INFLUENCE OF ELECTRON-PHONON INTERACTION
ON THE SCATTERING OF NEUTRONS BY
CONDUCTING CRYSTALS

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Synopsis

The theory of the influence of phonon-phonon interactions on the location and width of the one-phonon peaks in the spectrum of inelastically scattered neutrons by single crystals, as developed earlier [1]), is extended to the case of metals to include the interaction between phonons and conduction electrons. Expressions are derived for the shift and width as a result of electron-phonon coupling and estimates are given for these quantities. In general the influence of electron-phonon interaction on the line shape of the scattering peaks will be small.

1. *Introduction.* In a previous paper [1]), to be referred to hereafter as I, we have studied the influence of phonon-phonon interactions on the one-phonon peaks in the outgoing spectrum of coherently, inelastically scattered neutrons by single, non-conducting crystals. In the harmonic approximation these peaks are delta-function singularities, each peak corresponding to emission or absorption of a single phonon by the neutron. As a result of phonon-phonon interactions the peaks get a finite width and are shifted with respect to those predicted in the harmonic approximation. These anharmonic effects are treated in I by means of many particle perturbation theory, using diagram methods for the calculation of the various matrix elements. The essential point is that the formalism developed in I is restricted to the case where, independent of the strength of the coupling, the width of each peak is small compared to the value of its central frequency. Only then the peaks can be considered as being well defined with respect to the background (multi-phonon processes) to higher order in the interaction. This case is expected to be realized for temperatures which are not too high and values of the phonon wave vector q, which are not too large.

The aim of the present paper is to extend the above theory to the case of conducting crystals, where in addition to phonon-phonon interactions the interaction between phonons and conduction electrons gives a contribution to the displacement and broadening of the one-phonon peaks. Rough calculations of this latter contribution indicate that the effects of electron-

phonon interaction on the line shape will be small, presumably smaller than those arising from anharmonicities.

Of particular importance are those situations, where, for kinematical reasons (which do not affect phonon-phonon transitions), the contribution of the electron-phonon interactions to the shift and width, are strongly reduced. Such situations arise in the case where the phonon wave vector q becomes so large that it cannot be fitted into the Fermi sphere[2]), or in the case of superconductors where below the transition temperature the number of possible electron-phonon transitions is reduced because of the presence of an energy gap. Although very small and possibly hardly detectable, these latter effects are perhaps the most interesting ones from the point of view of the experimentalist.

In section 2 we discuss the effective Hamiltonian for our electron-phonon system, starting from the adiabatic principle and the one-electron approximation. In the next two sections the diagram formalism, introduced and developed in I, will be extended by including electron-phonon vertices. Special attention must be paid to the exclusion principle for the electrons. The summation of the one-phonon diagrams – which describe the scattering peaks if they are sufficiently narrow – in terms of so-called bubble functions, can also in this case be performed exactly. Finally in section 5 we derive the lowest order expressions for the shift and width due to electron-phonon coupling alone, and perform some approximate calculations.

2. *The Hamiltonian of the electron-phonon system.* In this section we present a brief sketch of the construction of the effective Hamiltonian for our electron-lattice system, as can be found in the current literature (see for instance reference 6). Consider a finite, perfect, conducting crystal of volume Ω, consisting of a lattice of ions and a number of conduction electrons, such, that the whole system is electrically neutral. The Hamiltonian of the system composed of ion lattice and conduction electrons can be written as follows:

$$H = \Sigma_{sn}\frac{|\boldsymbol{p}_{sn}|^2}{2M_n} + H_{ion\text{-}ion} + \Sigma_i \frac{|\boldsymbol{p}_i|^2}{2m} + H_{ee} + \Sigma_{isn} v(\boldsymbol{r}_i - \boldsymbol{r}_{sn}). \quad (2.1)$$

In this equation $\boldsymbol{r}_i$ and $\boldsymbol{p}_i$ are the electronic variables. The vectors $\boldsymbol{r}_{sn}$ designate the positions of the ions in the crystal; each vector $\boldsymbol{r}_{sn}$ is the sum of an equilibrium position vector $\boldsymbol{s} + \boldsymbol{R}_{0n}$ and a displacement vector $\boldsymbol{u}_{sn}$, where $\boldsymbol{s}$ is a crystal translation vector and $\boldsymbol{R}_{0n}$ the equilibrium position vector of ion n (mass M_n) in the unit cell containing the origin, n running from 1 to n_0, the number of ions per unit cell. The first two terms of the Hamiltonian (2.1) represent the kinetic and Coulomb energies of the ions and similarly the following two terms those of the electrons. The last term in (2.1) describes the electron-ion interaction. It is to be understood that in the above Hamiltonian all Coulomb interactions are still unscreened. In

this form the Hamiltonian is very unpractical for our investigations.

To obtain the „effective" Hamiltonian for our purpose the basic approach is that of the adiabatic approximation introduced by Born and Oppenheimer, in which it is assumed that, due to the smallness of the electron mass compared with the nuclear mass, the motion of the electrons is sufficiently rapid to follow the motion of the ions. We then first suppose that the ions are frozen in fixed positions r_{sn} and we calculate the energy $E(\ldots r_{sn} \ldots)$ of the electrons*). This energy, which depends parametrically on the positions of the ions, is added to the electrostatic ion-ion coupling $H_{ion\text{-}ion}$ to give the effective potential enery function $H_{ion\text{-}ion}(\ldots r_{sn}\ldots) +$ $+ E(\ldots r_{sn} \ldots)$ of the ionic motion, which together with the kinetic energy term of the ions forms the Hamiltonian H_p for the lattice vibrations (phonons). This Hamiltonian has been discussed in some detail in I. It is composed of two parts

$$H_p = H_p^{(2)} + V,$$

where $H_p^{(2)}$, the harmonic Hamiltonian, can be written in terms of phonon creation and annihilation operators A_{qj}^* and A_{qj} as follows (as far as eq. (5.10) we put $\hbar = 1$):

$$H_p^{(2)} = \varepsilon_0 + \varepsilon_{zp} + H_{0p}, \tag{2.2}$$

with ε_0 and ε_{zp} the rigid lattice energy and zero point energy respectively and with

$$H_{0p} = \Sigma_j \textstyle\int_q \omega_{qj} A_{qj}^* A_{qj}, \tag{2.3}$$

and similarly V, the anharmonic Hamiltonian:

$$V = \Sigma_{\nu=3}^\infty V^{(\nu)}$$

$$V^{(\nu)} = \Sigma_{j_1\ldots j_\nu} \textstyle\int_{q_1\ldots q_\nu} B^{(\nu)}_{q_1 j_1, \ldots, q_\nu j_\nu} [A_{q_1 j_1} + A^*_{-q_1 j_1}] \cdots \tag{2.4}$$

$$\cdots [A_{q_\nu j_\nu} + A^*_{-q_\nu j_\nu}] \Delta(q_1 + \ldots + q_\nu).$$

Here ω_{qj} is the frequency of the phonon with wave vector $q \pmod{2\pi\tau}$ and polarization index j (τ is a vector of the reciprocal lattice). We remark that as a result of thermal expansion the unperturbed phonon frequencies ω_{qj} and similarly the coefficients $B^{(\nu)}$ and $b^{(\nu)}$ (see 2.6) depend on temperature. The symbol $\int_q$ stands for $(8\pi^3/\Omega) \Sigma_q$ (summation over one unit cell in reciprocal space); it becomes $\int dq$ in the limit $\Omega \to \infty$.

The last three terms of the Hamiltonian (2.1), which describe the electrons, will be modified by applying the one-electron approximation. The electron-lattice interaction term $\Sigma_{isn} v(r_i - r_{sn})$ may be expanded in powers of the ionic displacements u_{sn}. The first term in this expansion, i.e. $\Sigma_{isn} v(r_i - R_{sn})$, is the interaction between the electrons and the ions in their equilibrium positions R_{sn}. In the one-electron approximation each electron is supposed to move in a potential field, which is the potential of the static ions

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*) From now on electrons are always meant to be conduction electrons.

compensated by some additional field which represents the average effect of all the other electrons. This effective potential may be combined with the kinetic energy of the electrons to give after second quantization the following Hamiltonian for the electrons in a static lattice:

$$H_{0e} = \Sigma_{\sigma m} \int_{k} \varepsilon_{km\sigma} \Gamma^*_{km\sigma} \Gamma_{km\sigma}. \tag{2.5}$$

Here $\varepsilon_{km\sigma}$ is the energy of a single Bloch electron, characterized by a wave vector k, a spin index σ and an index m distinguishing the Bloch bands. $\Gamma^*_{km\sigma}$ and $\Gamma_{km\sigma}$ are the creation and annihilation operators for this electron; they obey the usual anti-commutation rules for fermions. Just as in the case of phonons, k is only defined modulo $2\pi\tau$; for the energies we have $\varepsilon_{km} = \varepsilon_{k+2\pi\tau, m}$. Summations over k are to be restricted to the first Brillouin zone.

The remaining terms of the expansion of $\Sigma_{isn} v(r_i - r_{sn})$ determine in part the electron-phonon interaction. The motion of the ions changes the effective electrostatic potential acting on an electron. However, the electrons try to respond to the ionic motion in such a way as to screen out local charge fluctuations. Any shift of the ions will be accompanied by a shift in the electron charge cloud which tends to shield the electrostatic field of the ions and which considerably reduces the effective matrix elements for the electron-phonon coupling. A self-consistent field type of calculation of the effective matrix element to first order in the ionic displacements has been performed by Bardeen[3]). A more exact treatment of the whole screening question, based on the introduction of collective coordinates, can be found in a paper by Bardeen and Pines[4]).

In second quantization we may write the electron-phonon interaction energy W in the following form:

$$W = \Sigma_{\nu=1}^{\infty} W^{(\nu)}$$

$$W^{(\nu)} = \Sigma_{\sigma m m' j_1 \ldots j_\nu} \int_{kk' q_1 \ldots q_\nu} b^{(\nu)}_{km, k'm', q_1 j_1, \ldots, q_\nu j_\nu} \tag{2.6}$$

$$\Gamma^*_{km\sigma} \Gamma_{k'm'\sigma} [A_{q_1 j_1} + A^*_{-q_1 j_1}] \ldots [A_{q_\nu j_\nu} + A^*_{-q_\nu j_\nu}] \Delta(q_1 + \ldots + q_\nu + k' - k).$$

The ν'th order term in this expansion arises from the ν'th order term in the expansion of $\Sigma_{isn} v(r_i - r_{sn})$ in powers of the ionic displacements. As mentioned above an expression for the coefficient $b^{(1)}_{km, k'm', qj}$ has been derived by Bardeen[3]). In the limit of small q and considering only electrons within one Bloch band, one finds for a Bravais lattice[5]):

$$b^{(1)}_{k, k', qj} = iE_F (\hbar/36\pi^3 M \rho \omega_{qj})^{\frac{1}{2}} [e_{qj} \cdot (k - k')], \tag{2.7}$$

where M and ρ are the mass and number density of the ions, E_F is the Fermi energy and e_{qj} is the polarization vector of the phonon qj. Neglecting Umklappprocesses and noting that $k - k' = q$, we see that $b^{(1)}_{k, k', qj}$ is proportional to $|q|^{\frac{1}{2}}$ and therefore remains finite when q tends to zero. The

latter result is a consequence of the strong screening. The coefficients $b^{(\nu)}_{\dots}$ with $\nu > 1$ have never been calculated explicitly. The following relation can be proved:

$$b^{(\nu)*}_{k_1, k_2, q_1 j_1, \dots, q_\nu j_\nu} = b^{(\nu)}_{k_2, k_1, -q_1 j_1, \dots, -q_\nu j_\nu}, \qquad (2.8)$$

where the asterisk denotes the complex conjugate.

Summing up, the following Hamiltonian will now finally be adopted for our electron-phonon system (see (2.2), (2.4), (2.5) and (2.6)):

$$H = \varepsilon_0 + \varepsilon_{zp} + H_{0p} + H_{0e} + V + W, \qquad (2.9)$$

in which H_{0p} and H_{0e} describe the free phonons and free Bloch electrons and V and W are the phonon-phonon and electron-phonon interaction respectively. The relative strength of the various terms in both V and W will be governed by the same parameter u/d, where u is the average ionic displacement and d is the smallest interionic distance in the equilibrium lattice. Considering V and W as small terms in the Hamiltonian (2.9), which is justified as long as u/d is much less then one, we will investigate their effects by means of perturbation theory.

The eigenstates $|k_1 m_1 \sigma_1, \dots, k_n m_n \sigma_n; q_1 j_1, \dots, q_l j_l\rangle$ of the unperturbed Hamiltonian $\varepsilon_0 + \varepsilon_{zp} + H_{0p} + H_{0e}$ can be written in terms of electron and phonon creation operators as follows:

$$|k_1 m_1 \sigma_1, \dots, k_n m_n \sigma_n; q_1 j_1, \dots, q_l j_l\rangle = \Gamma^*_{k_1 m_1 \sigma_1} \dots \Gamma^*_{k_n m_n \sigma_n} A^*_{q_1 j_1} \dots A^*_{q_l j_l} |0\rangle, \quad (2.10)$$

where $|0\rangle$ is the vacuum (no electron, no phonon) state. The operation of the perturbation $V + W$ on these states may be easily seen. Each term from $V + W$, being a product of creation and annihilation operators, can induce a transition between the electron-phonon states in such a way that, as a consequence of the Δ-functions occurring in V and W, the new state has the same total wave vector, modulo $2\pi\tau$, as the initial one.

Before closing this section some remarks are necessary concerning the validity of the adiabatic approximation, on which we have based our discussion of the Hamiltonian. Questions, such as the use of perturbation theory and whether or not it makes sense in the framework of the adiabatic approach to include terms in the interaction up to general order in the ionic displacements, are of course closely connected with the problem of the validity of the adiabatic approximation as such. The adiabatic approximation as a starting point for quantum mechanical considerations of solids has been often discussed in the literature[6][7] without having led to a convincing criterion for its validity. Ziman[6] makes plausible the suggestion that the following condition should be necessary and probably even sufficient:

$$q\Lambda_e > 1, \qquad (2.11)$$

which says that the phonon wave length should be smaller than the mean free path Λ_e of the electron it scatters. This condition is satisfied except for

phonons of very long wave length; in the limit of very small q perturbation theory breaks down and relaxation phenomena become important.

Of course, one can try to escape the adiabatic approach and use more sophisticated methods for deriving the effective Hamiltonian. Such methods, based on the introduction of collective coordinates or on canonical transformation techniques, have indeed been proposed by Bardeen and Pines[4]), Nakajima[4]) and Chester[7]), but these methods also have their own difficulties. Fortunately all different methods lead essentially to the same effective matrix element (to first order in the ionic displacements, higher order terms being neglected by the abovementioned authors) for electron-phonon interaction.

We shall not enter into a more detailed discussion of this difficult question, but accept the Hamiltonian (2.9) for our further considerations with the interaction terms up to general order in the ionic displacements. This hardly complicates the formalism. Whether or not it makes any sense is not easy to decide; at any rate we may consider our Hamiltonian as a model Hamiltonian, which will describe the system correctly at least in lowest order in the interactions and for wave vectors, which are not too small*).

3. *The diagrams for calculating the scattering function.* The differential scattering cross section at temperature T per unit of solid angle $d\Omega$ and per unit of outgoing energy $d\varepsilon$ of the neutron for coherent scattering**) in the first Born approximation, is given by the following equation[8]):

$$\frac{d^2\sigma_T}{d\Omega \, d\varepsilon} = a^2 \frac{|\boldsymbol{k}|}{|\boldsymbol{k}_0|} S_T(\boldsymbol{\kappa}\omega), \qquad (3.1)$$

where the scattering function $S_T(\boldsymbol{\kappa}\omega)$, depending upon the momentum transfer $\boldsymbol{\kappa} = \boldsymbol{k}_0 - \boldsymbol{k}$ and energy transfer ω, can be written in the following form (compare I):

$$S_T(\boldsymbol{\kappa}\omega) = (2\pi Z_\beta)^{-1} \int_{-\infty}^{\infty} dt \exp[-i\omega t] \operatorname{Tr}\{U_\theta U_{-t} T_{-\boldsymbol{\kappa}} U_t T_{\boldsymbol{\kappa}}\}, \qquad (3.2)$$

with

$$Z_\beta = \operatorname{Tr}\{\exp[-\beta(H_{0p} + H_{0e} + V + W) + \alpha N]\}, \qquad (3.3)$$

$$U_{\pm t} = \exp[\pm it(H_{0p} + H_{0e} + V + W)], \qquad (3.4)$$

$$U_\theta \equiv U_{i\beta} = \exp[-\beta(H_{0p} + H_{0e} + V + W) + \alpha N], \qquad (3.5)$$

$$T_{\pm\boldsymbol{\kappa}} = \Sigma_{sn} \exp[\pm i\boldsymbol{\kappa} \cdot \boldsymbol{r}_{sn}]. \qquad (3.6)$$

The electrons are described by means of a grand canonical ensemble; $N = \Sigma_{km\sigma} \Gamma^*_{km\sigma} \Gamma_{km\sigma}$ is the number operator for the electrons and $\alpha = \mu\beta$, μ being the chemical potential.

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*) For very short wave lengths additional difficulties arise due to exchange effects [4]).

**) We only consider scattering of the neutrons by the nuclei; magnetic scattering by the electrons will not be taken into account.

In the representation of the electron-phonon states, defined by (2.10), the trace in (3.2) takes the form:

$$\text{Tr}\{O\} = \Sigma_{l=0}^{\infty} \Sigma_{n=0}^{\infty} \Sigma_{j_1...j_l;\sigma_1...\sigma_n;m_1...m_n} \int_{q_1...q_l;k_1...k_n} [(l+n)!]^{-1} \cdot$$

$$\cdot \langle q_l j_l,..., q_1 j_1; k_n \sigma_n m_n,..., k_1 \sigma_1 m_1 |\{O\}| k_1 \sigma_1 m_1,...,k_n \sigma_n m_n; q_1 j_1,...,q_l j_l \rangle. \quad (3.7)$$

We want to calculate the matrix elements (3.7) by means of perturbation theory. For that purpose we need expansions in powers of $V + W$ for the operators $U_{\pm t}$, U_θ and $T_{\pm \kappa}$. These expansions are written down in I ((4.1)–(4.5)) for the case of phonon-phonon interaction alone, but they can obviously be extended to include the electron-phonon interaction W. The only thing we have to do is to replace V by $V + W$. Substituting the expansions (2.4) and (2.6) for V and W, we see that the operator in the matrix element (3.7) is a linear combination of products of creation and annihilation operators for the electrons and the phonons.

Just as in I we introduce diagrams to classify the various matrix elements. These diagrams have a similar structure as the diagrams used in I. They are more complicated, however, because of the presence of two types of lines (phonon lines and electron lines) and of two types of vertices (V-vertices, in which only phonon lines join, and W-vertices, in which both phonon lines and electron lines join). From the structure of the terms in the expansion of W (see 2.6), we immediately conclude that in each W-vertex always one electron line comes in and always one electron line goes out, whereas the number of phonon lines which enter and/or leave a vertex may be one or more. No electron lines can be attached to a neutron vertex. In each V- or W-vertex we have conservation of wave vector due to the Δ-functions occurring in (2.4) and (2.6), while with the neutron vertex T_κ is associated a factor $\Delta(\kappa - q)$, where q is the sum of the wave vectors of the phonons created by T_κ minus the sum of the wave vectors annihilated by T_κ. In fig. 1 we have drawn an example of a diagram contributing to the trace in (3.2). This diagram contains four $W^{(3)}$-vertices in the U_t-region. For a more detailed description of these diagrams we must refer to I.
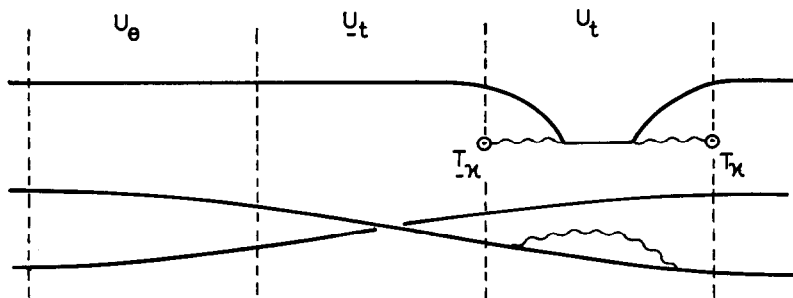

Fig. 1. Diagram contributing to the trace in (3.2). The full lines represent electrons, the wavy lines represent phonons. This diagram has two components; the component containing the neutron vertices is a one-phonon diagram (see § 4).

By continuously joining the external lines at the left and right of a diagram, which is always possible because the initial states of our diagrams are identical to the final states, we can consider each diagram as being rolled onto a cylinder. From the nature of the electron-phonon interaction terms it is then clear that the various electron lines of a diagram compose to closed loops on the cylinder, each loop consisting of one or more turns. For instance, the diagram of fig. 1 has two such loops.

At this stage a remark must be made concerning the Pauli principle for the electrons. It follows from (2.6) and (3.7) that in order to get the contribution of a particular diagram a summation must be performed over all variables $\mathbf{k}m\sigma$ for the electrons which occur. According to the exclusion principle terms with identical index triples should be excluded in this summation. It has been proved by Wick, however, that such a restriction on the summation can be dropped, because the errors one makes in forgetting the Pauli principle cancel each other exactly. This compensation of errors holds quite generally both for fermions (the exclusion principle) and for bosons (more than one boson in a particular state). In the following therefore we will treat the electron lines and phonon lines of our diagrams on an equal footing with the only difference that according to a well-known theorem of Wick[9]) each diagram gets an extra factor $(-1)^{n+l}$, where n is the number of external electron lines of the diagram and l the number of closed electron loops.

We define connectedness of our diagrams or parts of our diagrams as connectedness in the usual sense on the cylinder (see I) and call a connected part a component. According to a well-known theorem the contribution of a diagram to a matrix element can be determined from the contributions of its components. For the case of phonon-phonon interaction this theorem was formulated in I where it was used to prove that the contribution of all components without neutron vertices just cancels a factor Z_β in the expression for $S_T(\kappa\omega)$. These results can be taken over with minor modifications to our problem, to give

$$S_T(\kappa\omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} dt \exp[-i\omega t] \sum_{\delta}^{\text{neutron}} \text{Tr}\{U_\theta U_{-t}T_{-\kappa}U_t T_\kappa\}_\delta, \quad (3.8)$$

where the symbol $\sum_{\delta}^{\text{neutron}}$ indicates that in calculating the trace only diagrams δ, which consist of components containing neutron vertices, must be taken into account.

4. *One-phonon diagrams.* There are still two types of diagrams that contribute to the trace in (3.8). Firstly the diagrams that consist of two components, each component containing one neutron vertex. These diagrams produce the *elastic* scattering spectrum. It can be shown that phonon-phonon interactions and electron-phonon interactions only affect the elastic scattering intensity; the Bragg conditions remain exactly valid (compare I).

The second group of diagrams consists of one-component diagrams, which contain both of the neutron vertices. These diagrams give rise to the *inelastic* spectrum. In section 5 of I a particular class of diagrams, called *one-phonon diagrams*, was isolated from this group of one-component diagrams, which was expected to describe the one-phonon peaks provided the widths of the peaks were sufficiently small. In a completely analogous way these one-phonon diagrams can be defined and disentangled for the problem at hand. The general structure of these diagrams is a chain of bubbles connected by single phonon lines (q-lines), a chain beginning and ending at a neutron bubble (see fig. 1 and 2). A bubble is defined as a proper part which does not contain any q-line (for further details see I, § 6).
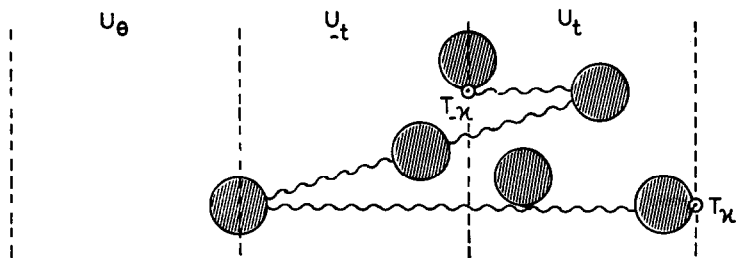

Fig. 2. General form of the one-phonon diagrams.

Our first task now is to perform the summation of the one-phonon diagrams defined above in order to obtain an expression for the partial scattering function which describes the peaks, in terms of the bubble functions which represent the contributions of the bubbles. This summation was demonstrated, at least schematically, in I for the case of phonon-phonon interaction alone. Although very complicated it turned out that this summation could be performed without any approximation by extending a method of Dyson[10]) and Beliaev[11]) to the case of arbitrary temperatures. The procedure can be directly extended to include the electron-phonon interaction as studied in this paper. The only difference is brought about by the enlarged number of types of bubbles; each q-line can be attached to a bubble at a V-vertex or at a W-vertex. This difference can be taken into account in a straightforward way. The summation process results in equations directly analogous to equations (8.1) and (8.2) of I, but where the bubble function, representing the general contribution of a (V, W)-bubble, now has the form:

$$G^{\pm}(\boldsymbol{q}\omega j j') =$$
$$= i \int_0^{\pm\infty} d\tau \exp[-i\omega\tau]\, \mathrm{Tr}\{U_\theta U_{-\tau}(V_{\boldsymbol{q}j} + W_{\boldsymbol{q}j})\, U_\tau(V_{\boldsymbol{q}j'} + W_{\boldsymbol{q}j'})\}_{C,n\boldsymbol{q}} +$$
$$+ i \int_0^{\mp\infty} d\tau \exp[i\omega\tau]\, \mathrm{Tr}\{U_\theta U_{-\tau}(V_{\boldsymbol{q}j'} + W_{\boldsymbol{q}j'})\, U_\tau(V_{\boldsymbol{q}j} + W_{\boldsymbol{q}j})\}_{C,n\boldsymbol{q}} +$$
$$+ \mathrm{Tr}\{U_\theta(V_{\boldsymbol{q}jj'} + W_{\boldsymbol{q}jj'})\}_C, \quad (4.1)$$

with U_θ and $U_{\pm\tau}$ given by (3.4) and (3.5). The subscript C, nq indicates that only connected diagrams involving no q-lines contribute to the traces in (4.1). Furthermore it is to be understood that V_{qj} and W_{qj} contain a creation operator for the phonon qj, $V_{qj'}$ and $W_{qj'}$ contain an annihilation operator for the phonon qj' and $V_{qjj'}$ and $W_{qjj'}$ contain both.

It was argued in I that for those cases where, independent of the strength of the interactions, the widths of the peaks remain small in such a way that the peaks are distinguishable from the background, the functions $G^\pm(q\omega jj')$ correctly describe the positions and widths of the peaks. Because of the irreducible character of the diagrams that contribute to the traces in (4.1) an expansion of $G^\pm(q\omega jj')$ in powers of $V + W$ converges rapidly for all values of ω, while for any particular order only a finite number of essentially different diagrams has to be calculated. It can be seen, that (at least for a Bravais lattice, see the next section) to lowest order in both interactions, that is to order $(u/d)^2$, there are no diagrams which involve both V-vertices and W-vertices, so that to lowest order the shift and width as a result of phonon-phonon interactions and of electron-phonon interactions are exactly additive. This no longer holds for higher orders in the coupling. Here ,,mixed" diagrams occur and the shift and width ensuing from the two types of interactions cease to be additive. In consistent higher order calculations of shift and width of the scattering peaks phonon-phonon interactions and electron-phonon interactions must be treated together. This also holds true for the scattering intensity.

We will not write down the general equations here but from now on restrict ourselves to the lowest order case. To lowest order in the interactions the following matrix equation is obtained:

$$\mp 2\pi i \sum_{j'} [(\omega_{qj} - \omega)\, \delta_{jj'} + G^\pm_{(0)}(q\omega jj')]\, C^\pm_{(0)}(q\omega j'j'') =$$
$$= f'(qj)\, \delta_{jj''} + \Theta^\pm_{(0)}(q\omega jj''). \quad (4.2)$$

The definitions of the various functions occurring in (4.2) are obvious generalizations of those in I. In the latter paper a discussion is given of this equation. It can be seen that equations (4.2) describe those peaks in the scattering spectrum whose central frequencies occur at positive values of ω and which therefore can be considered as corresponding to the emission of a single phonon by the neutron. The shift of each peak is determined by the hermitian part, the width by the anti-hermitian part of the quantity $G^\pm_{(0)}(q\omega jj')$. An analogous equation is valid for the absorption peaks.

5. *First order calculation of shift and width.* We restrict ourselves in this section to processes involving electron-phonon interactions; the shift and width as a result of phonon-phonon interactions *alone* have been considered in detail in I. The lowest order diagrams which contribute to $G^\pm(q\omega jj')$ are

shown in fig. 3, where again the full lines represent electrons and the wavy lines phonons.
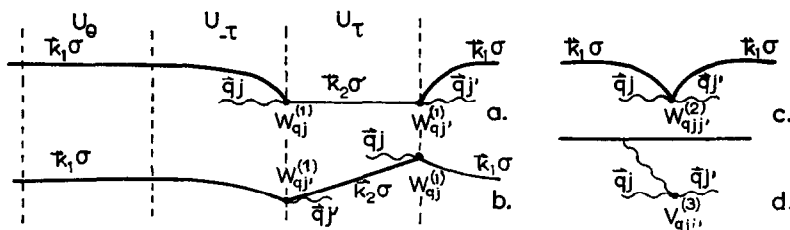

Fig. 3. Lowest order diagrams contributing to the traces in (4.1) and involving electron-phonon processes. Strictly speaking, the wavy lines representing the phonons qj and qj' do not belong to the diagrams; we have only drawn them to indicate that the appropriate vertices contain creation and/or annihilation operators for these phonons.

In addition to the diagrams drawn in fig. 3, there are classes of related diagrams, contributing to $G_{(0)}^{\pm}(q\omega jj')$, which only differ from the above-mentioned diagrams in that the internal and external electron lines and the internal phonon line of diagram d encircle the cylinder an arbitrary number of times. These additional turns can be easily summed[5][12] with the result that we can restrict ourselves to just calculating the diagrams of fig. 3, but substituting the following propagator functions (we drop the index m):
external electron line:

$$\frac{\exp[\alpha - \beta\varepsilon_{k\sigma} - i\tau\varepsilon_{k\sigma}]}{1 + \exp[\alpha - \beta\varepsilon_{k\sigma}]} , \tag{5.1}$$

internal electron line:

$$\frac{\exp[i\tau\varepsilon_{k\sigma}]}{1 + \exp[\alpha - \beta\varepsilon_{k\sigma}]} , \tag{5.2}$$

phonon line:

$$\frac{\exp[i\tau\omega_{qj}] + \exp[-(\beta + i\tau)\omega_{qj}]}{1 - \exp[-\beta\omega_{qj}]} . \tag{5.3}$$

The propagator functions now explicitly show up the difference in statistics for the electrons and phonons. In the summation this difference is brought about by the sign factor $(-1)^{n+l}$ for the electron lines, explained in section 3.*).

From the structure of diagram d we directly see that this diagram gives a non zero contribution only if the wave vector of the intermediate phonon is 0(mod $2\pi\tau$). Hence this intermediate phonon can only be an optical

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*) It is often convenient to make a slight reformulation of the diagram formalism in terms of electrons above the (spherical) Fermi sea and holes below it. In this formulation diagram a, for instance, can be interpreted at absolute zero as the decay of a phonon into an electron-hole pair.

phonon (acoustical phonons with zero wave vectors correspond to trans-
lations of the crystal as a whole, which we explicitly exclude from our
considerations). As a consequence diagram d only contributes for lattices
with more than one atom per unit cell. We shall restrict ourselves in the
following to Bravais lattices, i.e., to the first three diagrams of fig. 3; these
latter diagrams now involve only W-vertices, in contrast with diagram d
which contains both a V-vertex and a W-vertex.

From (2.6), (5.1) and (5.2) the following contributions to $G_{(0)}^{\pm}(q\omega jj')$ are
found of the diagrams a, b and c of fig. 3:

$$G_{(0)}^{\pm(a)}(q\omega jj') = \sum_\sigma \int_{k_1 k_2} b_{k_1, k_2, -qj}^{(1)} b_{k_2, k_1, qj'}^{(1)} \Delta(k_1 + q - k_2) \cdot$$
$$\cdot \exp[\alpha - \beta\varepsilon_{k_1\sigma}][\{1 + \exp[\alpha - \beta\varepsilon_{k_1\sigma}]\}\{1 + \exp[\alpha - \beta\varepsilon_{k_2\sigma}]\}]^{-1} \cdot$$
$$\cdot [(\omega + \varepsilon_{k_1\sigma} - \varepsilon_{k_2\sigma})_P^{-1} \pm \pi i\delta(\omega + \varepsilon_{k_1\sigma} - \varepsilon_{k_2\sigma})], \quad (5.4)$$

$$G_{(0)}^{\pm(b)}(q\omega jj') = \sum_\sigma \int_{k_1 k_2} b_{k_1, k_2, qj'}^{(1)} b_{k_2, k_1, -qj}^{(1)} \Delta(k_2 + q - k_1) \cdot$$
$$\cdot \exp[\alpha - \beta\varepsilon_{k_1\sigma}][\{1 + \exp[\alpha - \beta\varepsilon_{k_1\sigma}]\}\{1 + \exp[\alpha - \beta\varepsilon_{k_2\sigma}]\}]^{-1} \cdot$$
$$\cdot [-(\omega + \varepsilon_{k_2\sigma} - \varepsilon_{k_1\sigma})_P^{-1} \mp \pi i\delta(\omega + \varepsilon_{k_2\sigma} - \varepsilon_{k_1\sigma})], \quad (5.5)$$

$$G_{(0)}^{(c)}(qjj') = 2\sum_\sigma \int_{k_1} b_{k_1, k_1, qj, -qj'}^{(2)} \exp[\alpha - \beta\varepsilon_{k_1\sigma}]\{1 + \exp[\alpha - \beta\varepsilon_{k_1\sigma}]\}^{-1}. \quad (5.6)$$

Only electrons within one energy band are considered. In deriving the above
expressions use has been made of the formal relation:

$$\int_0^{\pm\infty} d\tau \exp[i\omega\tau] = (i/\omega)_P \pm \pi\delta(\omega),$$

which in connection with relation (2.8) immediately gives rise to a separation
in hermitian and anti-hermitian parts. The factor 2 in (5.6) is a combinatorial
factor. Analogous to the case of phonon-phonon interaction the contribution
of diagram c, being of second order in the ionic displacements, is hermitian
and hence only contributes to the line shift.

Combining equations (5.4), (5.5) and (5.6) we find for the shift $\Delta_{(0)}(q\omega jj')$
and the width $2\Gamma_{(0)}(q\omega jj')$ to lowest order in the electron-phonon coupling:

$$\Delta_{(0)}(q\omega jj') = \sum_\sigma \int_{k_1 k_2} b_{k_1, k_2, -qj}^{(1)} b_{k_2, k_1, qj'}^{(1)} \Delta(k_1 + q - k_2) \cdot$$
$$\cdot [n_{k_1\sigma} - n_{k_2\sigma}](\omega + \varepsilon_{k_1\sigma} - \varepsilon_{k_2\sigma})_P^{-1} + 2\sum_\sigma \int_{k_1} b_{k_1, k_1, qj, -qj'}^{(2)} n_{k_1\sigma}, \quad (5.7)$$

$$\Gamma_{(0)}(q\omega jj') = \pi \sum_\sigma \int_{k_1 k_2} b_{k_1, k_2, -qj}^{(1)} b_{k_2, k_1, qj'}^{(1)} \Delta(k_1 + q - k_2) \cdot$$
$$\cdot [n_{k_1\sigma} - n_{k_2\sigma}] \delta(\omega + \varepsilon_{k_1\sigma} - \varepsilon_{k_2\sigma}), \quad (5.8)$$

with

$$n_{k\sigma} = [1 + \exp(\beta\varepsilon_{k\sigma} - \alpha)]^{-1}. \quad (5.9)$$

These formulae have recently also been found by Krivoglaz[13] using
different methods. However, his treatment is restricted to terms in the
electron-phonon interaction potential which are linear in the ionic dis-

placements and so he does not find the second term at the right hand side of (5.7). This latter term, however, is expected to be of the same order of magnitude as the first term. A similar situation arises in phonon-phonon interactions[1]), where in calculating line shift effects cubic and quartic anharmonic terms must always be considered together.

In order to obtain orders of magnitude of the widths of the scattering peaks due to electron-phonon interaction we will evaluate formula (5.8) under the following simplifying assumptions (a) we consider long wave length acoustical phonons such that on the one hand condition (2.11) is satisfied and on the other hand the Bardeen formula in the simple form (2.7) is applicable, (b) we assume that the phonons are either longitudinal or transverse and (c) we neglect Umklappprocesses. These assumptions are reasonable for low temperatures and small energies of the incident neutrons. As a result of the factor $(e_{qj} \cdot q)$, occurring in (2.7), it follows in connection with the above assumptions that we get a non zero result only for longitudinal phonons; the electrons are coupled to transverse phonons via Umklappprocesses only (at least for a spherical Fermi surface). Substituting expression (2.7) in (5.8) and using the formulae $\varepsilon_k = \hbar^2 k^2 / 2m^*$ and $\omega_q = s_l q$, where m^* is the effective mass of the electron and s_l the longitudinal velocity of sound, we find after elementary but lengthy integrations:

$$\Gamma_{(0)}(q\omega)/\omega = (E_F^2 m^{*2}/9\pi M \rho s_l \hbar^3) \cdot$$

$$\cdot \left\{ 1 - (\beta \hbar \omega_q)^{-1} \ln \frac{1 + \exp[\beta(\tfrac{1}{2}m^* s_l^2 + \hbar^2 q^2/8m^* + \tfrac{1}{2}\hbar\omega_q - E_F)]}{1 + \exp[\beta(\tfrac{1}{2}m^* s_l^2 + \hbar^2 q^2/8m^* - \tfrac{1}{2}\hbar\omega_q - E_F)]} \right\} \quad (5.10)$$

where we have put $\alpha = \beta E_F$ and where it is assumed that the Fermi surface is spherical. The behaviour of the second term within braces of expression (5.10) is such that in the neighbourhood of $q = 2k_F$ (assuming for a moment the validity of (5.10) for such large values of q) it changes abruptly with q from the value zero for q immediately below $2k_F$ to the value 1 for q immediately above $2k_F$, k_F being the Fermi momentum. From this it follows that for $q > 2k_F$ the line width vanishes. Of course, this has a purely kinematical reason; for $q > 2k_F$ it is no longer possible to satisfy the conservation rules. (Note that this is only true under neglect of Umklappprocesses). For $q < 2k_F$ the logarithmic term in (5.10), which is the only temperature dependent term, may be neglected and we have obtained the following formula valid for longitudinal acoustical phonons of long wave length:

$$\Gamma_{(0)}(\omega)/\omega = E_F^2 m^{*2}/9\pi M \rho s_l \hbar^3 \quad (5.11)$$

Similar formulae can also be obtained using more intuitive arguments based on the exponential decay of one-particle states[14][15]). Only to first order in the coupling such simple techniques can be expected to be reliable. Formula (5.11) gives values for $\Gamma_{(0)}(\omega)/\omega$ which are of the order 10^{-3}–10^{-2} and hence are quite small.

When we admit Umklappprocesses, $\Gamma_{(0)}(q\omega)$ will display stepdiscontinuities, not only for $q = 2k_F$, but also for those values of q which satisfy the condition $|q + 2\pi\tau| = 2k_F$, for any reciprocal lattice vector τ. For further details about this question we refer to recent work of Woll and Kohn[2]. In fact these anomalies stem from the same grounds as the so-called Kohnanomalies in the frequency spectra of lattice vibrations in metals.

Concerning the shift of the scattering peaks, we remark that only the temperature dependent part is observable. It is to be expected that, due to the nature of the Fermi distribution of the electrons, this temperature dependence of the shift as a result of electron-phonon interactions will be very small and hardly observable. For this reason we shall not perform further calculations.

In the case of superconductors anomalies in the shift and width of the scattering peaks, due to electron-phonon coupling, can be expected as a result of the presence of an energy gap in the density of states of the electrons. Decay of a phonon into an electron-hole pair (see footnote on page 903), for instance, is energetically possible only when the phonon energy ω exceeds the gap. As a consequence at absolute zero there is an abrupt decrease of $\Gamma(q\omega)/\omega$ when ω becomes less than the gap[13]. But also the virtual transitions will be affected by the gap, leading to a change in the energy shift (5.7) of the phonons. It has recently been proposed by Ferrell[16] that this change in the frequency of the phonons in the superconducting state should account for the anomalous behaviour of the lattice specific heat of superconductors, discovered by Bryant and Keesom[17].

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