sec. III, as is the contribution of *intra*band processes within the *excited* band to quasielastic neutron scattering at elevated temperatures. The analyses in Secs. II and III are limited to the special case, discussed earlier, of one hydrogen occupancy site per primitive cell. In Sec. IV the effects of additional structure and of the degeneracy of the oscillator states on the cross sections are included. Section V contains a summary and discussion of the results. A further generalization of the results of Sec. IV is given in Appendix A.

II. THE GROUND STATE AND QUASIELASTIC SCATTERING

A. Intraband transitions

Neglecting, for the moment, the (usually dominant) incoherent contributions to the quasielastic peak, the sole source of its width is then derived from intraband scattering within the ground-state band in which a proton, initially with momentum $\vec{k}$ and energy $E_0(\vec{k})$, is scattered to

a state of momentum $\vec{k}-\vec{q}$ and energy $E_0(\vec{k}-\vec{q})$. The initial (I) and final (F) proton wave functions associated, in general, with bands labeled by α and α' are Bloch sums over the local-oscillator states centered at lattice sites $\vec{L}$. We have

$$\psi_I(\vec{x})=\psi_\alpha^{\vec{k}}(\vec{x})=(1/N)^{1/2}\sum_{\vec{L}} e^{i\vec{k}\cdot\vec{L}} f_\alpha(\vec{x}-\vec{L}) ,$$
$$\psi_F(\vec{x})=\psi_{\alpha'}^{\vec{k}'}(\vec{x})=(1/N)^{1/2}\sum_{\vec{L}'} e^{i\vec{k}'\cdot\vec{L}'} f_{\alpha'}(\vec{x}-\vec{L}') . \tag{4}$$

Here $\alpha'=\alpha=0$. Using the same normalization of the reduced T matrix t_{FI} as that employed in Ref. 1 and invoking the Fermi pseudopotential leads to the result

$$t_{FI}=(2\pi a/m)\int d^3x\, e^{-i\vec{q}\cdot\vec{x}}\psi_F^*(\vec{x})\psi_I(\vec{x})$$
$$=(2\pi a/m)\delta_{\vec{k}',\vec{k}-\vec{q}+\vec{K}}F(\vec{q}) , \tag{5}$$

where $F(\vec{q})$ is the oscillator ground-state form factor,

$$F(\vec{q})=\int d^3x\, e^{-i\vec{q}\cdot\vec{x}}\,|f_0(\vec{x})|^2 . \tag{6}$$

This leads to the differential cross section

$$\left[\frac{d^2\sigma}{d\Omega\, d\epsilon}\right]_I=\frac{k_F}{k_I}|\bar{a}|^2|F(\vec{q})|^2\delta(\omega+E_0(\vec{k}-\vec{q})-E_0(\vec{k})) \tag{7}$$

associated with the initial proton state $|I\rangle=|0,\vec{k}\rangle$. Averaging over these initial states,

$$\frac{d^2\sigma}{d\Omega\, d\epsilon}=Z^{-1}\sum_I e^{-\beta E_I}\left[\frac{d^2\sigma}{d\Omega\, d\epsilon}\right]_I , \tag{8}$$

where Z is the partition sum,

$$Z=\sum_I e^{-\beta E_I}=\sum_{\vec{k}} e^{-\beta E_0(\vec{k})} , \tag{9}$$

and $\beta=1/k_BT$. It is tacitly assumed here that the temperature T is sufficiently low that only the ground-state band is occupied. Typically, for H in V, Nb, or Ta, this condition is satisfied when $k_BT\ll O(100\text{ meV})$. I also assume that the temperature is sufficiently high that all states in the ground-state band are equally occupied, i.e., $k_BT>O(1\text{ meV})$ in the above examples. Then $e^{-\beta E_0}/Z=1/N$, where N is the number of unit cells. Hence

$$\frac{d^2\sigma}{d\Omega\, d\epsilon}=\frac{k_F}{k_I}|\bar{a}|^2|F(\vec{q})|^2 g_0(\vec{q},\omega) , \tag{10}$$

where

$$g_0(\vec{q},\omega)=\frac{1}{N}\sum_{\vec{k}}\delta(E_0(\vec{k}-\vec{q})-E_0(\vec{k})+\omega) . \tag{11}$$

Here $g_0(\vec{q},\omega)$ is the (normalized) oscillator ground-state intraband-transition density-of-states function. For arbitrary but fixed $\vec{q}$, it satisfies the relation $\int d\omega\, g_0(\vec{q},\omega)=1$. In the limit where this band is flat, E_0 is independent of $\vec{k}$ and $g_0=\delta(\omega)$. g_0 also assumes this form at $\vec{q}=0$ for arbitary dispersion in $E_0(\vec{k})$.

B. Incoherent hopping between local-oscillator states

For the purpose of later discussion, I include a brief review of the well-known CE method.[7] Let $P(\vec{L},t)$ be the probability that at time t the proton is at the discrete position $\vec{L}$. Classically, $P(\vec{L},t)$ satisfies the master equation

$$\frac{dP(\vec{L},t)}{dt}=-(1/\tau)P(\vec{L},t)+(1/n\tau)\sum_{\vec{l}}P(\vec{L}+\vec{l},t) , \tag{12}$$

where $1/\tau$ is the probability per unit time that the proton jumps to any of the n nearest-neighbor sites at $\vec{L}+\vec{l}$. Fourier transforming and assuming that for $t>0$, $P(\vec{q},t)=P(\vec{q},0)\exp[-\Gamma(\vec{q})t]$, leads to the CE result,

$$\Gamma(\vec{q})=(1/\tau)\left[1-(1/n)\sum_{\vec{l}}e^{i\vec{q}\cdot\vec{l}}\right] . \tag{13}$$

Under the CE factorization assumption,

$$G(\vec{q},t)=G_v(\vec{q},t)G_{\rm ih}(\vec{q},t) \tag{14}$$

(where, in my notation, v and ih denote vibrational and incoherent hopping, respectively) and requiring $P(\vec{L},0)=\delta_{\vec{L}O}$, leads to the identification $G_{\rm ih}(\vec{L},t)=P(\vec{L},t)$, whence[10]

$$G_{\rm ih}(\vec{q},t)=\exp[-\Gamma(\vec{q})t]\quad(t>0) . \tag{15}$$

Then under standard assumptions, by Fourier transform,

$$\frac{G_{\rm ih}(\vec{q},\omega)}{2\pi}=\frac{\Gamma(\vec{q})/\pi}{\omega^2+\Gamma(\vec{q})^2} \tag{16}$$

and

$$\frac{d^2\sigma}{d\Omega\, d\epsilon}=\frac{k_F}{k_I}|\hat{a}|^2\frac{G_{\rm ih}(\vec{q},\omega)}{2\pi} . \tag{17}$$

Here, by definition, $|\hat{a}|^2$ contains all effects associated with the vibrational part $G_v(\vec{q},t)$, properly convoluted. Thus, at fixed $\vec{q}$, the result for $G_{\rm ih}(\vec{q},\omega)/2\pi$ and, hence for $d^2\sigma/d\Omega\, d\epsilon$, is a Lorentzian function of ω of half-width $\Gamma(\vec{q})$. This completes the review of the CE method.

C. Coherent hopping between local-oscillator ground states

Let $\psi(\vec{L},t)=\langle\vec{L}\,|\,\psi(t)\rangle$ be the amplitude that at time t the proton is at site $\vec{L}$. That is, $P(\vec{L},t)=|\psi(\vec{L},t)|^2$. Then in the $|\vec{L}\rangle$ representation (and with $\hbar=1$), the Schrödinger equation, $i\partial/\partial t\,|\psi\rangle=H\,|\psi\rangle$, reads

$$i\frac{d\langle\vec{L}\,|\,\psi(t)\rangle}{dt}=\sum_{\vec{L}'}\langle\vec{L}\,|\,H\,|\,\vec{L}'\rangle\langle\vec{L}'\,|\,\psi(t)\rangle . \tag{18}$$

Assuming the hopping matrix elements have the form $\langle\vec{L}\,|\,H\,|\,\vec{L}\rangle=A$ for $\vec{L}'=\vec{L}$ and $\langle\vec{L}\,|\,H\,|\,\vec{L}+\vec{l}\rangle=B$ for all nearest-neighbor jumps, with $\langle\vec{L}\,|\,H\,|\,\vec{L}'\rangle=0$ otherwise,[11] the amplitude $\psi(\vec{L},t)$ satisfies

$$i\frac{d\psi(\vec{L},t)}{dt}=A\psi(\vec{L},t)+B\sum_{\vec{l}}\psi(\vec{L}+\vec{l},t) . \tag{19}$$

Letting

$$\psi(\vec{L},t)=(1/N)^{1/2}\sum_{\vec{q}}e^{i\vec{q}\cdot\vec{L}}\psi(\vec{q},t)\ , \tag{20}$$

and assuming $\psi(\vec{q},t)=\psi(\vec{q},0)\exp[-iE_0(\vec{q})t]$, leads to the band energy

$$E_0(\vec{q})=A+B\sum_{\vec{l}}e^{i\vec{q}\cdot\vec{l}}\ . \tag{21}$$

[When $B=-A/n$, Eq. (21) is the analog of Eq. (13) for the decay constant $\Gamma(\vec{q})$.]

I again factor $G(\vec{q},t)$ as in Eq. (14), but with $G_{\rm ch}(\vec{q},t)$ substituted for $G_{\rm ih}(\vec{q},t)$, where the notation ch signifies coherent hopping. Identifying $G_{\rm ch}(\vec{L},t)$ with $|\psi(\vec{L},t)|^2$ and employing Eq. (20),

$$\begin{aligned}G_{\rm ch}(\vec{q},t)&=\sum_{\vec{k}}\psi^*(\vec{k}-\vec{q},t)\psi(\vec{k},t)\\&=\sum_{\vec{k}}e^{-iE_0(\vec{k})t+iE_0(\vec{k}-\vec{q})t}\psi^*(\vec{k}-\vec{q},0)\psi(\vec{k},0)\ .\end{aligned} \tag{22}$$

Like $G_{\rm ih}(\vec{q},t)$, $G_{\rm ch}(\vec{q},t)$ is normalized such that $G_{\rm ch}(\vec{q},t=0)=1$, whence[10]

$$\sum_{\vec{k}}\psi^*(\vec{k}-\vec{q},0)\psi(\vec{k},0)=1\ . \tag{23}$$

If, consistent with Eq. (23), I impose the more stringent initial condition $\psi(\vec{L},t=0)=\delta_{\vec{L},0}$, then Eq. (22) becomes

$$G_{\rm ch}(\vec{q},t)=(1/N)\sum_{\vec{k}}e^{-iE_0(\vec{k})t+iE_0(\vec{k}-\vec{q})t}\ . \tag{24}$$

Hence its Fourier transform $G_{\rm ch}(\vec{q},\omega)$ satisfies

$$\frac{G_{\rm ch}(\vec{q},\omega)}{2\pi}=(1/N)\sum_{\vec{k}}\delta(E_0(\vec{k}-\vec{q})-E_0(\vec{k})+\omega) \tag{25}$$

and the cross section is given by [cf. Eq. (17)]

$$\frac{d^2\sigma}{d\Omega\,d\epsilon}=\frac{k_F}{k_I}|\hat{a}|^2\frac{G_{\rm ch}(\vec{q},\omega)}{2\pi}\ . \tag{26}$$

Comparison of Eq. (25) with Eq. (11) and of Eq. (26) with Eq. (10) allows identification of $G_{\rm ch}(\vec{q},\omega)/2\pi$ with the intraband density of states $g_0(\vec{q},\omega)$ and of $|\hat{a}|^2$ with $|\bar{a}|^2|F(\vec{q})|^2$. To complete the identification with the band picture discussed in Sec. II A, I further assume that the hopping matrix elements are such that the resulting eigenvalues $E_0(\vec{k})$ coincide with those determined by the relevant overlap integrals in the tight-binding picture based upon wave functions given by Eq. (4).

D. Coexistent coherent and incoherent transport between the local-oscillator ground states

Generalizing Eq. (14), I assume

$$G(\vec{q},t)=G_v(\vec{q},t)G_h(\vec{q},t)\ , \tag{27}$$

where $G_h(\vec{q},t)$ describes both incoherent hopping and coherent hopping (band transport), and furthermore, I assume

$$G_h(\vec{q},t)=G_{\rm ih}(\vec{q},t)G_{\rm ch}(\vec{q},t)\ , \tag{28}$$

where $G_{\rm ih}(\vec{q},t)$ and $G_{\rm ch}(\vec{q},t)$ are given by Eqs. (15) and (24), respectively. [As is true of each of its factors, $G_h(\vec{q},t=0)=1$.] Generalizing Eq. (26) by replacing $G_{\rm ch}(\vec{q},\omega)$ with $G_h(\vec{q},\omega)$, the Fourier transform of $G_h(\vec{q},t)$ as determined above, I find

$$\frac{d^2\sigma}{d\Omega\,d\epsilon}=\frac{k_F}{k_I}|\bar{a}|^2|F(\vec{q})|^2\frac{G_h(\vec{q},\omega)}{2\pi}\ , \tag{29}$$

where

$$\frac{G_h(\vec{q},\omega)}{2\pi}=\frac{1}{N}\sum_{\vec{k}}\frac{\Gamma(\vec{q})/\pi}{[\omega+E_0(\vec{k}-\vec{q})-E_0(\vec{k})]^2+[\Gamma(\vec{q})]^2}\ . \tag{30}$$

Together Eqs. (29) and (30) describe the quasielastic neutron scattering cross section when both incoherent hopping and coherent band transport are present. The differential cross section is seen to be given by a sum of Lorentzians (one for each $\vec{k}$, averaged over $\vec{k}$), each of which has a halfwidth $\Gamma(\vec{q})$ which depends upon the momentum transfer $\vec{q}$ but is independent of $\vec{k}$. This circumstance is a consequence of the factorization assumption [Eq. (28)]. As is true of the band density of states $g_0(\vec{q},\omega)$, $G_h(\vec{q},\omega)/2\pi$ satisfies the normalization condition

$$\int d\omega[G_h(\vec{q},\omega)/2\pi]=1\ . \tag{31}$$

I shall now demonstrate how one recovers the CE or coherent band results under the appropriate limiting conditions. (i) When the coherent bandwidth is much smaller than $\Gamma(\vec{q})$, the quantity $E_0(\vec{k}-\vec{q})-E_0(\vec{k})$ appearing in Eq. (30) may be neglected, whence

$$\frac{G_h(\vec{q},\omega)}{2\pi}=\frac{1}{N}\sum_{\vec{k}}\frac{\Gamma(\vec{q})/\pi}{\omega^2+\Gamma(\vec{q})^2}=\frac{G_{\rm ih}(\vec{q},\omega)}{2\pi}\ , \tag{32}$$

where $G_{\rm ih}(\vec{q},\omega)$ is given by Eq. (16). That is, the CE result is recovered in this limit. (ii) To consider the limiting case when $\Gamma(\vec{q})\to 0$, it is convenient to rewrite Eq. (30) in the form

$$\frac{G_h(\vec{q},\omega)}{2\pi}=\frac{1}{N}\sum_{\vec{k}}\frac{1}{2\pi i}\left[\frac{1}{\omega+E_0(\vec{k}-\vec{q})-E_0(\vec{k})-i\Gamma(\vec{q})}-\text{c.c.}\right]\ . \tag{33}$$

When $\Gamma(\vec{q})$ is treated as an infinitesimal γ, one can employ the identity

$$\frac{1}{x-x_0\mp i\gamma}=P\left[\frac{1}{x-x_0}\right]\pm i\pi\delta(x-x_0)\ , \tag{34}$$

which is valid as $\gamma\to 0^+$. Thus Eq. (33) is reduced to the form

$$\frac{G_h(\vec{q},\omega)}{2\pi}=(1/N)\sum_{\vec{k}}\delta(E_0(\vec{k}-\vec{q})-E_0(\vec{k})+\omega)\ . \quad (35)$$

That is, in this limit, $G_h(\vec{q},\omega)/2\pi=G_{ch}(\vec{q},\omega)/2\pi=g_0(\vec{q},\omega)$, where $g_0(\vec{q},\omega)$ is the intraband density of states.

The second limit generally applies when the coherent bandwidth is large compared with $\Gamma(\vec{q})$, a situation unlikely to occur for the oscillator ground state, but one which could in principle occur, especially when there is a contribution to the quasielastic scattering from protons present in the excited-state band. Independently of the width of the coherent band, the transition density of states $g_0(\vec{q},\omega)\to\delta(\omega)$ as $\vec{q}\to 0$. Hence, the limit described by Eq. (35) does not apply in the small-$\vec{q}$ regime. In this region, where ω is also small, one is in the domain of classical diffusion; the limit given by Eq. (32) applies; and $\Gamma(\vec{q})=D\,|\,\vec{q}\,|^2$, where D is the diffusion constant. However the analogous situation does not occur when one considers *inelastic* neutron scattering of the proton from the ground to excited oscillator states. There, in principle, either the band or the incoherent-transport limits can apply at all $\vec{q}$. Because of the existence of the band gap Δ for such processes, by definition $|\omega|>\Delta$ even as $\vec{q}\to 0$, and the small-$(\omega,\vec{q})$ correspondence limit is inaccessible. Inelastic scattering is discussed further in Sec. III.

III. THE ROLE OF EXCITED STATES IN INELASTIC AND QUASIELASTIC SCATTERING

A. Inelastic scattering

When the inelastic scattering of neutrons from hydrogen in the oscillator ground state, thereby inducing transitions to the excited states, can be described purely in terms of intraband scattering, the expression for $d^2\sigma/d\Omega\,d\epsilon$ is given by Eqs. (1)–(3). The development leading to these results is given in Ref. 1 and will not be repeated here. For our present purpose, it is convenient to consider a slightly more general expression for the density-of-states function g than is given by Eq. (2). Allowing for dispersion in the ground-state band, $g(\omega)\to g(\vec{q},\omega)$ and is given by the interband equivalent of Eq. (11):

$$g(\vec{q},\omega)=(1/N)\sum_{\vec{k}}\delta(E_{ex}(\vec{k}-\vec{q})-E_0(\vec{k})+\omega)\ . \quad (36)$$

[When dispersion of the ground-state band can be neglected, E_0 is independent of $\vec{k}$ and Eq. (36) reduces to Eq. (2).]

Within the local-oscillator picture, the appropriate generalization of the CE relation [cf. Eq. (12), Sec. II B] is

$$\frac{dP'(\vec{L},t)}{dt}=-(1/\tau_d'+1/\tau_h')P'(\vec{L},t)+(1/n\tau_h')\sum_{\vec{l}}P'(\vec{L}+\vec{l},t)\ . \quad (37)$$

Here $P'(\vec{L},t)$ is the probability that at time t the proton is present in an *excited*-oscillator state at $\vec{L}$, $1/\tau_h'$ is the probability per unit time that the proton hops (incoherently) to any of the n nearest-neighbor positions at $\vec{L}+\vec{l}$, and $1/\tau_d'$ is the probability per unit time that the proton in the excited-oscillator state undergoes spontaneous decay to the oscillator ground state. The analysis proceeds in parallel with that reviewed in Sec. II B, leading to the result

$$G_i'(\vec{q},t)=\exp[-\Gamma'(\vec{q})t]\quad (t>0)\ , \quad (38)$$

where

$$\Gamma'(\vec{q})=(1/\tau_d')+(1/\tau_h')\left[1-(1/n)\sum_{\vec{l}}e^{i\vec{q}\cdot\vec{l}}\right]\ . \quad (39)$$

To discuss interband transitions in the language of correlation functions, I shall consider the counterpart of Eq. (26),

$$\frac{d^2\sigma}{d\Omega\,d\epsilon}=\frac{k_F}{k_I}\,|\,\hat{a}'\,|^2\frac{G_{ch}'(\vec{q},\omega)}{2\pi}\ . \quad (40)$$

The quantity $G_{ch}'(\vec{q},\omega)/2\pi$ is associated with the coherent hopping (i.e., band transport) between excited-oscillator states, whereas $|\,\hat{a}'\,|^2$ contains all renormalizations to the Fermi scattering length due to the vibrations of the hydrogen. Invoking the equivalence between coherent hopping and band transport leads to the identification $G_{ch}'(\vec{q},\omega)/2\pi=g(\vec{q},\omega)$, as given by Eq. (36), whence comparison of Eq. (40) with Eq. (1) imples

$$|\,\hat{a}'\,|^2=|\,\bar{a}\,|^2\,|\,\tilde{F}(\vec{q})\,|^2\ ,$$

where $\tilde{F}(\vec{q})$ is given by Eq. (3).[12] (The lattice Debye-Waller factor is again, by definition, contained in $\bar{a}$.) This factorization is the same as that obtained for the case of intraband processes, discussed earlier, except that the quantities $F(\vec{q},\omega)$ and $g_0(\vec{q},\omega)$ which appear in the relevant intraband expressions are replaced by the quantities $\tilde{F}(\vec{q},\omega)$ and $g(\vec{q},\omega)$, respectively [cf. Eqs. (11) and (36), Eqs. (6) and (3).]

To include both coherent and incoherent processes, Eq. (40) is generalized by substituting the quantity $G'(\vec{q},\omega)$ for the quantity $G_{ch}'(\vec{q},\omega)$ therein, where $G'(\vec{q},\omega)$ is the Fourier transform of $G'(\vec{q},t)$, which is assumed, as in the intraband case, to be equal to a product of incoherent and coherent factors,[13]

$$G'(\vec{q},t)=G_i'(\vec{q},t)G_{ch}'(\vec{q},t)=e^{-\Gamma'(\vec{q})t}G_{ch}'(\vec{q},t)\ . \quad (41)$$

From the above it is clear that $G_{ch}'(\vec{q},t)/2\pi$ is the inverse Fourier transform of the interband density-of-states function $g(\vec{q},\omega)$, which is given by Eq. (36). Thus Eq. (41) can be expressed in the form

$$G'(\vec{q},t)=e^{-\Gamma'(\vec{q})t}(1/N)\sum_{\vec{k}}e^{iE_{ex}(\vec{k}-\vec{q})t-iE_0(\vec{k})t}\ . \quad (42)$$

It follows that the general result for the inelastic cross section is

$$\frac{d^2\sigma}{d\Omega\,d\epsilon}=\frac{k_F}{k_I}\,|\,\bar{a}\,|^2\,|\,\tilde{F}(\vec{q})\,|^2\frac{G'(\vec{q},\omega)}{2\pi}\ , \quad (43)$$

where

$$\frac{G'(\vec{q},\omega)}{2\pi}=\frac{1}{N}\sum_{\vec{k}}\frac{\Gamma'(\vec{q})/\pi}{[\omega+E_{ex}(\vec{k}-\vec{q})-E_0(\vec{k})]^2+\Gamma'(\vec{q})^2} . \tag{44}$$

When dispersion within the ground-state band can be ignored, we can set $E_0(\vec{k})=0$ without loss of generality. Then

$$\frac{G'(\vec{q},\omega)}{2\pi}=\frac{1}{N}\sum_{\vec{k}}\frac{\Gamma'(\vec{q})/\pi}{[\omega+E_{ex}(\vec{k})]^2+\Gamma'(\vec{q})^2} . \tag{45}$$

Equations (43) and (44) or (45) constitute the main results of this section. It remains to examine the two limiting cases when (i) the contribution due to incoherent processes (spontaneous decay and incoherent hopping) greatly exceeds the coherent width induced by overlap of the wave functions, or (ii) the incoherent width $\Gamma'(\vec{q})$ can be treated as an infinitesimal. To discuss case (i), let Δ be the band gap for excitation from the ground-state to the excited-state bands. When the coherent bandwidths are small compared with $\Gamma'(\vec{q})$, we may set $E_{ex}(\vec{k}-\vec{q})-E_0(\vec{k})=\Delta$ in Eq. (44) and identify Δ with the excitation energy of the local oscillator. The summand is then independent of $\vec{k}$, leading to a factor N under summation. This leads to the simplification

$$\frac{G'(\vec{q},\omega)}{2\pi}=\frac{\Gamma'(\vec{q})/\pi}{(\omega+\Delta)^2+[\Gamma'(\vec{q})]^2} . \tag{46}$$

Equation (46) is the natural generalization of the CE result given by Eq. (16). When case (ii) applies, Eq. (44) can be written in a form analogous to Eq. (33) and, treating $\Gamma'(\vec{q})$ as an infinitesimal, use can be made of the identity Eq. (34), whence

$$\frac{G'(\vec{q},\omega)}{2\pi}=(1/N)\sum_{\vec{k}}\delta(E_{ex}(\vec{k}-\vec{q})-E_0(\vec{k})+\omega) . \tag{47}$$

That is, in case (ii) we recover the result $G'(\vec{q},\omega)/2\pi=g(\vec{q},\omega)$, the interband density of states as given by Eq. (36). (Similar manipulation of the approximate result [Eq. (45)] leads to the density $g(\omega)$, as given by Eq. (2).)

B. Quasielastic scattering

The considerations in this section differ from those in the earlier discussion in that, heretofore, it has been universally assumed that the equilibrium occupation of the excited-state bands is negligible [i.e., $k_BT\ll\Delta$, where typically $\Delta=O(100\text{ meV})$ for H in bcc metals]. Here I shall consider the case when $k_BT<\Delta$ but thermal occupation of the excited-state band of lowest energy is not wholly negligible. When this situation occurs, quasielastic scattering of neutrons from protons initially in the excited band must be included. Under this condition

$$\frac{d^2\sigma}{d\Omega\,d\epsilon}=\frac{1}{z}\left[\left[\frac{d^2\sigma}{d\Omega\,d\epsilon}\right]_0+e^{-\beta\Delta}\left[\frac{d^2\sigma}{d\Omega\,d\epsilon}\right]_{ex}\right] , \tag{48}$$

where $z=1+\exp(-\beta\Delta)$ and it has been assumed that k_BT exceeds the width of the excited-state band at these elevated temperatures. The quantity $(d^2\sigma/d\Omega\,d\epsilon)_0$ is the quasielastic cross section associated with the ground state, as given by Eqs. (29) and (30) and $(d^2\sigma/d\Omega\,d\epsilon)_{ex}$ is the cross section associated with quasielastic scattering from protons in the excited-state band. The latter is given by an expression of the form displayed by Eq. (29) with the quantities $F(\vec{q})$ and $G_h(\vec{q},\omega)$ therein replaced by $F_{ex}(\vec{q})$ and $G_h''(\vec{q},\omega)$, respectively. $F_{ex}(\vec{q})$, which is be distinguished from the transition form factor $\tilde{F}(\vec{q})$, is given by the relation

$$F_{ex}(\vec{q})=\int d^3x\, e^{-i\vec{q}\cdot\vec{x}}\,|f_{ex}(\vec{x})|^2 . \tag{49}$$

The quantity $G''(\vec{q},\omega)$ can be obtained from the corresponding interband expression for $G'(\vec{q},\omega)$ [Eq. (44)] by replacing the function $E_0(\vec{k})$ therein by $E_{ex}(\vec{k})$. Equation (48) allows an additional temperature dependence of the quasielastic scattering cross section, above and beyond that implicit in the T dependence of $\Gamma(\vec{q})$ [and $\Gamma'(\vec{q})$] through the temperature dependence of the hopping probabilities $1/\tau$ (and $1/\tau_h'$) as provided, for example, by small-polaron theory. Since both terms in Eq. (48) contribute in the small-$(\vec{q},\omega)$ regime, a similar additional temperature dependence is implied for the diffusion constant.

IV. REALISTIC COMPLICATIONS

Here the complications due to crystal structure and degeneracy of the local-oscillator states are included. Let h be the number of energetically equivalent hydrogen occupancy sites in the primitive cell and d be the degree of degeneracy of the oscillator states. I shall again assume the temperature is such that only the subbands associated with the oscillator ground-state band are occupied by the proton and that all states within these subbands are equally likely to be occupied.

A. Band transitions

The general case was treated in Ref. 1. The result for the cross section is

$$\frac{d^2\sigma}{d\Omega\,d\epsilon}=\frac{k_F}{k_I}|\bar{a}|^2\frac{1}{Nh}\times\sum_{\vec{k}}\sum_{\alpha}\sum_{\alpha'}|F_{\alpha'\alpha}(\vec{q},\vec{k})|^2\delta(\omega+E_{\alpha'}(\vec{k}-\vec{q})-E_\alpha(\vec{k})) \tag{50}$$

where the sum on α is restricted to the subbands within the ground-state band. For intraband transitions the sum on α' is similarly restricted, whereas for interband transitions the sum on α' extends over those subbands associated with a particular excitation of the local oscillator (in narrow-band approximation). In general, the expression for $F_{\alpha'\alpha}(\vec{q},\vec{k})$ depends upon the expansion coefficients of the band eigenstates and the form factor $F^a_{n'n}(\vec{q})$ associated with the (generally anisotropic) local oscillator at position $\vec{\rho}_a$ is the unit cell. The latter is given by the general relation

$$F^{a}_{n'n}(\vec{q})=\int d^3x\, e^{-i\vec{q}\cdot\vec{x}} f^{*}_{n'a}(\vec{x}) f_{na}(\vec{x}) . \tag{51}$$

Here by assumption, only the ground state is initially occupied, whence $n=0$. As shown in Ref. 1, in first approximation, the expression for the cross section takes on the simpler form

$$\frac{d^2\sigma}{d\Omega\, d\epsilon}=\frac{k_F}{k_I}\,|\bar{a}|^2\,|\hat{F}(\vec{q})|^2 g(\vec{q},\omega) , \tag{52}$$

where

$$|\hat{F}(\vec{q})|^2=(1/h)\sum_{a=1}^{h}\sum_{n'=1}^{d}|F^{a}_{n'n}(\vec{q})|^2 \tag{53}$$

and

$$g(\vec{q},\omega)=(1/Nh^2d)\sum_{\alpha'=1}^{hd}\sum_{\alpha=1}^{h}\sum_{\vec{k}}\delta(\omega+E_{\alpha'}(\vec{k}-\vec{q})-E_{\alpha}(\vec{k})) . \tag{54}$$

This $g(\vec{q},\omega)$ is the transition density of states for either intraband or interband processes. As such, it represents a slight generalization of the result given in Ref. 1. When, for interband transitions, dispersion of the ground-state band can be neglected, we can set $E_{\alpha}(\vec{k})=0$ without loss of generality and Eq. (54) reduces to the simpler form[1]

$$g(\omega)=(1/Nhd)\sum_{\alpha'=1}^{hd}\sum_{\vec{k}}\delta(\omega+E_{\alpha'}(\vec{k})) . \tag{55}$$

That is, $g(\omega)$ is the normalized sum of the ordinary densities of states associated with each subband in the excited band being probed by the neutron. Like $g(\vec{q},\omega)$, it satisfies the relation $\int d\omega\, g(\omega)=1$.

B. Incoherent hopping

The effect of including structure within the CE framework was shown by Rowe *et al.*[3] to lead to a set of coupled master equations. The resulting cross section is of the CE form [cf. Eq. (17), Sec. II B], except that $G_{\rm ih}(\vec{q},\omega)$ is the Fourier transform of a quantity more general than that given here by Eq. (15). That is

$$G_{\rm ih}(\vec{q},t)=\frac{1}{h}\sum_{j=1}^{h}\left|\sum_{a=1}^{h}e^{-i\vec{q}\cdot\vec{\rho}_a}\langle a\,|\,\Gamma_j(\vec{q})\rangle\right|^2 e^{-\Gamma_j(\vec{q})t} . \tag{56}$$

In the present notation, the quantities $\langle a\,|\,\Gamma_j(\vec{q})\rangle$ are the expansion coefficients of the eigenvectors belonging to the decay-constant eigenvalues $\Gamma_j(\vec{q})$ of the Hermitian matrix which results from the coupled master equations in the method of Ref. 3. They satisfy the normalization condition

$$\sum_{a=1}^{h}|\langle a\,|\,\Gamma_j(\vec{q})\rangle|^2=1 . \tag{57}$$

This completes the brief summary of the method of Ref. 3. For the purpose of later discussion, it is convenient to approximate Eq. (56) by replacing the coefficients $\langle a\,|\,\Gamma_j(\vec{q})\rangle$ by their rms value $(1/h)^{1/2}$ times $\vec{q}$-dependent phase factors of modulus one. Then, averaging over these phases, $G_{\rm ih}(\vec{q},t)$ takes on the simpler approximate form

$$G_{\rm ih}(\vec{q},t)=(1/h)\sum_{j=1}^{h}e^{-\Gamma_j(\vec{q})t} . \tag{58}$$

C. Simultaneous coherent and incoherent contributions to the widths

Again employing the connection between coherent hopping and band transport, the transition density-of-states function $g(\vec{q},\omega)$, given by Eq. (54), is identified with the Fourier transform of the proton self-correlation function for coherent hopping, i.e., $G_{\rm ch}(\vec{q},\omega)/2\pi=g(\vec{q},\omega)$. Hence

$$G_{\rm ch}(\vec{q},t)=(1/Nh^2d)\sum_{\alpha'=1}^{hd}\sum_{\alpha=1}^{h}\sum_{\vec{k}}e^{iE_{\alpha'}(\vec{k}-\vec{q})t-iE_{\alpha}(\vec{k})t} . \tag{59}$$

Letting

$$G(\vec{q},t)=G_{\rm ih}(\vec{q},t)G_{\rm ch}(\vec{q},t) , \tag{60}$$

where $G_{\rm ih}$ is given by Eq. (58), and generalizing Eq. (52), expressed in terms of $G_{\rm ch}(\vec{q},\omega)$, by replacing the latter with $G(\vec{q},\omega)$, leads to the result[14]

$$\frac{d^2\sigma}{d\Omega\, d\epsilon}=\frac{k_F}{k_I}\,|\bar{a}|^2\,|\hat{F}(\vec{q})|^2\frac{G(\vec{q},\omega)}{(2\pi)} , \tag{61}$$

where

$$\frac{G(\vec{q},\omega)}{2\pi}=\frac{1}{Nh^3d}\sum_{j=1}^{h}\sum_{\alpha'=1}^{hd}\sum_{\alpha=1}^{h}\sum_{\vec{k}}\frac{\Gamma_j(\vec{q})/\pi}{[\omega+E_{\alpha'}(\vec{k}-\vec{q})-E_{\alpha}(\vec{k})]^2+[\Gamma_j(\vec{q})]^2} . \tag{62}$$

These equations, together with Eqs. (51) and (53), express the cross section for neutron scattering from hydrogen in metals under the general conditions that both coherent and incoherent processes contribute to the bandwidths, when the complications of structure and oscillator degeneracy are included. They apply to either intraband or interband transitions depending upon whether α' is summed over the subbands associated with the oscillator ground state (in which case the set $\{\alpha'\}$ coincides with the set $\{\alpha\}$ and $d=1$) or α' is summed over the subbands associated with the excited state of the local oscillator. When applied to inelastic scattering, the incoherent aspects, as analyzed in Ref. 3, have been generalized slightly to account for spontaneous decay of the excited oscillator to the ground state, in a way that is illustrated in Sec. III A for the special case of one hydrogen occupancy site per unit cell.

To evaluate $G(\vec{q},\omega)$ as given by Eq. (62) requires a knowledge of the band-state eigenvalues $E_\alpha(\vec{k})$ as determined for the case of H in bcc metals in Ref. 1.[15] It is also necessary to know the eigenvalues $\Gamma_j(\vec{q})$ of the decay matrix which result from the solution of the coupled master equations in the method of Ref. 3. However, it is *not* necessary to input the eigen*vectors* of either the band problem or the decay-matrix problem. This circumstance is a consequence of the rms., random-phase approximations made in reducing Eq. (50) to the form given by Eqs. (52)–(54) for the band case and in reducing Eq. (56) to the simpler Eq. (58) for the decay matrix. [In the latter case, the simplification achieved is manifest, whereas for the former, since the initial complexity is hidden in the quantity $F_{\alpha'\alpha}(\vec{q},\vec{k})$, the considerable simplification attained is not immediately obvious.[16]] It is possible to eliminate the rms., random-phase approximation that entered into the derivation of Eq. (62), but at the cost of introducing considerable complexity. To evaluate the analog of Eqs. (53) and (62) which is obtained in the more general analysis for the product $|\hat{F}(\vec{q})|^2 G(\vec{q},\omega)$ requires inputting not only the eigenvalues, but also the eigenvectors of both the band and decay-matrix problems. Because of this requirement, the present discussion is limited to the result given by Eqs. (61), (62), and (53). (For completeness, a brief sketch of the extended analysis is given in Appendix A.)

Within the framework defined by Eqs. (61), (62), and (53), it remains to be shown that the expression for the cross section reduces to the earlier results under the relevant limiting conditions. When the incoherent contributions to the neutron widths dominate in either quasielastic or inelastic scattering, we may approximate Eq. (62) by setting

$$E_{\alpha'}(\vec{k}-\vec{q})-E_\alpha(\vec{k})=\Delta' , \tag{63}$$

where $\Delta'=0$ for quasielastic scattering, and $\Delta'=\Delta$ for inelastic scattering. In this incoherent limit Δ can be identified with the excitation energy of the local oscillator. Given Eq. (63), many of the sums in Eq. (62) can be done trivially, leading to the result

$$\frac{G(\vec{q},\omega)}{2\pi}=\frac{1}{h}\sum_{j=1}^{h}\frac{\Gamma_j(\vec{q})/\pi}{(\omega+\Delta')^2+[\Gamma_j(\vec{q})]^2} . \tag{64}$$

Conversely, when the quantities $\Gamma_j(\vec{q})$ can be treated as infinitesimals, use of the identity [Eq. (34)] renders trivial the sum on j in Eq. (62), with the consequence that $G(\vec{q},\omega)/2\pi$, as given by Eq. (62), is reduced to the transition density-of-states functions $g(\vec{q},\omega)$ of Eq. (54) [or the simpler $g(\omega)$ of Eq. (55), when dispersion of the ground-state band is ignored]. Thus the band results are recovered in this limit.

V. SUMMARY AND DISCUSSION

A general formalism for treating quasielastic and inelastic scattering of neutrons from dilute hydrogen in metals in the α phase has been developed.[17] Basically, the results of Ref. 1 for inelastic interband scattering have been generalized to include incoherent processes such as spontaneous decay of the proton from excited-oscillator states and hopping among them to nearby sites with loss of phase memory. Also, earlier analyses[3,7] of quasielastic scattering in terms of incoherent hopping of the proton among local-oscillator ground states centered at neighboring sties have been generalized to include coherent hopping (intraband scattering) and decay. The analysis has proceeded by identifying the Fourier transform of the proton self-correlation function describing coherent hopping with the appropriate intraband or interband transition density-of-states function $g(\vec{q},\omega)$, which enters in a pure band picture. Then the Chudley-Elliott factorization assumption concerning the space Fourier transform $G(\vec{q},t)$ of the correlation function is extended to include not only the vibrational and incoherent-hopping motion of the proton, but also that due to coherent hopping.

When the analysis is limited to one hydrogen occupancy site per primitive cell, the main results are given by Eqs. (29) and (30) for quasielastic scattering of protons within the ground-state band, Eqs. (43) and (44) or (45) for inelastic interband scattering, and Eq. (48) which applies to quasielastic scattering at elevated temperatures when account must be taken of equilibrium occupancy of the excited-state band by the proton. In each case, the general expressions are shown to reduce to earlier results in the limits when either coherent or incoherent processes can be neglected. Applied to quasielastic scattering, the original Chudley-Elliott result [Eqs. (16) and (17)] or the intraband cross section [Eqs. (10) and (11)] are recovered in these limits, respectively. As for inelastic scattering, in the limit when incoherent processes dominate, Eq. (46) follows. It represents a modification of the CE result to apply to inelastic scattering. In the limit when this process is dominated by the coherent interband scattering, the expression for the cross section reduces to a form given by Eqs. (1)–(3), obtained earlier by Casella.[1]

When there is more than one hydrogen occupancy site per unit cell and account is taken of the degeneracy of the local-oscillator excited states, the most general expression for the neutron cross section is quite complex and is given by Eqs. (A5), (A6), and (A3) in Appendix A. These relations apply to either quasielastic or inelastic scattering (depending upon the assignment of the band or local-oscillator indices) and include incoherent as well as coherent contributions to the proton self-correlation function. In the incoherent limit the expression for the cross section reduces to the form given by Eq. (A7), which represents a generalization of the earlier results of Rowe *et al.*[3] to apply to inelastic as well as the quasielastic scattering. In the coherent limit the cross section is given by Eq. (50), the band result given earlier by Casella.[1] Implementation of the general results [Eqs. (A5) and (A6)] requires obtaining the eigenvalues *and* eigenvectors of the energy-band *and* decay-matrix equations of Refs. 1 and 3, respectively.

The analysis can be simplified considerably by making the rms random-phase approximation discussed in Sec. V and employed earlier for pure interband transitions in Ref. 1. Within this approximation, the general expression for the cross section is given by Eqs. (61), (62), and (53). Implementation of these equations requires knowledge of the

eigenvalues of the energy-band and decay-matrix problems, but not of their eigenvectors. In the band limit these equations reduce to the forms given by Eqs. (52)—(54), obtained in Ref. 1, whereas in the incoherent regime, the result is given by Eq. (64). The latter represents, on the one hand, a generalization of the earlier result of Ref. 3 to apply to inelastic as well as quasielastic scattering, and on the other hand, a simplifying approximation in that the decay-matrix eigenvectors are not required to evaluate it.

The general results obtained are essentially model-independent in that the form of the incoherent hopping and decay probabilities are left unspecified, as are the few irreducible overlap integrals which determine[1] the scale of the energy bands. As is well known,[4] the hopping probabilities are sometimes described in terms of small-polaron theory, which introduces a known temperature dependence for the quasielastic neutron scattering, and for hydrogen diffusion. Equation (48) allows an additional temperature dependence associated with the occupancy of the excited-state band at elevated temperatures. Experimentally, there is some evidence for this effect in the diffusion of H in Nb, but more complex behavior is found for H in other bcc metals.[4] As was pointed out in Ref. 1, the band picture correctly orders the observed[2] magnitudes of the peak widths in inelastic neutron scattering from dilute hydrogen in the bcc metals: $\Gamma(\mathrm{V}) > \Gamma(\mathrm{Nb}) > \Gamma(\mathrm{Ta})$. The band picture was also shown[1] to be consistent with data[2] for inelastic scattering from hydrogen trapped near dilute O or N in Nb, although none of these experiments can yet be thought of as providing direct evidence for the existence of protonic energy bands in metals. Recently, Richter, Rush, and Rowe[18] have fitted their data on inelastic scattering of neutrons from hydrogen trapped near Ti and Cr impurities in Nb with a few Lorentzians, a result which is obtained here for hydrogen in the α phase of undefected samples in the incoherent limit [cf. Eqs. (46) and (64)].

To conclude, the formalism developed here is sufficiently general so that, together with specific model assumptions, it provides a framework for expressing the results of quasielastic and inelastic scattering of neutrons from dilute hydrogen in metals under a wide variety of experimental conditions. Perhaps the best approach is to adopt the simplest form which suffices to describe the data of any given experiment, proceeding to the next level of complexity as required.

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APPENDIX A

Here the differential cross section for neutron scattering from hydrogen initially in the oscillator ground state is derived when structural effects are included, as in Sec. IV, but without making the rms., random-phase approximation, which was emplolyed to obtain Eqs. (61) and (62) of the text. That is, the exact Eq. (56), rather than the approximate Eq. (58), is employed for $G_{\mathrm{ih}}(\vec{q},t)$. Similarly, $G_{\mathrm{ch}}(\vec{q},\omega)/2\pi$ is no longer equated with $g(\vec{q},\omega)$, as given by Eq. (54). Instead, it is defined by the relation [cf. Eq. (52)],

$$\frac{d^2\sigma}{d\Omega\, d\epsilon}=\frac{k_F}{k_I}\,|\bar{a}\,|^2\,|\hat{F}(\vec{q})\,|^2\frac{G_{\mathrm{ch}}(\vec{q},\omega)}{(2\pi)}\ , \tag{A1}$$

when $d^2\sigma/d\Omega\, d\epsilon$ is equated to the *exact* expression given by Eq. (50) and $|\hat{F}(\vec{q},\omega)|^2$ remains defined by Eqs. (51) and (53). [Of course, when the rms random-phase approximation is made, $G_{\mathrm{ch}}(\vec{q},\omega)/2\pi$ can again be identified with $g(\vec{q},\omega)$, as defined by Eq. (54).] From Eqs. (A1) and (50), inverting the time Fourier transform $G_{\mathrm{ch}}(\vec{q},\omega)$ leads to the result

$$G_{\mathrm{ch}}(\vec{q},t)=[1/Nh\ |\hat{F}(\vec{q})\,|^2]\sum_{\alpha=1}^{h}\sum_{\alpha'=1}^{hd}\sum_{\vec{k}}|F_{\alpha'\alpha}(\vec{q},\vec{k})\,|^2\exp[iE_{\alpha'}(\vec{k}-\vec{q})t-iE_{\alpha}(\vec{k})t]\ , \tag{A2}$$

where[1]

$$F_{\alpha'\alpha}(\vec{q},\vec{k})=\sum_{a=1}^{h}\sum_{n'=1}^{d}e^{-i\vec{q}\cdot\vec{\rho}_a}\langle E_{\alpha'}(\vec{k}-\vec{q})\,|\,n'a\,\rangle\langle na\,|\,E_{\alpha}(\vec{k})\rangle F^{a}_{n'n}(\vec{q})\ . \tag{A3}$$

The quantities $\langle na\,|\,E_{\alpha}(\vec{k})\rangle$ are expansion coefficients of the band eigenstates $\psi^{\vec{k}}_{\alpha}(\vec{x})$ in terms of the basis $\psi^{\vec{k}}_{na}(\vec{x})$:

$$\psi^{\vec{k}}_{na}(\vec{x})=(1/N)^{1/2}\sum_{\vec{L}}e^{i\vec{k}\cdot\vec{L}}f_{na}(\vec{x}-\vec{L}-\vec{\rho}_a)\ . \tag{A4}$$

It can be verified from Eqs. (A2) and (A3) that $G_{\mathrm{ch}}(\vec{q},t=0)=1$. Similarly, from Eq. (56), $G_{\mathrm{ih}}(\vec{q},t=0)=1$. Again letting $G(\vec{q},t)=G_{\mathrm{ih}}(\vec{q},t)G_{\mathrm{ch}}(\vec{q},t)$, it follows that the generalized function $G(\vec{q},t)$ satisfies the same initial condition. Substituting its Fourier transform $G(\vec{q},\omega)$ for the quantity $G_{\mathrm{ch}}(\vec{q},\omega)$ in Eq. (A1), I obtain

$$\frac{d^2\sigma}{d\Omega\, d\epsilon}=\frac{k_F}{k_I}\,|\bar{a}\,|^2S(\vec{q},\omega)\ , \tag{A5}$$

where

$$S(\vec{q},\omega)=(1/Nh^2)\sum_{j=1}^{h}\sum_{\alpha'=1}^{hd}\sum_{\alpha=1}^{h}\sum_{\vec{k}}|F_{\alpha'\alpha}(\vec{q},\vec{k})|^2\left|\sum_a e^{-i\vec{q}\cdot\vec{\rho}_a}\langle a\,|\,\Gamma_j(\vec{q})\rangle\right|^2\frac{\Gamma_j(\vec{q})/\pi}{[\omega+E_{\alpha'}(\vec{k}-\vec{q})-E_\alpha(\vec{k})]^2+[\Gamma_j(\vec{q})]^2}\ . \tag{A6}$$

Taken together with Eqs. (A3) and (51), Eqs. (A5) and (A6) constitute the generalization of Eqs. (61), (62), and (53) of the text. Evaluation of $S(\vec{q},\omega)$ requires inputing not only the eigenvalues $E_\alpha(\vec{k})$ and $\Gamma_j(\vec{q})$ of the energy-band and decay-matrix problems, but also the expansion coefficients $\langle na\,|\,E_\alpha(\vec{k})\rangle$ and $\langle a\,|\,\Gamma_j(\vec{q})\rangle$ of their respective eigenvectors.

When incoherent effects dominate, it can be shown that the expression for the cross section reduces to the approximate form

$$\frac{d^2\sigma}{d\Omega\,d\epsilon}=\frac{k_F}{k_I}|\bar{a}|^2|\hat{F}(\vec{q})|^2(1/h)\sum_j\left|\sum_a e^{-i\vec{q}\cdot\vec{\rho}_a}\langle a\,|\,\Gamma_j(\vec{q})\rangle\right|^2\left[\frac{\Gamma_j(\vec{q})/\pi}{(\omega+\Delta')^2+[\Gamma_j(\vec{q})]^2}\right], \tag{A7}$$

where Δ' is defined in the text. If, moreover, the rms, random-phase approximation is made, then the absolute square of the sum on a reduces to unity, and Eq. (A7) reduces to the result given by Eqs. (61) and (64) of the text. Conversely, when the incoherent widths $\Gamma_j(\vec{q})$ can be treated as infinitesimals, Eq. (A6) reduces to a form such that, together with Eq. (A5), the general band expression given by Eq. (50) of the text is recovered. Finally, when, in addition, the rms random-phase approximation is made, the approximate form for the cross section given by Eqs. (52), (53), and (54) or (55) is recovered.

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[9]In Ref. 1, the quantity E_0 was chosen as a reference level and set equal to zero.

[10]Here $G_{ih}(\vec{q},t)=NG^D_{ih}(\vec{q},t)$ where N is the number of unit cells and $G^D_{ih}(\vec{q},t)$ is the Fourier transform of the discrete correlation function $G_{ih}(\vec{L},t)$. That is,

$$G^D_{ih}(\vec{q},t)=(1/N)\exp[-i\Gamma(\vec{q})t]\ .$$

Thus $G_{ih}(\vec{q},t=0)=1$. It is the continuum function $G_{ih}(\vec{q},\omega)$ which appears in the scattering function $S(\vec{q},\omega)$. Similarly, $G_{ch}(\vec{q},t=0)=NG^D_{ch}(\vec{q},t=0)=1$.

[11]The restriction to nearest-neighor jumps, both here and in the discussion of the CE method is not essential.

[12]In making this comparison, the quantity $g(\omega)$ in Eq. (1) is to be thought of as replaced by the more general function $g(\vec{q},\omega)$ as defined by Eq. (36).

[13]Since the incoherent function $G_i'(\vec{q},t)$ includes spontaneous decay as well as hopping, the subscript i is used in place of ih and the product function $G'(\vec{q},t)$ is written without subscript, even though the vibrations have been factored out. Henceforth, the latter practive is employed throughout.

[14]Here the symbol G_{ih} applies to either quasielastic or inelastic processes and the quantity $\Gamma_j(\vec{q})$ is no longer distinguished by a prime when referring to the latter.

[15]In Ref. 1, the bands are only determined modulo a few irreducible overlap integrals, which are treated as disposable parameters. Moreover, consideration is limited to the structure of the first two excited-state bands in bcc metals.

[16]The somewhat involved expression for $F_{\alpha'\alpha}(\vec{q},\vec{k})$ need not concern us here, but is required for the further generalization affected in Appendix A [cf. Eq. (A3)].

[17]As noted in Refs. 1 and 2, the inelastic cross sections for the scattering of neutrons from hydrogen associated with interstitial traps, such as O and N in Nb, resemble that for scattering from dilute hydrogen in the undefected α phase. Thus the analysis of the pure α phase is of some relevance for these defected systems as well. Moreover, hydrogen trapping by these impurities inhibits the transition to the ϵ phase permitting low-temperature studies of systems related to the theory developed here.

[18]D. Richter, J. J. Rush, and J. M. Rowe, Phys. Rev. B 27, 6227 (1983).