

Appearance and Effect of the Debye-Waller Factor in the Transport Coefficients of Simple Normal Metals*

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Analogous to the theory of the diffraction of x rays and neutrons by the lattice vibrations of crystals, the scattering of electrons in a metal by thermal vibrations gives rise to a temperature-dependent Debye-Waller factor in the matrix element. The factor is derived and its possible effects on electrical resistivity discussed for the case where Bloch functions are used for the electron wave function. A detailed numerical calculation for an umklapp process involving a particular phonon was performed, for cesium at room temperature, with the result that the new matrix element is about 0.7 times the 1937 Bardeen result, and consequently the contribution to the resistivity about 0.5 times the Bardeen value. It is even a possibility that, for some phonons, the matrix element may increase.

1. INTRODUCTION

IN the scattering of x rays, neutrons, and γ rays by crystals, it has long been known that the temperature-dependent Debye-Waller factor enters in the expressions for the scattering cross sections. This factor represents the effect of the "system fluctuations" of the lattice vibrations on the scattering, and tends to smooth out sharp peaks in the coherent scattering. This results in broadened Laue spots, for example, and puts a limit on the proportion of recoilless transitions in the Mössbauer effect, for another example. One is tempted to ask: Does this factor appear in the ordinary scattering of electrons by lattice vibrations; i.e., in the transport properties of a metal, and if so, what sort of alterations would it cause?

As may be expected, the Debye-Waller factor enters in a simple way on the rigid-ion model with shielding if we use plane waves for the electron wave functions. [See the $\mathbf{K}=0$ term of Eq. (27) below.] It would decrease the resistivity, a result entirely analogous to that in the above-mentioned topics. The situation for the electrons in a metal is slightly different since they are not plane waves, but Bloch functions. That this might be significant can be seen from the observation that the details of the lattice vibrations that the Debye-Waller factor takes into account have to do with the motion of a charge which is the rigid-ion core, and at the same time the deviation of the Bloch wave from a plane wave is mainly significant in the region of the cell which is near the core. Thus, we might expect that if the effect of the deviation of the Bloch functions from plane waves is large, then the Debye-Waller factor may be important. Our calculations have shown for a particular phonon that the plane-wave result is very close to the Bardeen value (which used the nearly free electron type Bloch function), but that this is fortuitous in the following sense. If one forms the Bardeen result

by adding to the plane-wave term the other waves which correspond to the (nonzero) vectors of the reciprocal lattice (see below), then the series does not immediately begin to converge, nor does it seem to converge after many thousands of such vectors are taken into account. The effect of the Debye-Waller factor sets in well before the convergence does. We made such a calculation for a particular phonon at high temperatures, and there is involved considerable computational error; nevertheless we believe it allows us to say that the effect of the Debye-Waller factor appears not to be a minor matter, at least at first glance. In order to get entirely significant results, one should compute the total effect on the electrical resistivity, say. But it would require such an enormous amount of numerical work that it was rejected as unfeasible at the present time.

The derivation of the effect in the electrical resistivity is contained in Sec. 2 below, with some intermediate steps taken in the Appendices. In Sec. 3, we discuss a former calculation of Bardeen in which the effect of the deviation of the electron wave functions from plane waves had been estimated. It is convenient to discuss the Debye-Waller factor effect in terms of the Bardeen treatment, and such a discussion concludes Sec. 3. We end the paper with a short summary of the characteristics of the matrix element that appears in the transport coefficients of metals.

2. DERIVATION

We start from the results of the variational theory for the electrical resistivity ρ . We shall have to appeal to a previous paper¹ to get our basic expression; the details are given in Appendix A. We start then with

$$\rho = C \int u^2 du \left\langle \hbar \omega \int dE' P(\mathbf{k}, \mathbf{k}') [(1 - e^{-z})^{-1} \delta_{E', E + \hbar \omega} + (e^z - 1)^{-1} \delta_{E', E - \hbar \omega}] \right\rangle, \quad (1)$$

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¹ M. Bailyn, Phys. Rev. **120**, 381 (1960).

where C is given by Eq. (A12) in Appendix A. We list below some of the notation in (1) and elsewhere.

- \mathbf{k} =initial-electron wave vector; $E \equiv E(\mathbf{k})$.
- \mathbf{k}' =final-electron wave vector (after collision with a phonon); $E' \equiv E(\mathbf{k}')$;
- \mathbf{K} =vector of reciprocal lattice,
- $\mathbf{s} \equiv -\mathbf{k}' + \mathbf{k}$,
- $\mathbf{e}(j\sigma)$ =unit vector in direction of polarization of $j\sigma$ phonon,
- $\mathbf{k} \cdot \mathbf{k}' / k k' = \cos \theta$,
- $u = \sin(\theta/2)$, ($u = 0 \cdots 1$),
- $\mathbf{u}(l)$ =displacement of l th ion from its equilibrium position $\mathbf{R}(l)$,
- $u(\mathbf{k}, \mathbf{r})$ =coefficient in the Bloch function [see Eq. (10)],
- σ =phonon wave vector,
- j =phonon polarization index ($j = 1, 2, 3$),
- $\omega(j\sigma)$ =phonon frequency,
- $\omega(\mathfrak{N})$ =probability expression in Eq. (5),
- $z = \hbar\omega/\kappa T$,
- N =number of atoms in crystal,
- Δ =volume of crystal,
- $\Delta_0 = \Delta/N$ =atomic volume,
- $\Omega(x) = [\sin(xt/2\hbar)/(xt/2\hbar)]^2 t$.

The pseudomomentum law that emerges from the transition probability $P(\mathbf{k}, \mathbf{k}')$ is of the form [see Eq. (21) below]

$$\mathbf{s} = -\mathbf{k}' + \mathbf{k} = \sigma + \mathbf{K}. \quad (2)$$

The angle brackets in (1) mean an average over all interactions \mathbf{k}, \mathbf{k}' which have the same $|\mathbf{k} - \mathbf{k}'|$ magnitude (i.e., over all directions \mathbf{s} for a given s). The first term in the square bracket of Eq. (1) represents the absorption of a phonon; the second term, the emission of a phonon.

The quantity $P(\mathbf{k}, \mathbf{k}')$ is what concerns us in this article. It is defined from first order perturbation theory as

$$P(\mathbf{k}, \mathbf{k}') = \sum (\mathfrak{N}) \omega(\mathfrak{N}) \sum (\mathfrak{N}') \hbar^{-2} |\langle \mathbf{k}' \mathfrak{N}' | \delta V | \mathbf{k} \mathfrak{N} \rangle|^2 \times \Omega[E(\mathbf{k}) + E(\mathfrak{N}) - E(\mathbf{k}') - E(\mathfrak{N}')], \quad (4)$$

i.e., a sum over the final phonon configurations \mathfrak{N}' and an average over the initial configurations \mathfrak{N} , the weighting factor in the average being

$$\omega(\mathfrak{N}) = \prod_{\sigma j} (1 - e^{-z}) \exp[-n(j\sigma)z]. \quad (5)$$

A configuration for the phonons specifies the $3N$ occupation numbers $n(j\sigma)$. These numbers are designated as $n(j\sigma)'$ in the configuration \mathfrak{N}' , etc. The quantity Ω acts like a delta function and gives as usual

$$\int dE' \Omega[E' - E + E(\mathfrak{N}') - E(\mathfrak{N})] = 2\hbar \int dy \left(\frac{\sin y}{y} \right)^2 = 2\pi \hbar \delta[E' - E + E(\mathfrak{N}') - E(\mathfrak{N})], \quad (6)$$

where δ is a Kronecker delta function. The wave function Ψ for the system is written as a product of an electron wave function $\psi(\mathbf{k}', \mathbf{r})$ and the phonon configuration wave function $\Phi(\mathfrak{N})$, the latter itself a product of $3N$ functions for the phonon modes. Thus the matrix element can be written

$$\langle \mathbf{k}' \mathfrak{N}' | \delta V | \mathbf{k} \mathfrak{N} \rangle = \langle \mathfrak{N}' | \langle \mathbf{k}' | \delta V | \mathbf{k} \rangle | \mathfrak{N} \rangle. \quad (7)$$

Now the perturbation in the potential will be assumed to be such that the shielding of the ion by the conduction electrons, and the "antishielding" of the given electron by its accompanying hole can be accounted for in the form

$$\langle \mathbf{k}' | \delta V | \mathbf{k} \rangle = S(\mathbf{k}, \mathbf{k}') \langle \mathbf{k}' | \delta V_{\text{ion}} | \mathbf{k} \rangle, \quad (8)$$

where δV_{ion} is the perturbation from the ions alone. The justification for (8) is that there are many calculations which yield precisely this result.^{2,3} Even if the electron wave function is not a plane wave, but a Bloch function, a sum of such terms will result, and our considerations will then apply to each term.⁴ The shielding factor S thus can be removed from the matrix element.

δV_{ion} is computed on the rigid ion model as

$$\delta V_{\text{ion}}(\mathbf{r}) = \sum_l [v(\mathbf{r} - \mathbf{R}(l) - \mathbf{u}(l)) - v(\mathbf{r} - \mathbf{R}(l))], \quad (9)$$

where $\mathbf{u}(l)$ is the displacement of the l ion from its equilibrium position $\mathbf{R}(l)$, and $v(\mathbf{r})$ is the potential at the point \mathbf{r} from an ion at the origin. $v(\mathbf{r})$ should contain exchange effects between conduction and core electrons, and core polarization effects. We shall use Bloch functions

$$\psi(\mathbf{k}, \mathbf{r}) = \Delta^{-1/2} e^{i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{k}, \mathbf{r}) = \Delta^{-1/2} e^{i\mathbf{k} \cdot \mathbf{r}} [u_0(\mathbf{r}) + u_1(\mathbf{r}) + \cdots], \quad (10)$$

where $u(\mathbf{k})$ [not to be confused with $\mathbf{u}(l)$] is periodic with the periodicity of the lattice. We can then write

$$\begin{aligned} \langle \mathbf{k}' | \delta V_{\text{ion}} | \mathbf{k} \rangle &= \sum_l \Delta^{-1} \int d^3 \mathbf{r} e^{i\mathbf{s} \cdot \mathbf{r}} u(\mathbf{k}, \mathbf{r}) u(\mathbf{k}', \mathbf{r})^* \\ &\quad \times [v(\mathbf{r} - \mathbf{R}(l) - \mathbf{u}(l)) - v(\mathbf{r} - \mathbf{R}(l))] \end{aligned} \quad (11a)$$

$$\begin{aligned} &= \sum_l e^{i\mathbf{s} \cdot \mathbf{R}(l)} \int d^3 \mathbf{x} \psi(\mathbf{k}, \mathbf{x}) \psi(\mathbf{k}', \mathbf{x})^* \\ &\quad \times [v(\mathbf{x} - \mathbf{u}(l)) - v(\mathbf{x})]. \end{aligned} \quad (11b)$$

In going from (11a) to (11b) we have changed the variable of integration from \mathbf{r} to $\mathbf{x} = \mathbf{r} - \mathbf{R}(l)$ and employed the periodic nature of $u(\mathbf{k}, \mathbf{r})$; i.e., $u(\mathbf{k}, \mathbf{r} + \mathbf{R}) = u(\mathbf{k}, \mathbf{r})$. To proceed, we Fourier-analyze the ion

² J. Bardeen, Phys. Rev. **52**, 688 (1937).

³ M. Bailyn, Phys. Rev. **117**, 974 (1960); see Eq. (29). See also D. Hone, Phys. Rev. **120**, 1600 (1960).

⁴ See reference 3, left-hand column of p. 981, Eq. (24) would keep the sum over n that appears in Eq. (15).

potential:

$$v(\mathbf{r}) = N^{-1} \sum_{\mathbf{q}} v_{\mathbf{q}} e^{-i\mathbf{q} \cdot \mathbf{r}}$$

$$v_{\mathbf{q}} = \frac{1}{\Delta_0} \int_{\Delta_0}^{\infty} e^{i\mathbf{q} \cdot \mathbf{r}} v(\mathbf{r}) d^3\mathbf{r}, \quad (12a)$$

giving

$$v(\mathbf{x} - \mathbf{u}(l)) - v(\mathbf{x}) = N^{-1} \sum_{\mathbf{q}} v_{\mathbf{q}} e^{-i\mathbf{q} \cdot \mathbf{x}} [e^{i\mathbf{q} \cdot \mathbf{u}(l)} - 1]. \quad (12b)$$

Thus we find upon substituting (12b) into (11b), and the result into (7),

$$\langle \mathbf{k}' \mathfrak{N}' | \delta V_{\text{ion}} | \mathbf{k} \mathfrak{N} \rangle = N^{-1} \sum_{l\mathbf{q}} e^{i\mathbf{s} \cdot \mathbf{R}(l)} v_{\mathbf{q}} U(\mathbf{k}\mathbf{k}', \mathbf{q}) \times \langle \mathfrak{N}' | e^{i\mathbf{q} \cdot \mathbf{u}(l)} - 1 | \mathfrak{N} \rangle, \quad (13)$$

where

$$U(\mathbf{k}\mathbf{k}', \mathbf{q}) = \int_{\text{crystal}} d^3\mathbf{r} \psi(\mathbf{k}, \mathbf{r}) \psi(\mathbf{k}', \mathbf{r})^* e^{-i\mathbf{q} \cdot \mathbf{r}}. \quad (14)$$

In the plane wave approximation, $U(\mathbf{k}\mathbf{k}', \mathbf{q}) = \delta_{\mathbf{s}, \mathbf{q}}$. The crux of our discussion lies in obtaining the displacement $\mathbf{u}(l)$ in the exponential in (13). For we see immediately that the techniques used in neutron diffraction work are now applicable without further ado.

Substituting (13) and (8) into (4) and then integrating over E' and using (6), we get

$$\int P(\mathbf{k}\mathbf{k}') dE' = \frac{2\pi}{\hbar} \frac{|S(\mathbf{k}, \mathbf{k}')|^2}{N^2} \sum_{l\mathbf{q}} \sum_{l'\mathbf{q}'} e^{i\mathbf{s} \cdot [\mathbf{R}(l) - \mathbf{R}(l')]} v_{\mathbf{q}} v_{\mathbf{q}'}^* \times U(\mathbf{k}\mathbf{k}', \mathbf{q}) U(\mathbf{k}\mathbf{k}', \mathbf{q}')^* T(\mathbf{q}l, \mathbf{q}'l'), \quad (15)$$

where

$$T(\mathbf{q}l, \mathbf{q}'l') = \sum_{\mathfrak{N}} \omega(\mathfrak{N}) \sum_{\mathfrak{N}'} \delta[E' - E + E(\mathfrak{N}') - E(\mathfrak{N})] \times \langle \mathfrak{N}' | e^{i\mathbf{q} \cdot \mathbf{u}(l)} - 1 | \mathfrak{N} \rangle \langle \mathfrak{N}' | e^{i\mathbf{q}' \cdot \mathbf{u}(l')} - 1 | \mathfrak{N} \rangle^*. \quad (16)$$

We shall consider only single phonon processes defined by the state \mathfrak{N}' differing from \mathfrak{N} by one mode having one more or one less quantum. In Appendix B we derive from the published methods⁵ the following expression for T :

$$T(\mathbf{q}l, \mathbf{q}'l') = \sum_{j\sigma} Q_{\mathbf{q}}(j\sigma) Q_{\mathbf{q}'}(j\sigma)^* \times \{ \exp\{i\sigma \cdot [\mathbf{R}(l) - \mathbf{R}(l')]\} n_0(j\sigma) \delta(E' - E - \hbar\omega) + \exp\{-i\sigma \cdot [\mathbf{R}(l) - \mathbf{R}(l')]\} [n_0(j\sigma) + 1] \times \delta(E' - E + \hbar\omega) \} \exp\{-[W(\mathbf{q}) + W(\mathbf{q}')]\}, \quad (17)$$

where W is the well-known quantity appearing in the Debye-Waller factor:

$$W(\mathbf{q}) = \frac{1}{2} \sum_{j\sigma} \frac{\hbar}{2MN\omega(j\sigma)} (\mathbf{q} \cdot \boldsymbol{\epsilon})^2 \coth \frac{\hbar\omega}{2kT}$$

$$\cong \frac{1}{3} \cdot \frac{1}{2} \sum_{j\sigma} \frac{\hbar}{2MN\omega(j\sigma)} q^2 \coth \frac{\hbar\omega}{2kT} \dots$$

cubic symmetry, (18)

where $n_0(j\sigma)$ is the equilibrium occupation number of $j\sigma$ phonons

$$n_0(j\sigma) = (e^z - 1)^{-1}, \quad (19)$$

and where Q (differing slightly from the notation of reference 5) is

$$Q_{\mathbf{q}}(j\sigma) = \left(\frac{\hbar}{2MN\omega} \right)^{\frac{1}{2}} \mathbf{q} \cdot \boldsymbol{\epsilon}(j\sigma). \quad (20)$$

The second form in (18) follows because of cubic symmetry.⁶

Substituting (17) into (15), we get momentum delta functions

$$\sum_l \exp[i(\mathbf{s} \pm \boldsymbol{\sigma}) \cdot \mathbf{R}(l)] = N \delta(\mathbf{s} \pm \boldsymbol{\sigma} \pm \mathbf{K}), \quad (21)$$

which select out, for a given \mathbf{s} , one and only one $\boldsymbol{\sigma}$, \mathbf{K} in the $\boldsymbol{\sigma}$ sum in (17). \mathbf{K} is a vector of the reciprocal lattice. For the rest, we get

$$\int P(\mathbf{k}\mathbf{k}') dE' = \sum_j \frac{2\pi}{\hbar} \{ n_0(j\sigma) \delta(E' - E - \hbar\omega) + [n_0(j\sigma) + 1] \delta(E' - E + \hbar\omega) \} (\mathbf{Y} \cdot \boldsymbol{\epsilon})^2 \times |S(\mathbf{k}, \mathbf{k}')|^2 \frac{\hbar}{2MN\omega}, \quad (22)$$

where

$$\mathbf{Y}(\mathbf{k}, \mathbf{k}') = \sum_{\mathbf{q}} \mathbf{q} v_{\mathbf{q}} U(\mathbf{k}\mathbf{k}', \mathbf{q}) e^{-W(\mathbf{q})}. \quad (23)$$

This is our basic result. Instead of the usual matrix element, we get \mathbf{Y} , which is temperature dependent through W .

Substituting (23) into (1), we get finally

$$\rho = A \frac{2\pi}{\hbar} \frac{\hbar^2}{2MN} \int u^3 du \left\langle \frac{|\mathbf{Y} \cdot \boldsymbol{\epsilon}|^2}{(e^z - 1)(1 - e^{-z})} \right\rangle \times |S(\mathbf{k}, \mathbf{k}')|^2. \quad (24)$$

It is worthwhile making a simplification here. From Eq. (14) we have

$$U(\mathbf{k}\mathbf{k}', \mathbf{q}) = \frac{1}{\Delta_{\text{crystal}}} \int_{\Delta_{\text{crystal}}} d^3\mathbf{r} e^{i(\mathbf{k} - \mathbf{k}' - \mathbf{q}) \cdot \mathbf{r}} u(\mathbf{k}, \mathbf{r}) u(\mathbf{k}', \mathbf{r})^* = \delta(\mathbf{s} - \mathbf{q} - \mathbf{K}') U_{\mathbf{k}\mathbf{k}'}^{\mathbf{K}'}, \quad (25)$$

where

$$U_{\mathbf{k}\mathbf{k}'}^{\mathbf{K}'} = \frac{1}{\Delta_0} \int_{\text{cell}} d^3\mathbf{r} e^{i\mathbf{K}' \cdot \mathbf{r}} u(\mathbf{k}, \mathbf{r}) u(\mathbf{k}', \mathbf{r})^*, \quad (26)$$

(i.e., \mathbf{q} can differ from \mathbf{s} only by some reciprocal lattice vector \mathbf{K}'). Hence

$$\mathbf{Y}(\mathbf{k}, \mathbf{k}') = \sum_{\mathbf{K}'} (\mathbf{s} - \mathbf{K}') v_{\mathbf{s} - \mathbf{K}'} U_{\mathbf{k}\mathbf{k}'}^{\mathbf{K}'} e^{-W(\mathbf{s} - \mathbf{K}')}. \quad (27)$$

In the case of plane waves, $U_{\mathbf{k}\mathbf{k}'}^{\mathbf{K}'} = \delta_{\mathbf{K}', 0}$, and we get

$$\mathbf{Y}(\mathbf{k}, \mathbf{k}') = \mathbf{s} v_{\mathbf{s}} e^{-W(\mathbf{s})} \dots \text{plane waves.} \quad (27')$$

⁵ L. S. Kothari and K. S. Singwi, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1959), Vol. 8, p. 109. The relevant pages are 117, 118, 125, and 126. Some errors there will be corrected by the authors at a later date.

⁶ The author is indebted to Dr. A. Maradudin for pointing out that this is rigorous for cubic crystals. See for example R. E. Peierls, *Quantum Theory of Solids* (Clarendon Press, Oxford, 1955), p. 66.

Thus, for plane waves, the new effect is to multiply the old matrix element squared by $e^{-2W(s)}$, the Debye-Waller factor. This factor would then enter linearly in the integrands of the electrical and thermal resistivities, and all other transport coefficients involving thermal scattering, and would always decrease the resistivity. The case of Bloch waves is discussed in the next section.

3. COMPARISON WITH THE BARDEEN CALCULATION

The by now standard calculation of the electron-phonon scattering matrix element was originally presented by Bardeen²; and subsequent discussions³ have only extended his approach. Therefore it is instructive to compare the calculation here with the work of Bardeen. In the latter, the plane-wave approximation was used in obtaining the shielding factor, so that Eq. (8) is valid. The potential in (9) was expanded in powers of \mathbf{u} and only the linear terms kept. The linear terms there correspond to the terms linear in \mathbf{u} in the expansion of the exponential in Eq. (13). If the two treatments are then compared, it is not difficult to show that our \mathbf{Y} corresponds to the integral

$$\mathbf{Y}_{\text{Bardeen}} \equiv iN \langle \mathbf{k}' | \nabla v | \mathbf{k} \rangle \quad (28)$$

of Bardeen's treatment. If we wish to further compare the two, we should drop the e^{-W} factors in \mathbf{Y} [for this factor corresponds to taking the terms nonlinear in \mathbf{u} in the expansion of the exponential in (13)]. Thus we should identify (28) with

$$\mathbf{Y} = \sum_{\mathbf{k}'} v_{\mathbf{s}-\mathbf{K}'} U_{\mathbf{k}\mathbf{k}'}^{K'} (\mathbf{s}-\mathbf{K}'). \quad (29)$$

That (28) and (29) are identical can be seen by expanding the quantity u_0^2 in a Fourier series. In terms of the U^K of (26), we have

$$u_0(r)^2 = \sum_{\mathbf{K}} U^K e^{i\mathbf{K} \cdot \mathbf{r}}. \quad (30)$$

Substitution of this into (28) yields by integration by parts

$$\begin{aligned} \mathbf{Y}_{\text{Bardeen}} &\equiv i \sum_{\mathbf{K}'} U^{K'} \int e^{i(\mathbf{s}-\mathbf{K}') \cdot \mathbf{r}} \nabla v d^3r \\ &= \sum_{\mathbf{K}'} U^{K'} \int e^{i(\mathbf{s}-\mathbf{K}') \cdot \mathbf{r}} v (\mathbf{s}-\mathbf{K}') d^3r \\ &= \sum_{\mathbf{K}'} (\mathbf{s}-\mathbf{K}') U^{K'} v_{\mathbf{s}-\mathbf{K}'}, \end{aligned} \quad (31)$$

which is precisely (29).

Bardeen then separated the integral in (28) into an integral \mathbf{Y}_1 over the zeroth cell plus an integral \mathbf{Y}_2 over the rest of the cells. In \mathbf{Y}_2 , the potential was approximated as e^2/r and the wave function, for the purpose of calculation, as a plane wave. Thus \mathbf{Y}_2 is just the Fourier coefficient of the potential, with the zeroth cell

removed. In \mathbf{Y}_1 , Bardeen set

$$\begin{aligned} \mathbf{Y}_1 &= \langle \mathbf{k}' | \nabla v | \mathbf{k} \rangle_{\text{cell}} = \mathbf{Y}_1^{(T)} + \mathbf{Y}_1', \\ \mathbf{Y}_1^{(T)} &= \langle \mathbf{k}' | \nabla v_T | \mathbf{k} \rangle_{\text{cell}}, \\ \mathbf{Y}_1' &= -\langle \mathbf{k}' | \nabla v_e | \mathbf{k} \rangle_{\text{cell}}, \end{aligned} \quad (32)$$

where $v_T(\mathbf{r})$ is the total potential of the electron in the zeroth cell, and where the ion part (v) of this is obtained by subtracting off v_e which was taken by Bardeen to be the potential of a uniform negative charge, representative of the other conduction electrons. Strictly speaking, one should add a term $\mathbf{Y}_1'' = -\langle \mathbf{k}' | \nabla v_{\text{ex}} | \mathbf{k} \rangle_{\text{cell}}$ which would represent the subtracting off of the exchange potential v_{ex} of the conduction electrons from one another. However the exchange potential is fairly constant as a function of \mathbf{r} (i.e., the exchange hole "follows" the electron), and its gradient is neglected. Thus \mathbf{Y}_1' is the "zeroth cell Fourier coefficient" of a uniform *positive* charge distribution. Now it turns out numerically that the first term on the right, $\mathbf{Y}_1^{(T)}$, in (32) is usually very small. Hence $\mathbf{Y}_{\text{Bardeen}} \cong \mathbf{Y}_1' + \mathbf{Y}_2$, corresponds to the Fourier coefficient of a potential arising from a uniform positive charge when \mathbf{r} is in the zeroth cell and from a point charge (which amounts to the same thing) when \mathbf{r} is outside the zeroth cell. That this is in effect an almost equivalent "pseudo-potential" to the Bardeen model was pointed out by Brooks.⁷ Thus one can use either modulated plane-wave functions and the correct potential, or modulated or unmodulated plane waves and the pseudopotential

$$\begin{aligned} V &= \frac{e^2}{2} \frac{r^2}{r_s^3} - \frac{3}{2} \frac{e^2}{r_s}, \quad r < r_s; \\ V &= -\frac{e^2}{r}, \quad r > r_s. \end{aligned} \quad (33)$$

The true potential and (33) are rather similar ($\cong -e^2/r$) near the edge of the cell, but they differ enormously near the center.

Thus if we leave off the Debye-Waller factor, there are two equivalent ways of computing \mathbf{Y} : (1) by summing the series (31); and (2) by using the closed form result of Bardeen (i.e., $\mathbf{Y} = \mathbf{Y}_1' + \mathbf{Y}_2$). Unfortunately, when we include the Debye-Waller factor, there does not seem to be any closed form expression (although some hope for this still exists), and we are reduced to evaluating the series (27). In the calculations described in the next section, we have for a particular \mathbf{s} computed both series (27) and (31). In the final section we compare the various cases.

4. A DETAILED CALCULATION FOR A PARTICULAR PHONON

In order to get some idea of the effect of the e^{-W} factors in (27), we have not been able to avoid doing a

⁷ H. Brooks (unpublished notes).

detailed calculation of each \mathbf{K} term, and then summing over \mathbf{K} . To do this we must choose a particular \mathbf{s} , i.e., a particular phonon. To get from such a calculation to the electrical resistivity, one would have to add the results from many \mathbf{s} 's and average the result in the appropriate way. Such a comprehensive calculation seems unfeasible at the present time, and we have restricted ourselves to just one \mathbf{s} , hoping that this glimpse will give us some idea of whether or not the Debye-Waller factors may be important.

Fortunately, Callaway and co-workers and others⁸ have calculated the potentials and the wave functions for the alkali metals. We chose rubidium for our example, and for our \mathbf{s} we chose an umklapp process with

$$\mathbf{s} = 2\frac{1}{2}k_0(1.1, 0.9, 0), \quad (34)$$

where k_0 is the wave vector at the Fermi level. The magnitude of this \mathbf{s} is about $2k_0$, and its direction is approximately (but by design not precisely) in the $[110]$ direction. Thus it corresponds to an umklapp process involving a phonon of very small wave vector in which the electron changes direction by 180° , i.e., it corresponds to an important scattering process. We chose a room temperature value for the coefficient of q^2 in (18):

$$W(q) = (qa_h)^2 A, \quad (35)$$

$$A = 0.3304.$$

Here a_h is the Bohr radius so that qa_h is dimensionless.

The wave functions we used from Callaway and Morgan⁸ were of the form (10) including only the u_0 term. Hence the quantity $U_{\mathbf{kk}'}^{\mathbf{K}}$ of (26) depends only on K , and we can relabel it U^K . The angle integrals in U^K and v_s can be performed immediately, and the resulting expression from which we computed was

$$\mathbf{Y} = -B\mathbf{Z}, \quad (36)$$

$$B = -\frac{9}{2} \frac{e^2}{a_h^2 \rho_s^6}, \quad (37)$$

$$\mathbf{Z} = \sum_{\mathbf{\kappa}} (\boldsymbol{\tau} - \mathbf{\kappa}) \int_0^{\rho_s} (\rho u_0)^2 \frac{\sin \kappa \rho}{\kappa \rho} d\rho \exp(-A|\boldsymbol{\tau} - \mathbf{\kappa}|^2) \\ \times \left\{ \frac{2 \cos(|\boldsymbol{\tau} - \mathbf{\kappa}| \rho_s)}{|\boldsymbol{\tau} - \mathbf{\kappa}|^2} + \int_0^{\rho_s} \rho^2 \Phi \frac{\sin(|\boldsymbol{\tau} - \mathbf{\kappa}| \rho)}{|\boldsymbol{\tau} - \mathbf{\kappa}| \rho} \right\}. \quad (38)$$

Here we introduced the dimensionless quantities $\tau = a_h s$; $\kappa = a_h K$; $\rho = r/a_h$; $\rho_s = r_s/a_h$; $\Phi = v(r)[e^2/(2a_h)]^{-1}$. In the v_s integral we made the same approximation as Bardeen²; namely in the region $r > r_s$, we used plane waves and $v(r) = e^2/r$.

The reciprocal lattice vectors \mathbf{K} for the body-centered

TABLE I. The numbers here are the components of \mathbf{Z} in Eq. (38). The results denoted by the superscript DW are those including the Debye-Waller factor. The row "Bardeen" corresponds to the result from a computation similar to that in reference 2.

Box	Z_x	Z_y	Z_z	Z_x^{DW}	Z_y^{DW}	Z_z^{DW}
0	-13.12	-10.73	0	-10.94	-8.95	0
1	-11.29	-9.38	0	-9.86	-8.21	0
2	-11.31	-8.80	0	-9.23	-7.11	0
3	-15.17	-11.99	0	-8.97	-6.96	0
4	-16.19	-12.80	0	-8.84	-6.85	0
5	-15.99	-12.64	0	-8.83	-6.84	0
6	-15.39	-12.13	0	-8.85	-6.86	0
7	-15.53	-12.27	0	-8.85	-6.86	0
8	-15.87	-12.53	0	-8.85	-6.86	0
9	-16.50	-13.06	0	-8.85	-6.86	0
10	-17.06	-13.52	0	-8.85	-6.86	0
11	-17.56	-13.92	0	-8.85	-6.86	0
Bardeen	-12.4	-10.2	0			

alkali metals form a face-centered lattice with points at

$$\mathbf{K} = (2\pi/a)(g_1, g_2, g_3), \quad (39)$$

$$a = (8\pi/3)^{1/3} r_s.$$

The components refer to the orthogonal axes of the crystal of unit cube edge a . Not all combinations of integers $g_1 g_2 g_3$ are allowed: only those for which the sum $g_1 + g_2 + g_3$ is even correspond to a reciprocal lattice vector.

The various \mathbf{K} 's were regarded as lying on "shells" and in "boxes." A shell is the surface of a cube, the box is the volume. The first box is bounded by $-1 \leq g_i \leq 1$ ($i=1, 2, 3$), and its surface is the first shell. The second box is bounded by $-2 \leq g_i \leq 2$, and the second shell is its surface. And so on. The number of possible combinations $g_1 g_2 g_3$ in the n th box is $(2n+1)^3$. Of these the number of reciprocal lattice points is almost exactly one-half, the error being less than unity. For example, for $n=1$, the true number is 13, the computed number 13.5. The zeroth box contains the one term $K=0$, and corresponds to the plane-wave result.

In this way, we computed the series (27) and (31) up to 11 boxes, that is, including 6083 reciprocal lattice vectors. The results are in Table I. See also Table II.

5. DISCUSSION

We see from Table I that the series not including the Debye-Waller factor does not appear to begin to converge even after about 6000 reciprocal lattice vectors have been calculated. (The converged value should be the Bardeen result in Table II.) A possible explanation of this, and a significant fact anyway is that the integrals U^K and v_s performed by the machine only computed 36 points in the region $r < r_s$, these points corresponding to some of the points listed by Callaway and Morgan.⁸ However the convergence of the series at large K depends to a great extent on the heavy canceling of plus and minus contributions in these integrals arising from the presence of the factors

⁸ The following articles contain the potentials for Li, Na, K, Rb, and Cs in that order. W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954); E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); J. Callaway, Phys. Rev. **103**, 1219 (1956); J. Callaway and D. F. Morgan, Jr., Phys. Rev. **112**, 334 (1958); J. Callaway and E. L. Haase, Phys. Rev. **108**, 217 (1957).

$\sin K r$ and $\sin(|\mathbf{s}-\mathbf{K}|r)$. Therefore the details of the convergence are not significant in the series not including the Debye-Waller factor. At best the first few shells and the converged value of the case including the Debye-Waller factor may be qualitatively reliable. As a check we computed graphically by hand the factor

$$\int_0^{r_s} (\rho u_0)^2 \frac{\sin \kappa \rho}{\kappa \rho} d\rho \sim U^K$$

for a \mathbf{K} in the 11th shell (with $K=10.99$), interpolating between the values the machine used. Our result was -1.08 , the machine gave -1.28 . Thus an error of 25% in the individual term resulted in this extreme case; in the lower shells the error is far less, of course. Just as the whole terms tend to cancel, so do we expect the errors to; nevertheless, the numerical results must be regarded very cautiously in the light of this consideration. We believe that the first few shells are reliable, and our subsequent discussion presumes this.

For the case calculated, we notice that with the Debye-Waller factor, we get a resultant value of Y about 0.7 times the Bardeen result (this is about twice the plane-wave Debye-Waller effect), implying a corresponding reduction by $\frac{1}{2}$ [$= (0.7)^2$] of the contribution to the resistivity. It is not safe to assume, however, that this would be the way in which the total resistivity does change, because for different \mathbf{s} vectors (even with the same s magnitude), the alteration might be a greater decrease or even an increase possibly. It is hard to see how to estimate the total effect.

The case calculated was for room temperatures. For low temperatures, the coefficient A in (35) becomes smaller (see Table III). The Debye-Waller factor effect we anticipate would then be smaller, although even this is not certain, since so much depends on the details of the cancelation of different \mathbf{K} terms.

Finally we remark that the direction of the resulting matrix element is not the same with the Debye-Waller factors included. The ratio of the y component to the x component is given in parentheses in Table II. It is a change of only a few degrees. There seems to be no formal reason why it should be the same.

In a naive way, one can argue that the Debye-Waller factor effect may be larger at high temperatures for cesium and rubidium than for sodium and potassium (since A is larger, see Table III), and hence, if the trend indicated by our spot calculation is representative

TABLE II. The values for the magnitude of Z [see Eq. (38)], with the ratio Z_y/Z_x in parentheses. The Bardeen result is that provided by the model of reference 2; the D-W value is the converged result of (38) including the Debye-Waller factor, as obtained from Table I; the PW entries are the values for the $K=0$ term in (38) with and without the Debye-Waller factor.

Bardeen	D-W	PW _B	PW _{DW}
16.1 (0.817)	11.2 (0.78)	17.0 (0.817)	14.1 (0.817)

TABLE III. Values for A [see Eq. (35)] at high and low temperatures. These are rough values.

	Li	Na	K	Rb	Cs
A (0°K)	0.035	0.032	0.030	0.027	0.022
A (300°K)	0.070	0.150	0.270	0.330 ₄	0.388
r_s/a_h (300°K)	3.21	4.00	4.84	5.21	5.64

for an average over all \mathbf{s} 's, the resistivities will be reduced by greater and greater amounts as we go from sodium to cesium. This at high temperatures would make agreement with experiment *worse* than it already is.¹ However, we regard such an estimate as idle speculation since the actual effect on the transport coefficients can hardly be estimated from the solitary example so very crudely computed in this paper.

6. SUMMARY

It has long been known that deviations of electrons in metals from perfectly free electrons play an important role in understanding metallic phenomena. This deviation can be discussed in terms of the deviation of the energy surfaces from perfect spheres in \mathbf{k} space, and also in terms of the deviations of the wave functions from plane waves. In semiclassical transport theory, the former gives rise to effective mass and velocity considerations, and considerations concerning the geometry of momentum transfer. The wave-function deviations give rise to the details of the scattering matrix element. The two are of course closely related. Bardeen² has given an account of how the deviation from plane waves will alter the cross section of the scattering. Some additions to his approach have been considered in reference 1. These reflected the details of the wave function also, and tended to *increase* the matrix element over the Bardeen value, especially in the umklapp region of scattering. We have shown in this paper that when the phonon "system fluctuations" are taken into account in the single-phonon processes, Debye-Waller factors enter into the ion potential perturbation matrix element in a rather complicated way that indicates a kind of interference of the detailed ion motion and the detailed nature of the wave function. Very tentative indications of a not altogether reliable spot calculation are that this results in a *decrease* of the matrix element from the Bardeen value. For quantitative results for the transport coefficients, we feel that in addition to matrix element improvements, the details of the spectrum are also very important,¹ and that the theoretical estimates now available must be improved.

Finally there are questions of a more general nature that one is stimulated to ask, once there is a possibility that effects of the higher order terms in the potential expansion in powers of \mathbf{u} , the ionic displacements, may not be negligible. First there is the question of higher order perturbation theory. Everything so far has been

in the context of first order perturbation theory, but the n th order perturbation effects are proportional to u^n , and these then resemble our "higher first order" effects which lead to the Debye-Waller factor. Unfortunately higher order perturbation theory in this problem seems to be orders of magnitude more difficult to calculate than first order perturbation theory, and we can do little more at present than point wistfully in this direction. On the other hand, one can do something about relaxing the restriction to single-phonon processes in first order perturbation theory. The effect of two-phonon processes has been calculated,⁹ and has been shown to be of the order of 4% or less in the electrical resistivity. Hence we suspect that no major effects are to be looked for in this direction. However, multiphonon processes occur in higher order perturbation theory, and may well play an important role there.

Another question that can be raised is how good the potential model is. What we have done in this paper is to take the rigid-ion model with shielding seriously. But one can question whether the model is that accurate to warrant such seriousness. One can argue that the model might be all right for first order effects, but anything of greater detail cannot be expected of it. In particular, one can recall that the "deformable-ion" model has some validity to it, whereas the rigid-ion model ignores any deformation of the ion core. Here again all we can do is point and say that possibly an improvement of significance lies in this direction. Our attitude is that *if* one takes the rigid-ion model with shielding seriously in first order perturbation theory and with single-phonon processes, *then* it leads to the Debye-Waller type effect as discussed above.

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APPENDIX A. DERIVATION OF EQ. (1)

We start from the variational principle¹ expression for the electrical resistivity $\rho = d_{00}/\alpha^2$, where on the effective mass approximation [see reference 1, Eq. (A8)]

$$\alpha_0 = -\frac{m}{m^*} \frac{e}{\hbar \Delta_0}, \quad (\text{A1})$$

⁹ E. Franzak and M. Bailyn, *Bull. Am. Phys. Soc.* **5**, 280 (1960).

and where

$$d_{00} = \frac{1}{4\pi^3} \frac{\Delta}{8\pi^3 \kappa T} \left(\frac{m_0}{\hbar^2}\right)^2 \frac{1}{6} \iint dS_E dS_{E'} \int \frac{dE}{|\nabla E| |\nabla E'|} \\ \times \left(\int dE' P(\mathbf{k}, \mathbf{k}') \right) f_0(1-f_0') |\nabla E' - \nabla E|^2. \quad (\text{A2})$$

This latter comes about from substituting into [see reference 1, Eq. (A6)]

$$d_{00} = -\frac{1}{4\pi^3} \left(\frac{m_0}{\hbar^2}\right)^2 \int \nabla E_x L\{\nabla E_x\} d^3k \quad (\text{A3})$$

the expression¹⁰

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}} \equiv L(\chi) = \frac{\Delta}{8\pi^3 \kappa T} \int P(\mathbf{k}, \mathbf{k}') f_0(E) \\ \times [1 - f_0(E')] [\chi(\mathbf{k}') - \chi(\mathbf{k})] d^3k'. \quad (\text{A4})$$

Here the electron distribution is

$$f = f_0 - (\partial f_0 / \partial E) \chi(\mathbf{k}), \quad (\text{A5})$$

where f_0 is the Fermi function. We have assumed cubic symmetry so that vector component products $\nabla E_x \cdot \nabla E_{x'}$ were replaced by $\nabla E \cdot \nabla E' / 3$. The integral dS_E is over the surface of constant energy E . The differential volume element was written

$$d^3k = (dS_E / |\nabla E|) dE. \quad (\text{A6})$$

The E' integral will employ the delta function of energy for single-phonon processes so that E' will equal $E \pm \hbar\omega$. We anticipate this result [see Eq. (6) above]. The E integral will then be simplified because of the presence of $f_0(1-f_0')$ which also acts as a kind of delta function. For the two cases of emission and absorption of a phonon, we get

$$\int_0^\infty dE f_0(E) [1 - f_0(E \pm \hbar\omega)] \\ = \hbar\omega (1 - e^{-z})^{-1} \dots, \quad E' = E + \hbar\omega \\ = \hbar\omega (e^z - 1)^{-1} \dots, \quad E' = E - \hbar\omega. \quad (\text{A7})$$

The rest of the integrand is taken out at its value on the Fermi surface, and the two surface integrals are over the Fermi surface.

$$d_{00} = \frac{1}{4\pi^3} \frac{\Delta}{8\pi^3 \kappa T} \left(\frac{m_0}{\hbar^2}\right)^2 \frac{1}{6} \iint dS_\xi dS_{\xi'} \frac{|\nabla E' - \nabla E|^2}{|\nabla E| |\nabla E'|} \hbar\omega \\ \times \int dE' P(\mathbf{k}, \mathbf{k}') \{ (1 - e^{-z})^{-1} \delta(E' - E - \hbar\omega) \\ + (e^z - 1)^{-1} \delta(E' - E + \hbar\omega) \}. \quad (\text{A8})$$

The surface elements can be written

$$dS_\xi dS_{\xi'} = \left(\frac{2M^*}{\hbar^2}\right)^2 \xi^2 \iiint d\cos\theta d\phi d\phi' \int d\cos\theta', \quad (\text{A9})$$

¹⁰ H. Jones, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. 19.

where θ' , ϕ' are the polar and azimuthal angles of \mathbf{k}' relative to \mathbf{k} as polar axis; and θ , ϕ are the angles \mathbf{k} makes with respect to some arbitrary polar direction. θ' is thus the angle of scattering.

Now if we keep $|\mathbf{k}-\mathbf{k}'|$ magnitude fixed, and the tip of \mathbf{k} fixed (i.e., $\theta\phi$), then the tip of \mathbf{k}' traces a circle on the Fermi surface as ϕ' takes on values $0 \cdots 2\pi$. The \mathbf{k} integral $\int \int d(\cos\theta)d\phi$ then in effect moves this circle over the Fermi surface to all possible positions with equal weighting. Thus for a given θ' (i.e., for a given $\mathbf{k}-\mathbf{k}'$ magnitude), the three integrals $\int \int \int d(\cos\theta)d\phi d\phi'$ correspond to averaging $\mathbf{k}-\mathbf{k}'$ over all directions with equal probability:

$$\int \int \int d(\cos\theta)d\phi d\phi' = 8\pi^2 \langle \rangle_{\mathbf{k}-\mathbf{k}'}. \quad (\text{A10})$$

The angle brackets designate this average. The factor $8\pi^2$ arises from the product of 2 (from the $\cos\theta$ range) 2π (from the ϕ range) and 2π (from the ϕ' range). A more general discussion of the integration of (A2) was made in reference 1. The above is a short-cut to the result for a spherical Fermi surface. (The important point is that for a given $|\mathbf{k}-\mathbf{k}'|$, one must average over many σ 's if one is in the umklapp range. This point is discussed in reference 1, but is not relevant to the argument of the present paper. However, it was thought worthwhile to derive here the resistivity expression incorporating this average.)

Defining $u = \sin(\theta/2)$, we get

$$\frac{|\nabla E' - \nabla E|^2}{|\nabla E| |\nabla E'|} = 4u^2, \quad (\text{A11})$$

whence from (A8) we obtain Eq. (1) above, with

$$C = \frac{N}{\kappa T} \frac{8}{3\pi^4} \frac{\Delta_0^2 \zeta^2(m^*)^4}{\hbar^6 e^2}. \quad (\text{A12})$$

APPENDIX B. DERIVATION OF $T(ql; q'l')$

In Eq. (16), we consider only "single-phonon processes," defined as processes for which \mathfrak{N}' differs from \mathfrak{N} by one phonon mode having an occupation number of one greater or less. These can differ from the single-phonon processes which are defined as processes in which one phonon mode changes its occupation number by ± 1 in that in the former, processes are taken into account in which a second phonon may get emitted and absorbed, and in which still a third may get emitted and absorbed and so on, all of which additional emissions and absorptions appear in emission-absorption pairs so that there is no effect on the state \mathfrak{N}' from these other phonon transitions.

The factors 1 in the matrix element in Eq. (16) will yield zero for single-phonon processes.

The quantity $\mathbf{u}(l)$ is expanded in normal modes in the customary way⁵:

$$\mathbf{q} \cdot \mathbf{u}(l) = \sum_{j\sigma} Q_q(j\sigma) \{a(j\sigma) \exp[i\sigma \cdot \mathbf{R}(l)] + a(j\sigma)^* \exp[-i\sigma \cdot \mathbf{R}(l)]\}, \quad (\text{B1})$$

where the Q 's are given by Eq. (20) above. The matrix elements of the a 's are then

$$\langle n|a|n+1\rangle = \langle n+1|a^*|n\rangle = (n+1)^{\frac{1}{2}}. \quad (\text{B2})$$

From Eq. (4.6) of reference 5 we have

$$\begin{aligned} \langle \mathfrak{N}' | \exp[i\mathbf{q} \cdot \mathbf{u}(l)] | \mathfrak{N} \rangle &= in(j_1\sigma_1)^{\frac{1}{2}} Q_q(j_1\sigma_1) \exp[i\sigma_1 \cdot \mathbf{R}(l)] F(\mathfrak{N}, \mathbf{q}), \\ \mathfrak{N} &= \{n(j_1\sigma_1), n(j_2\sigma_2), \dots, n(j_{3N}\sigma_{3N})\}, \\ \mathfrak{N}' &= \{n(j_1\sigma_1) \pm 1, n(j_2\sigma_2), \dots, n(j_{3N}\sigma_{3N})\}, \end{aligned} \quad (\text{B3})$$

where

$$\begin{aligned} F(\mathfrak{N}, \mathbf{q}) &= \prod_{j\sigma} F_{n,j\sigma}(j\sigma, \mathbf{q}), \\ F_{n,j\sigma}(j\sigma, \mathbf{q}) &= \langle n(j\sigma) | \exp\{iQ_q(j\sigma) \\ &\quad \times [\exp[i\sigma \cdot \mathbf{R}(l)] a(j\sigma) \\ &\quad + \exp[-i\sigma \cdot \mathbf{R}(l)] a^*(j\sigma)]\} | n(j\sigma) \rangle. \end{aligned} \quad (\text{B4})$$

In a parallel manner one can show

$$\begin{aligned} \langle \mathfrak{N}' | \exp[i\mathbf{q} \cdot \mathbf{u}(l)] | \mathfrak{N} \rangle &= i[n(j_1\sigma_1) + 1]^{\frac{1}{2}} Q_q(j_1\sigma_1) \\ &\quad \times \exp[-i\sigma_1 \cdot \mathbf{R}(l)] F(\mathfrak{N}, \mathbf{q}), \quad (\text{B5}) \\ \mathfrak{N}' &= \{n(j_1\sigma_1) + 1, n(j_2\sigma_2), \dots, n(j_{3N}\sigma_{3N})\}, \\ \mathfrak{N} &= \text{as in (B3)}. \end{aligned}$$

For a given \mathfrak{N} , the sum over \mathfrak{N}' in (16) will then be a sum over (B3) and (B5) and over the $j_1\sigma_1$ singled out in (B3) and (B5) (there labeled $j_1\sigma_1$). Thus

$$\begin{aligned} T(ql; q'l') &= \sum_{j_1\sigma_1} Q_q(j_1\sigma_1) Q_{q'}(j_1\sigma_1) \\ &\quad \times \{\exp\{i\sigma_1 \cdot [\mathbf{R}(l) - \mathbf{R}(l')]\} X(j_1\sigma_1; \mathbf{q}\mathbf{q}') \\ &\quad + \exp\{-i\sigma_1 \cdot [\mathbf{R}(l) - \mathbf{R}(l')]\} \\ &\quad \times [X(j_1\sigma_1; \mathbf{q}\mathbf{q}') + X'(\mathbf{q}\mathbf{q}')]\}, \quad (\text{B6}) \end{aligned}$$

where

$$X'(\mathbf{q}\mathbf{q}') = \sum_{\mathfrak{N}} \omega(\mathfrak{N}) F(\mathfrak{N}, \mathbf{q}) F(\mathfrak{N}, \mathbf{q}')^*, \quad (\text{B7})$$

$$X(j_1\sigma_1; \mathbf{q}\mathbf{q}') = \sum_{\mathfrak{N}} \omega(\mathfrak{N}) n(j_1\sigma_1) F(\mathfrak{N}, \mathbf{q}) F(\mathfrak{N}, \mathbf{q}')^*. \quad (\text{B8})$$

Methods for evaluating X and X' can be found in reference 5 [see Eqs. (4.8) and (3.9) of that reference] and in the paper by Weinstock.¹¹ In our case, we do not have $F(\mathfrak{N}, \mathbf{q})^2$ as in these references, but rather $F(\mathfrak{N}, \mathbf{q}) F(\mathfrak{N}, \mathbf{q}')$. By exactly the same methods, however, it is not difficult to show that the difference between \mathbf{q} and \mathbf{q}' can be taken into account by the result

$$X'(\mathbf{q}\mathbf{q}') = e^{-[W(\mathbf{q}) + W(\mathbf{q}')]}, \quad (\text{B9})$$

$$X(j_1\sigma_1; \mathbf{q}\mathbf{q}') = n_0(j_1\sigma_1) e^{-[W(\mathbf{q}) + W(\mathbf{q}')]}, \quad (\text{B10})$$

where $W(\mathbf{q})$ and $n_0(j\sigma)$ are given by Eqs. (18) and (19) of the text. Substitution of (B9) and (B10) into (B6) yields the desired result: Eq. (17).

¹¹ R. Weinstock, Phys. Rev. **65**, 1 (1944).