$$S(\omega)=\frac{A^2}{2\pi}e^{\overline{\Delta\omega^2}/\alpha^2} \tag{18}$$

$$\times\sum_{m=0}^{\infty}\frac{(-1)^m}{m!}\left(\frac{\overline{\Delta\omega^2}}{\alpha^2}\right)^m\frac{(\overline{\Delta\omega^2}/\alpha)+\alpha m}{[(\overline{\Delta\omega^2}/\alpha)+\alpha m]^2+(\omega_0-\omega)^2}.$$

If $\overline{\Delta\omega^2}\ll\alpha^2$, then only the first terms in the series (18) are important:

$$S(\omega)=\frac{A^2}{2\pi}\left[\frac{\overline{\Delta\omega^2}/\alpha}{(\overline{\Delta\omega^2}/\alpha)^2+(\omega_0-\omega)^2}-\frac{\overline{\Delta\omega^2}/\alpha}{\alpha^2+(\omega_0-\omega)^2}+\ldots\right]$$

where, as expected, the first term of the series coincides with Eq. (17).

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[1] I. L. Bershtein, Dokl. Akad. Nauk SSSR 20, 11 (1938).

[2] I. L. Bershtein, J. Tech. Phys. (U.S.S.R.) 11, 305 (1941).

[3] I. L. Bershtein, Izv. Akad. Nauk SSSR, Ser. Fiz. 14, 145 (1950).

[4] G. S. Gorelik, J. Exptl. Theoret. Phys. (U.S.S.R.) 20, 351 (1950).

[5] G. S. Gorelik, Izv. Akad. Nauk SSSR, Ser. Fiz. 14, 187 (1950).

[6] M. A. Leontovich, *Statistical Physics* (Moscow, Leningrad), 1944.

[7] D. Middleton, Phil. Mag. 42, 689 (1951).

[8] S. M. Rytov, J. Exptl. Theoret. Phys. (U.S.S.R.) 29, 304, 315 (1955); Soviet Phys. JETP 2, 217, 225 (1956).

[9] S. M. Rytov, Radiotekhnika i elektronika 1, 114 (1956).

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Vibration Spectrum of Disordered Crystal Lattices

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The vibration spectrum of a disordered crystal is studied. Calculations are made for an isotopic mixture, although the method could be applied under more general conditions. The mass of each atom is taken to be a random variable, and the deviation of the mass from its average value is not assumed to be small. The spectral density and the vibrational part of the free energy of the mixed crystal are determined.

THE determination of the vibration spectrum of a disordered system, for example a mixed solid, is a highly interesting problem. A similar problem was considered by one of the authors[1] in connection with the optical properties of mixed solids; at that time we investigated thoroughly only those aspects of the problem which are directly relevant to infra-red spectroscopy, (in particular the question of the existence of impurity frequencies). Dyson[2] considered the same problem for the special case of a disordered linear chain with nearest-neighbor interactions. But Dyson's method is by its very nature not capable of extension to three-dimensional systems.

In the present paper we describe a method which is free from these limitations. The method is an extension of earlier work by one of us.[3-6] We apply the method here to the case in which the atoms in the system differ only in mass (a mixture of isotopes). For the sake of clarity and simplicity of exposition, we consider only an idealized lattice in which all vibrations take place in one direction. This shortens the analysis considerably, without changing the essential nature of the problem.

There exists a deep-lying similarity in the effects of the destruction of translational invariance upon the energy spectra of phonons and of electrons. Hence the results of this investigation should be qualitatively valid also for electronic spectra.

1. THE METHOD OF TRACES

The equation for the vibrations of a lattice composed of a mixture of isotopes of a single element has the form

$$\sum_{\mathbf{r}'}\frac{A_{\mathbf{r}-\mathbf{r}'}}{m_{\mathbf{r}}}\chi(\mathbf{r}')-\omega^2\chi(\mathbf{r})=0. \tag{1}$$

Here $\chi(r)$ is the displacement of an atom from its equilibrium position, and $A_{r-r'}$ is an interaction coefficient; $r=n_1a_1+n_2a_2+n_3a_3$, where the n_i are integers and the a_i are the periods of the lattice. In what follows we take the periods to be the unit of length. The masses m_r are random variables taking two values (for a binary mixture) with probabilities equal to the corresponding isotopic abundances. The quantity to be determined is the expectation value of the spectral density, or of the number of energy levels in a given interval. For a sufficiently large crystal, the actual value of the spectral density will coincide with its expectation value.

Considering the difference between m_r and a constant mass m as a perturbation, we may write equation (1) in the form

$$(\hat{L}+\hat{\varepsilon}\hat{L})\chi-\omega^2\chi=0, \tag{2}$$

with

$$L_{\mathbf{r},\mathbf{r}'}\equiv L_{\mathbf{r}-\mathbf{r}'}=A_{\mathbf{r}-\mathbf{r}'}/m; \tag{3}$$

$$\hat{\varepsilon}_{\mathbf{r},\mathbf{r}'}=\varepsilon'_{\mathbf{r}}\delta_{\mathbf{r}\mathbf{r}'}, \qquad \varepsilon'_{\mathbf{r}}=(m-m_{\mathbf{r}})/m_{\mathbf{r}}. \tag{4}$$

To make the operators Hermitian, we write Equation (2) in the symmetrized form

$$(\hat{L}+\hat{\Lambda})\chi'=\omega^2\chi', \tag{5}$$

$$\hat{\Lambda}=\hat{L}^{1/2}\hat{\varepsilon}\hat{L}^{1/2}, \qquad \chi'=\hat{L}^{1/2}\chi.$$

In future we drop the primes and write χ for χ'. The eigenfunctions of the unperturbed operator $\hat{L}$ are the plane waves $\chi^0_k=e^{2\pi ikr}$. The corresponding eigenvalues are the squares of the unperturbed frequencies

$$\omega^2(\mathbf{k})=\sum_{\mathbf{r}}L_{\mathbf{r}}e^{-2\pi i\mathbf{k}\mathbf{r}}.$$

In the representation defined by the states χ^0_k, the perturbation $\hat{\Lambda}$ has matrix elements given by

$$\Lambda_{\mathbf{k},\mathbf{k}'}=(\hat{L}^{1/2}\hat{\varepsilon}\hat{L}^{1/2}\chi^0_{\mathbf{k}},\chi^0_{\mathbf{k}'})=(\hat{\varepsilon}\hat{L}^{1/2}\chi^0_{\mathbf{k}},\hat{L}^{1/2}\chi^0_{\mathbf{k}'}) \tag{6}$$

$$=\omega(\mathbf{k})\,\omega(\mathbf{k}')\sum_{\mathbf{r}}\varepsilon'_{\mathbf{r}}e^{2\pi i(\mathbf{k}-\mathbf{k}')\mathbf{r}}.$$

We shall calculate the difference in vibrational free energy between the unperturbed and perturbed crystals, namely

$$F-F_0=\mathrm{Sp}\,\{\varphi(\hat{L}+\hat{\Lambda})-\varphi(\hat{L})\}, \tag{7}$$

$$\varphi(z)=\Theta\ln(1-e^{-\hbar\sqrt{z}/\Theta})+{}^1\!/_2\,\hbar\sqrt{z}. \tag{8}$$

Here Θ is the temperature and h is Planck's constant. In principle we could equally well carry through the calculation with some other function ϕ, but this choice has the advantage of yielding directly the free energy which is a physically interesting quantity.

The quantity (7) is related to the difference between the spectral densities by the equation

$$F-F_0=N\int\varphi(z)\,[\nu(z)-\nu_0(z)]\,dz \tag{9}$$

$$=-N\int dz\varphi'(z)\int_0^z[\nu(\mu)-\nu_0(\mu)]\,d\mu.$$

Here and henceforth, the letter z denotes the square of a frequency, $z=\omega^2$. N is the number of atoms if the lattice and $N\nu(z)$ is the spectral density. For the unperturbed lattice,

$$\nu_0(z)=\int d\Omega/|\nabla\omega^2|, \tag{10}$$

the integration being over the surface $\omega^2(k)=z$ in k-space; $d\Omega$ is an element of area on the surface, and $\nabla\omega^2$ means the gradient of ω^2 in k-space.

2. EXPANSION IN POWERS OF CONCENTRATION

We set the "unperturbed mass" m equal to the mass m_1 of one isotope, and consider as a perturbation the replacement of m_1 by the mass m_2 of the other isotope at certain lattice-points. Asymptotically for large N, the expansion of the vibrational free energy in powers of the concentration c of the second isotope has the form

$$F-F_0=Ncf_1+N\frac{c^2}{2}f_2+\ldots, \tag{11}$$

$$Nf_1=(\partial F/\partial c)|_{c=0}=N(\bar{F}_1-F_0), \tag{12}$$

$$Nf_2=(\partial^2F/\partial c^2)|_{c=0}=N^2(\bar{F}_2-2\bar{F}_1+F_0). \tag{13}$$

Here F_n is the free energy of a lattice containing precisely n impurity atoms, averaged over the possible positions of these atoms. Let $\psi_n(r_1,\ldots,r_n$ (be the addition to the unperturbed free energy, in the case when the impurity atoms are at the positions $r_1,\ldots,r_n$. Clearly $\psi_1(r)=\psi_1$ is independent of r, and $\psi_2(r_1,r_2)\equiv\psi_2(r_1-r_2)$, while $\psi_2(r)\to 2\psi_1$ as $r\to\infty$. Further, let $W_{r_1-r_2,\ldots,r_{n-1}-r_n}$

be the correlation function defining the probability $P_{r_1 \ldots r_n}$ for finding n impurity atoms at the positions $r_1, \ldots, r_n$,

$$P_{\mathbf{r}} = c, \quad P_{\mathbf{r}_1, \mathbf{r}_2} = c^2 W_{\mathbf{r}_1 - \mathbf{r}_2} \cdots$$

In the absence of long-range order, $W_r \to 1$ as $r \to \infty$. If there is no correlation between the positions of impurity atoms, then $W_r = 1$ for all r. In any case,

$$f_1 = \psi_1, \quad f_2 = \sum_{\mathbf{r} \neq 0} W_{\mathbf{r}} [\psi_2(\mathbf{r}) - 2\psi_1], \tag{14}$$

and therefore

$$F - F_0 = N \left\{ c\psi_1 + \frac{c^2}{2} \sum_{\mathbf{r} \neq 0} W_{\mathbf{r}} [\psi_2(\mathbf{r}) - 2\psi_1] + \ldots \right\}. \tag{15}$$

If there is no correlation ($W_r = 1$), then

$$F - F_0 = N \left\{ c\psi_1 + \frac{c^2}{2} \sum_{\mathbf{r} \neq 0} [\psi_2(\mathbf{r}) - 2\psi_1] + \ldots \right\}. \tag{16}$$

Thus, to determine the free energy of the mixture correctly to terms of the order c^n, it is sufficient to calculate the addition to the free energy produced by inserting not more than n impurity atoms into the lattice. When n atoms are inserted, the contribution to the free energy is

$$\psi_n(\mathbf{r}_1, \ldots, \mathbf{r}_n) = \operatorname{Sp} \{ \varphi(\hat{L} + \hat{\Lambda}_n(\mathbf{r}_1, \ldots, \mathbf{r}_n)) - \varphi(\hat{L}) \}, \tag{17}$$

with

$$(\hat{\Lambda}_n)_{\mathbf{k},\mathbf{k}'} = \varepsilon' \omega(\mathbf{k}) \omega(\mathbf{k}') \sum_{p=1}^{n} e^{2\pi i (\mathbf{k} - \mathbf{k}') \mathbf{r}_p}, \tag{18}$$

$$\varepsilon' = (m_1 - m_2)/m_2. \tag{19}$$

In our problem, the perturbation operator is finite-dimensional, the number of dimensions being equal to the number of impurity atoms. The analysis of such perturbation operators in the physics of crystal lattices has been carried out earlier.[3-6] The problem of calculating the trace of a difference of two operators of the form (7) has been solved[6,7] quite generally. Using the results of the earlier papers, we have

$$\psi_n(\mathbf{r}_1, \ldots, \mathbf{r}_n) = \int \xi_n(z, \mathbf{r}_1, \ldots, \mathbf{r}_n) \varphi'(z) \, dz; \tag{20}$$

$$\xi_n(z, \mathbf{r}_1, \ldots, \mathbf{r}_n) = \frac{1}{\pi} \arg D \tag{21}$$

$$\times \left(\delta_{pk} + \varepsilon z \int_0^{z_g^0} \frac{J_{\mathbf{r}_p - \mathbf{r}_k}(\mu)}{\mu - z - i0} d\mu \right) \quad (p, k = 1, \ldots, n);$$

$$\varepsilon = (m_1 - m_2)/m_1, \tag{22}$$

$$J_{\mathbf{r}}(\mu) = \int_{\omega^2(\mathbf{k}) = \mu} \frac{d\Omega}{|\nabla \omega^2|} e^{2\pi i \mathbf{k} \mathbf{r}}. \tag{23}$$

Here $D(\alpha_{ik})$ means the determinant whose elements are α_{ik}. For $z > z_g^0$, the determinant D is real, and ξ_n takes the value zero or one according as D is positive or negative. The contribution to ψ_n supplied by the function ξ_n in this range is

$$\sum_j (\varphi(z_j) - \varphi(z_g^0)), \tag{24}$$

where the z_i are the roots of the equation

$$D \left(\delta_{ik} + \varepsilon z \int_0^{z_g^0} \frac{J_{\mathbf{r}_i - \mathbf{r}_k}(\mu)}{\mu - z} d\mu \right) = 0. \tag{25}$$

In the region of the continuous spectrum ($0 < z < z_g^0$) we have

$$\int \frac{J_{\mathbf{r}_i - \mathbf{r}_k}(\mu)}{\mu - z - i0} d\mu = \int' \frac{J_{\mathbf{r}_i - \mathbf{r}_k}(\mu)}{\mu - z} d\mu + i\pi J_{\mathbf{r}_i - \mathbf{r}_k}(z),$$

where $\int'$ means a principal value integral, and so the argument of the determinant may take any value from $-\pi$ to π. In the special case of one impurity atom, with z in the continuous spectrum range,

$$\xi_1(z) = \frac{1}{\pi} \operatorname{arctg} \left\{ \pi \varepsilon z \nu_0(z) \left[1 + \varepsilon z \int' \frac{\nu_0(\mu)}{\mu - z} d\mu \right]^{-1} \right\}. \tag{26}$$

To make the meaning of the above equations clear, we now carry through the calculations of Ref. 6 for the simplest case, in which there is only one impurity atom. Without loss of generality we suppose this atom to be placed at the coordinate origin. Then the perturbation operator becomes

$$(\hat{\Lambda}_1)_{\mathbf{k},\mathbf{k}'} = \varepsilon'\omega(\mathbf{k})\,\omega(\mathbf{k}').$$

We introduce a sequence of operators L_α, having the same eigenfunctions $X_k^0 = e^{2\pi ikr}$ as L, but with eigenvalues $\mu_n = \alpha[\omega^2(k)/\alpha]$, where $[q]$ denotes the integer part of a real number q. Each eigenvalue $\mu_n = \alpha n$ of $\hat{L}_\alpha$ is infinitely degenerate, the crystal being supposed infinite. It was proved previously[3] that, for an operator with a degenerate spectrum, the addition of a one-dimensional operator $\hat{\Lambda}_1$ produces a decrease by one unit in the multiplicity of each eigenvalue, the multiple eigenvalues maintaining their positions unchanged. One eigenvalue is split off from each multiplet and takes a displaced position between μ_n and μ_{n+1}. Thus the new eigenvalues of $(L_\alpha + \hat{\Lambda}_1)$ may be written in the form

$$z_n = \mu_n + \alpha\xi_1(\mu_n). \tag{27}$$

with an error small compared with α. The equation for the eigenfunctions corresponding to the new eigenvalues is

$$f(\mathbf{r}) = -(\hat{L}_\alpha - z)^{-1}\hat{\Lambda}_1 f(\mathbf{r}) \tag{28}$$

$$= \sum_n \frac{1}{z-\mu_n} \int\limits_{\alpha n<\omega^2(\mathbf{k})<\alpha(n+1)} (\hat{\Lambda}_1 f, \chi_{\mathbf{k}})\,\chi_{\mathbf{k}}\,d\mathbf{k}$$

$$= \varepsilon' f(0) \sum_n \frac{\alpha\mu_n}{z-\mu_n} \int\limits_{\omega^2(\mathbf{k})=\mu_n} \frac{d\Omega}{|\nabla\omega^2|} e^{2\pi i\mathbf{kr}}.$$

Putting $r = 0$ on both sides of this equation and dividing by $f(0)$, we obtain

$$1 = \varepsilon' \sum_n \frac{\alpha\mu_n\nu_0(\mu_n)}{z-\mu_n}. \tag{29}$$

We now write $z_n = \mu_n + \alpha\xi_1(\mu_n)$, and go to the limit $\alpha \to 0$. After a few transforamtions,[6], we obtain

$$1 = \pi\varepsilon' z\nu_0(z)\,\mathrm{ctg}\,\pi\xi_1(z) + \varepsilon' \int^{\prime} \frac{\mu\nu_0(\mu)}{z-\mu}\,d\mu, \tag{30}$$

Remembering that $\int d\mathbf{k} = 1$ and $\varepsilon = \varepsilon'/(1+\varepsilon')$, we find that (30) reduces to the desired result (26). These displaced eigenvalues tend to a continuous spectrum as $\alpha \to 0$. If there exist other eigenvalues in the range $z < z_g^0$ of the discrete spectrum, they are solutions of the limiting equation

$$1 = \varepsilon' \int_0^{z_g^0} \frac{\mu\nu_0(\mu)}{z-\mu}\,d\mu. \tag{31}$$

In our case, such discrete eigenvalues can exist only if ϵ' is positive and sufficiently large, i.e., if the impurity atom is much lighter than the others. In what follows, except in Sec. 4, we assume that such discrete eigenvalues are absent.

From the foregoing expressions for the eigenvalues of the perturbed operator, we deduce the value of the difference of traces.

$$\psi_1 = \mathrm{Sp}\,\{\varphi(\hat{L} + \hat{\Lambda}_1) - \varphi(\hat{L})\} \tag{32}$$

$$= \lim_{\alpha\to 0} \mathrm{Sp}\,\{\varphi(\hat{L}_\alpha + \hat{\Lambda}_1) - \varphi(\hat{L}_\alpha)\}$$

$$= \lim_{\alpha\to 0} \sum_n [\varphi(\mu_n + \alpha\xi_1(\mu_n)) - \varphi(\mu_n)]$$

$$= \int \xi_1(\mu)\,\varphi'(\mu)\,d\mu,$$

in agreement with Eq. (20).

Turning now to the evaluation of the free energy (15) and using Eq. (20), we find

$$F - F_0 = N\int dz\varphi'(z)\Big\{c\xi_1(z) + \frac{c^2}{2} \tag{33}$$

$$\times \sum_{\mathbf{r}\neq 0} W_{\mathbf{r}}[\xi_2(z,\mathbf{r}) - 2\xi_1(z)] + \ldots\Big\}.$$

The sum over r in Eq. (33) is convergent. In fact, the quantity $(\xi_2(r) - 2\xi_1)$ is according to Eq. (21)

$$\xi_2(\mathbf{r}) - 2\xi_1 \tag{34}$$

$$= \frac{1}{\pi}\arg\left(1 - \frac{\varepsilon^2 z^2 \int \frac{J_{\mathbf{r}}'(\mu)}{\mu - z - i0}\,d\mu \int \frac{J_{-\mathbf{r}}(\mu')}{\mu' - z - i0}\,d\mu'}{\left(1 + \varepsilon z \int \frac{\nu_0(\mu'')}{\mu'' - z - i0}\,d\mu''\right)^2}\right),$$

and decreases rapidly for large r by virtue of the decrease of the integrands $J_r(\mu)$ which contain exponential factors. If there is no correlation, the sum in Eq. (33) becomes

$$\sum_{\mathbf{r}} (\xi_2(z,\mathbf{r}) - 2\xi_1(z)) = \frac{1}{\pi}\arg\prod_{\mathbf{r}} \tag{35}$$

$$\times\left(1 - \frac{\varepsilon^2 z^2 \int \frac{J_{\mathbf{r}}(\mu)}{\mu - z - i0}\,d\mu \int \frac{J_{-\mathbf{r}}(\mu')}{\mu' - z - i0}\,d\mu'}{\left(1 + \varepsilon z \int \frac{\nu_0(\mu'')}{\mu'' - z - i0}\,d\mu''\right)^2}\right).$$

We used the fact that the argument of a product is equal to the sum of the arguments of the factors.

Within the interval of unperturbed frequencies ($0 < z < z^0_g$), the vibrational spectrum density $\nu(z)$ of the mixed crystal is obtained by a comparison of Eq. (9) with (33),

$$\nu(z) - \nu_0(z) = -\frac{d}{dz}\Big\{c\xi_1(z) + \frac{c^2}{2} \times \sum_{\mathbf{r}\neq 0} W_{\mathbf{r}}\,[\xi_2(z,\mathbf{r}) - 2\xi_1(z)] + \dots\Big\}. \tag{36}$$

Near the end-frequency z^0_g this formula is incorrect. Indeed, the endpoints of the continuous spectrum of the perturbed and unperturbed crystals will not be identical. In Sec. 4 we determine the perturbation of the end-points, and the spectral density throughout the whole range of perturbed frequencies.

3. EXPANSION IN POWERS OF ϵ

When the mass-differences are small ($\epsilon << 1$), the foregoing results simplify greatly. Retaining terms up to the order ϵ^2, we find

$$\xi_1(z) = \varepsilon z \nu_0(z)\left[1 - \varepsilon z \int' \frac{\nu_0(\mu)}{\mu - z}\,d\mu\right], \tag{37}$$

$$\xi_2(z, \mathbf{r}) - 2\xi_1(z) = -2\varepsilon^2 z^2 \operatorname{Re} J_{-\mathbf{r}}(z) \int' \frac{J_{\mathbf{r}}(\mu)}{\mu - z}\,d\mu. \tag{38}$$

Substituting Eqs. (37) and (38) into the expressions (33) for the free energy and (36) for the vibration spectrum density, we obtain to the same accuracy, assuming no correlations exist,

$$F - F_0 = N\Big\{\varepsilon c \int z\varphi'(z)\,\nu_0(z)\,dz + \varepsilon^2\Big[c^2 \int z\varphi'(z)\,\nu_0(z)\,dz + \frac{c^2}{2}\int z^2\varphi''(z)\,\nu_0(z)\,dz + \frac{c(1-c)}{2} \times \int \frac{z^2\varphi'(z) - \mu^2\varphi'(\mu)}{z - \mu}\,\nu_0(z)\,\nu_0(\mu)\,dz\,d\mu\Big] + \dots\Big\}; \tag{39}$$

$$\nu(z) - \nu_0(z) = -\frac{d}{dz}\Big\{\varepsilon c z \nu_0(z) - \varepsilon^2\Big[c(1-c)\,z^2\nu_0(z)\int' \frac{\nu_0(\mu)}{\mu - z}\,d\mu + \frac{c^2}{2} z^2 \nu_0'(z)\Big] + \dots\Big\}. \tag{40}$$

In the derivation we have used the identity

$$\int\limits_{\omega(k)=z} \frac{d\Omega}{|\nabla\omega^2|} \int d\mathbf{k}'\, f(\mathbf{k}, \mathbf{k}') = \int d\mathbf{k}\, d\mathbf{k}'\, \delta(\omega^2(\mathbf{k}) - z)\, f(\mathbf{k}, \mathbf{k}').$$

Equations (39) and (40), considered as expansions in powers of ϵ, are valid for any value of the concentration c. This is because the higher terms in the expansion in powers of c all carry higher powers of ϵ.

Equation (39) could have been derived directly from Equations (2)–(6) by making an expansion in powers of ϵ. If we apply the analogs of Equations (17), (20) and (21)) to the entire perturbation operator $\hat{\Lambda}$ (Equation 6) and expand $\xi(z)$ in powers of ϵ, we find*

$$F - F_0 = \sum_{\mathbf{r}} \overline{\varepsilon_{\mathbf{r}}} \int z\varphi'(z)\,\nu_0(z)\,dz + \sum_{\mathbf{r},\mathbf{r}'} \overline{\varepsilon_{\mathbf{r}}\varepsilon_{\mathbf{r}'}} \int' \frac{z^2\varphi'(z)}{z - \mu}\, J_{\mathbf{r}-\mathbf{r}'}(z)\, J_{\mathbf{r}'-\mathbf{r}}(\mu)\,dz\,d\mu. \tag{41}$$

Here $\varepsilon_{\mathbf{r}} = (m - m_{\mathbf{r}})/m_{\mathbf{r}}$ is treated as a random variable, and the bar means a statistical average. The ϵ_r appear in Equation (41) in place of the ϵ'_r which appear in Eq (6), because we changed from integrals of the form $\int' \frac{\mu J_{\mathbf{r}}(\mu)}{\mu - z}\,d\mu$ to integrals of the form $\int' \frac{J_{\mathbf{r}}(\mu)}{\mu - z}\,d\mu$. The same thing happened in passing from Eq. (30) to (26). If the original unperturbed mass was m_1, then

$$\overline{\varepsilon_{\mathbf{r}}} = c(m_1 - m_2)/m_1 = c\varepsilon,$$

$$\overline{\varepsilon^2_{\mathbf{r}}} = c\varepsilon^2, \quad \overline{\varepsilon_{\mathbf{r}'}\varepsilon_{\mathbf{r}'+\mathbf{r}}} = c^2 W_{\mathbf{r}}\varepsilon^2,$$

and Eqs. (39) and (40) follow.

If ϵ is small, it is convenient to choose for the unperturbed mass the mean mass $m = m_1(1-\epsilon)$. In this case Equation (41) should be used with

$$\overline{\varepsilon_{\mathbf{r}}} = 0, \quad \overline{\varepsilon^2_{\mathbf{r}}} = c(1-c)\,\varepsilon^2, \quad \overline{\varepsilon_{\mathbf{r}'}\varepsilon_{\mathbf{r}'+\mathbf{r}}} = 0$$

if there are no correlations. The correction to the free energy is then quadratic in ϵ. The unperturbed spectrum density in this case will be $\nu^0(z) = \nu_0[z/(1 - \varepsilon c)]$.

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*To justify the use of these equations, we should imagine that we have an infinite crystal composed of identical atoms of mass m, with a finite perturbed region containing N lattice-sites at which the perturbation operator $\hat{\Lambda}$ is different from zero. Afterwards the value of N can be made as large as we please.

Finally, we shall state without proof the formula for the correction to the free energy for $\epsilon \ll 1$, in a real crystal where the vibrations have several modes of polarization. The unperturbed mass is again the mean mass $\overline{m}$.

$$F - F_0 = \sum_{\mathbf{r},\mathbf{r}'} \overline{\varepsilon_{\mathbf{r}}\varepsilon_{\mathbf{r}'}} \int' \frac{z^2\varphi'(z)}{z-\mu} \times \sum_{\beta,\beta'} J^{\beta\beta'}_{\mathbf{r}-\mathbf{r}'}(z)\, J^{\beta\beta'}_{\mathbf{r}'-\mathbf{r}}(\mu)\, dz\, d\mu, \tag{42}$$

$$J^{\beta'\beta}_{\mathbf{r}}(z) = \sum_{j} \int_{\omega_j^2(\mathbf{k})=z} \frac{d\Omega}{|\nabla\omega_j{}^2|}\, u^j_\beta(\mathbf{k})\, u^{j*}_{\beta'}(\mathbf{k}')\, e^{2\pi i\mathbf{kr}}. \tag{43}$$

Here the index j denotes a particular mode of polarization of the unperturbed crystal vibration, and u^j (u^j_1, u^j_2, u^j_3) is the corresponding normalized polarization vector. The eigenfunctions of the unperturbed system are now of the form $\mathbf{u}^j(\mathbf{k})\, e^{2\pi i\mathbf{kr}}$). . It is more convenient to write Equation (42) as an integral over k-space, the integration volume being one cell of the reciprocal lattice.

$$F - F_0 = \frac{1}{2} \sum_{\mathbf{r},\mathbf{r}'} \overline{\varepsilon_{\mathbf{r}}\varepsilon_{\mathbf{r}'}} \times \int d\mathbf{k}\, d\mathbf{k}'\, e^{2\pi i(\mathbf{k}-\mathbf{k}')(\mathbf{r}-\mathbf{r}')}\Phi(\mathbf{k}, \mathbf{k}'), \tag{44}$$

$$\Phi(\mathbf{k}, \mathbf{k}') = \sum_{jj'} |\, \mathbf{u}^{j'}(\mathbf{k}), \mathbf{u}^{j'}(\mathbf{k}')\, |^2 \times \frac{\omega_j^4(\mathbf{k})\,\varphi'(\omega_j^2(\mathbf{k})) - \omega_{j'}^4(\mathbf{k}')\,\varphi'(\omega_{j'}^2(\mathbf{k}'))}{\omega_j^2(\mathbf{k}) - \omega_{j'}^2(\mathbf{k}')}. \tag{45}$$

If there is no correlation, then

$$F - F_0 = \frac{1}{2} Nc(1-c)\,\varepsilon^2 \int dk\, dk'\, \Phi(\mathbf{k}, \mathbf{k}'). \tag{46}$$

4. STRUCTURE OF THE SPECTRUM

Equations (36) and (40), obtained formally from the difference of traces, are incorrect near the end-points z^0_g of the unperturbed spectrum. This is connected with the fact that the range of eigenvalues of the perturbed operator $\hat{L} + \Lambda$ does not coincide with the range $(0, z^0_g)$ of the continuous spectrum of the unperturbed operator $\hat{L}$ (i.e., the range of frequencies of the monoisotopic crystal). The difficulty arises mathematically from the singularities of the derivatives $\nu_0^{(n)}(z)$ at the point z^0_g. In the neighborhood of z^0_g, the spectrum usually has the shape $\nu_0(z) \sim (z^0_g - z)^{1/2}$, and the expansion (40) containing the $\nu_0^{(n)}(z)$ is meaningless. It is not difficult to express $\nu(z)$ in a form free from divergences, and to determine the displacement of the end-point. For this purpose we consider first the case $\epsilon \ll 1$. Then Eq. (39) may be written in the form

$$F = N\int \nu_0(z) \Big\{\varphi(z) + \Big[\varepsilon cz + \varepsilon^2c^2z + \varepsilon^2 c(1-c)z^2 \int' \frac{\nu_0(\mu)}{z-\mu}\, d\mu\Big]\varphi'(z) + \frac{\varepsilon^2z^2c^2}{2}\varphi''(z) + \ldots\Big\}\, dz. \tag{47}$$

The point z^0_g is not a singularity of the function $\phi(z)$, and the coefficients of $\phi'(z), \phi''(z), \ldots$ in the curly bracket are finite at z^0_g. Therefore we may regard the whole expression in the curly bracket as an expansion in powers of ϵ of the quantity

$$\varphi(z + \varepsilon cz + \varepsilon^2\eta(z) + \ldots), \tag{48}$$

$$\eta(z) = c^2z + c(1-c)z^2 \int' \frac{\nu_0(\mu)}{z-\mu}\, d\mu. \tag{49}$$

Then a simple change of variable in the integral gives

$$F = \int_0^{z^0_g} \nu_0(t)\,\varphi(t + \varepsilon ct + \varepsilon^2\eta(t))\, dt = \int_0^{z_g} \nu_0(t(z))\,\frac{dt}{dz}\,\varphi(z)\, dz, \tag{50}$$

$$z = t + \varepsilon ct + \varepsilon^2\eta(t), \qquad z_g = z^0_g + \varepsilon c z^0_g + \varepsilon^2\eta(z^0_g). \tag{51}$$

Hence

$$\nu(z) = \nu_0(t(z))\,(dt/dz). \tag{52}$$

A similar method applies to the case when we make an expansion in powers of the concentration of one isotope. The result, correct to terms of order c, is then

$$\nu(z) = \nu_0\left(z - c\frac{\xi_1(z)}{\nu_0(z)}\right)\left[1 + c\left(\frac{\xi_1(z)}{\nu_0(z)}\right)'\right]^{-1}, \quad (53)$$

$$z_g = z_g^0 + c\xi_1(z_g^0)/\nu_0(z_g^0). \quad (54)$$

Up to now we assumed that there were no discrete eigenvalues of the perturbed operator. If such eigenvalues exist, then terms of the form (24) must be added to the expression (33) for the free energy. Let $z_j^{(n)}$ be the j'th discrete eigenvalue for a crystal with n impurity atoms. The value of $z_j^{(n)}$ is determined by Equation (25). Then the relevant difference between free energies becomes

$$F - F_0 = N\left\{\int \varphi'(z)\left[c\xi_1(z) + \frac{c^2}{2}\right.\right. \quad (55)$$

$$\left.\times \sum_{\mathbf{r}\neq 0} W_{\mathbf{r}}(\xi_2(z, \mathbf{r}) - 2\xi_1(z)) + \ldots\right]dz$$

$$+ c\,[\varphi(z_1^{(1)}) - \varphi(z_g^0)] + \frac{c^2}{2}$$

$$\left.\times \sum_{\mathbf{r}\neq 0} W_{\mathbf{r}}[\varphi(z_1^{(2)}(\mathbf{r})) + \varphi(z_2^{(2)}(r)) - 2\varphi(z_1^{(1)})] + \ldots\right\}.$$

Since $z_{1,2}^{(2)} \to z_1^{(1)}$ as $r \to \infty$, the terms in square brackets decrease rapidly, and the sum over r converges.

From equation (21), or from a consideration of the physical meaning of the eigenvalues, the value $z_1^{(1)}$ is the limit of a sequence of values $z^{(2)}$ which appear in the terms of order c^2. Each value $z^{(2)}$ is in turn the limit of a sequence of values $z^{(3)}$, belonging to the crystal with three impurity atoms and appearing in terms of order c^3. And so on.

The correction to the free energy arising from the discrete eigenvalues van be expanded in powers of the concentration c, and this expansion formally corresponds to a spectrum with the peculiar structure which we have described. However, an expression for the expectation value of the spectral density cannot be immediately obtained. A formal expansion of the density function gives a meaningless and divergent sum of δ– functions. We are always interested physically, not in the spectral density itself, but only in expectation values of the form (7) constructed from the spectral density. For example, the vibrational energy of the crystal is given by Eq. 7 with

$$\varphi(z) = \hbar\sqrt{z}\left[(e^{\hbar\sqrt{z}/\theta} - 1)^{-1} + \frac{1}{2}\right]),$$

Thus the expansion in powers of the concentration provides in principle the solution of our problem.

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[1] I. M. Lifshitz, J. Exptl. Theoret. Phys. (U.S.S.R.) 12, 117 (1942).

[2] F. J. Dyson, Phys. Rev. 92, 1331 (1953).

[3] I. M. Lifshitz, J. Exptl. Theoret. Phys. (U.S.S.R.) 17, 1017 (1947).

[4] I. M. Lifshitz, J. Exptl Theoret. Phys. (U.S.S.R.) 17, 1076 (1947).

[5] I. M. Lifshitz, J. Exptl. Theoret. Phys. (U.S.S.R.) 18, 233 (1948) .

[6] I. M. Lifshitz, Usp. Mat. Nauk 7, 171 (1952).

[7] M. G. Krein, Mat. Sbornik 33 (75), 597 (1953).

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