The possibility of conservation of singularities of the phonon state density in the case of isotropic disordering of perfect crystals

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It is shown that part of the Van Hove singularities in the phonon spectrum are conserved following isotopic disordering in certain sublattices of perfect crystals with several atoms in a unit cell. This occurs when the singularity corresponds to a critical oscillation, the amplitude of which vanishes at those sites where atoms of an isotopically inhomogeneous element are located.

The phonon state density $g_0(\omega^2)$ in an ideal crystal has the singularities $\Delta^{\pm} g_0(\Omega)$ at the frequencies $\omega = \omega_i + \Omega$, $\Omega \to \pm 0$, most of which as a consequence of the invariance of the Hamiltonian under symmetry transformations of the crystal.[1]

We assume that an isotopic disordering takes place in such a crystal, i.e., it is "converted" into a solid substitution solution, in which the masses of the atoms are randomly distributed. Will the phonon state density $g(\omega^2)$ in the solid solution have the singularities $\Delta^{\pm} g(\Omega)$ at $\omega - \omega_i = \Omega \pm 0$, i.e., at the same frequencies as the initial perfect crystal?[1)]

Phonon excitations of the plane wave type have a finite lifetime in the solid solution, even in the harmonic approximation (to which we limit ourselves in what follows). As noted by Krivoglaz,[2] this leads in the general case to a smearing out of the singularities.

It will be shown below that, in spite of the applicability of this physical picture to the spectrum as a whole, some of the singularities of $g_0(\omega^2)$ can persist in certain solid solutions, albeit in modified form, since the phonons corresponding to these singularities of $g(\omega^2)$ are scattered with limiting weakness in such solid solutions. The results were obtained without use of perturbation theory in terms of the potential of the interaction with the components of the solid solution and without expansion in powers of the concentration of the latter.

THE HAMILTONIAN OF THE PROBLEM

The Hamiltonian H of the phonons in the solid solution is of the form

$$H=\sum_{l,k}\frac{p^2(l,k)}{2M(l,k)}+\frac{1}{2}\sum_{l,l',k,k'}\varphi_{\alpha\beta}(l,k;l',k')\,u_\alpha(l,k)\,u_\beta(l',k'), \tag{1}$$

$$\sum_{l',k'}\varphi_{\alpha\beta}(l,k;l',k')=0, \tag{2}$$

where $M(l, k)$, $p(l, k)$ and $u_\alpha(l, k)$ are the mass, momentum and α-th component of the displacement of the k-th atom in the l-th unit cell from a position of equilibrium $\mathbf{R}(l, k)$; $\varphi_{\alpha\beta}(l, k; l', k')$ are the spin constants. Repeated Greek indices mean summation from 1 to f (f is the dimensionality of the crystal).

For analysis of the singularities of $g(\omega^2)$, we need a number of values which characterize the perfect crystal. The Hamiltonian H_0 of the phonons in the perfect crystal is obtained by replacement of the mass $M(l, k)$ in H by the mass $M^0(k)$, and the polarization vector $W(k, q, j)$ and frequency $\omega(q, j)$ of the phonon with momentum q and polarization j are determined from the dispersion equation[3]

$$\sum_{k'}\Big\{\omega^2(\mathbf{q},j)\,\delta_{\alpha\beta}\delta_{kk'}-\sum_{l'}\varphi_{\alpha\beta}(l,k;l'k')\,(M^0(k)M^0(k'))^{-1/2}\times\exp(i\mathbf{q}(\mathbf{R}(l',k')-\mathbf{R}(l,k)))\Big\}W_\beta(k',\mathbf{q},j)=0. \tag{3}$$

The quantity $g(\omega^2)$ is expressed in terms of the trace of the Green's function averaged (which operation is denoted by the symbol $\langle \ldots \rangle_c$) over all configurations of the solid solution:

$$g(\omega^2)=\frac{1}{\pi rfN}\operatorname{Im}\sum_{\mathbf{q},j}\langle\!\langle \mathbf{q},j|G|\mathbf{q}',j'\rangle\!\rangle_c,$$
$$\langle \mathbf{q},j|G^{-1}|\mathbf{q}',j'\rangle=((\omega+i\varepsilon)^2-\omega^2(q,j))\,\delta_{\mathbf{q}\mathbf{q}'}\delta_{jj'}-\langle \mathbf{q},j|\Phi|\mathbf{q}',j'\rangle,\quad \varepsilon\to+0, \tag{4}$$

where the matrix element of the random potential is

$$\langle \mathbf{q},j|\Phi|\mathbf{q}',j'\rangle=\frac{1}{N}\sum_{l,l',k,k'}W_\alpha^*(k,\mathbf{q},j)\,W_\beta(k',\mathbf{q}',j')\,\varphi_{\alpha\beta}(l,k;l'k') \tag{5}$$
$$\times\left(\sqrt{\frac{M^0(k)}{M^0(k')}}\frac{1}{M(l,k)}-\frac{1}{\sqrt{M^0(k)M^0(k')}}\right)\exp(-i\mathbf{q}\mathbf{R}(l,k)+i\mathbf{q}'\mathbf{R}(l',k')),$$

r and N are respectively the number of atoms in the unit cell and the number of the latter in the crystal.

Let G_q be the group of the wave vector q in the Brillouin zone of a perfect crystal. For simplicity, we further assume that the latter does not have screw axes and slip planes. Under the action of the elements of G_q, the displacements $u(l, k)$ are transformed according to the law

$$u_\alpha'(l,k)=S_{\beta\alpha}u_\beta(l,k)\exp(iq_\nu S_{\mu\nu}R_\mu(0,k)), \tag{6}$$

where S is the transformation matrix corresponding to G_q.

We now expand the representation (6), which is denoted by Γ_k^u in terms of the irreducible representations $\Gamma^{(\alpha)}G_q$:

$$\Gamma_k^u=\sum_\alpha a_k^{(\alpha)}\Gamma^{(\alpha)}. \tag{7}$$

If we have $a_k^{(\alpha)} = 0$, and $a_{k'}^{(\alpha)} \neq 0$ for any α, $k \neq k'$, then the k-th atom in the unit cell does take part in the oscillations of $\Gamma^{(\alpha)}$ of the perfect crystal, and isotopic disordering of the masses of the k-th atoms in the solid solution does not change the oscillations of $\Gamma^{(\alpha)}$. If for the same $g_0(\omega^2)$, there is a singularity produced by states extremely close to $\Gamma^{(\alpha)}$, then it can also be conserved in the solid solution, as is shown below. The con-

ditions $a_k^{(\alpha)} = 0$, $a_k^{(\alpha)} \neq 0$ are not satisfied for the common critical point and, as a rule, for points lying on the axes and planes of symmetry inside the Brillouin zone of the perfect crystal, and the corresponding singularities $g_0(\omega^2)$ are smeared in the solid solution. For simplicity, the calculations are carried out with separate examples. In particular, it is assumed that the unit cell of the perfect crystal with lattice constant a contains two different atoms, and the inversion center is located at the point R(0, 1).

LINEAR CHAIN

We now consider a perfect crystal in the form of a linear chain. Assuming that G_q is an inversion group at q = 0 and q = π/a,[4] we obtain

$$\Gamma_1^u(q=0)=A_u, \quad \Gamma_2^u(q=0)=A_u; \qquad \Gamma_1^u(q=\pi/a)=A_u, \quad \Gamma_2^u(q=\pi/a)=A_g. \tag{8}$$

For definiteness, we limit ourselves in what follows to the case of isotopic disordering in the sublattice k = 1, defining $M^0(1)$ by the condition $M^0(1) = 1/\langle 1/M(l, 1)\rangle_c$. The singularities $g_0(\omega^2)$ created by the optical[2] phonons (q = 0) and phonons of polarization A_u at q = π/a are smeared in the solid solution by virtue of (8). For phonons of momentum $q_1 = \pi/a + Q$, $|Q| \to 0$ and polarization A_g we have

$$W(1, q, A_q) \approx QW(1, A_u)\langle A_u|\nabla_1\omega^2|A_g\rangle(\omega^2(A_g)-\omega^2(A_u))^{-1},$$
$$\omega^2(q, A_g) \approx \omega^2(A_g) + \frac{1}{2}Q^2\langle A_g|\nabla_1^2\omega^2|A_g\rangle + \frac{1}{2}Q^2\frac{|\langle A_u|\nabla_1\omega^2|A_g\rangle|^2}{\omega^2(A_g)-\omega^2(A_u)} \equiv \omega^2(A_g)+c^2Q^2,$$
$$\omega^2(A_{g,u}) \equiv \omega^2(\pi/a, A_{g,u}), \qquad |A_{g,u}\rangle \equiv |\pi/a, A_{g,u}\rangle, \quad W(1, A_{g,u}) \equiv W(1, \pi/a, A_{g,u}). \tag{9}$$

Here and below, the value of the wave vector is omitted, for simplicity of notation, from the expressions for quantities which refer directly to the critical point.

We now choose a very small number Q_0, such that $|\Omega|^{1/2} \ll Q_0 \ll \pi/a$, and introduce the projection operators P and $\bar{P}$ on the states $|q, A_g\rangle$ ($q_1 = \pi/a + Q$, $|Q| \ll Q_0$) and on the orthogonal complements to them, respectively:

$$\bar{P}=1-P, \quad P\Phi\bar{P}\sim\bar{P}\Phi P\sim Q, \quad \Phi=\bar{P}\Phi\bar{P}+P\Phi\bar{P}+\bar{P}\Phi P+P\Phi P. \tag{10}$$

Let $G_P \equiv G_P(\omega^2)$ and $G_{\bar{P}} \equiv G_{\bar{P}}(\omega^2)$ ($\omega = \omega(\pi/a, A_g) + \Omega$) be the Green's functions corresponding to the Hamiltonian $H_0 + \bar{P}(H - H_0)\bar{P}$:

$$\langle q, j||G_P^{-1}|q', j'\rangle = \delta_{qq'}\delta_{jj'}(\omega^2-\omega^2(q, j))\langle q, j|P|q', j'\rangle,$$
$$\langle q, j|G_{\bar{P}}^{-1}|q', j'\rangle \equiv \delta_{qq'}\delta_{jj'}(\omega^2-\omega^2(q, j))\langle q, j|\bar{P}|q', j'\rangle - \langle q, j|\bar{P}\Phi\bar{P}|q', j'\rangle. \tag{11}$$

Neglecting the potential PΦP for the present, we expand $g(\omega^2)$ in powers of $P\Phi\bar{P} + \bar{P}\Phi P$:

$$g(\omega^2) = \langle g_1(P)\rangle_c + \langle g_1(\bar{P})\rangle_c; \tag{12}$$

$$g_1(P) = -\frac{1}{2\pi N}\operatorname{Im}\operatorname{Sp}P(G_P + G_P\Phi G_{\bar{P}}\Phi G_P + \ldots) \equiv \sum_{s=0}^{\infty} g_1^{(s)}(P),$$
$$g_1^{(s)}(P) \sim \Phi^s, \quad s = 0, 2, 4, \ldots \tag{13}$$

The quantity $g_1(\bar{P})$ is obtained by replacing in $g_1(P)$ the quantity P by $\bar{P}$ and $\bar{P}$; G_P corresponds to phonons that are intensively scattered by the potential $\bar{P}\Phi\bar{P}$ and therefore we shall assume that the corresponding spectral density $g_1^{(0)}(P)$ is a smooth function as $|\Omega| \to 0$ and that $G_{\bar{P}}$ has a "radius of action" $\rho \ll Q_0^{-1}$ ($G_{\bar{P}}(l, k); (l', k') \sim 0$ for $|R(l, k) - R\,l', k'| > \rho$). We obtain

$$\langle g_1^{(0)}(\bar{P})\rangle_c \sim 1,$$
$$\langle g_1^{(2)}(\bar{P})\rangle_c \sim \operatorname{Im}\int_{-Q_0}^{+Q_0}(2\omega(A_g)\Omega - c^2Q^2 + i\varepsilon)^{-1}Q^2\,dQ \sim A|\Omega|^{1/2}, \quad |A| \sim 1.$$

Inasmuch as $Q_0 \ll \pi/a$ and $\Delta^{\pm}g_0(\Omega) \sim |\Omega|^{-1/2}$, it follows that we can neglect the contribution $\langle g_1^{(2)}(P)\rangle_c$ and, similarly, $\langle g_1^{(4)}(\bar{P})\rangle_c$, $\langle g_1^{(6)}(P)\rangle_c$, . . . , i.e., the effect of the states $|q, A_g\rangle$ on the remaining states.

We now calculate $\langle g_1(P)\rangle_c$. We have

$$\langle g_1^{(0)}(P)\rangle_c = -\frac{a}{2\pi^2}\operatorname{Im}\int_{-Q_0}^{+Q_0}(2\omega(A_g)\Omega - c^2Q^2 + i\varepsilon)^{-1}\,dQ,$$
$$\langle g_1^{(2)}(P)\rangle_c = -\frac{a}{2\pi^2}\operatorname{Im}\int_{-Q_0}^{+Q_0}(2\omega(A_g)\Omega - c^2Q^2 + i\varepsilon)^{-2}|\xi|^2F_1(G_{\bar{P}})Q^2\,dQ, \tag{14}$$

$$\xi = \langle A_u|\nabla_1\omega^2|A_g\rangle(\omega^2(A_g)-\omega^2(A_u))^{-1},$$
$$F_1(G_{\bar{P}}) = \sum_{\substack{l', l'', q', q'' \\ j', j''}}\left\langle\left(\frac{M^0(1)}{M(l', 1)}-1\right)\left(\frac{M^0(1)}{M(l'', 1)}-1\right)\langle q', j'|G_{\bar{P}}|q'', j''\rangle\right\rangle_c \times\frac{\omega^2(q', j')\omega^2(A_g)}{N^2}W_1(1, q', j')W_1(1, q'', j'') \times\exp\left(i\left(q_1' - \frac{\pi}{a}\right)R_1(l', 1) - i\left(q_1'' - \frac{\pi}{a}\right)R_1(l'', 1)\right), \tag{15}$$

$$\langle g_1^{(4)}(P)\rangle_c = -\frac{a}{2\pi^2}\operatorname{Im}\int_{-Q_0}^{+Q_0}\frac{|\xi|^4F_1^2(G_{\bar{P}})Q^4}{(2\omega(A_g)\Omega - c^2Q^2 + i\varepsilon)^3}\,dQ + \langle S^{(4)}(P)\rangle_c. \tag{16}$$

As $|\Omega| \to 0$, Eqs. (14), (15) and the first term of (16) become $\sim|\Omega|^{-1/2}$, while

$$\langle S^4(P)\rangle_c \sim \int_{-Q_0}^{+Q_0}(2\omega(A_g)\Omega - c^2Q^2 + i\varepsilon)^{-1}Q^2(AQ_0 + B|\Omega|^{1/2})\,dQ, \quad |A| \sim |B| \sim 1$$

and can be neglected. Thus, separating the most significant terms of $\langle g_1(P)\rangle_c$, and assuming that $Q_0\rho \ll 1$, we get

$$\langle g_1(P)\rangle_c = -\frac{a}{2\pi^2}\operatorname{Im}\int_{-Q_0}^{+Q_0}(2\omega(A_g)\Omega - c^2Q^2 - |\xi|^2F_1(G_{\bar{P}})Q^2 + i\varepsilon)^{-1}\,dQ. \tag{17}$$

The part PΦP of the random potential Φ (10), not previously considered gives the contribution $g^{(\mu)} \sim \Phi^\mu$ (μ = 2, 4, . . .) to $g(\omega^2)$:

$$g^{(2)} \sim \operatorname{Im}\iint_{-Q_0}^{+Q_0}(2\omega(A_g)\Omega - c^2Q^2 + i\varepsilon)^{-2}(2\omega(A_g)\Omega - c^2Q_1^2 + i\varepsilon)^{-1}Q^2Q_1^2\,dQ\,dQ_1$$
$$\sim AQ_0|\Omega|^{-1/2} + B + CQ_0|\Omega|^{1/2} + D|\Omega|^{3/2}, \quad |A| \sim |B| \sim |C| \sim |D| \sim 1.$$

Therefore, as $|\Omega| \to 0$, we can neglect $g^{(2)}$ and, similarly $g^{(4)}$, $g^{(6)}$, ...

It is well known[5] that in the one-dimensional case the small but finite interaction between the particles with a square law of dispersion and the impurities leads to a complete renormalization of the spectrum of the states have a limitingly small group velocity. More exactly, because of the diagrams with overlapping lines from different impurities, new excitation branches appear. In our case (8) and (9), the simplest diagram of such a type leads to a phonon polarization operator Π.

$$\Pi(Q, \Omega) \sim \iint_{-Q_0}^{+Q_0}(2\omega(A_g)\Omega - c^2Q_1^2 + i\varepsilon)^{-1}(2\omega(A_g)\Omega - c^2Q_2^2 + i\varepsilon)^{-1} \times(2\omega(A_g)\Omega - c^2(Q - Q_1 - Q_2)^2 + i\varepsilon)^{-1}Q_1^2Q_2^2(Q - Q_1 - Q_2)^2\,dQ_1\,dQ_2.$$

Isolating the singularity of Π(Q, Ω) by the Landau method,[6] (the effect of the remaining terms of Π(Q, Ω) on $\Delta^{\pm}g(\Omega)$ can be neglected), we obtain the operator Π and the Green's function G_1 for $\Omega \to c^2Q^2/(18\omega(A_g))$:

$$\Pi(Q,\Omega)\sim\Omega^3(\Omega-c^2Q^2/(18\omega(A_g)))^{-1},$$
$$G_1\sim\Omega(\Omega-c^2Q^2/(18\omega(A_g)))^{-1}.$$

It is seen that although there is a new excitation branch in the spectrum with frequency $\omega = \omega(A_g) + c^2Q^2/18\omega A_g))$, the residue of the corresponding Green's function is $\sim\Omega$, and in contrast with (17), the role of these excitations in the singularity of $\Delta^{\pm}g(\Omega)$ is negligibly small. The same is true of the other similar diagrams.

Long-wave fluctuations of the composition of the solid solution are in the general case very important[7] for analysis of $\Delta^{\pm}g(\Omega)$. In the considered problem, they do not change the frequency for which there is a singularity of $g(\omega^2)$ and therefore are not important (the possible renormalization of $F_1(G_{\overline{P}})$ can be neglected because of the low probability of such fluctuations). Finally, because of the small effect of PΦP on $\Delta^{\pm}g(\Omega)$, we can replace $G_{\overline{P}}$ in (15) by the complete Green's function G [Eq. (5)] of the phonon in the solid solution, so that we finally obtain

$$\Delta^{\pm}g(\Omega)=-\frac{a}{2\pi^2}\operatorname{Im}\int_{-Q_0}^{+Q_0}(2\omega(A_g)\Omega-c^2Q^2+|\xi|^2F_1(G)Q^2+i\varepsilon)^{-1}dQ,$$
$$\Delta^{\pm}g(\Omega)=C^{\pm}|\Omega|^{-1/2},\quad C^{\pm}\geqslant 0,\quad \Omega\to\pm 0. \tag{18}$$

If the isotopic disordering exists in both sublattices, then the singularity (18) becomes smeared.

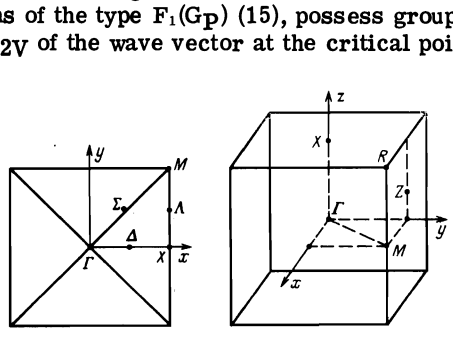
TWO-DIMENSIONAL LATTICE

As an example, we consider a square lattice, constructed of atoms of the type k = 0, and containing atoms of the type k = 1 at the centers of the squares, in the case of isotopic disordering of the latter. With the help of (7), we can show that the singularities of $\Delta^{\pm}g(\Omega)$, which arise because of the critical points Σ, Δ, Λ, M, Γ in the Brillouin zone of the perfect crystal (drawing a), are blurred in the solid solution. At the critical point $X(q_1=\pi/a,\ q_2=0)$ which corresponds to the group C_{2V}[4] of the wave vector, $\Gamma_1^u = B_1 + B_2$, $\Gamma_2^u = A_1 + A_2$, so that $g(\omega^2)$ will not have a singularity for $\omega = \omega(B_1)$, $\omega = \omega(B_2)$.

We now calculate $\Delta^{\pm}g(\Omega)$ for $\omega = \omega(A_1) + \Omega$, $|\Omega| \to 0$. For states with momentum $q_1 = \pi/a + Q_1$, $q_2 = Q_2$, $|Q| \to 0$, we have

$$\omega^2(q,A_1)\sim\omega^2(A_1)+\frac{Q_\alpha^2}{2}\langle A_1|\nabla_\alpha^2\omega^2|A_1\rangle+Q_\alpha^2\frac{|\langle B_\alpha|\nabla_\alpha\omega^2|A_1\rangle|^2}{\omega^2(A_1)-\omega^2(B_\alpha)},$$
$$W_\alpha(1,q,A_1)\approx\delta_{\alpha\beta}Q_\beta W_\beta(1,q,B_\beta)\frac{\langle B_\beta|\nabla_\beta\omega^2|A_1\rangle}{\omega^2(A_1)-\omega^2(B_\beta)}. \tag{19}$$

Inasmuch as the phonons (19) are weakly scattered in the solid solution, we obtain the following strongest singularity of $\Delta^{\pm}g(\Omega)$ from (4), (5), (19) under the same assumptions and similarly (10)–(18), neglecting quantities $\sim Q_0^2$, $|\Omega|$, and $|\Omega|\ln|\Omega|$, and assuming that, after averaging over the configurations of the solid solution, expressions of the type $F_1(G_P)$ (15), possess group symmetry C_{2V} of the wave vector at the critical point X;



$$\frac{d}{d\Omega}\Delta^{\pm}g(\Omega)=-\frac{a^2}{2\pi^3}\omega(A_1)\operatorname{Im}\iint_{-Q_0}^{+Q_0}(2\omega(A_1)\Omega+Q_1^2F_{2,1}+Q_2^2F_{2,2}+i\varepsilon)^{-1}dQ_1dQ_2$$
$$=\frac{a^2}{8\pi^2}\left\{\frac{1}{\Omega}\operatorname{Im}\int_0^{2\pi}(F_{2,1}\cos^2\varphi+F_{2,2}\sin^2\varphi+i\varepsilon)^{-1}d\varphi\right.$$
$$\left.-\pi\delta(\Omega_2)\operatorname{Re}\int_0^{2\pi}(F_{2,1}\cos^2\varphi+F_{2,2}\sin^2\varphi+i\varepsilon)^{-1}d\varphi\right\}, \tag{20}$$

$$F_{2,s}=-\frac{1}{2}\langle A_1|\nabla_s\omega^2|A_1\rangle-\frac{|\langle B_s|\nabla_s\omega^2|A_1\rangle|^2}{\omega^2(A_1)-\omega^2(B_s)}-\left|\frac{\langle B_s|\nabla_s\omega^2|A_1\rangle}{\omega^2(A_1)-\omega^2(B_s)}\right|^2\times\sum_{\substack{l',l'',\mathbf{q}',\mathbf{q}'',\\ j',j''}}\left\langle\left(\frac{M^0(1)}{M(l',1)}-1\right)\left(\frac{M^0(1)}{M(l'',1)}-1\right)\langle\mathbf{q}',j'|G|\mathbf{q}'',j''\rangle\right\rangle$$
$$\times\frac{\omega^2(\mathbf{q}',j')\,\omega^2(A_1)}{N^2}W_s(1,\mathbf{q}',j')W_s(1,\mathbf{q}'',j'')$$
$$\times\exp\left(i\mathbf{q}'\mathbf{R}(l',1)-i\mathbf{q}''\mathbf{R}(l'',1)-i\frac{\pi}{a}R_1(l',1)+i\frac{\pi}{a}R_1(l'',1)\right),$$
$$s=1,2;$$
$$\Delta^{\pm}g(\Omega)=C\ln|\Omega|+D\Theta(\Omega),\quad C\geqslant 0,\ |D|\sim 1,\quad \Omega\to\pm 0. \tag{21}$$

Thus, in the case of isotopic disordering in the sublattice k = 1, the function $g(\omega^2)$ has a symmetric logarithmic singularity and (or) a weaker singularity of the discontinuity type for $\omega = \omega(A_1)$, and also, as can be shown, for $\omega = \omega(A_2)$. These singularities are smeared in the presence of isotopic disordering in the sublattice k = 2.

THREE-DIMENSIONAL LATTICE OF THE CsCl TYPE

For definiteness, we assume that atoms of the sorts k = 1 and k = 2 occupy the centers and vertices of cubes, respectively. The strongest singularities of $\Delta^{\pm}g(\Omega_2)$ can correspond to the critical points X, M, R, Γ in the Brillouin zone of the perfect crystal (Fig. b).

We consider[3)] the critical point X, the wave vector of which the symmetry group D_{4h}:[4]

$$\Gamma_1^u=A_2'+E',\quad \Gamma_2^u=A_1+E.$$

We shall show that there will be sharp singularities in the cases $\omega = \omega(A_1)$ and $\omega = \omega(E')$ for isotopic disordering in the sublattice k = 1 of $g(\omega^2)$ in contrast to the situation for $\omega = \omega(A_2')$ and $\omega = \omega(E')$. Inasmuch as the results for $\omega = \omega(A_1)$ and $\omega = \omega(E)$ are similar, we limit ourselves to the analysis of $g(\omega^2)$ for $\omega = \omega(E) + \Omega$, $\Omega \pm 0$.

Let $|E_1\rangle$ $|E_2\rangle$, $|E_1'\rangle$, $|E_2'\rangle$ be solutions of (3) at the critical points of the Brillouin zone, which transform respectively as the x and y components of the doubly degenerate E and E′ of the representations of the group D_{4h}. Near the critical point $X(q_1 = Q_1, q_2 = Q_2, q_3 = \pi/a + Q_3, |Q\rangle \to 0)$, the dynamic matrix of the perfect crystal D_0 takes in the basis $|E_1\rangle$, $|E_2\rangle$ the form

$$\langle E_1|D_0|E_1\rangle\approx\omega^2(E)+\frac{Q_\alpha^2}{2}\langle E_1|\nabla_\alpha^2\omega^2|E_1\rangle+Q_3^2\frac{|\langle E_2'|\nabla_3\omega^2|E_1\rangle|^2}{\omega^2(E)-\omega^2(E')}+Q_\alpha^2\frac{|\langle A_2'|\nabla_2\omega^2|E_1\rangle|^2}{\omega^2(E)-\omega^2(A_2')}, \tag{22}$$

$$\langle E_1|D_0|E_2\rangle=\langle E_2|D_0|E_1\rangle\approx Q_1Q_2\left\{2\langle E_2|\nabla_1\nabla_2\omega^2|E_1\rangle-\frac{|\langle A_2'|\nabla_2\omega^2|E_1\rangle|^2}{\omega^2(E)-\omega^2(A_2')}\right\};$$
$$W_\alpha(1,q,E_\beta)\approx\delta_{\alpha 3}e_{3\beta\gamma}Q_\gamma\langle A_2'|\nabla_2\omega^2|E_1\rangle/(\omega^2(E)-\omega^2(A_2'))+e_{3\beta\alpha}Q_3\langle S_2'|\nabla_3\omega^2|E_1\rangle/(\omega^2(E)-\omega^2(E')). \tag{23}$$

The quantity $\langle E_2|D_0|E_2\rangle$ is obtained from $\langle E_1|D_0|E_1\rangle$ by replacement of Q_1 by Q_2 and Q_2 by Q_1.

The phonons (23) are weakly scattered in the solid solution. By a method similar to that used above for the derivation of (18) and (21), we obtain

$$\Delta^{\pm}g(\Omega)=-\frac{3a^3}{8\pi^4}\operatorname{Im}\int\int\int_{-Q_0}^{+Q_0}d^3Q\sum_{\alpha=1}^{2}\langle E_\alpha|[(\omega+i\varepsilon)^2-D_0-F_3]^{-1}|E_\alpha\rangle,$$

$$\Delta^{\pm}g(\Omega)=-\frac{3a^3}{8\pi^4}\operatorname{Im}\int_0^{\pi}\sin\vartheta\,d\vartheta\int_0^{2\pi}d\varphi\int_0^{Q_0}Q^2\,dQ\sum_{\alpha=1}^{2}(2\omega(E)\Omega+i\varepsilon-f_\alpha(\vartheta,\varphi)Q^2)^{-1}, \tag{24}$$

where

$$\langle E_1|F_3|E_1\rangle=\left|\frac{\langle A_2'|\nabla_2\omega^2|E_1\rangle}{\omega^2(E)-\omega^2(A_2')}\right|^2\psi_{11}Q_2^2+\left|\frac{\langle E_2'|\nabla_3\omega^2|E_1\rangle}{\omega^2(E)-\omega^2(E')}\right|^2\psi_{33}Q_3^2,$$

$$\langle E_2|F_3|E_2\rangle=\left|\frac{\langle A_2'|\nabla_2\omega^2|E_1\rangle}{\omega^2(E)-\omega^2(A_2')}\right|^2\psi_{11}Q_1^2+\left|\frac{\langle E_2'|\nabla_3\omega^2|E_1\rangle}{\omega^2(E)-\omega^2(E')}\right|^2\psi_{33}Q_3^2,$$

$$\langle E_1|F_3|E_2\rangle=\langle E_2|F_3|E_1\rangle=-\left|\frac{\langle A_2'|\nabla_2\omega^2|E_1\rangle}{\omega^2(E)-\omega^2(A_2')}\right|^2\psi_{11}Q_1Q_2,$$

$$\psi_{\alpha\beta}=\sum_{\substack{l',l'',\mathbf{q}',\mathbf{q}'',\\ j',j''}}\left\langle\left(\frac{M^0(1)}{M(l',1)}-1\right)\left(\frac{M^0(1)}{M(l'',1)}-1\right)\langle\mathbf{q}',j'|G|\mathbf{q}'',j''\rangle\right\rangle_c$$

$$\times\frac{\omega^2(\mathbf{q}',j')\,\omega^2(E)}{N^2}W_\alpha(1,\mathbf{q}',j')W_\beta(1,\mathbf{q}'',j'') \tag{25}$$

$$\times\exp\left(i\mathbf{q}'(\mathbf{R}(l',1)-\mathbf{R}(l'',1))-i\frac{\pi}{a}(R_3(l',1)-R_3(l'',1))\right)$$

and $f_\alpha(\vartheta$ and $\varphi)Q^2$ are the eigenvalues of the matrix $D_0 + F_3$. Calculating $(d/d\Omega)\Delta^{\pm}g(\Omega)$ from (24), and leaving only the most divergent terms as $\Omega \to \pm 0$, we obtain

$$\Delta^{\pm}g(\Omega)=C^{\pm}|\Omega|^{1/2}\quad |C^{\pm}|\sim 1. \tag{26}$$

For isotopic disordering in the sublattice k = 2, the singularities $g(\omega^2)$ for $\omega = \omega(A_1)$ and $\omega = \omega(E)$ become smeared.

We have considered above the so-called ordinary[3] critical points, in which $\partial\omega(\mathbf{q}, j)/\partial q_\alpha = 0$ for $\alpha = 1$, 2, and 3 for phonons of any polarization j. Are the singularities in $g(\omega^2)$ that are produced in $g_0(\omega^2)$ by the singularities of the critical points preserved, i.e., those produced by the points where certain components of $\partial\omega(\mathbf{q}, j)/\partial q_\alpha \neq 0$? Such critical points develop most frequently as a consequence of the intersection of the branches of the phonon spectrum of the perfect crystal. We consider, for example, the critical point Z (Fig. b), which corresponds to group C_{2V} of the wave vector, and let, for definiteness, the branch of the phonon spectrum with symmetry A_2 intersect in the critical point Z as a consequence of the random degeneracy with B_2:

$$\Gamma_1^u=A_1+B_1+B_2,\quad \Gamma_2^u=A_1+A_2+B_1,$$
$$\langle A_2|\nabla_1\omega^2|A_2\rangle=\langle A_2|\nabla_2\omega^2|A_2\rangle=\langle B_2|\nabla_1\omega^2|B_2\rangle=\langle B_2|\nabla_2\omega^2|B_2\rangle=0, \tag{27}$$
$$\langle A_2|\nabla_3\omega^2|A_2\rangle\neq 0,\quad \langle B_2|\nabla_3\omega^2|B_2\rangle\neq 0.$$

Inasmuch as the nondiagonal matrix element $\langle B_2|\nabla_1\omega^2|A_2\rangle \neq 0$, it follows that near the critical point Z the states $|A_2\rangle$ and $|B_2\rangle$ are strongly mixed. In a perfect crystal, this leads to $\Delta^{\pm}g_0(\Omega) \sim |\Omega|$, i.e., to a discontinuity of the derivative of $g_0(\omega^2)$. For isotopic disordering in the sublattice k = 1, the states $|B_2\rangle$, in contrast with $|A_2\rangle$, are strongly scattered. Therefore, the singularity of $g_0(\omega^2)$ in the solid solution, formed by the critical point Z, becomes smeared. If the singular critical point is formed by the intersection of the phonon branches, each of which is not scattered (at the point of intersection) in the solid solution, then the corresponding singularity of $g(\omega^2)$ will also exist in the solid solution.

CONCLUSION

It was shown above that in the phonon state density $g(\omega^2)$ of substitutional solid solutions formed by isotopic disordering of the masses in certain sublattices, the preserved singularities of the phonon state density $g(\omega^2)$ of perfect crystals are those due to phonons that are weakly scattered in the solid solution. The interaction potential of the phonons with the components of the solid solution is not assumed to be small in this case. However, this weak scattering is sufficient for a significant change in the singularity of $g(\omega^2)$ in comparison with $\Delta^{\pm}g_0(\Omega)$. Thus, in the two-dimensional case (f = 2), the situation is possible in which $\Delta^{\pm}g_0(\Omega)$ is discontinuous, while in the solid solution $\Delta^{\pm}g(\Omega) \sim \ln|\Omega|$ (21). Such an enhancement of the singularity of the phonon state density in the solid solution, in compoarison with the perfect crystal, is due to the increase (as a consequence of the finiteness of the lifetime and change in the dispersion law of the corresponding phonons in the solid solution) of the phase folume of the states that are important in $\Delta^{\pm}g(\Omega)$. In the one-dimensional (three-dimensional) case of a solid solution, the singularity of $g(\omega^2)$ (18), (26) is bilateral ($C^+ \neq 0$, $C^- \neq 0$) while in the perfect crystal, either $C^+ = 0$ or $C^- = 0$. Naturally, in certain solid solutions, a situation can arise in which, for f = 1 and 3, either $C^+ = 0$ or $C^- = 0$, while for f = 2, $g(\omega^2)$ has a singularity of the discontinuous type. Such will be the case, in particular, when the singularity of $g(\omega^2)$ is located at the edge of a gap or some other boundary in the solid state spectrum.

For example, let us consider a solid solution in the form of a linear chain (8) with interaction between nearest neighbors. Let atoms of the type k = 1 have a mass m_1 or m_0 with probabilities t and $1-t$. We have

$$\varphi_{11}(l,1;l',2)=-h(\delta_{l,l'}+\delta_{l,l'-1}), \tag{28}$$
$$\varphi_{11}(l,1;l',1)=\varphi_{11}(l,2;l',2)=2h\delta_{l,l'},$$
$$M^0(1)=(t/m_1+(1-t)/m_0)^{-1}. \tag{29}$$

The functions $g(\omega^2)$ will have a singularity (18) for $\omega = \omega(A_u) = \sqrt{2h/M^0(2)}$. The transfer matrix[8] T_l at the frequency ω is equal to either $T_{(0)}$ or $T_{(0)}^l$:

$$\begin{pmatrix}u_1(l-1,1)\\ u_1(l,1)\end{pmatrix}=T_{l-1}\begin{pmatrix}u_1(l,1)\\ u_1(l+1,1)\end{pmatrix},\quad T_{(\alpha)}=\begin{pmatrix}\lambda_\alpha & -1\\ 1 & 0\end{pmatrix}, \tag{30}$$
$$\lambda_\alpha=((2h-\omega^2m_\alpha)(2h-\omega^2M^0(2))-2h^2)h^{-2},\quad \alpha=0,\ 1.$$

The transfer matrix T_l of the entire chain is the product of the matrices $T_{(1)}T_{(0)}$ ($l = 0, 1, \ldots$).

Let $E_\pm(l)$, $(x_\pm(l), y_\pm(l))$, $\delta_\pm(l)$ be the eigenvalues, eigenvectors, and phases of $T_{(1)}T_{(0)}^l$, and

$$\exp(i\delta_\pm(l))=-\frac{x_\pm(l)-iy_\pm(l)}{x_\pm(l)+iy_\pm(l)}. \tag{31}$$

According to Hori[8], $g(\omega^2) = 0$ if $|E_+(l)| > |E_-(l)|$ for all l and the intervals of the phases $\delta_+(l)$ and $\delta_-(l)$ do not overlap. The quantities γ^2 and γ^{-2} are eigenvalues of $T_{(0)}(\gamma^2 + \gamma^{-2} = \lambda_0)$. Near the frequency $\omega(A_u)$ of interest to us, we have

$$\gamma^2=e^{i\pi-\mu},$$
$$\omega\approx\omega(A_u)+\frac{M^0(2)}{8(M^0(2)-m_0)}\omega(A_u)\mu^2, \tag{32}$$

where $|\mu| \ll 1$.

Transforming to the representation in which the matrix $T_{(0)}$ is diagonal, we find that only for $\operatorname{Im}\mu = 0(m_1-m_0)/(M^0(2)-m_0) < 1$, $|E_+(l)|| > ||E_-(l)$ and the intervals of the phases $\delta_+(l)$ and $\delta_-(l)$ do not overlap for all $l = 0, 1, \ldots$. Therefore, if $M^0(2) > m_0$ and $M^0(2) > m_1$ ($M^0(2) < m_0$ and $M^0(2) < m_1$), then the singularity of $g(\omega^2)$ of the type (18) coincides with the boundaries of the gap in the phonon state density of the solid solution and is unilateral.

The calculations given above were carried out in the harmonic approximation. If we take into account the anharmonism and the interaction of the phonons with the other elementary excitations, then the singularities (18), (21), and (26) will be smeared out over the energy width Γ_0' or Γ' in perfect crystals[2] or solid solutions, respectively. Generally speaking, $\Gamma' \sim \Gamma_0'$ but the specific values of Γ' and Γ_0' depend strongly on the parameters of the solid solution. Thus, for example, a situation is possible in which $\Gamma_0' = 0$ at any order in the constant of the anharmonism (by virtue of the laws of conservation of energy and quasimomentum), while $\Gamma' \neq 0$. Finally, as a consequence of the inexactness of the adiabatic approximation, the force constants in the isotropic disordering of the solid solution and the perfect crystal are different, which makes an additional, but very small, contribution to Γ'.

In practice, Eqs. (18), (21), and (26) are applicable principally to two cases:

1) the crystal consists chiefly of light atoms, the isotopic scattering of the phonons in the solid solution is large,[2] so that Γ' is relatively small;

2) the substitution solid solution is not isotopically disordered, but its components are such that the difference in the force constants in the solid solution and in the ideal crystal is small while the mass of the atoms is large.

Results similar to (18), (21) and (26), can be obtained also for the electron state density in a substitutional solid solution with a delta-shaped interaction potential, the intensity of which Φ_l in the l-th node is a random function. Those singularities of the electron state density in the perfect crystal are preserved in the form (18), (21), and (26) in the solid solution which are determined by the wave functions which have very small amplitude at the lattice sites. It must be emphasized that Bychkov[9] and Ovchinnikov[10] recently succeeded (by assuming a Lorentzian distribution of Φ_l[11]) in solving exactly the problem of the electron state density in such a system.

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[1)]The term "perfect crystal" will be used precisely in this sense in the rest of the paper.

[2)]Analysis of $g(\omega^2)$ as $\omega \to +0$ is outside the limits of this research.

[3)]Similar results are obtained for the critical points M, R. The singularity of $g_0(\omega^2)$ corresponding to the critical point Γ is smeared in the solid solution.

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