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THEORY OF INELASTIC SCATTERING OF NEUTRONS BY IMPERFECT CRYSTALS

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We consider inelastic one-phonon scattering of neutrons by solid solutions or by crystals containing defects. Phonon scattering by static inhomogeneities in a crystal results in broadening of the peaks in the energy distribution of coherently scattered neutrons. This broadening depends strongly on the degree of order in the arrangement of the atoms of the solution and becomes anomalously large near critical points on the decomposition curve and near points of second-order phase transitions. We consider the peculiarities of the broadening in the scattering by vibrations corresponding to extrema of the vibration spectrum. It is shown that including the effects of defects and correlations in the solution results in the appearance of an angular dependence of the intensity of incoherent scattering, and that imperfection of the crystal leads to a smearing out of singularities in the energy spectrum of this scattering and in the distribution function of the vibration frequencies. The incoherent scattering increases sharply near critical points on the decomposition curve. We consider the scattering of neutrons by local vibrations.

It is known that in the elastic scattering of neutrons by imperfect crystals (where the imperfection of the crystal may be related to the presence of atoms of different sorts, or of defects at the sites of some sublattice, or of distortions of the crystal), in addition to the allowed Bragg reflections which are characteristic of the ideal crystal, there appears a diffuse scattering. The fact that the crystal is not ideal should also lead to important peculiarities in the inelastic scattering of neutrons by the thermal vibrations of the atoms, resulting in a change not only in the angular distribution but also in the energy distribution after scattering. The scattering of neutrons by vibrations of an ideal crystal have been studied in detail, for the harmonic approximation, in many papers (cf., for example, references 1 — 3, where references are given to other work). It was found that, in addition to a smooth distribution, the energy spectrum of the scattered neutrons contains terms proportional to δ functions which correspond to the case where the energy and momentum conservation laws are satisfied in the processes of absorption or emission of a phonon during the scattering. The investigation of the location of these peaks in the energy distribution at various scattering angles is the basis of the widely used method for determining the energy distribution of the crystal vibrations.

It is obvious that the δ functions are associated with perfectly monochromatic waves propagating in an ideal crystal. The presence of inhomogeneities in the crystal, or interaction of phonons with one another or with other elementary excitations, leads to scattering and damping of the waves and to a smearing of the δ function distribution in the energy spectrum. Since the determination of the vibration spectrum is possible only when the distribution is sufficiently sharp, it is of interest to investigate theoretically the width and shape of the distribution (for the scattering of neutrons by superfluid He, this problem was studied in references 4 and 5).

Moreover, the study of the broadening may give new and valuable information concerning the interaction of phonons with crystal inhomogeneities and with one another, concerning their relaxation times, concerning singularities in the vibration spectrum, concerning order in the arrangement of atoms in solution, etc. In addition to a broadening of the peaks, corresponding to one-phonon coherent scattering, imperfection of the crystal may also cause a smearing out of the singularities in the spectrum of incoherent scattering and the appearance of an angular dependence of this scattering. We shall also consider these questions.

In this paper we consider effects associated with the influence of the interaction of phonons with static inhomogeneities in the crystal on the nuclear scattering of neutrons (effects associated with anharmonicity and with phonon-magnon interaction in ferromagnets will be discussed elsewhere[6]). Nonideal crystals include solid solutions (including solutions of isotopes) and crystals containing vacancies, interstitial atoms, etc. Since the scattering depends strongly on the order in the arrangement of the atoms of different types, we shall not assume that the solutions are ideal, and will explicitly include correlations. In particular, we shall investigate the important special phenomena which must occur near critical points on the decomposition curve and near points of second order phase transition. In most cases the interaction of phonons with static inhomogeneities will be assumed to be small, which permits us to use perturbation theory and to disregard local vibrations. We shall consider separately the case where defects have a strong influence on the vibrations and lead to the appearance of new local frequencies.

1. GENERAL FORMULAS FOR THE DIFFERENTIAL SCATTERING CROSS SECTION

For simplicity of presentation, we shall carry through the treatment for the case of a binary solution A-B. The differential cross section, $d^2\Sigma/d\Omega\, dE = \sigma(\mathbf{q}_1, \omega)$, for the nuclear scattering of monochromatic neutrons by a single crystal, per unit solid angle and per unit energy, is given by the expression:[3,4]

$$\frac{d^2\Sigma}{d\Omega\, dE} = \sigma(\mathbf{q}_1, \omega) = \frac{m^2}{8\pi^3\hbar^5}\frac{k_2}{k_1}\,\mathrm{Sp}\Big\{\sum_{ss'\gamma\gamma'}(A_{s\gamma}A_{s'\gamma'} + \delta_{ss'}\delta_{\gamma\gamma'}B^2_{s\gamma})$$
$$\times\exp(i\mathbf{q}_1, \mathbf{R}_{s\gamma} - \mathbf{R}_{s'\gamma'})\exp(i\mathbf{q}_1, \delta\mathbf{R}_{s\gamma} - \delta\mathbf{R}_{s'\gamma'})$$
$$\times\int_{-\infty}^{\infty} dt\, e^{-i\omega t}\exp[i\mathbf{q}_1, \mathbf{u}_{s\gamma}(t)]\exp[-i\mathbf{q}_1, \mathbf{u}_{s'\gamma'}(0)]\,e^{-\lambda H}\Big\}$$
$$\times(\mathrm{Sp}\, e^{-\lambda H})^{-1}. \tag{1}$$

Here m is the neutron mass; $\mathbf{q}_1$ is the difference of the wave vectors $\mathbf{k}_2$ and $\mathbf{k}_1$ of the scattered and incident waves; $\mathbf{q} = \mathbf{q}_1 - 2\pi\mathbf{K}_n$, where $\mathbf{K}_n$ is the vector of the reciprocal lattice which is closest to the end of the vector $\mathbf{q}_1/2\pi$; s is the number labelling the elementary cell; γ is the number of the site in the lattice; $\mathbf{R}_{s\gamma}$ is the radius vector to a site in the "average" periodic lattice; $\delta\mathbf{R}_{s\gamma}$ is the static displacement of the atom from this site; $A_{s\gamma}$ and $B_{s\gamma}$ are constants in the expression for the interaction of the neutron with the nucleus at the site labelled $s\gamma$:

$$V_{s\gamma}(\mathbf{r}) = \{A_{s\gamma} + 2B_{s\gamma}(\mathbf{s}\mathbf{S}_{s\gamma})\,[S_{s\gamma}(S_{s\gamma}+1)]^{-1/2}\}\,\delta(\mathbf{r})$$

($\mathbf{s}$ and $\mathbf{S}_{s\gamma}$ are the operators for the spin of the neutron and the spin of the nucleus $s\gamma$); $A_{s\gamma}$ and $B_{s\gamma}$ take on the values A_1, A_2, B_1, B_2, depending on the sort of atom which is located at the $s\gamma$ site;

$$E = \hbar\omega = \hbar^2(k_2^2 - k_1^2)/2m$$

is the change in energy of the neutron in the scattering; $\lambda = (kT)^{-1}$; H is the Hamiltonian for the vibrations of the atoms;

$$\mathbf{u}_{s\gamma}(t) = \exp(iHt/\hbar)\,\mathbf{u}_{s\gamma}(0)\exp(-iHt/\hbar)$$

is the operator for the thermal displacement of the $s\gamma$ atom, in the Heisenberg representation. In taking the trace in (1), it is understood that we also average over all configurations corresponding to the given values of the order and correlation parameters.

In the case of a nonideal crystal, the normal vibrations are no longer described by plane waves, which complicates the computation of the trace in (1). Making use of the fact that the imperfection is small, we can carry out the computation in two ways. First, by using perturbation theory we can find the approximate normal coordinates of the problem, as was done by I. Lifshitz[7] in treating the problem of the absorption of light by imperfect crystals, and then evaluate the trace in these coordinates. However it is more convenient to solve the problem by expanding the displacements, not in the normal coordinates of the nonideal crystal, but rather in plane waves, and to use perturbation theory directly for computing the trace. This method is more general, and is also applicable, for example, to the treatment of anharmonicity.

We expand the thermal displacement vector in plane waves describing the normal vibrations in the zero'th approximation, which corresponds to an ideal crystal consisting of atoms with the average (for sites of the particular type) reciprocal masses and force constants:

$$\mathbf{u}_{s\gamma} = \sum_{\mathbf{k}j}\sqrt{\frac{\hbar}{2\rho N v\omega_{\mathbf{k}j}}}\,\mathbf{e}_{\mathbf{k}j\gamma}\exp(i\mathbf{k}\mathbf{R}_{s\gamma})\,(a_{\mathbf{k}j} - a^{+}_{-\mathbf{k}j}),$$
$$\mathbf{e}^{*}_{-\mathbf{k}j\gamma} = -\mathbf{e}_{\mathbf{k}j\gamma},$$
$$\frac{\partial}{\partial\mathbf{u}_{s\gamma}} = \sum_{\mathbf{k}j}M_\gamma\sqrt{\frac{\omega_{\mathbf{k}j}}{2\rho N v\hbar}}\,\mathbf{e}_{\mathbf{k}j\gamma}\exp(i\mathbf{k}\mathbf{R}_{s\gamma})\,(a_{\mathbf{k}j} + a^{+}_{-\mathbf{k}j}),$$
$$[a_{\mathbf{k}j}(0)\,a^{+}_{\mathbf{k}'j'}(0)] = \delta_{\mathbf{k}\mathbf{k}'}\delta_{jj'}. \tag{2}$$

Here ρ is the density of the crystal, N the number of elementary cells, v the volume of a cell; $\omega_{\mathbf{k}j}$ is the vibration frequency for the j-th branch with wave number $\mathbf{k}$; the values $\mathbf{k}/2\pi$ lie inside a unit cell of the reciprocal lattice; $\mathbf{e}_{\mathbf{k}j\gamma}$ are polarization vectors satisfying the normalization condition

$$\sum_{s\gamma} \mathbf{e}_{\mathbf{k}j\gamma}\overset{*}{\mathbf{e}}_{\mathbf{k}'j'\gamma} M_\gamma \exp\left(i(\mathbf{k}-\mathbf{k}'),\ \mathbf{R}_{s\gamma}\right) = MN\delta_{\mathbf{k}\mathbf{k}'}\delta_{jj'},$$

M_γ are the masses of the atoms at the γ sites, and M is the mass of a cell.

The Hamiltonian for the vibrations of the nonideal crystal has the following form, when expressed in terms of the operators $a_{\mathbf{k}j}$ and $a^{+}_{\mathbf{k}j}$:[8]

$$H = \sum_{\mathbf{k}j} \hbar\omega_{\mathbf{k}j} a^{+}_{\mathbf{k}j} a_{\mathbf{k}j} + \sum_{\mathbf{k}j\mathbf{k}'j'} V_{\mathbf{k}j\mathbf{k}'j'} a^{+}_{\mathbf{k}j} a_{\mathbf{k}'j'}$$

$$-\frac{1}{2}\sum_{\mathbf{k}j\mathbf{k}'j'} \left(V'_{\mathbf{k}j\mathbf{k}'j'} a^{+}_{\mathbf{k}j} a^{+}_{\mathbf{k}'j'} + V'^{*}_{\mathbf{k}j\mathbf{k}'j'} a_{\mathbf{k}j} a_{\mathbf{k}'j'}\right). \tag{3}$$

The quantities V and V′, which characterize the probability of scattering of phonons by static inhomogeneities, are determined by the values of the differences in masses of the atoms, by the force constants of the interaction and by the static imperfections. Explicit expressions for these quantities were obtained earlier[8] and are given below for various cases. Here we mention only that $V_{\mathbf{k}j\mathbf{k}'j'} = V^{*}_{\mathbf{k}'j\mathbf{k}j'}$, that $V_{\mathbf{k}j\mathbf{k}j'} = 0$, and that the average of $V_{\mathbf{k}j\mathbf{k}'j'}$ over the configurations of the atoms is also equal to zero.

The thermal vibrations result in a weakening of the intensity of the allowed Bragg reflections and the appearance of inelastic diffuse scattering. The reduction in intensity of allowed reflections and the multiphonon diffuse scattering by nonideal crystals will be treated elsewhere. Here we shall consider only processes which are accompanied by the absorption or emission of one (real or virtual) phonon, so that in the expansion of $\exp(i\mathbf{q}_1\cdot\mathbf{u}_{s\gamma})$ we need keep only the linear terms. In addition we shall treat the case when there are no static imperfections present ($\delta\mathbf{R}_s = 0$) or when both $\delta\mathbf{R}_s$ and $A_1 - A_2$ can be treated as small quantities, and we can neglect cubic terms in these quantities. We split the quantities $B^2_{s\gamma}$ and $A_{s\gamma} = \overline{A}_\gamma + (c_{s\gamma} - c_\gamma)(A_1 - A_2)$ into an average value (for the particular sublattice), $\overline{A}_\gamma = c_\gamma A_1 + (1 - c_\gamma)A_2$, and a fluctuating part, $(c_{s\gamma} - c_\gamma) \times (A_1 - A_2)$ (where $c_{s\gamma}$ take on the values one or zero, depending on whether the atom at the $s\gamma$ site is of type A or type B; c_γ is the concentration of atoms A at the γ sites). Expanding in $\delta\mathbf{R}_{s\gamma}$ and $\mathbf{u}_{s\gamma}$, we find the expression for the differential inelastic scattering of neutrons

$$\sigma(\mathbf{q}_1, \omega) = \sigma_1(\mathbf{q}_1, \omega) + \sigma_2(\mathbf{q}_1, \omega) + \sigma_3(\mathbf{q}_1, \omega), \tag{4}$$

$$\sigma_1(\mathbf{q}_1, \omega) = CN\frac{k_2}{k_1}\sum_{jj'} \frac{Q_{j\mathbf{q}_1}Q^{*}_{j'\mathbf{q}_1}}{\sqrt{\omega_{\mathbf{q}j}\omega_{\mathbf{q}j'}}}\varphi_{\mathbf{q}j\mathbf{q}j'}(\omega), \tag{5}$$

$$\sigma_2(\mathbf{q}_1, \omega) = CN\frac{k_2}{k_1}\sum_{jj'}\Bigg\{-2\,\mathrm{Re}\sum_{\mathbf{k}} \frac{Q_{j\mathbf{q}_1}S^{*}_{j'\mathbf{q}_1}(\mathbf{k})}{\sqrt{\omega_{\mathbf{q}j}\omega_{\mathbf{k}j'}}}\varphi_{\mathbf{q}j-\mathbf{k}j'}(\omega)$$

$$+\sum_{\mathbf{k}\mathbf{k}'} \frac{S_{j\mathbf{q}_1}(\mathbf{k})S^{*}_{j'\mathbf{q}_1}(\mathbf{k}')}{\sqrt{\omega_{\mathbf{k}j}\omega_{\mathbf{k}'j'}}}\varphi_{\mathbf{k}j\mathbf{k}'j'}(\omega)\Bigg\}, \tag{6}$$

$$\sigma_3(\mathbf{q}_1, \omega) = C\frac{k_2}{k_1}\sum_{jj'}\Bigg\{\sum_{\mathbf{k}} \frac{b_{jj'\mathbf{q}_1}(\mathbf{k})}{\sqrt{\omega_{\mathbf{q}j}\omega_{\mathbf{k}j'}}}\varphi_{\mathbf{k}j\mathbf{k}j'}(\omega)$$

$$+(B_1^2 - B_2^2)\sum_{\mathbf{k}\mathbf{k}'}\sum_{\gamma} \frac{(\mathbf{q}_1\mathbf{e}_{\mathbf{k}j\gamma})(\mathbf{q}_1\overset{*}{\mathbf{e}}_{\mathbf{k}'j'\gamma})c_{\mathbf{k}-\mathbf{k}'\gamma}}{\sqrt{\omega_{\mathbf{k}j}\omega_{\mathbf{k}'j'}}}\varphi_{\mathbf{k}j\mathbf{k}'j'}(\omega)\Bigg\}. \tag{7}$$

We have introduced the notation

$$C = \frac{m^2}{8\pi^2\hbar^4\rho v}, \qquad c_{\mathbf{k}\gamma} = \frac{1}{N}\sum_s (c_{s\gamma} - c_\gamma)\exp(i\mathbf{k}\mathbf{R}_{s\gamma}),$$

$$\mathbf{R}_{\mathbf{k}\gamma} = -\frac{i}{N}\sum_s \delta\mathbf{R}_{s\gamma}\exp(i\mathbf{k}\mathbf{R}_{s\gamma}),$$

$$Q_{j\mathbf{q}_1} = \sum_\gamma \overline{A}_\gamma\,\mathbf{q}_1\mathbf{e}_{\mathbf{q}j\gamma}\exp(2\pi i\,\mathbf{K}_n\mathbf{R}_{s\gamma}),$$

$$S_{j\mathbf{q}_1}(\mathbf{k}) = \sum_\gamma [(A_1 - A_2)\,c_{\mathbf{q}+\mathbf{k}\gamma}$$

$$-\overline{A}_\gamma\mathbf{q}_1\mathbf{R}_{\mathbf{q}+\mathbf{k}\gamma}]\,\mathbf{q}_1\mathbf{e}_{\mathbf{k}j\gamma}\exp(2\pi i\,\mathbf{K}_n\mathbf{R}_{s\gamma}),$$

$$b_{jj'\mathbf{q}_1}(\mathbf{k}) = \sum_\gamma \overline{B}^2_\gamma(\mathbf{q}_1\mathbf{e}_{\mathbf{k}j\gamma})(\mathbf{q}_1\overset{*}{\mathbf{e}}_{\mathbf{k}j'\gamma}),$$

$$\varphi_{\mathbf{k}j\mathbf{k}'j'}(\omega) = \varphi'_{\mathbf{k}j\mathbf{k}'j'}(\omega) + \varphi''_{\mathbf{k}j\mathbf{k}'j'}(\omega),$$

$$\varphi'_{\mathbf{k}j\mathbf{k}'j'}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{-i\omega t}\,\mathrm{Sp}\,[e^{-\lambda H}a_{\mathbf{k}j}(t)\,a^{+}_{\mathbf{k}'j'}(0)]\,(\mathrm{Sp}\,e^{-\lambda H})^{-1},$$

$$\varphi''_{\mathbf{k}j\mathbf{k}'j'} = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{-i\omega t}\,\mathrm{Sp}\,[e^{-\lambda H}a^{+}_{\mathbf{k}j}(t)\,a_{\mathbf{k}'j'}(0)]\,(\mathrm{Sp}\,e^{-\lambda H})^{-1}. \tag{8}$$

In expressions (5) — (7) it is understood that we average over all configurations of the atoms.

As we see from these formulas, the problem of determining the energy distribution of the scattered neutrons has been reduced to the computation of the spectral representations $\varphi_{\mathbf{k}j\mathbf{k}'j'}(\omega)$ for the product of two single-particle operators. These quantities are most simply found by using the method of temperature Green's functions.[9] In the following we shall use a variant of this method, based on the use of spectral representations of two-time retarded and advanced Green's functions[9e] G(ω). For a system with the Hamiltonian (3), these functions are given in the Appendix. Remembering that (cf. reference 9e):

$$\varphi''_{\mathbf{k}j\mathbf{k}'j'}(\omega) = \varphi'_{\mathbf{k}'j'\mathbf{k}j}(-\omega)\,e^{-\lambda\hbar\omega},$$

$$\varphi''_{\mathbf{k}'j'\mathbf{k}j}(\omega) = i\,(e^{\lambda\hbar\omega} - 1)^{-1}\lim_{\varepsilon\to 0}\,[G_{\mathbf{k}j\mathbf{k}'j'}(\omega + i\varepsilon)$$

$$-G_{\mathbf{k}j\mathbf{k}'j'}(\omega - i\varepsilon)],$$

and also using the relation $(x + i\epsilon)^{-1} = Px^{-1} - i\pi\delta(x)$ (where P denotes the principal value), we can obtain the expressions for the functions φ' and φ'' from formulas (A.4) – (A.7) of the Appendix:

$$\varphi''_{\mathbf{k}j\mathbf{k}j}(\omega) = \varphi''_{\mathbf{k}j}(\omega) = \varphi'_{\mathbf{k}j}(-\omega)\frac{n(\omega)}{n(\omega)+1}$$

$$= \frac{1}{\pi}\frac{\Gamma_{\mathbf{k}j}(\omega)\,n(\omega)}{[\omega - \omega_{\mathbf{k}j} - P_{\mathbf{k}j}(\omega)]^2 + \Gamma^2_{\mathbf{k}j}(\omega)}, \tag{9}$$

$$\varphi''_{\mathbf{k}j'\mathbf{k}j}(\omega) = \varphi''_{\mathbf{k}j'j}(\omega) = \frac{P_{\mathbf{k}jj'}\varphi''_{\mathbf{k}j'}(\omega)}{\omega - \omega_{\mathbf{k}j}}$$

$$+ \frac{1}{\pi}\frac{\Gamma_{\mathbf{k}jj'}n(\omega)}{\omega - \omega_{\mathbf{k}j}}\frac{\omega - \omega_{\mathbf{k}j'} - P_{\mathbf{k}j'}}{[\omega - \omega_{\mathbf{k}j'} - P_{\mathbf{k}j'}]^2 + \Gamma^2_{\mathbf{k}j'}} \quad (\text{for } \omega \approx \omega_{\mathbf{k}j'}), \tag{10}$$

$$\varphi'_{\mathbf{k}'j'\mathbf{k}j}(\omega) = \frac{V_{\mathbf{k}j\mathbf{k}'j'}}{\hbar}\varphi'_{\mathbf{k}'j'}(\omega)\,\mathrm{P}\frac{1}{\omega - \omega_{\mathbf{k}j}} \quad (\text{for } \omega \neq \omega_{\mathbf{k}j}), \tag{11}$$

where

$$n(\omega) = [e^{\lambda\hbar\omega} - 1]^{-1},$$

$$P_{\mathbf{k}jj'}(\omega) = \frac{1}{\hbar^2}\mathrm{P}\sum_{\mathbf{k}''j''}\left[\frac{V_{\mathbf{k}j\mathbf{k}''j''}V_{\mathbf{k}''j''\mathbf{k}j'}}{\omega - \omega_{\mathbf{k}''j''}} - \frac{V'_{\mathbf{k}j\mathbf{k}''j''}V'^{*}_{\mathbf{k}''j''\mathbf{k}j'}}{\omega + \omega_{\mathbf{k}''j''}}\right],$$

$$\Gamma_{\mathbf{k}jj'}(\omega) = \frac{\pi}{\hbar^2}\sum_{\mathbf{k}''j''}[V_{\mathbf{k}j\mathbf{k}''j''}V_{\mathbf{k}''j''\mathbf{k}j'}\delta(\omega - \omega_{\mathbf{k}''j''})$$

$$- V'_{\mathbf{k}j\mathbf{k}''j''}V'^{*}_{\mathbf{k}''j''\mathbf{k}j'}\delta(\omega + \omega_{\mathbf{k}''j''})]. \tag{12}$$

From (9) and (12) we see that, in the second approximation of perturbation theory, the quantity $P_{\mathbf{k}j} = P_{\mathbf{k}jj}$ determines the displacement of the $(\mathbf{k}j)$ vibration frequency associated with the imperfection of the crystal, while $\Gamma_{\mathbf{k}j} = \Gamma_{\mathbf{k}jj}$ determines the damping.

In the limiting transition to the ideal crystal, when V and V′ → 0, $\varphi''_{\mathbf{k}j}(\omega)$ goes over into the δ function, while the other functions $\varphi''_{\mathbf{k}j\mathbf{k}'j'}(\omega)$ vanish. At the same time, the expression (5) for σ_1 goes over into the usual formula for coherent inelastic scattering, and the expressions (6) and (7) for σ_2 and σ_3 into the formulas for incoherent scattering. We shall continue to use the convention, even for the case of nonideal crystals, of calling the scattering corresponding to σ_1 coherent scattering, and the scattering corresponding to the sum $\sigma_2 + \sigma_3$, incoherent scattering. Let us now separately consider the coherent and incoherent scattering.

2. COHERENT INELASTIC SCATTERING

As we see from (5), (9) and (10), the main contribution to the coherent scattering comes from the diagonal terms σ_{1jj} in the sum (5), which correspond to absorption of a phonon,

$$\sigma'_{1jj}(\mathbf{q}_1, \omega) = CN\frac{k_2}{k_1}\frac{|Q_{j\mathbf{q}_1}|^2}{\pi\omega_{\mathbf{q}j}}\frac{\Gamma_{\mathbf{q}j}(\omega)\,n(\omega)}{[\omega - \omega_{\mathbf{q}j} - P_{\mathbf{q}j}(\omega)]^2 + \Gamma^2_{\mathbf{q}j}(\omega)}, \tag{13a}$$

or to its emission:

$$\sigma''_{1jj}(\mathbf{q}_1, -\omega) = CN\frac{k_2}{k_1}\frac{|Q_{j\mathbf{q}_1}|^2}{\pi\omega_{\mathbf{q}j}}\frac{\Gamma_{\mathbf{q}j}(\omega)\,[n(\omega) + 1]}{[\omega - \omega_{\mathbf{q}j} - P_{\mathbf{q}j}(\omega)]^2 + \Gamma^2_{\mathbf{q}j}(\omega)}\cdot \tag{13b}$$

For each $\mathbf{q}_1$, these terms determine the intensity of the series of peaks in the energy distribution of the scattered neutrons whose maxima lie at $\pm\omega \approx \omega_{\mathbf{q}j} + P_{\mathbf{q}j}$, and which correspond to the different branches of the vibration spectrum. The peak intensities are proportional to the squares of the "structure amplitudes" $Q_{j\mathbf{q}_1}$ [cf. Eq. (8)], which are different for the different peaks, and depend on the temperature through the factors $n(\omega)$ and $n(\omega) + 1$. The peak widths $\Gamma_{\mathbf{q}j}$, according to (12), do not depend explicitly on the temperature, and are essentially determined by the magnitude of the inhomogeneities and the amount of order in the arrangement of the atoms. The temperature dependence of $\Gamma_{\mathbf{q}j}$ shows itself when we include the effects of anharmonicity.[6] If the peaks are sufficiently narrow, and $\Gamma(\omega)$ does not depend very strongly on frequency, so that $d\Gamma_{\mathbf{q}j}/d\omega \ll 1$, the shape of each peak is described by a symmetric Lorentz curve. In the general case, because of the dependence of Γ on ω, the shape of the curve is more complicated.

The nondiagonal terms in (5) correspond to more complicated scattering processes, in which phonons belonging to two different zones participate. As we see from (10), they are also most important when $\pm\omega \approx \omega_{\mathbf{q}j'} + P_{\mathbf{q}j'}$, and vanish for $V = V' = 0$. These terms lead to a slight change in the peak intensities [the first term in Eq. (10)] and to the appearance of an asymmetry of the distribution, which is associated with the second term in (10). (Analogous effects also occur in the exciton absorption spectrum.[10]). The degree of asymmetry is of order $\Gamma_{\mathbf{q}jj'}(\omega_{\mathbf{q}j'} - \omega_{\mathbf{q}j})^{-1}$ (if all the $Q_{j\mathbf{q}_1}$ are of the same order) and increases rapidly when the vibration frequencies of different branches approach one another. For sufficiently small values of $|\omega_{\mathbf{q}j'} - \omega_{\mathbf{q}j}|$, the expression (10) ceases to be applicable to the most important part of the frequency range, around $\omega \approx \omega_{\mathbf{q}j'}$. In this case the function $\varphi_{\mathbf{q}j\mathbf{q}j'}(\omega)$ can be gotten by starting from the more exact expression (A.8) for the Green's function. Without giving the resulting very complicated formulas, we merely remark that the values of the displacements and broadenings of the levels are determined in this case not only by $P_{\mathbf{q}j}$ and $\Gamma_{\mathbf{q}j}$, but also by $P_{\mathbf{q}jj'}$ and $\Gamma_{\mathbf{q}jj'}$, and depend strongly on the frequency difference $\omega - \omega_{\mathbf{q}j}$

(since the energy bands begin to "interact" strongly as they approach one another).

Now let us compute the $\Gamma_{\mathbf{q}j}$. To do this we must have explicit expressions for the $V_{\mathbf{k}j\mathbf{k}'j'}$. We shall assume that quantities like the density of the crystal and the elastic moduli depend linearly on the concentrations c_γ. Then the $V_{\mathbf{k}j\mathbf{k}'j'}$ will depend linearly on the Fourier components of the fluctuations of these concentrations. In the following we shall, for the most part, treat solutions in which the atoms of the two types can only be at the sites of one of the sublattices, while there are identical atoms at the sites of the other sublattices (for example, crystals with one site per unit cell, solutions like NaKCl with two sites per unit cell, etc). In this case the quantity $c_{\mathbf{k}'-\mathbf{k},\gamma} = c_{\mathbf{k}'-\mathbf{k}}$ is different from zero for only one value of γ (so that we can drop the index γ), and

$$V_{\mathbf{k}j\mathbf{k}'j'} = h_{\mathbf{k}j\mathbf{k}'j'} c_{\mathbf{k}'-\mathbf{k}}, \quad V'_{\mathbf{k}j\mathbf{k}'j'} = h_{\mathbf{k}j\mathbf{k}'j'} c_{\mathbf{k}'+\mathbf{k}} \tag{14}$$

(the expressions for h are given below). Substituting (14) in formula (12) for the $\Gamma_{\mathbf{q}j}$, dropping the second term in this formula (which is important only for negative ω, when the scattering is very small), and going over from a sum to a surface integral over the surfaces $S_{j'}$ on which the conditions $\omega = \omega_{\mathbf{k}j'}$ are satisfied, we get

$$\Gamma_{\mathbf{q}j}(\omega) = \frac{vN}{8\pi^2\hbar^2} \sum_{j'} \int_{S_{j'}} \frac{dS_{j'}}{|\nabla_{\mathbf{k}}\omega_{\mathbf{k}j'}|} h^2_{\mathbf{q}j\mathbf{k}j'} \overline{|c_{\mathbf{k}-\mathbf{q}}|^2}. \tag{15}$$

If the $c_{\mathbf{k}\gamma}$ are different from zero for several sublattices, we must replace $h^2_{\mathbf{q}j\mathbf{k}j'} |c_{\mathbf{k}-\mathbf{q}}|^2$ in (15) by $\left|\sum_\gamma h^\gamma_{\mathbf{q}j\mathbf{k}j'} c_{\mathbf{k}-\mathbf{q},\gamma}\right|^2$.

The average values of the $|c_{\mathbf{k}-\mathbf{q}}|^2$, and consequently $\Gamma_{\mathbf{q}j}$, are essentially related to the degree of order of the atomic arrangement. We shall therefore treat separately the cases of different types of correlation in the solid solution.

Ideal solutions. In ideal solutions there is no correlation, and the atoms of different types are distributed completely at random over the sites of the particular sublattice. Then the $\overline{|c_\mathbf{k}|^2}$ are given by the simple formula:

$$\overline{|c_\mathbf{k}|^2} = c(1-c)/N \tag{16}$$

(where c is the concentration in the particular sublattice). As we see from (16), in this case $|c_\mathbf{k}|^2$ does not depend on $\mathbf{k}$, which greatly simplifies the integration in (15). The integral (15) can be calculated explicitly for the long wave acoustical and optical vibrations.

In the case of the acoustic vibrations, in the approximation of an elastic isotropic continuum, the quantities $h_{\mathbf{k}j\mathbf{k}'j'}$ and $\omega_{\mathbf{k}j}$, according to reference 8a, are given by the formulas

$$\begin{aligned} h_{\mathbf{k}j\mathbf{k}'j'} &= \frac{\hbar}{2\rho\sqrt{\omega_{\mathbf{k}j}\omega_{\mathbf{k}'j'}}} \\ &\times \Big\{\mathbf{e}_{\mathbf{k}j}\mathbf{e}_{\mathbf{k}'j'}\omega_{\mathbf{k}j}\omega_{\mathbf{k}'j'}\rho' + (\mathbf{e}_{\mathbf{k}j}\mathbf{k})(\mathbf{e}_{\mathbf{k}'j'}\mathbf{k}')\left(K' - \tfrac{2}{3}\mu'\right) \\ &+ [(\mathbf{e}_{\mathbf{k}j}\mathbf{e}_{\mathbf{k}'j'})(\mathbf{k}\mathbf{k}') + (\mathbf{k}\mathbf{e}_{\mathbf{k}'j'})(\mathbf{k}'\mathbf{e}_{\mathbf{k}j})]\mu'\Big\}, \\ \omega_{\mathbf{k}1} &= c_1 k = \sqrt{\frac{K + 4\mu/3}{\rho}}\, k, \qquad \omega_{\mathbf{k}2} = c_2 k = \sqrt{\frac{\mu}{\rho}}\, k. \end{aligned} \tag{17}$$

Here j = 1 corresponds to longitudinal vibrations ($\mathbf{e}_{\mathbf{k}_1} \parallel \mathbf{k}$), while j = 2, 3 correspond to transverse vibrations ($\mathbf{e}_{\mathbf{k}j} \perp \mathbf{k}$); K and μ are the bulk and shear moduli; ρ', K′ and μ' are the derivatives of the corresponding unprimed quantities with respect to c; c_j is the velocity of propagation of the vibrations. Substituting (16) and (17) in (15) and carrying out the integration, for j = 1 and j = 2, over the surfaces of the three spheres $S_{j'}$ (for the three vibration branches), we find the widths $\Gamma_{\mathbf{q}_1}$ and $\Gamma_{\mathbf{q}_2}$ of the energy distributions for the longitudinal and transverse acoustic vibrations:

$$\begin{aligned} \Gamma_{\mathbf{q}1}(\omega) &= \frac{vc_1q^4}{24\pi}\left(\frac{\omega}{\omega_\mathbf{q}}\right)^3 \Big[(1 + 2\varkappa^3)\left(\frac{\rho'}{\rho}\right)^2 \\ &+ \frac{45K'^2 + 8(2 + 3\varkappa^5)\mu'^2}{15\varkappa^4\mu^2}\Big] c(1-c) \\ &\sim 10\left(\frac{q}{q_m}\right)^3 \omega\varepsilon_1^2 c(1-c), \end{aligned} \tag{18}$$

$$\begin{aligned} \Gamma_{\mathbf{q}2}(\omega) &= \frac{vc_2q^4}{12\pi}\left(\frac{\omega}{\omega_\mathbf{q}}\right)^3 \left[\frac{1 + 2\varkappa^3}{2\varkappa^3}\left(\frac{\rho'}{\rho}\right)^2 + \frac{2 + 3\varkappa^5}{5\varkappa^5}\left(\frac{\mu'}{\mu}\right)^2\right] c(1-c) \\ &\sim \left(\frac{q}{q_m}\right)^3 \omega\varepsilon_1^2 c(1-c). \end{aligned} \tag{19}$$

Here $\kappa = c_1/c_2$; $\omega_\mathbf{q}$ is the frequency of the $\mathbf{q}$-th vibration (and, if we can neglect the dependence of Γ on ω, $\omega/\omega_\mathbf{q} \approx 1$); q_m is the maximum value of the phonon wave vector; ϵ_1 is the largest of the quantities ρ'/ρ, K′/K, μ'/μ; the last equalities in (18) and (19) determine the order of magnitude of $\Gamma_\mathbf{q}$. For frequencies of longitudinal vibrations which are greater than the maximum frequency of transverse vibration $\omega_{\perp\max}$, those scattering processes are excluded in which a longitudinal phonon is annihilated and a transverse phonon is created, and we must replace the square bracket in (18) by the expression $(\rho'/\rho)^2 + (45K'^2 + 16\mu'^2)/15\kappa^4\mu^2$ [and also drop the factor 10 in the estimate given in Eq. (18)].

It is obvious that, except for singular points in the vibration spectrum, (cf. below) formulas (18) and (19) give the correct order of the widths $\Gamma_\mathbf{q}$ of the distribution for ideal solutions. As we see from these formulas, for large q ($q \sim q_m$), for components which differ markedly in their properties ($\epsilon_1 \sim 1$), and for high concentrations ($c \sim 1/2$), $\Gamma_{\mathbf{q}}$ is of the same order of magnitude as ω, i.e., the peak in the energy distribution is almost completely smeared out. In solutions of isotopes (except for the lightest elements) usually $\epsilon_1 < 1/10$, and the broadening of the peaks due to the presence of different isotopes is usually small ($\Gamma_{\mathbf{q}} < 1/100\, \omega$) and less than the broadening due to anharmonicity. Since for low frequencies $\Gamma_{\mathbf{q}} \sim q^4$, for the scattering by the low frequency vibrations, one should in all cases observe sharp peaks.

A different dependence of $\Gamma_{\mathbf{q}}$ on q is obtained for the case of long-wave optical vibrations. To avoid giving very involved formulas, we shall restrict ourselves to the usually occurring case where the effects due to the mass difference of the atoms of the solution are considerably greater than the effects due to differences in force constants and to imperfections. We then have for all the vibration branches and all **k** and **k′** (cf. reference 8b):

$$h_{\mathbf{k}j\mathbf{k}'j'} = \frac{1}{2}\hbar\sqrt{\omega_{\mathbf{k}j}\omega_{\mathbf{k}'j'}}\, \mathbf{e}_{\mathbf{k}j\gamma}\mathbf{e}_{\mathbf{k}'j'\gamma}\,\varepsilon, \qquad \varepsilon = \frac{\rho'}{\rho} = \frac{M_1 - M_2}{M} \tag{20}$$

(where M_1, M_2 and M are the masses of the component atoms and the average mass per cell).

Let us consider the case when there is an analytic minimum or maximum of $\omega_j(\mathbf{k})$ at the point $\mathbf{k} = 0$ and the other branches have no vibrations with this frequency. Then for cubic crystals $\omega_j(\mathbf{k}) = \omega_0 + 1/2\,\omega_2 k^2$ (we neglect retardation effects, which are important only for very small k) and, according to (15), (16) and (20), $\Gamma_{\mathbf{q}\parallel}$ and $\Gamma_{\mathbf{q}\perp}$ for the longitudinal and transverse optical vibrations are equal to:

$$\Gamma_{\mathbf{q}\parallel}(\omega) = \frac{v\omega_{\mathbf{q}}\omega q(\omega)}{24\pi|\omega_2|} n^4\varepsilon^2 c(1-c) \sim \frac{\omega_0^2}{\Delta\omega}\frac{q}{q_m}\varepsilon^2 c(1-c),$$

$$\Gamma_{\mathbf{q}\perp}(\omega) = \frac{v\omega_q\omega q(\omega)}{12\pi|\omega_2|} n^4\varepsilon^2 c(1-c), \tag{21}$$

where the quantity $n = n_j$ is equal to the length of the polarization vector $e_{\mathbf{k}j\gamma}(k \rightarrow 0)$ for the particular sublattice (in which the atoms are arranged at random), $q(\omega)$ is the wave vector corresponding to the frequency ω (for narrow peaks $\omega \approx \omega_{\mathbf{q}}$, $q(\omega) \approx q$), $\Delta\omega \sim 1/2\,|\omega_2|\, q_m^2$ is the width of the particular frequency band. According to (12), expressions for the $\Gamma_{\mathbf{q}jj'}(\omega)$, for frequencies ω corresponding to optical vibrations can be obtained from (21) by replacing $\omega_{\mathbf{q}} n_j^2$ by $\sqrt{\omega_{\mathbf{q}j}\omega_{\mathbf{q}j'}}\, n_j n_{j'}$, if the two branches j and j′ both describe longitudinal or transverse (optical or acoustical) vibrations. If one of the branches is longitudinal and the other transverse, then $\Gamma_{\mathbf{q}jj'}(\omega) = 0$.

As we see from (21), now as q decreases the quantity $\Gamma_{\mathbf{q}}$ falls off not like q^4 but like q, i.e., the broadening may be sizable even for small q. For a given ϵ, the broadening is especially large for narrow zones (small $\Delta\omega$), for example for optical vibrations in molecular crystals. The same type of formula for the $\Gamma_{\mathbf{q}}(\omega)$ is also valid for other minima and maxima in the dependence of $\omega_j(\mathbf{k})$ (including the case of the maximum frequency of acoustic vibration), so long as only this one branch occurs near the frequency ω. Then q in (21) denotes the distance to the extremal point in **k** space. If other branches have this same frequency, then in evaluating $\Gamma_{\mathbf{q}}$ for small q the terms corresponding to these branches are very important. Their order of magnitude is given by formulas (18) or (19).

As Van Hove[11] has shown, for each vibration branch there must exist critical points (c.p.) of the vibration spectrum, i.e., minima, maxima and saddle points, at which $\nabla_{\mathbf{k}}\omega_{\mathbf{k}} = 0$. As follows from (15), the occurrence of such an analytic c.p. for one of the branches at the frequency ω_1 leads to the appearance of a singularity in the dependence of Γ on ω of the form $|\omega - \omega_1|^{1/2}$ for all the other vibration branches (whose frequencies coincide with ω_1). Here the term proportional to $|\omega - \omega_1|^{1/2}$ appears only for those frequencies ω which lie on that side of the point ω_1 for which new poles appear on the surface $\omega_j(\mathbf{k}) = \omega$. The same kind of singularity also occurs if a nonanalytic c.p. is a minimum or maximum for not one but two vibration branches, and $\nabla_{\mathbf{k}}\omega_{\mathbf{k}} = 0$ at the point. If however the c.p. is singular, i.e., if some of the components $\nabla_{\mathbf{k}}\omega_{\mathbf{k}}$ do not vanish at it but instead have discontinuities, then the singularity of the function $\Gamma_{\mathbf{q}}(\omega)$ is weaker.

It should be emphasized that the singularity of $\Gamma_{\mathbf{q}}(\omega)$ was found only in this particular approximation of perturbation theory. The next approximation leads to a smearing out of the singularity over a frequency interval $\sim \Gamma_{\mathbf{q}}$, analogous to the smearing of the singularity in the spectrum of incoherently scattered neutrons (cf. Sec. 3). For small values of $\Gamma_{\mathbf{q}}$, the singularity will still manifest itself in experimental studies of the dependence of $\Gamma_{\mathbf{q}}(\omega)$, which can be used as an independent method for locating the frequencies of c.p.'s.

It is easy to show that for multicomponent ideal solutions we should make the following replacements in formulas (18), (19), and (21):

$$c(1-c)\,\varepsilon^2 = c(1-c)\frac{(M_1-M_2)^2}{M^2} \to \sum_{\mu_1<\mu_2} c_{\mu_1}c_{\mu_2}(M_{\mu_1}^{\Gamma}-M_{\mu_2})^2/M^2,$$

where c_μ is the concentration of the μ-th component, whose atoms have mass M_μ.

Nonideal solutions. In nonideal solutions the correlation between positions of atoms is important. In this case the expression for $|c_{\mathbf{k}}|^2$ becomes more complicated, and its dependence on **k** becomes important. A simple formula for $|c_{\mathbf{k}}|^2$ can be given only for small values of k. In this case, as it follows from the thermodynamic theory of fluctuations, for disordered solutions

$$\overline{|c_{k'}|^2} = kT/Nv\,(\varphi_{cc}+\beta k'^2). \tag{22}$$

Here k is the Boltzmann constant, T is the temperature at which short range order is established in the solution (and is not necessarily the same as the temperature at which the experiment is done), $\varphi_{cc} = \partial^2\varphi/\partial c^2$ is the second derivative of the thermodynamic potential per unit volume, β is a quantity of order kTr_0^2/v (where r_0 is the interatomic separation). From a comparison of (16) and (22), we see that in the case of long wave acoustical or optical vibrations, when $\beta q^2 \ll \varphi_{cc}$, the formulas obtained above for $\Gamma_{\mathbf{q}}$ can also be applied to nonideal solutions, if we replace $c(1-c)$ by $kT/v\varphi_{cc}$. Since φ_{cc} is usually greater for ordering nonideal solutions (which go over into the ordered state at low temperatures) than for ideal solutions, whereas it is smaller in dissociating solutions, the establishment of short range order leads to a reduction of $\Gamma_{\mathbf{q}}$ in the first case and to its increase in the second case.*

A marked decrease in the value of $\Gamma_{\mathbf{q}}$ should occur when a high degree of long range order is established in the solution. In almost completely ordered solutions having two types of sites, just as in ideal solutions, the atoms are distributed chaotically over the sites of each sublattice, and in the expressions for $|c_{\mathbf{k}}|^2$ and $\Gamma_{\mathbf{q}}$ we must simply replace $c(1-c)$ by $c(1-c) - \nu(1-\nu)\eta^2$, where ν is the ratio of the number of sites of the first type to the total number of sites and η is the long range order parameter, which is equal to unity in an alloy having stoichiometric composition and complete order. In particular, for this composition $(c = \nu)$, $\Gamma_{\mathbf{q}} \sim (1-\eta^2)$, i.e., $\Gamma_{\mathbf{q}}$ actually falls off rapidly in the transition from a disordered to an almost completely ordered solution.

Solutions near a critical point on the decomposition curve. Characteristic features of the energy distribution of the scattered neutrons should appear near a critical point on the decomposition curve (d.p.), i.e., a point at which the decomposition curve has a maximum. It is known[12] that $\varphi_{cc} = 0$ at a d.p. Therefore, near such a point, as we see from (22), the probability for scattering of phonons with a small change in momentum increases markedly, so that $\Gamma_{\mathbf{q}}$ should decrease markedly. It follows from (15), (17) and (22) that for long wave acoustical vibrations, in the case where $K' = \mu' = 0$, the $\Gamma_{\mathbf{q}}$ are equal to:

$$\Gamma_{\mathbf{q}1}(\omega) = \frac{c_1 q^2}{32\pi}\frac{kT}{\beta}\varepsilon^2\left[\ln\frac{2}{ae^2} + \varkappa(1+\varkappa^2) - \frac{1}{2}(\varkappa^2-1)^2\ln\frac{\varkappa+1}{\varkappa-1}\right] \sim \frac{q}{q_m}\omega\varepsilon^2\ln\frac{2}{ae^2}, \tag{23}$$

$$\Gamma_{\mathbf{q}2}(\omega) = \frac{c_2 q^2}{32\pi}\frac{kT}{\beta}\varepsilon^2\left[\ln\frac{2}{ae} + \frac{1}{2}\frac{1+\varkappa^2}{\varkappa^3} - \frac{(\varkappa^2-1)^2}{4\varkappa^4}\ln\frac{\varkappa+1}{\varkappa-1}\right] \sim \frac{q}{q_m}\omega\varepsilon^2\ln\frac{2}{ae}. \tag{24}$$

Here e is the base of the natural logarithms, and

$$a = \{\varphi_{cc} + \beta\,[q - q(\omega)]^2\}/2\beta q q(\omega), \tag{25}$$

$q(\omega)$ is the wave vector for the same branch that contains q corresponding to the frequency ω, and we have used the fact that $\omega \approx \omega_{\mathbf{q}}$, $\varphi_{cc}/\beta q^2 \ll 1$. (For $\omega > \omega_{\perp\,\max}$, only the first term in the square brackets in (23) should be kept.)

Comparison of (23), (24) and (18), (19) shows that the transition from the ideal solution to the solution in the neighborhood of the d.p. leads to a considerable increase in $\Gamma_{\mathbf{q}}$ (by a factor of $\sim (q_m/q)^2 \ln a^{-1}$). This effect makes itself felt more strongly for long waves, since then, as q decreases, $\Gamma_{\mathbf{q}}$ falls off not like q^4, but almost like q^2. For a given q, and for $\omega = \omega_{\mathbf{q}}$, the value of $\Gamma_{\mathbf{q}}$ goes to infinity logarithmically as we approach the d.p. (while $\varphi_{cc} \to 0$).

An especially sharp rise in $\Gamma_{\mathbf{q}}$ near the d.p. should occur for values of **q** which are in the neighborhood of a c.p. For example, for the mini-

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*A very sharp increase in Γ_q should be observed when large groups of impurity atoms are formed, for example when particles of a new phase separate out in the crystal. According to reference 8b, when n atoms are joined into a group, then for long wave oscillations whose wavelength $\lambda_0 > r$ (where r is the linear size of the particles), Γ_q increases by a factor $\sim n$, i.e., it may increase by several orders of magnitude. For shorter waves, for which $\lambda_0 \ll r$ and $(\varepsilon r/\lambda)^2 \ll 1$, Γ_q increases by a factor $\sim n^{1/3}(q_m/q)^2$ compared to the case of individual impurity atoms. Finally, for vibrations of such short wave length that $\lambda_0 \ll r$ and $(\varepsilon r/\lambda_0)^2 \gg 1$, Γ_q changes by a factor $\sim(q_m/q)^4 n^{-1/3}$ and falls off with increasing n. The transition from the $\Gamma_q \sim q^4$ law to the q^2 law (or to $\Gamma q \sim q^0$) for $\lambda_0 \sim r$ may make it possible to determine experimentally the dimensions of the particles which separate out.

mum or maximum points of long wave optical vibrations, we obtain from (15), (20) and (22) the following expressions in place of (21):

$$\Gamma_{\mathbf{q}\parallel}(\omega) = \frac{\omega_{\mathbf{q}}\omega}{32\pi\,|\,\omega_2\,|\,q(\omega)}\frac{kT}{\beta}n^4\varepsilon^2(1+a)$$

$$\times\left[(1+a)\ \ln\left(1+\frac{2}{a}\right)-2\right],$$

$$\Gamma_{\mathbf{q}\perp}(\omega) = \frac{\omega_{\mathbf{q}}\omega}{34\pi\,|\,\omega_2\,|\,q(\omega)}\frac{kT}{\beta}n^4\varepsilon^2\left[(2+2a+a^2)\ln\left(1+\frac{2}{a}\right)\right.$$

$$\left.-2(1+a)\right];$$

$$\Gamma_{\mathbf{q}\parallel} \sim \Gamma_{\mathbf{q}\perp} \sim \frac{\omega_0^2}{\Delta\omega}\varepsilon^2\frac{q_m}{q}\ln\frac{1}{a}\ \text{for}\ a\ll 1,$$

$$\Gamma_{\mathbf{q}\parallel} \sim \Gamma_{\mathbf{q}\perp} \sim \frac{\omega_0^2}{\Delta\omega}\varepsilon^2\frac{q_m}{q}\frac{1}{a}\ \text{for}\ a\gg 1. \tag{26}$$

From (26) we see that for $\omega = \omega_{\mathbf{q}}$ and for very small q, when $a \gg 1$ $(\varphi_{cc} \gg \beta q^2)$, just as in ideal solutions, $\Gamma_{\mathbf{q}}$ is proportional to q, but the coefficient of proportionality is increased by a factor $\sim \beta q_m^2/\varphi_{cc}$, and tends to infinity as we approach the d.p. Thus, even for small ϵ, near the d.p. the peaks in the energy distribution which correspond to values of q in the neighborhood of the c.p. are smeared out badly. For somewhat larger values of q (but still small compared with q_m), when $a \ll 1$, $\Gamma_{\mathbf{q}}$ varies inversely with q instead of being proportional to it.

As we see from (26) and (25), in this case $\Gamma_{\mathbf{q}}$ depends strongly on ω, i.e., the curve describing the energy distribution may differ markedly from the Lorentz shape. Since $\Gamma_{\mathbf{q}jj'}$, just as for formula (21), differs from $\Gamma_{\mathbf{q}j'}$ only by the replacement of $n^2\omega_{\mathbf{q}j'}$ by $\sqrt{\omega_{\mathbf{q}j}\omega_{\mathbf{q}j'}}\,n_j n_{j'}$, the value of $\Gamma_{\mathbf{q}jj'}$ should also increase sharply, i.e., the role of two-zone processes becomes more important, leading to an asymmetry in the energy distribution.

Near a d.p. there should also be a considerable shift of the vibration frequencies (or of the energy levels of conduction electrons). In the case of minimum or maximum points of long wave longitudinal optical vibrations, the value of the shift $P_0(\omega_0)$ as given by (12), (14), (20) and (22), is

$$P_0(\omega_0) = -\frac{\omega_0^2}{24\pi\omega_2}\frac{kTn^4}{\sqrt{\varphi_{cc}\beta}}\varepsilon^2 \sim -\frac{\omega_0^2}{\Delta\omega}\sqrt{\frac{kT}{v\varphi_{cc}}}\varepsilon^2 \tag{26a}$$

(and twice this for transverse vibrations), and increases like $\varphi_{cc}^{-1/2}$ as we approach the d.p. It should be emphasized that near the d.p. the perturbation expansion is actually not in powers of the small quantity ϵ, but in the quantity $\epsilon^2\sqrt{kT/v\varphi_{cc}}$; i.e., right near the d.p. the method we are using, which is based on the application of perturbation theory, ceases to be valid. In the case of small ϵ, we can however approach sufficiently close to the d.p.

The same type of expression for $\Gamma_{\mathbf{q}}(\omega)$ is obtained for any analytic minimum or maximum point (at which $\nabla_{\mathbf{k}}\omega_{\mathbf{k}} = 0$), where q denotes the distance from this point in the reciprocal lattice space, and an additional factor of order unity appears in the expression for $\Gamma_{\mathbf{q}}$ for the case of nonspherical isofrequency surfaces. In the case of analytic c.p.'s which are saddle points, again $\nabla_{\mathbf{k}}\omega_{\mathbf{k}} = 0$, and $\Gamma_{\mathbf{q}}$ increases sharply near the d.p. In the two limiting cases $a \ll 1$ and $a \gg 1$, the formulas for $\Gamma_{\mathbf{q}}$ then have the form

$$\Gamma_{\mathbf{q}} = \frac{\omega^2 kTn^4\varepsilon^2}{32\pi q\omega_{2q}\beta\cos\psi}\ln\frac{\zeta}{a}\ \text{for}\ a\ll 1,$$

$$\Gamma_{\mathbf{q}} = \frac{\omega^2 DkT\varepsilon^2}{32\pi^2\sqrt{\beta\varphi_{cc}}}\ \text{for}\ a\gg 1. \tag{27}$$

Here $\omega_{2\mathbf{q}} = |\nabla_{\mathbf{q}}\omega_{\mathbf{q}}|/q$; ψ is the angle between $\nabla_{\mathbf{q}}\omega_{\mathbf{q}}$ and $\mathbf{q}$; $\zeta \sim 1$; the constant $D \sim \omega_2^{-1}$ is defined by the relation

$$Ddk = \int(\mathbf{e}_{\mathbf{q}j\gamma}\,\mathbf{e}_{\mathbf{k}j\gamma})^2\frac{dS}{|\nabla_{\mathbf{k}}\omega_{\mathbf{k}}|},$$

where the integral extends over the belt on the surface S which is cut out by two spheres with radii k and k + dk. Thus, in this case, for very small q $(\beta q^2 \ll \varphi_{cc})$ $\Gamma_{\mathbf{q}}$ increases like $\varphi_{cc}^{-1/2}$ as we approach the d.p.

As one can show by using the formula which relates the mean square fluctuations at high temperatures to the corresponding susceptibility at zero frequency (see Chap. XIII of reference 13), the integral of the coherent scattering intensity over frequency near the d.p. has a singularity of the type $\sqrt{\varphi_{cc}}$.

Solutions near a point of second-order phase transition. A marked increase in $\Gamma_{\mathbf{q}}$ for certain values of $\mathbf{q}$ may also occur near points where there is a second-order phase transition (t.p.). To be specific, we shall consider processes of ordering in solutions which in the disordered state have one sublattice, while in the ordered state there are two sublattices with the same number of sites (for example solutions of the type of β-brass). Effects of anomalously large scattering of phonons are related to the anomalously large fluctuations of the degree of long range order, η, near the t.p.

First let us treat disordered solutions. In the neighborhood of values $\mathbf{k}' = 2\pi\mathbf{K}_1$, where $\mathbf{K}_1$ is a vector of the reciprocal lattice of the ordered crystal which is absent in the disordered crystal, according to references 14 and 15,

$$\overline{|c_{\mathbf{k}'}|^2} = \frac{kT}{4Nv}[\varphi_{\eta\eta} + \alpha(\mathbf{k}' - 2\pi\mathrm{K}_1)^2]^{-1},$$

where $\varphi_{\eta\eta} = \partial^2\varphi/\partial\eta^2$. Since $\varphi_{\eta\eta} = 0$ at the t.p.,[12] $|c_{\mathbf{k}'}|^2$ increases markedly near these values of $\mathbf{k}'$. As we see from (14) and (15), such a marked increase in $|c_{\mathbf{k}-\mathbf{q}}|^2$ manifests itself in the value of $\Gamma_{\mathbf{q}}$ if vibrations with vectors $\mathbf{q}$ and $\mathbf{k}$, such that $\mathbf{q} - \mathbf{k} \approx 2\pi\mathbf{K}_1$, have the same energy. Such a situation can occur in two cases: first, if the vector $\mathbf{q}/2\pi$ lies near the surface of a new Brillouin zone which appears when ordering occurs, and secondly if the optical and acoustical vibration branches, which are obtained in the reduction of the vibration spectrum to the cell of the reciprocal lattice of the ordered solution, intersect, and $\mathbf{q}$ lies near the surface of intersection of these branches. In both cases, after integration we obtain for $\Gamma_{\mathbf{q}}$ an estimate of the type of (23) and (24):

$$\Gamma_{\mathbf{q}} \sim \frac{c_1 q^2}{100}\frac{kT}{\alpha}\varepsilon^2 \ln\frac{\zeta}{a'} \sim \frac{q}{q_m}\omega\varepsilon^2 \ln\frac{\zeta}{a'}, \qquad a' = \frac{\varphi_{\eta\eta} + \zeta' q'^2}{2\alpha q^2}, \tag{28}$$

where ζ and $\zeta' \sim 1$, and q' is the distance to the surface of the new Brillouin zone or the surface of intersection of the branches. If there is a c.p. near such a surface, then in the neighborhood of such a point there occurs an even greater broadening as we approach the t.p., and $\Gamma_{\mathbf{q}}$ is given by formulas like (26). The expression (28) is also valid for certain points and lines in the reciprocal lattice space which lie on isofrequency surfaces and are connected by the vector $2\pi\mathbf{K}_1$; however, in contrast to the case of a d.p., there will not be a sizable increase of $\Gamma_{\mathbf{q}}$ at arbitrary points of the reciprocal lattice.

A similar picture exists near a t.p. in an ordered solution. Since in this case the ratio $|\mathbf{e}_{\mathbf{k}j\gamma}| : |\mathbf{e}_{\mathbf{k}j\gamma'}|$ for different γ and γ' is not equal to unity, but differs from it by an amount $\sim \epsilon^2\eta^2$, the probability of scattering of a phonon will contain a term proportional to $[\varphi_{\eta\eta} + \alpha(\mathbf{q} - \mathbf{k})^2]^{-1}$ not just when the momentum change $\mathbf{q} - \mathbf{k}$ is $2\pi\mathbf{K}_1$, but in general (for example, for $\mathbf{k} \approx \mathbf{q}$). However this term contains a factor $\epsilon^2\eta^2$ which is small in just that region where $\varphi_{\eta\eta}^{-1}$ is large. Therefore, in this case, when ordering occurs $\Gamma_{\mathbf{q}}$ changes only somewhat, without changing its order of magnitude. In the case of a second-order phase transition near a critical point on the curve of t.p.'s, η^2 can already take on sizable values when $\varphi_{\eta\eta}$ is still small,[16] and there may be a considerable increase in $\Gamma_{\mathbf{q}}$, especially near a c.p., if the factor η^2 which appears in formulas (26) (in which φ_{cc} is replaced by $\varphi_{\eta\eta}$) is not small.

As Landau has shown,[16] at the critical point, at which the curve of t.p.'s changes into the decomposition curve, we have $\varphi_{cc} = 0$ and $\varphi_{\eta\eta} = 0$ for the ordered phase, while for the disordered phase only $\varphi_{\eta\eta} = 0$. Therefore in this case, in the ordered phase, as we approach the critical point there should occur a sharp rise in $\Gamma_{\mathbf{q}}$, just as in the case of an ordinary d.p. In the disordered phase, the rise in $\Gamma_{\mathbf{q}}$, as it occurs in the neighborhood of an ordinary t.p., will occur only near the surfaces of new Brillouin zones and the surfaces of intersection of the acoustical and optical branches. We also note that in certain cases, for example in Rochelle salt crystals, near a t.p. the frequencies of certain vibration branches (the transverse optical branches) become extremely small.[17,18a] Then, as we see from formulas (5) — (7), the intensity of inelastic scattering of neutrons by these frequencies increases sharply.

3. INCOHERENT INELASTIC SCATTERING

The cross section $\sigma_2 + \sigma_3$ for incoherent scattering of neutrons is given by expressions (6) and (7). These expressions contain terms of zeroth, first, and second order in the constant V of interaction of the phonons with inhomogeneities. Here we shall consider only the leading terms of zeroth order (since the first and second order corrections can easily be obtained from the formulas given). As we see from formulas (A.4) — (A.7) of the Appendix, we may retain in the sums of (6) and (7) only those terms which contain functions $\varphi_{\mathbf{k}j\mathbf{k}'j}$ with $\mathbf{k} = \mathbf{k}'$, $j = j'$. The expressions for σ_2, σ_3 simplify considerably in this case, and take the form

$$\sigma_2(\mathbf{q}_1, \omega) = CN\frac{k_2}{k_1}\sum_j\sum_{\mathbf{k}}\omega_{\mathbf{k}j}^{-1}[A_1 - A_2 - \overline{A}(\mathbf{q}_1\mathbf{B}_{\mathbf{k}+\mathbf{q}})]^2$$

$$\times(\mathbf{q}_1\mathbf{e}_{\mathbf{k}j})^2\,\overline{|c_{\mathbf{k}+\mathbf{q}}|^2}\varphi_{\mathbf{k}j}(\omega), \tag{29}$$

$$\sigma_3(\mathbf{q}_1, \omega) = C\frac{k_2}{k_1}\overline{B^2}\sum_j\sum_{\mathbf{k}}\omega_{\mathbf{k}j}^{-1}(\mathbf{q}_1\mathbf{e}_{\mathbf{k}j})^2\varphi_{\mathbf{k}j}(\omega), \tag{30}$$

where we have used the assumption that the lattice constant is linearly dependent on composition, i.e., that $\mathbf{R}_{\mathbf{k}}$ depends linearly on $c_{\mathbf{k}}$: $R_{\mathbf{k}} = B_{\mathbf{k}} \cdot c_{\mathbf{k}}$. Explicit expressions for the $\mathbf{B}_{\mathbf{k}}$ were obtained earlier.[15] In particular, in the approximation of an isotropic elastic continuum,

$$\mathbf{B}_{\mathbf{k}} = b\frac{\mathbf{k}}{k^2}, \qquad b = \frac{1+\sigma}{3(1-\sigma)}\frac{1}{v}\frac{\partial v}{\partial c}$$

(where σ is the Poisson ratio).

The inclusion of defects and imperfections of the solution and the scattering of phonons by inhomogeneities leads to two effects which were not previously considered in treating incoherent scattering. First of all, imperfection of the solution and defects lead to a change in the value of σ_2 and to the appearance of a dependence on $\mathbf{q}$. Secondly, the broadening of the levels results in a smearing out of the singularities which, according to Placzek and Van Hove,[2] should be present in the energy distribution of $\sigma_2 + \sigma_3$.

Let us begin by treating the first effect for ideal solutions, where $|c_{\mathbf{k}}|^2$ is given by formula (16). For sufficiently small $V_{\mathbf{k}jk'j'}$ and $\Gamma_{\mathbf{q}}$, the functions $\varphi'_{\mathbf{k}jk'j'}$ and $\varphi''_{\mathbf{k}jk'j'}$ can, according to (9), be replaced by δ functions (except at the singular points of the frequency distribution function). We shall further restrict ourselves to treating a cubic crystal in the isotropic continuum approximation. We denote by $g_j(\omega)$ the distribution function for the vibration frequencies of the j-th branch (normalized to $1/3$), and by $q_{\omega j}$ the length of the wave vector of the j-th branch which corresponds to the frequency ω. The expression for σ_2 simplifies in the two limiting cases when $q \gg q_{\omega j}$ and $q \ll q_{\omega j}$. Then for processes in which a phonon is absorbed,

$$\sigma_2(\mathbf{q}_1, \omega) = CN \frac{k_2}{k_1} \frac{n(\omega)}{\omega} q_1^2 c(1-c) \sum_j g_j(\omega) \times \left[A_1 - A_2 - \overline{A} b \frac{\mathbf{q}_1 \mathbf{q}}{q^2}\right], \qquad q \gg q_{\omega j};$$

$$\sigma_2(\mathbf{q}_1, \omega) = CN \frac{k_2}{k_1} \frac{n(\omega)}{\omega} q_1^2 c(1-c) \sum_j g_j(\omega) \times \left[(A_2 - A_1)^2 + \chi_j \overline{A}^2 b^2 \frac{q_1^2}{q_{\omega j}^2}\right], \qquad q \ll q_{\omega j}, \tag{31}$$

where $\chi_j = 3/5$ for longitudinal vibrations and $\chi_j = 2/5$ for transverse vibrations. For arbitrary $\mathbf{q}$, the expression for σ_3 has the form

$$\sigma_3(\mathbf{q}_1, \omega) = CN \frac{k_2}{k_1} \frac{n(\omega)}{\omega} g(\omega) q_1^2 \overline{B^2}, \qquad g(\omega) = \sum_j g_j(\omega). \tag{32}$$

In the case of processes in which a phonon is emitted, one should replace $n(\omega)$ by $n(\omega) + 1$ in (31) and (32).

Thus, inclusion of defects leads to the result that σ_2 depends not only on the vibration frequency but also on $\mathbf{q}$. The effects associated with defects are especially large if the change in energy of the neutron, $\hbar\omega$, in the scattering is very small or close to the energy of the long wave optical vibrations, and if the end of the vector $\mathbf{q}_1/2\pi$ lies near a point of the reciprocal lattice. Then, if q and and $q_{\omega j}$ are sufficiently small, even in slightly distorted crystals (small b) the terms in (31) caused by defects become dominant, and as $q, q_{\omega j} \to 0$ the value of σ_2 goes to infinity like q^{-2} or $q_{\omega j}^{-2}$. This characteristic dependence of σ_2 on q and ω can be used for the experimental determination of the limiting frequencies of optical vibrations. As we see from (32), σ_3 is independent of defects.

It follows from a comparison of (16) and (22), and from (29), that for small q and $q_{\omega j}$ the formulas (31) for σ_2 can also be applied to nonideal solutions, if we replace $c(1-c)$ by $kT/v\varphi_{cc}$. Thus, in this range of values of q and $q_{\omega j}$, σ_2 changes when short range order is established in the solution, increasing in solutions which decompose and decreasing in solutions which become ordered. When long-range order is established in an almost completely ordered solution, we must replace $c(1-c)$ in (31) by $c(1-c) - \nu(1-\nu)\eta^2$, i.e., σ_2 decreases sharply. In the case of solutions, close to a d.p. we must keep the second term in the denominator of (22) even for small k′. It follows from (29) and (22) that we have (for the case of absorption of the phonon)

$$\sigma_2(\mathbf{q}_1, \omega) = CN \frac{k_2}{k_2} \frac{n(\omega)}{\omega} g(\omega) q_1^2 \frac{kT}{v(\varphi_{cc} + \beta q^2)} \left(A_1 - A_2 - \overline{A} b \frac{\mathbf{q}_1 \mathbf{q}}{q^2}\right)^2, \qquad q \gg q_{\omega j};$$

$$\sigma_2(\mathbf{q}_1, \omega) = CN \frac{k_2}{k_1} \frac{n(\omega)}{\omega} q_1^2 \sum_j g_j(\omega) \frac{kT}{v(\varphi_{cc} + \beta q_{\omega j}^2)} \times \left[(A_1 - A_2)^2 + \chi_j \overline{A}^2 b^2 \frac{q_1^2}{q_{\omega j}^2}\right], \qquad q \ll q_{\omega j}. \tag{33}$$

From (33) we see that for small q and $q_{\omega j}$, the cross section σ_2 increases markedly when we approach the d.p., when $\varphi_{cc} \to 0$. From the results obtained above it follows that anomalous changes should occur not only in the intensity distribution of the elastic scattering of x-rays and neutrons near t.p.'s[14,15,18] and d.p.'s,[15,18] and in the magnetic scattering of neutrons near the Curie and Neel points,[19] but one should also observe singularities in the energy distribution of neutrons coherently scattered by thermal vibrations near d.p.'s and t.p.'s, and in the energy and angular distributions of incoherent scattering near a d.p.

Now let us consider the smearing out of singularities in the energy spectrum of the incoherent scattering by ideal solutions. If we replace the $\varphi_{\mathbf{k}j}(\omega)$ in (29) and (30) by δ functions, then for frequencies ω_1 corresponding to c.p.'s, at which $\nabla_{\mathbf{k}}\omega_{\mathbf{k}} = 0$, the quantities $g(\omega)$, σ_2 and σ_3 will, according to the results of Placzek and Van Hove,[2] have singularities of the type $|\omega - \omega_1|^{1/2}$. The change from the δ functions to the smoothed functions (9) obviously leads to a smearing out of these singularities. Except for cases where there are no vibrations of other branches at the frequency ω_1 corresponding to the minimum or maximum for a particular branch, we can neglect the change in $\Gamma_{\mathbf{q}}(\omega)$ over the narrow frequency range $\omega - \omega_{\mathbf{q}} \sim \Gamma_{\mathbf{q}}$. Integrating with respect to $\mathbf{k}$ in (29) and (30), and using (9), we find that the term $A(\omega - \omega_1)^{1/2}$, which describes the singularity near a minimum, must when we include damping be replaced by

$$A\,(\omega - \omega_1)^{1/2} \to A\Gamma_{\mathbf{q}}/2\,[(\omega - \omega_1)^2 + \Gamma_{\mathbf{q}}^2]^{1/4}\sin\frac{\theta}{2},$$

$$\operatorname{tg}\theta = \frac{\Gamma_{\mathbf{q}}}{\omega - \omega_1}, \quad 0 < \theta < \pi. \tag{34*}$$

Here ω_1 is the frequency at the particular c.p. when we include the shift by an amount $p(\omega_1)$ and drop terms of the form $P(\omega_1)/\omega_1$. For $\omega - \omega_1 \gg \Gamma_{\mathbf{q}}$ the expression (34) goes over into $A(\omega - \omega_1)^{1/2}$, i.e., the damping is unimportant. For $\omega - \omega_1 = 0$, the right side is however equal to $A\sqrt{\Gamma_{\mathbf{q}}/2}$, and does not vanish. For negative $\omega - \omega_1$, when $\omega_1 - \omega \gg \Gamma_{\mathbf{q}}$, the right side of (34) is equal to $A\Gamma_{\mathbf{q}}/2\sqrt{\omega_1 - \omega}$, i.e., it falls off like $(\omega_1 - \omega)^{1/2}$. Thus the singularity in $g(\omega)$ and in the spectrum of incoherent scattering is smeared out over an interval of frequencies $\sim \Gamma_{\mathbf{q}}$. Obviously such a smearing may also be associated with anharmonicity, electron-phonon interaction, etc. If other branches have no vibrations at the frequency of the minimum or maximum ω_1, then according to (21), $\Gamma_{\mathbf{q}}(\omega) \to 0$ for $\omega \to \omega_1$, and in this approximation $g(\omega)$ has a singularity of the type $|\omega - \omega_1|^{1/2}$.

In the discussion given above it was assumed that no local oscillations occur in the crystal. For small ϵ, local vibrations in the neighborhood of impurity atoms actually do not occur.[20] However, no matter how small ϵ, if a sufficiently large group of impurity atoms is formed which are located close to one another, such levels must necessarily appear. As a result of the concentration fluctuations in the large crystal, there is a finite (though small) probability of formation of large groups of impurity atoms. Since the groups differ from one another in the number and location of the impurity atoms, and since the local vibrations of the different groups interacting with one another are split up in a very complicated way, the local levels associated with the different groups will give a resultant continuous spectrum which lies either below or above the point of minimum or maximum frequency ω_1 (and has a very rapidly decreasing level density). Thus, in concentrated solutions the smearing out of extremal points occurs because of fluctuational deviations from the average concentration, and because of the local levels which appear in regions where there are such concentration changes. It can be shown that the smearing associated with this effect in ideal solutions leads to a smearing out of the singularity $|\omega - \omega_1|^{1/2}$ over a very narrow range (for small ϵ) of frequencies $\sim \lambda'\omega_1$, where

$$\lambda' = c^2(1 - c)^2\varepsilon^4(\omega_1/\omega_2 q_m^2)^3.$$

As we move away from the point ω_1, at large distances the level density first falls off exponentially according to the law $\exp[-(\omega - \omega_1)^2/\lambda'^2\omega_1^2]$, and then even faster. This level density goes to zero only at the frequency ω' which is equal to the frequency of vibration of a crystal containing only the atoms of the heavier element (in the case of a minimum frequency) or of the lighter element (in the case of a maximum frequency). The same argument is obviously equally applicable to the energy levels of conduction electrons in a crystal.

4. SCATTERING OF NEUTRONS BY LOCAL VIBRATIONS

Now let us consider the case when the impurity atoms (or other defects) strongly perturb the crystal vibrations and lead to the appearance of local levels.[7,20] We shall assume that the concentration of defects is small. For determining the scattering cross section from formula (1), it is more convenient in this case to expand not in plane waves but in exact normal coordinates. We shall denote by

$$\sqrt{\hbar/2\rho v\omega_\varkappa}\,\mathbf{e}_{\varkappa s\gamma}\,(a_\varkappa - a^{+}_{-\varkappa})$$

the term in the expansion of the displacement of the $s\gamma$ atom corresponding to the local vibration κ. Then the cross section for scattering with absorption or emission of a phonon κ is equal to

$$\sigma_\varkappa(\mathbf{q}_1, \omega) = C\frac{k_2}{k_1}\frac{1}{\omega_\varkappa}\Big[\Big|\sum_{s\gamma} A_{s\gamma}\exp(i\mathbf{q}_1\delta\mathbf{R}_{s\gamma})\exp(i\mathbf{q}_1\mathbf{R}_{s\gamma})\mathbf{e}_{\varkappa s\gamma}\mathbf{q}_1\Big|^2 + \sum_{s\gamma} B_{s\gamma}^2(\mathbf{e}_{\varkappa s\gamma}\mathbf{q}_1)^2\Big]\varphi_{\varkappa\varkappa}(\omega), \tag{35}$$

where $A_{s\gamma}$ and $B_{s\gamma}$ are now fixed, $\varphi_{\kappa\kappa}(\omega)$ is

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*tg = tan

given by formula (8) with $a_{\mathbf{k}j}$ replaced by a_κ, and we have dropped the small terms corresponding to $\varphi_{\kappa\kappa'}(\omega)$ with $\kappa \neq \kappa'$. In the harmonic approximation, the Hamiltonian is diagonal in the variables a_κ, a_κ^+, so that $\varphi_{\kappa\kappa}(\omega)$ reduces to $\delta(\pm\omega - \omega_\kappa)$ (and $\varphi_{\kappa\kappa'}^{(\omega)} = 0$). However, because of anharmonicity, there is an interaction between the vibrations which leads to a broadening of the distribution. We shall assume that the frequency ω_κ is such that processes are possible in which a local phonon κ is annihilated and two phonons $\mathbf{k}j$ and $\mathbf{k}'j'$ are created. The Hamiltonian describing such processes can be written in the form

$$H = \hbar\omega_\varkappa a_\varkappa^+ a_\varkappa + \frac{1}{2} \sum_{\mathbf{k}j\mathbf{k}'j'} (V_{\varkappa\mathbf{k}j\mathbf{k}'j'} a_\varkappa^+ a_{\mathbf{k}j} a_{\mathbf{k}'j'} + V^*_{\varkappa\mathbf{k}j\mathbf{k}'j'} a_\varkappa a_{\mathbf{k}j}^+ a_{\mathbf{k}'j'}^+)$$

$$+ \sum_{\mathbf{k}j} \hbar\omega_{\mathbf{k}j} a_{\mathbf{k}j}^+ a_{\mathbf{k}j}. \tag{36}$$

Setting up the equations for the Green's function corresponding to this Hamiltonian and breaking off the chain of equations in the second approximation of perturbation theory, as is done in the Appendix for the Hamiltonian (3), we find that $\varphi_{\kappa\kappa}(\omega)$ is given by a formula of the type of (9), in which $\Gamma_{\mathbf{k}j}$ and $P_{\mathbf{k}j}$ must be replaced by Γ_κ and P_κ, where

$$\Gamma_\varkappa = \frac{\pi}{\hbar^2} \sum_{\mathbf{k}j\mathbf{k}'j'} |V_{\varkappa\mathbf{k}j\mathbf{k}'j'}|^2 \delta(\omega - \omega_{\mathbf{k}j} - \omega_{\mathbf{k}'j'})$$

$$\times [1 + n(\omega_{\mathbf{k}j}) + n(\omega_{\mathbf{k}'j'})],$$

$$P_\varkappa = \frac{1}{\hbar^2} \mathrm{P} \sum_{\mathbf{k}j\mathbf{k}'j'} \frac{|V_{\varkappa\mathbf{k}j\mathbf{k}'j'}|^2}{\omega - \omega_{\mathbf{k}j} - \omega_{\mathbf{k}'j'}} [1 + n(\omega_{\mathbf{k}j}) + n(\omega_{\mathbf{k}'j'})]. \tag{37}$$

From (35), (9), and (37), it follows that the width of the distribution in this case depends on temperature (and is proportional to T for high temperatures). It can be shown that as ω_κ approaches the edge of the frequency band, Γ_κ increases rapidly and the distribution is smeared out. On the other hand, with increasing ω_κ the processes treated here, in which one local vibration is changed into two crystal vibrations, cease to be possible, and broadening can occur only because of multiphonon thermal transitions, whose probability is small and very strongly dependent on temperature (cf., for example, reference 21). The essential point is that when the scattering angle changes the position of the coherent scattering peaks changes in general, while the position of peaks associated with local vibrations remains unchanged.

APPENDIX

According to reference 9e, the retarded Green's function for the operators $a_{\mathbf{k}j}$, $a_{\mathbf{k}'j'}^+$ is given by the expression

$$G_{\mathbf{k}j\mathbf{k}'j'}(t, 0) = -i\theta(t)\,\mathrm{Sp}\,\{e^{-\lambda H}\,[a_{\mathbf{k}j}(t)\,a_{\mathbf{k}'j'}^+(0)$$

$$- a_{\mathbf{k}'j'}^+(0)\,a_{\mathbf{k}j}(t)]\}\,(\mathrm{Sp}\,e^{-\lambda H})^{-1} \tag{A.1}$$

(where $\theta(t) = 1$ for $t > 0$ and $\theta(t) = 0$ for $t < 0$), while the advanced Green's function differs in sign and has $-t$ in place of t. Similarly we can introduce a Green's function $F_{\mathbf{k}j\mathbf{k}'j'}$ for $a_{\mathbf{k}j}^+$ and $a_{\mathbf{k}'j'}^+$. If the Hamiltonian is given by formula (3), the equations of motion for these functions have the form

$$i\frac{dG_{\mathbf{k}j\mathbf{k}'j'}}{dt} = \delta(t)\,\delta_{\mathbf{k}\mathbf{k}'}\delta_{jj'} + \omega_{\mathbf{k}j}G_{\mathbf{k}j\mathbf{k}'j'}$$

$$+ \frac{1}{\hbar} \sum_{\mathbf{k}''j''} (V_{\mathbf{k}j\mathbf{k}''j''}G_{\mathbf{k}''j''\mathbf{k}'j'} - V'_{\mathbf{k}j\mathbf{k}''j''}F_{\mathbf{k}''j''\mathbf{k}'j'}),$$

$$i\frac{dF_{\mathbf{k}j\mathbf{k}'j'}}{dt} = -\omega_{\mathbf{k}j}F_{\mathbf{k}j\mathbf{k}'j'} - \frac{1}{\hbar} \sum_{\mathbf{k}''j''} (V_{\mathbf{k}''j''\mathbf{k}j}F_{\mathbf{k}''j''\mathbf{k}'j'}$$

$$- V'^*_{\mathbf{k}j\mathbf{k}''j''}G_{\mathbf{k}''j''\mathbf{k}'j'}). \tag{A.2}$$

For the Fourier components we get the integral equations

$$(\omega - \omega_{\mathbf{k}j})\,G_{\mathbf{k}j\mathbf{k}'j'}(\omega) - \frac{1}{\hbar} \sum_{\mathbf{k}''j''} [V_{\mathbf{k}j\mathbf{k}''j''}G_{\mathbf{k}''j''\mathbf{k}'j'}(\omega)$$

$$- V'_{\mathbf{k}j\mathbf{k}''j''}F_{\mathbf{k}''j''\mathbf{k}'j'}(\omega)] = \frac{1}{2\pi}\,\delta_{\mathbf{k}\mathbf{k}'}\delta_{jj'},$$

$$(\omega + \omega_{\mathbf{k}j})\,F_{\mathbf{k}j\mathbf{k}'j'}(\omega) + \frac{1}{\hbar} \sum_{\mathbf{k}''j''} [V_{\mathbf{k}''j''\mathbf{k}j}F_{\mathbf{k}''j''\mathbf{k}'j'}(\omega)$$

$$- V'^*_{\mathbf{k}j\mathbf{k}''j''}\,G_{\mathbf{k}''j''\mathbf{k}'j'}(\omega)] = 0. \tag{A.3}$$

These equations can be solved by the method of successive approximations, assuming that V and V′ are small quantities. The result is

$$G_{\mathbf{k}j\mathbf{k}'j'}(\omega) = \frac{V_{\mathbf{k}j\mathbf{k}'j'}}{\hbar(\omega - \omega_{\mathbf{k}j})}\,G_{\mathbf{k}'j'}(\omega), \quad \mathbf{k} \neq \mathbf{k}', \quad j \neq j', \tag{A.4}$$

$$G_{\mathbf{k}j\mathbf{k}j'}(\omega) = G_{\mathbf{k}jj'}(\omega) = \frac{R_{\mathbf{k}jj'}(\omega)}{\omega - \omega_{\mathbf{k}j}}\,G_{\mathbf{k}j'}(\omega), \quad j \neq j', \quad \omega \approx \omega_{\mathbf{k}j'}, \tag{A.5}$$

$$G_{\mathbf{k}j\mathbf{k}j}(\omega) = G_{\mathbf{k}j}(\omega) = 1/2\pi\,[\omega - \omega_{\mathbf{k}j} - R_{\mathbf{k}jj}(\omega)], \tag{A.6}$$

where

$$R_{\mathbf{k}jj'}(\omega) = \frac{1}{\hbar^2} \sum_{\mathbf{k}''j''} \left[\frac{V_{\mathbf{k}j\mathbf{k}''j''}V_{\mathbf{k}''j''\mathbf{k}j'}}{\omega - \omega_{\mathbf{k}''j''}} - \frac{V'_{\mathbf{k}j\mathbf{k}''j''}V'^*_{\mathbf{k}''j''\mathbf{k}j'}}{\omega + \omega_{\mathbf{k}''j''}} \right]. \tag{A.7}$$

If the levels $\omega_{\mathbf{k}j}$ and $\omega_{\mathbf{k}j'}$ are close to one another, perturbation theory is no longer applicable. The convergence can be improved in the same way as one does in ordinary perturbation theory when there are two close levels, by treating both $G_{\mathbf{k}j}$ and $G_{\mathbf{k}jj'}$ as zeroth order quantities. We then obtain

$$G_{\mathbf{k}j}(\omega) = \frac{1}{2\pi} \frac{\omega - \omega_{\mathbf{k}j'} - R_{\mathbf{k}j'j'}}{(\omega - \omega_{\mathbf{k}j} - R_{\mathbf{k}jj})(\omega - \omega_{\mathbf{k}j'} - R_{\mathbf{k}j'j'}) - R_{\mathbf{k}jj'}R_{\mathbf{k}j'j}},$$

$$G_{\mathbf{k}jj'}(\omega) = R_{\mathbf{k}jj'}G_{\mathbf{k}j'}(\omega)\,/\,(\omega - \omega_{\mathbf{k}j} - R_{\mathbf{k}jj}). \tag{A.8}$$

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