SOVIET PHYSICS JETP VOLUME 19, NUMBER 6 DECEMBER, 1964

IMPURITY ATOMS IN LATTICES WITH OPTICAL OSCILLATION MODES. MÖSSBAUER EFFECT. INFRARED ABSORPTION

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Submitted to JETP editor December 29, 1963

J. Exptl. Theoret. Phys. (U.S.S.R.) **46**, 2165-2182 (June, 1964)

The problem of the oscillation of an impurity atom in a crystal with arbitrary number of atoms per unit cell is considered. The value of the mass of the impurity atom is arbitrary, and the variation of the force constants is taken into account within the framework of perturbation theory. A detailed analysis is made of the spectral density of the square of the displacement of the impurity atom, particularly in the presence of "free" local, "gap" local, and quasilocal levels in the perturbed frequency spectrum. The results are used to determine and analyze the probability of the Mössbauer effect on the impurity nucleus for the entire range of temperatures. The probability of infrared absorption by isolated impurity atoms is also determined.

1. INTRODUCTION

THE authors have previously developed [1] (see also [2]) the theory of the Mössbauer effect for isolated impurity nuclei in a crystal, in the entire temperature interval. We considered an impurity atom with perfectly arbitrary mass in a one-atom crystal lattice, and the variation of the force constants was taken into account within the framework of perturbation theory. The scattering of slow neutrons by crystals with impurity atoms was investigated in [3] [1] under the same assumptions.

Since the publication of the first paper, many other works were reported, connected with the theory of the Mössbauer effect on impurity nuclei. Maradudin and Flynn [4] considered in detail the probability of the Mössbauer effect in the classical limit of high temperatures. Dzyub and Lubchenko [5], using a formally different method, again obtained part of the results of I and II. Visscher [6] carried out computer calculations using for the matrix a model of a simple cubic lattice with allowance for the near-order interactions and taking into consideration the variation in the force constants (single-parameter approximation). A recent paper was also published by Dawber and Elliott [7]. Unfortunately, these authors apparently were unacquainted with paper I, for the results of Dawber and Elliott (and even the methods used) are practically equivalent to the results of that paper, corresponding to the case when there is no variation of the force constants ($\gamma = 0$).

In I and II, as in all the other cited papers, only the case of a single-atom matrix was actually considered. However, the transition to crystals with arbitrary number of atoms per unit cell leads to many new qualitative results. In the present paper we made a detailed analysis of the oscillation of an impurity atom, which replaces an arbitrary atom in the unit cell of a complex anisotropic crystal. The basic analysis (Sec. 2) is made for the case when the mass of the impurity atom is arbitrary, and the variation of the force constants can be neglected. (An account of the variation of the force constants, using perturbation theory, is considered in Appendix 1). It must be noted that the experimental results obtained recently [8-10] give grounds for believing that this assumption has a rather broad range of applicability even from the purely quantitative point of view.

The results of Sec. 2 are used in Sec. 3 to describe the Mössbauer effect in the entire range of temperatures. Sec. 4 deals with the question of infrared absorption by isolated impurity atoms. It must be noted that the latter problem was recently considered by Dawber and Elliott [11] for a single-atom matrix.

2. OSCILLATION OF AN IMPURITY ATOM IN A LATTICE WITH OPTICAL MODES

A. We consider a crystal lattice of arbitrary symmetry and with an arbitrary number of atoms per unit cell. Let one of the atoms of the ideal lattice be replaced by an impurity atom, the mass

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[1] References[1, 2, 3] will be sited henceforth as I, II, and III, respectively.

m′ of the latter being arbitrary. We neglect the variation of the force constants. (In Appendix 1 we present the solution of the problem within the framework of perturbation theory for the case when the variation of the force constants is relatively small.) Then the general equation, describing the lattice vibration, can be written in the following form (the impurity atom is located at the site of the t-th atom in the unit cell $\mathbf{r_n} = 0$)

$$\omega^2\Phi^i(\mathbf{r_n}, j) = \sum_{\mathbf{n}'j'} (m_{\mathbf{n}j}m_{\mathbf{n}'j'})^{-1/2} A_{0jj'}{}^{ii'} (\mathbf{r_n} - \mathbf{r_{n'}})\, \Phi^{i'}(\mathbf{r_{n'}}, j'); \tag{2.1}$$

$$m_{\mathbf{n}j} = m_j(1 - \varepsilon_t\delta_{\mathbf{n}0}\delta_{jt}), \qquad \varepsilon_t = 1 - m'/m_t. \tag{2.2}$$

All the symbols used in (2.1) are standard; summation over repeated superior coordinate indices is implied here and throughout.

If we put $\epsilon_t = 0$, we arrive at an equation for the initial regular lattice. The solutions of this equation normalized to unity have, as is well known, the following form (s —number of atoms per unit cell)

$$\varphi_{\mathbf{f}\alpha}{}^i(\mathbf{r_n}, j) = N^{-1/2} e_j{}^i(\mathbf{f}, \alpha) \exp(i\mathbf{f}\mathbf{r_n}); \tag{2.3}$$

$$\sum_{j=1}^{s} e_j{}^i(\mathbf{f}, \alpha)\, e_j{}^{i*}(\mathbf{f}, \alpha') = \delta_{\alpha\alpha'},$$

$$\sum_{\alpha=1}^{3s} e_j{}^i(\mathbf{f}, \alpha)\, e_{j'}{}^{i'*}(\mathbf{f}, \alpha) = \delta^{ii'}\delta_{jj'},$$

$$e_j{}^{i*}(\mathbf{f}, \alpha) = e_j{}^i(-\mathbf{f}, \alpha). \tag{2.4}$$

The solution of (2.1) will be sought in the form of an expansion in the complete system of functions (2.3):

$$\Phi^i(\mathbf{r_n}, j) = \sum_{\mathbf{f}\alpha} C(\mathbf{f}, \alpha)\, \varphi_{\mathbf{f}\alpha}{}^i(\mathbf{r_n}, j). \tag{2.5}$$

We substitute (2.5) in (2.1), multiply both halves of the equation by $(1 - \epsilon_t\delta_{\mathbf{n}0}\delta_{jt})^{1/2}\varphi^{i*}_{\mathbf{f}\alpha}(\mathbf{r_n}, j)$ and sum over i, n, and j. We then obtain after simple transformation

$$[\omega^2 - \omega_0{}^2(\mathbf{f}, \alpha)]\, C(\mathbf{f}, \alpha) = (1 - \varepsilon_t)^{-1/2} \{\varepsilon_t\omega^2 + (\sqrt{1 - \varepsilon_t} - 1) \times [\omega^2 - \omega_0{}^2(\mathbf{f}, \alpha)]\}\, \Phi^i(0, t)\, \varphi_{\mathbf{f}\alpha}{}^{i*}(0, t). \tag{2.6}$$

By $\omega_0^2(\mathbf{f}, \alpha)$ we denote here the square of the natural frequencies of an ideal lattice, corresponding to the wave vector f and to the mode number α.

In describing the Mössbauer effect for the infrared absorption, we are interested only in the displacement of the impurity atom itself. From (2.6) it follows that, as in the case of the single-atom lattice (see I and III), $\Phi(0,t) \neq 0$ only for the classic solutions which correspond to split frequencies, i.e., the frequencies which result from a partial lifting of the degeneracy from each multiply-degenerate level in the ideal lattice (see III). In all the remaining cases we have $\omega^2 = \omega_0^2$ and $\Phi(0, t) = 0$, and these solutions can be disregarded (unlike for example, the problem of the scattering of neutrons by impurity nuclei in a crystal—see III for more details).

For the class of solutions of interest to us we obtain formulas (2.5) and (2.6), with allowance for (2.3)

$$\Phi^i(\mathbf{r_n}, j) = \Phi^k(0, t) \times \frac{1}{\sqrt{1 - \varepsilon_t}} \left\{ \frac{\varepsilon_t\omega^2}{N} \sum_{\mathbf{f}\alpha} \frac{e_j{}^i(\mathbf{f}, \alpha)\, e_t{}^{k*}(\mathbf{f}, \alpha)}{\omega^2 - \omega_0{}^2(\mathbf{f}, \alpha)} \exp(i\mathbf{f}\mathbf{r_n}) + (\sqrt{1 - \varepsilon_t} - 1)\, \delta^{ik}\delta_{\mathbf{n}0}\delta_{jt} \right\}. \tag{2.7}$$

We note that the solutions (27) are real, as can be readily verified by using (2.4).

We put $\mathbf{n} = 0$ and $j = t$ in (2.7). Introducing the notation

$$\Phi(0, t) = \Phi(t)\, \mathbf{j}(t) \tag{2.8}$$

[j(t) —unit vector], we arrive at a system of equations for the determination of the frequencies of the perturbed spectrum and the corresponding values of j(t):

$$D_t{}^{ik}(\omega^2)\, j^k(t) = j^i(t),$$

$$D_t{}^{ik}(\omega^2) \equiv \frac{\varepsilon_t\omega^2}{N} \sum_{\mathbf{f}\alpha} \frac{e_t{}^i(\mathbf{f}, \alpha)\, e_t{}^{k*}(\mathbf{f}, \alpha)}{\omega^2 - \omega_0{}^2(\mathbf{f}, \alpha)}. \tag{2.9}$$

For the single-atom lattice, (2.9) coincides directly with the corresponding expressions used in I and III. The difference lies only in the fact that now (2.9) contains the polarization vectors $e_t^i(\mathbf{f}, \alpha)$ corresponding to the t-th atom in the unit cell. We therefore can leave out here many intermediate steps and present only the results, referring the reader to I and II for details. Thus, we can show directly that the functions $\Phi^i(\mathbf{r_n}, j)$ (2.7), corresponding to different normal modes, are mutually orthogonal.

The condition that these functions are normalized to unity leads to the relation

$$\sum_{\mathbf{n}j} \Phi^2(\mathbf{r_n}, j) = \Phi^2(t) \times \frac{1}{\sqrt{1 - \varepsilon_t}} \left\{ \frac{\varepsilon_t{}^2\omega^4}{N} \sum_{\mathbf{f}\alpha} \frac{|\mathbf{e}_t(\mathbf{f}, \alpha)\, \mathbf{j}(t)|^2}{[\omega^2 - \omega_0{}^2(\mathbf{f}, \alpha)]^2} - \varepsilon_t \right\} = 1. \tag{2.10}$$

On the other hand, if we recognize that $\omega^2 = \omega^2(\epsilon_t)$ and differentiate both sides of (2.9) with respect to ϵ_t, after which we multiply by $\epsilon_t\omega^2 j^i(t)$ and use (2.9) again, as well as the condition $|\mathbf{j}(t)| = 1$, we obtain after simple transformations

$$\frac{d \ln \omega^2}{d\varepsilon_t} = \left\{ \frac{\varepsilon_t{}^2\omega^4}{N} \sum_{\mathbf{f}\alpha} \frac{|\mathbf{e}_t(\mathbf{f}, \alpha)\, \mathbf{j}(t)|^2}{[\omega^2 - \omega_0{}^2(\mathbf{f}, \alpha)]^2} - \varepsilon_t \right\}^{-1}. \tag{2.10'}$$

Comparing this result with (2.10), we get immediately

$$\Phi(t) = (1-\varepsilon_t)^{1/2}\left(\frac{d\ln\omega^2}{d\varepsilon_t}\right)^{1/2}. \tag{2.11}$$

The expression for the true displacement $u^i(0,t)$ of the impurity atom in terms of the real dimensionless normal coordinates q_β is written as follows

$$u^i(0,t) = \sum_\beta j_\beta^i(t)\sqrt{\frac{\hbar}{m'\omega_\beta}}\,\Phi_\beta(t)\,q_\beta. \tag{2.12}$$

B. The tensor $D_t^{ik}(\omega^2)$ (2.9), as follows from (2.4), is symmetrical and real. Unfortunately, the presence of the index t in this tensor leads in the general case to a situation wherein its properties are not determined merely by the corresponding crystal system, as is the case with a single-atom lattice. However, in order not to clutter up unnecessarily the analysis that follows, we shall consider only lattices with symmetry not lower than rhombic, and we assume that the atom t in the unit cell occupies a sufficiently symmetrical position to make the tensor $D_t^{ik}(\omega^2)$ reducible to diagonal form in terms of the same principal axes as any macroscopic tensor of second rank. In this case Eq. (2.9) breaks up into three independent equations for the determination of three frequencies that split up each level:

$$\frac{\varepsilon_t\omega_\nu^2}{N}\sum_{f\alpha}\frac{|e_t^\nu(\mathfrak{f},\alpha)|^2}{\omega_\nu^2-\omega_0^2(\mathfrak{f},\alpha)} = 1, \tag{2.13}$$

and the corresponding eigenvectors $j_\nu^i(t) = \delta^{i\nu}$ ($\nu = x, y, z$) are directed along coordinate axes chosen to coincide with the principal axes. We shall arrange the solutions of (2.13) in increasing order and designate them by ω^2. It is obvious that β in (2.12) represents precisely the combined index (p, ν).

We make use of the fact that when $n = 0$ and $j = t$ only the functions (2.7) differ from zero in the complete system of eigenfunctions for the vibration problem with impurity atom. Then, in accordance with the completeness condition

$$\sum_\beta \Phi_\beta^i(0,t)\,\Phi_\beta^{i'}(0,t) = \delta^{ii'},$$

we have for each ν [see (2.8), (2.11), and (2.13)]

$$\sum_p [\Phi_{p\nu}^\nu(t)]^2 = 1. \tag{2.14}$$

In I—III there is, for the case of a single-atom lattice, a detailed description of the limiting transition from summation to integration in expressions of the type (2.14). Purposely omitting here the analogous intermediate steps, we present only the final results for the integral relation that replaces (2.16) in the general case of a many-atom lattice under consideration:

$$\int_0^\infty G_t^{(\nu)}(\omega^2)\,d\omega^2 = 1, \tag{2.15}$$

$$G_t^{(\nu)}(\omega^2) = (1-\varepsilon_t)\,g_t^{(\nu)}(\omega^2)\left\{\left[1-\varepsilon_t\omega^2 -\!\!\!\!\!\!\int_0^{\omega_0^2 max}\frac{g_t^{(\nu)}(\omega_0^2)\,d\omega_0^2}{\omega^2-\omega_0^2}\right]^2 + [\pi\varepsilon_t\omega^2 g_t^{(\nu)}(\omega^2)]^2\right\}^{-1}, \tag{2.16}$$

$$g_t^{(\nu)}(\omega^2) = \frac{v_0}{(2\pi)^3}\sum_{\alpha=1}^{3s}\int_{\omega_0^2(\mathfrak{f},\alpha)=\omega^2}\frac{|e_t^\nu(\mathfrak{f},\alpha)|^2}{|\nabla\omega_0^2(\mathfrak{f},\alpha)|}\,dS_{\mathfrak{f}},$$

$$\times\int_0^{\omega_0^2 max} g_t^{(\nu)}(\omega^2)\,d\omega^2 = 1. \tag{2.17}$$

In this case the correctness of relation (2.15), with account of (2.16) and of the normalization relation (2.17), can also be proved directly (see Appendix 2).

It follows from (2.14) and (2.15) that the function $G_t^{(\nu)}(\omega^2)$ (in the single-atom lattice (see II) the corresponding quantity was designated by $(1-\epsilon)\varphi_\nu(\omega^2)$; we use only one letter here for brevity) is the spectral density of the square of the displacement of the impurity along the principal crystal axes, normalized to unity. But this is precisely the quantity which determines the probability of the Mössbauer effect, and also the intensity of the infrared absorption in the entire range of temperatures (see below, and also II).

C. The vibrational spectrum of the crystal with impurity atoms consists of quasicontinuous bands, which coincide with the corresponding bands of the ideal crystal, and a series of discrete levels. In (2.15) the integration is carried out over the entire interval of frequencies from zero to infinity, and not only, as usual, over the quasicontinuous bands. In this case the spectral density of the square of the impurity-atom displacement also contains automatically the discrete levels. Indeed, these levels are known to be located in the frequency region where $g_t^\nu(\omega^2) = 0$. Letting $g_t^\nu(\omega^2)$ go to zero in (2.16), we obtain directly

$$G_t^{(\nu)}(\omega^2) = \frac{1-\varepsilon_t}{\varepsilon_t\omega^2}\,\delta\left(1-\varepsilon_t\omega^2\int_0^{\omega_0^2 max}\frac{g_t^{(\nu)}(\omega_0^2)\,d\omega_0^2}{\omega^2-\omega_0^2}\right)$$

$$= (1-\varepsilon_t)\sum_d\frac{d\ln\omega_{d\nu}^2}{d\varepsilon_i}\,\delta(\omega^2-\omega_{d\nu}^2), \tag{2.18}$$

where the discrete frequencies $\omega_{d\nu}^2$ are the roots of the equation

$$1-\varepsilon_t\omega^2\int_0^{\omega_0^2 max}\frac{g_t^{(\nu)}(\omega_0^2)\,d\omega_0^2}{\omega^2-\omega_0^2} = 0 \qquad (g_t^{(\nu)}(\omega^2) = 0). \tag{2.19}$$

Here

$$\frac{d \ln \omega_{d\nu}^2}{d\varepsilon_t} = \left\{\varepsilon_t^2 \omega_{d\nu}^4 \int\limits_0^{\omega_0^2 max} \frac{g_t^{(\nu)}(\omega_0^2)\, d\omega_0^2}{\omega^2 - \omega_0^2} - \varepsilon_t\right\}^{-1}. \quad (2.10'')$$

But the roots of (2.19) (if they exist) coincide with the roots of (2.13) that correspond to discrete frequencies, i.e., when the corresponding value of ω^2 lies outside the band of the quasicontinuous spectrum (outside the quasicontinuous bands (2.13) and (2.19) they are simply identical). Thus, (2.16) encompasses the entire spectrum of the crystal with impurity atom.

The discrete frequencies, which are the solutions of (2.19), can in the general case appear both above the limiting frequency of the phonon spectrum of the ideal matrix $\omega_{0\,\max}$ ("free" discrete frequencies), and in the gap between the quasicontinuous bands ("gap" discrete frequencies). It turns out, from the point of view of the behavior of the function $G_t^{(\nu)}(\omega^2)$, and consequently also of the Mossbauer effect and of infrared absorption, that these discrete frequencies behave differently.

In order to simplify the notation, we introduce the symbol

$$x = \omega^2/\omega_0^2{}_{max} \quad (2.20)$$

and rewrite (2.19) in the form

$$1 - \varepsilon_t x \int\limits_0^1 \frac{g_t^{(\nu)}(x')\, dx'}{x - x'} = 0. \quad (2.19')$$

It is obvious that "free" discrete frequencies occur under the condition ($\epsilon_t > 0$)

$$\varepsilon_t \langle (1 - x)^{-1} \rangle_t^{(\nu)} > 1, \quad (2.21)$$

which is the analog of the known condition for the single-atom lattice (see I, III, and [12]). By $\langle \ldots \rangle^{(\nu)}$ we denote here averaging with the function $g_t^{(\nu)}(x)$ (2.17). (The maximum number of "free" discrete frequencies, neglecting the variation of the force constants, is equal to 3, of which two coincide in a uniaxial crystal and three in a cubic crystal.)

It follows from (2.21) that the possibility of appearance of a "free" discrete frequency depends essentially on the place in the unit cell on which the impurity atom has landed. The heavier the cell atom replaced by the impurity atom, the easier, other conditions being equal, it is to satisfy the inequality (2.21). Thus, for example, in a two-atom lattice with strongly different masses, if $m_1 < m' < m_2$, the replacement of the light atom by an impurity atom does not lead at all to the occurrence of "free" discrete frequencies, whereas replacement of the heavy atom may lead to the appearance of such frequencies.

It must be specially noted that Eq. (2.19) and the inequality (2.21) differ essentially from the corresponding expressions for the single-atom lattice, owing to the dependence on the polarization vectors of the replaced atom. Thus, the stronger the relative coupling of the t-th atom in the ideal lattice to the low-lying acoustic modes, the more difficult it is to satisfy (2.21). Conversely, (2.21) is easier to satisfy if the t-th atom vibrates principally in the high-lying optical modes. Therefore, with decreasing mass of the impurity atom, the "free" discrete frequencies can first appear in principle when the substituted site corresponds not at all to the maximum value of ϵ_t (for given m′).

If inequality (2.21) is satisfied, then, obviously, all the considerations which held in the case of the single-atom lattice remain in force. Thus, in particular, as $\epsilon_t \to 1$ (see I, II) we have

$$x_{d\nu} = \frac{\omega_{d\nu}^2}{\omega^2{}_{0\,max}} = \frac{\langle x \rangle_t^{(\nu)}}{1 - \varepsilon_t}\left[1 + (1 - \varepsilon_t)\frac{\langle x^2 \rangle_t^{(\nu)} - \langle x \rangle_t^{(\nu)2}}{\langle x \rangle_t^{(\nu)2}}\right] \quad (2.22)$$

and

$$(1 - \varepsilon_t)\frac{d \ln \omega_{d\nu}^2}{d\varepsilon_t} = 1 - (1 - \varepsilon_t)\frac{\langle x^2 \rangle_t^{(\nu)} - \langle x \rangle_t^{(\nu)2}}{\langle x \rangle_t^{(\nu)2}}. \quad (2.23)$$

Thus, taking (2.15) and (2.18) into consideration, we see that the impurity atoms will actually oscillate under these conditions in the "free" discrete frequencies.

We now consider a case when the spectrum of the frequencies of the matrix contained forbidden bands. We consider one such "gap" and denote by $x_1 = \omega_1^2/\omega_{0\,\max}^2$ the upper limits of the lower energy band, and by $x_2 = \omega_2^2/\omega_{0\,\max}^2$ the lower limit of the upper energy band. Bearing in mind the solution corresponding to the discrete frequency inside the "gap" in question, we rewrite (2.19′) in the form

$$\varepsilon_t x \left[\int\limits_0^{x_1} \frac{g_t^{(\nu)}(x')\, dx'}{x - x'} + \int\limits_{x_2}^1 \frac{g_t^{(\nu)}(x')\, dx'}{x - x'}\right] \equiv \varepsilon_t x\, [I_1(x) + I_2(x)] = 1. \quad (2.24)$$

If $\epsilon_t > 0$, then the necessary condition for the occurrence of a "gap" discrete level is the inequality ($\epsilon_t < 1$)

$$x_1\, [I_1(x_1) - |I_2(x_1)|] > 1/\varepsilon_t, \quad (2.25)$$

which is also sufficient if

$$|I_2(x_2)| > I_1(x_2).$$

In the opposite case the band ϵ_t, for which the discrete frequencies take place, is bounded from above by the condition

$$x_2[I_1(x_2) - |I_2(x_2)|] < 1/\varepsilon_t. \quad (2.26)$$

If $\epsilon_t < 0$, then the necessary condition for the occurrence of a "gap" discrete level is the inequality

$$x_2[|I_2(x_2)| - I_1(x_2)] > 1/|\varepsilon_t|, \qquad (2.27)$$

which is sufficient if

$$I_1(x_1) > |I_2(x_1)|.$$

In the opposite case, the discrete frequencies appear only when $|\epsilon_t|$ is bounded from above by the condition

$$x_1[|I_2(x_1)| - I_1(x_1)] < 1/|\varepsilon_t|. \qquad (2.28)$$

In a three-dimensional crystal $I_1(x)$ and $|I_2(x)|$ are bounded in magnitude. By virtue of this, conditions (2.25)—(2.28) limit the possibility of occurrence of "gap" discrete frequencies. Let us analyze the character of the oscillations of the impurity atom in "gap" discrete frequencies. We use for this purpose expression (2.10″).

A characteristic feature of the "gap" frequencies is their boundedness from above (x_2) and below (x_1). If we take this into consideration, then it follows directly from (2.10″) and (2.11) that both for very light impurity atoms ($\epsilon_t \to 1$) and for very heavy ones ($\epsilon_t \to -\infty$) we have

$$\Phi^2{}_{d\nu}(t) \to 0. \qquad (2.29)$$

(This quantity, of course, vanishes also when $\epsilon_t = 0$.) At all other intermediate values of ϵ_t, satisfying conditions (2.25)—(2.28), the quantity $\Phi^2_{d\nu}(t)$ will have a value different from zero. However, in all cases these quantities will be noticeably smaller than unity. Thus, the "gap" localized oscillations cannot take on, under known values of ϵ_t, the main fraction of the oscillation energy of the impurity atom. In this lies their essential difference from the "free" discrete frequencies.

Along with the truly discrete frequencies, the oscillation of the impurity atom is characterized by the appearance of quasi discrete frequencies. Indeed, if in some frequency interval Δx of the quasicontinuous spectrum the function $g_t^{(\nu)}(x)$ is small and at the same time the equation

$$1 - \varepsilon_t x \int\limits_0^1 \frac{g_t^{(\nu)}(x')dx'}{x - x'} = 0 \qquad (2.30)$$

has a solution $x = x_t^{(\nu)}$ lying in the same interval, then the spectral density $G_t^{(\nu)}(x)$ (2.16) will be large within the limits Δx, and this section of the spectrum can have a relatively large statistical weight in the oscillation of the impurity atom. If, moreover, the width of the spectral distribution $G_t^{(\nu)}(x)$ in this section, which width is defined by the function $g_t^{(\nu)}(x)$, turns out to be smaller than Δx, then $G_t^{(\nu)}(x)$ will have within the interval Δx a Lorentz form with sharp localization near $x_t^{(\nu)}$, denoting indeed the appearance of the quasidiscrete level. (If (2.30) does not have a solution in this interval, then $G^{(\nu)}(x) \sim g_t^{(\nu)}(x)$.)

In the spectrum of the regular lattice $g_t^{(\nu)}(x)$ vanishes regularly at $x = 0$ and on all the boundaries of the quasicontinuous bands. Therefore, for definite values of ϵ_t, quasidiscrete levels can occur in principle both in the limiting low frequency region of the spectrum and near the limits of the bands; at least there will occur a noticeable increase in the statistical rate of the corresponding sections of the spectra.

However, $g_t^{(\nu)}(x)$ can also be small in a broad interval of frequencies inside the energy bands. This occurs when the t-th atom of the principal lattice oscillates relatively weakly in some modes of the phonon spectrum (i.e., in these modes the corresponding polarization vectors are small). It is remarkable that in this case quasilocal levels can arise inside the energy bands at arbitrary values of x, which are the solution of (2.30), or else a noticeable increase will again occur in the statistical weight of these sections of the spectrum. Of greatest interest is in this case the occurrence of a quasidiscrete level at $|\epsilon_t| \gg 1$ in the region of small x. In the case of a single-atom lattice we have already encountered the appearance of a sharp localization of the spectral density of the square of the displacement of the impurity atom (i.e., the quasidiscrete level), when the mass of the impurity atom was large compared with the mass of the atom of the principal lattice (see I, II). The same result was later pointed out by Brout and Visscher[13].

In a complex lattice with $|\epsilon_t| \gg 1$, there also exists always such a level, with

$$x_t^{(\nu)} = (|\varepsilon_t| \langle x^{-1} \rangle_t^{(\nu)})^{-1} \ll 1 \qquad (2.31)$$

and

$$G_t^{(\nu)}(x) = \frac{1}{\pi} \sqrt{\frac{x}{x_t^{(\nu)}}} \frac{\lambda_t^{(\nu)}}{(x - x_t^{(\nu)})^2 + \lambda_t^{(\nu)2}},$$

$$\lambda_t^{(\nu)} = \frac{\pi d_t^{(\nu)}}{|\varepsilon_t|^{3/2} \langle x^{-1} \rangle_t^{(\nu)5/2}}. \qquad (2.32)$$

Here $d_t^{(\nu)}$ —constant connected with the low frequency limit for the spectrum

$$g_t^{(\nu)}(x) = d_t^{(\nu)} \sqrt{x}.$$

If we integrate (2.32) over the region near (2.31), then we readily obtain

$$\int G_t^{(\nu)}(x)\, dx \approx 1. \qquad (2.33)$$

It follows therefore that a sufficiently heavy impurity atom, when substituted in the unit cell for the t-th atom, for which $|\epsilon_t| \gg 1$, oscillates essentially in a narrow frequency region near (2.31).

Expression (2.32) is valid only when the root $x_t^{(\nu)}$ of (2.30) is sufficiently small. It is easy to conclude from (2.30) and (2.31) that the situation depends radically on the predominant oscillation frequencies of the replaced atom. If it is coupled principally to the acoustic modes, then the occurrence of a quasidiscrete level is facilitated; however, if it oscillates predominantly in the high-lying optical modes, then this increases radically the minimum value of $|\epsilon_t|$ necessary for the appearance of such a level. (This picture is the opposite of the condition for the appearance of "free" discrete frequencies.)

It must be noted that the result (2.33) can be realized only for low-frequency quasidiscrete levels. In this sense these levels are analogous to the "free" discrete levels. The remaining quasidiscrete levels are analogous to the "gap" discrete levels—the amplitude of oscillation of the impurity atom tends in them to zero both when $\epsilon_t \to 1$ and when $\epsilon_t \to -\infty$. At intermediate values they can serve as a center for a considerable part of the oscillation of the impurity atom.

3. PROBABILITY OF THE MÖSSBAUER EFFECT. DISCUSSION OF RESULTS

A. We now proceed to determine the probability of the Mössbauer effect. We use for this purpose the procedure described in I and II. We confine ourselves to an examination of cases when the width of the discrete levels, due to the interaction between the normal oscillations resulting from the usual anharmonicity, is much larger than the natural width of the γ line. Then the Bessel function no longer arises in the expression for the probability of the Mössbauer effect proper (see [14]), and for the impurity nucleus that replaces the t-th atom in the unit cell we obtain from (2.12)

$$W_t = \exp\{-Z_t\}, \tag{3.1}$$

$$Z_t = R' \sum_{\beta} \frac{(\varkappa \mathbf{j}_\beta(t))^2}{\hbar\omega_\beta} \Phi_\beta{}^2(t) \operatorname{cth} \frac{\hbar\omega_\beta}{2T}. \qquad (3.2)^*$$

Here $R' = \hbar^2 k^2/2m'$ —recoil energy on the free impurity nucleus; $\kappa = \mathbf{k}/k$ —unit vector in the direction of the γ-quantum momentum; T —temperature in energy units. The summation in (3.2) is carried out over all normal oscillations of the perturbed spectrum, including the discrete frequencies.

In the general case the probability of the Mössbauer effect will be determined by the expression

$$W = \sum_{t=1}^{s} c_t W_t, \qquad \sum_{t=1}^{s} c_t = 1, \tag{3.3}$$

where c_t is the relative probability that the impurity atom will be in the site t of the unit cell.

If the system (2.9) separates into three independent equations of the type (2.13), the polarization vectors for the three frequencies which split off from each degenerate level form a fixed system of unit vectors that coincide with the principal axes of the crystal. In this case, if we use (2.14)—(2.16) and go over in (3.2) from summation to integration, we obtain directly

$$Z_t = \frac{R'}{\hbar\omega_{0\,max}} \sum_{\nu=1}^{3} (\varkappa \mathbf{j}_\nu)^2 \times \int_0^\infty \frac{G_t^{(\nu)}(x)}{\sqrt{x}} \operatorname{cth}\left(\frac{\hbar\omega_{0\,max}\sqrt{x}}{2T}\right) dx. \tag{3.4}$$

This is indeed the final expression which must be analyzed by using the results of the preceding section.

However, one result can be obtained from (3.4) without any specific analysis—the classical limit corresponding to $T \gtrsim \hbar\omega_{max}$, where ω_{max} is the limiting frequency of the perturbed spectrum. It is easy to show (either as was done in II or by using the explicit form (2.16) of the function $G_t^{(\nu)}(x)$—see Appendix 2) that in this case

$$Z_t = \frac{2TR_t}{\hbar^2} \frac{v_0}{(2\pi)^3} \sum_{\alpha=1}^{3s} \int d^3f \frac{|\varkappa \mathbf{e}_t(\mathbf{f}, \alpha)|^2}{\omega_0{}^2(\mathbf{f}, \alpha)} + \frac{R'}{6T},$$

$$R_t = \hbar^2 k^2/2m_t. \tag{3.5}$$

It follows from (3.5) that at such temperatures, if the force constants do not change, W_t is practically independent of the mass of the impurity atom and coincides with the corresponding expression for the ideal crystal. (The dependence on the mass of the impurity atom remains only in the small second term on the right in (3.5).) This result has already been given in I and II.

B. Let us analyze now (3.1), (3.3), and (3.4) in detail. We first put $c_t = 1$. When $T = 0$ the probability W_t of the effect depends on the value of $\omega^{-1} = 1/\omega_{0\,max}\sqrt{x}$ averaged over the spectrum, and the role of the probability density is assumed by the quantity

$$G_t(x) = \sum_{\nu=1}^{3} (\varkappa \mathbf{j}_\nu)^2 G_t^{(\nu)}(x),$$

which, in accordance with (2.15), is normalized to unity. It is clear that the probability of the Mössbauer effect depends in decisive fashion on the character of the behavior of the spectral density $G_t(x)$.

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*cth = coth.

Let $m' > m_t$. Then there are no "free" discrete frequencies and the entire perturbed spectrum lies in the range $0 \leq x \leq 1$. For values of m' close to m_t there are likewise no "gap" discrete frequencies, and the frequency distribution of the oscillation is close to the distribution of the ideal lattice. With increasing m', the "gap" frequencies begin to appear, and the spectrum $G_t^{(\nu)}(x)$ is deformed and moves towards smaller x. At the same time the quantity Z_t/R' increases continuously. The shift of $G_t^{(\nu)}(x)$ towards the lower frequencies causes the temperature dependence to become sharper—the probability of the Mössbauer effect decreases more rapidly with increasing temperature.

In the limiting cases of large m', when $|\epsilon_t| \gg 1$, $G_t^{(\nu)}(x)$ assumes the form (2.32) and we arrive at the following simple expression for the probability of the Mössbauer effect at $T = 0$:

$$W_t = \exp\left\{-\frac{R'}{\hbar\omega_{0\,max}}|\varepsilon_t|^{1/2}\sum_{\nu=1}^{3}(\varkappa \mathbf{j}_\nu)^2\left\langle\frac{1}{x}\right\rangle_t^{(\nu)}\right\}. \quad (3.6)$$

The appearance of the large quantity $|\epsilon_t|^{1/2}$ in the exponent in conjunction with the obvious inequality $\langle x^{-1}\rangle_t^{(\nu)1/2} > \langle x^{-1/2}\rangle_t^{(\nu)}$ causes the probability of the effect to decrease appreciably compared with the case of the regular lattice in which all the atoms m_t are replaced by m', and the oscillation spectrum is close to the initial spectrum. On the other hand, in the general case (3.6) greatly exceeds the probability of the effect for the initial regular crystal, produced if γ quanta of the same energy were to be emitted by the t-th atom.

The decrease of the effect with the temperature becomes particularly abrupt in the case under consideration, because now the characteristic frequency for the spectrum is given by (2.31). Using again (2.32), we readily obtain for W_t

$$W_t = \exp\left\{-\frac{R'}{\hbar\omega_{0\,max}}\sum_{\nu=1}^{3}\frac{(\varkappa \mathbf{j}_\nu)^2}{\sqrt{x_t^{(\nu)}}}\operatorname{cth}\frac{\hbar\omega_{0\,max}\sqrt{x_t^{(\nu)}}}{2T}\right\}. \quad (3.7)$$

The transition to the classical limit (3.5) is realized in our case at low temperatures

$$T \gtrsim \hbar\omega_{0\,max}\sqrt{x_t^{(\nu)}} = \hbar\omega_{0\,max}/|\varepsilon_t|^{1/2}\langle x^{-1}\rangle_t^{(\nu)1/2}.$$

We now consider the case $m' < m_t$. With decreasing m' the spectral density of the oscillations of the impurity atom shifts continuously into the region of higher frequencies. "Gap" local and possibly also quasilocal levels appear. Then Z_t/R' decreases, and the temperature decrease in the probability of the effect becomes continuously weaker. With further decrease of m', the values of function $G_t^{(\nu)}(x)$ cluster more and more near the upper limit of the spectrum of the ideal lattice, "free" discrete frequencies appear, and transfer of the entire spectral density into these frequencies begins [see (2.23)]. All is now determined by the frequency (2.22), and we have as a consequence a large effect at $T = 0$ and a weak decrease with the temperature.

We give here the limiting value of (3.1) corresponding to $1 - \epsilon_t \ll 1$ at $T = 0$:

$$W_t = \exp\left\{-\frac{R'}{\hbar\omega_{0\,max}}(1-\varepsilon_t)^{1/2}\sum_{\nu=1}^{3}\frac{(\varkappa \mathbf{j}_\nu)^2}{\langle x\rangle_t^{(\nu)1/2}}\times\left[1-\frac{3}{2}(1-\varepsilon_t)\frac{\langle x^2\rangle_t^{(\nu)}-\langle x\rangle_t^{(\nu)2}}{\langle x\rangle_t^{(\nu)2}}\right]\right\}. \quad (3.8)$$

The low value of the argument of the exponent in (3.8) is connected primarily with the appearance of the factor $(1 - \epsilon_t)^{1/2}$ and, in addition, with the fact that $\langle x\rangle_t^{(\nu)-1/2} < \langle x^{-1/2}\rangle_t^{(\nu)}$. The temperature dependence will be determined in the case in question by expression (3.7) with the substitution $x_t^{(\nu)} \rightarrow x_d$. Now the transition to the classical limit will occur already at high temperatures, which are determined by the inequality [see (2.22)]

$$T \gtrsim \hbar\omega_{0\,max}\sqrt{x_{d\nu}} \approx \hbar\omega_{0\,max}\langle x\rangle_t^{(\nu)1/2}/(1-\varepsilon_t)^{1/2}.$$

We note that all the results of this section coincide in the case of the single-atom lattice with the results of I and II. In the case of lattices with two identical atoms in the unit cell, both positions of these atoms are equivalent. In each normal oscillation, the squares of the polarization vectors coincide for both atoms, by virtue of which we can reduce (2.13) and consequently also the succeeding formulas to a form equivalent to the case of the single-atom lattice (eliminate the index t). The difference will lie only in the oscillation spectrum itself.

We shall not stop specially to determine the probability of the single-quantum excitations for a γ transition in the nucleus. By using the result of II and of the present work it is easy to derive all the final relations.

C. If the impurity atom can replace different atoms in the unit cell, then the value of the Mössbauer-effect probability [see (3.3)] and its temperature variation can display a very complicated and in some cases utterly anomalous picture. Let us consider, for example, a two-atom lattice with $m_2 \gg m_1$, and let m' have some intermediate value. In addition, let c_1 and $c_2 = 1 - c_1$ be quantities of the same order. In this case it may turn out that $W_2(T = 0) \gg W_1(T = 0)$ and the decrease in W_1 with temperature will be much more rapid.

The result is an unusual over-all picture. Indeed, when $T = 0$, W will have a relatively low value, but at the same time it will decrease slowly with temperature (a relatively small interval can occur, in which W decreases rapidly by a small amount at the expense of W_1 prior to going over to the slowly varying curve connected with W_2). If the force constants change following the intrusion of the impurity atom, then the appearance of two distinctly different sites in the unit cell with respect to the Mössbauer effect can occur also for comparable values of the masses of all atoms. (If one of the two atoms of the regular lattice oscillates primarily in the low-frequency part of the spectrum and the other in the high frequency part, then an anomalous picture can occur also when the force constants remain unchanged and the relation between all three masses is relatively arbitrary.)

It must be noted that the occurrence of an anomalous temperature variation of the Mössbauer-effect probability is not an exclusive privilege of the single-atom crystals. Thus, if two or several nonequivalent positions can exist in a single-atom crystal (for example, a site and an interstice or a position on the surface and in the volume in a finely dispersed polycrystal, particularly when the impurity atoms are poorly soluble, etc.), then we can obtain an analogous picture[2)]. In our opinion it is possible that this is why the results obtained by Craig et al.[15] (in measurements of the probability of the Mössbauer effect on Fe^{57} nuclei imbedded in an indium matrix) showed a low value of the effect for $T = 0$ and a very weak temperature dependence of the effect up to room temperature.

We have considered here only one type of anomaly connected with the presence of nonequivalent sites in the crystal. However, an analogous analysis can be carried out also for any other case.

4. INFRARED ABSORPTION

If the impurity atom occupies the position of the t-th atom in the unit cell of an ideal lattice, then we have in the rigid-ion approximation for the Hamiltonian of the interaction between the external electromagnetic field and the individual impurity atom

$$H' = c^{-1}e_{eff}\mathbf{A}(0, t)\,\dot{\mathbf{u}}(0, t) \tag{4.1}$$

(e_{eff} —effective charge of the impurity ion). Let us use expression (2.12). Then the probability of photon absorption per unit impurity atom turns out to be proportional to the following expression (we have left out inessential factors):

$$\frac{e_{eff}^2}{m'}\sum_{\beta}\Phi_\beta{}^2\,(\mathbf{v}\mathbf{j}_\beta(t))^2\,\delta(\omega_0-\omega_\beta). \tag{4.2}$$

Here $\mathbf{v}$ —unit vector of photon polarization and ω_0 —photon frequency. We change over from summation to integration. Taking into consideration (2.14) —(2.16) and (2.20), we readily obtain

$$\frac{e_{eff}^2}{m'\omega_{0\,max}}\sum_{\nu=1}^{3}(\mathbf{v}\mathbf{j}_\nu)^2\sqrt{x_0}\,G_t{}^{(\nu)}(x_0). \tag{4.3}$$

This is indeed the final expression for the absorption probability. We note that the probability of the single-quantum excitations in γ decay of the nucleus is determined by an analogous expression (see II).

Measurement of infrared absorption by isolated impurity atoms, as can be seen from (4.3), uncovers the attractive possibility of directly determining $G_t^{(\nu)}(x)$. (In the case of an anisotropic lattice, the measurements must be made with a single crystal, using (depending on the symmetry) two or three orientations of the single crystal relative to the photon incidence direction.) We can thus find the positions of the "free" and "gap" local levels, the quasilocal levels, and the relative intensity of the oscillation of the impurity atom at all the frequencies. For the analysis of $G_t^{(\nu)}(x)$ we can use here the results of the preceding sections. (We note that, as was already noted many times, the local levels in the crystal will have a finite width. Because of this, $G_t^{(\nu)}(x)$ will have near the discrete levels a Lorentz form with a width determined by the width of the local level; see II.)

Experiments on infrared absorption by impurity atoms could uncover still another interesting possibility. We have in mind here the determination of the spectral characteristics of the ideal matrix. Indeed, experiments on the determination of the Mossbauer effect on impurity atoms have shown that, at least for a definite type crystal, the force constants vary very little[8-10]. But then, measuring the intensity of the infrared absorption, and at the same time also $G_t^{(\nu)}(x)$, we can obtain $g_t^{(\nu)}(x)$ and consequently, in particular,

$$g_t(x)=\frac{1}{3}\sum_{\nu=1}^{3}g_t{}^{(\nu)}(x).$$

In a single-atom crystal and in crystals with two identical atoms in the unit cell, the latter quantity yields simply the distribution function of the square root of the frequencies of the matrix—the fundamental spectral characteristics for all the thermo-

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[2)] A temperature dependence of a type described above can also occur in a polycrystalline specimen if the Mossbauer effect in the single crystal has a strong anisotropy.

dynamic quantities. We shall not dwell in detail here on the analysis of all the aspects of this problem, inasmuch as a corresponding discussion was carried out in II and III in connection with the single-quantum excitations for γ transitions in nuclei and for scattering of slow neutrons.

APPENDIX 1

In the general case of a crystal with a complex unit cell, one of the sites of which $(0, t)$ contains the impurity atom, the force-constant matrix can be written in the form

$$A^{ii'}(\mathbf{r}_\mathbf{n}, j; \mathbf{r}_{\mathbf{n}'}, j') = A^{ii'}_{0jj'}(\mathbf{r}_\mathbf{n} - \mathbf{r}_{\mathbf{n}'}) + \gamma\Lambda^{ii'}_{(0,t)}(\mathbf{r}_\mathbf{n}, j; \mathbf{r}_{\mathbf{n}'}, j'), \tag{A1.1}$$

where $\gamma\Lambda^{ii'}_{(0,t)}(\mathbf{r}_\mathbf{n}, j, \mathbf{r}'_\mathbf{n}, j)$ is the perturbation operator, which satisfies the usual invariance relations and usually attenuates rapidly with increasing distance from the impurity atom, particularly with increasing $|\mathbf{r}_\mathbf{n}|$ and $|\mathbf{r}'_\mathbf{n}|$. In this case the equation for the oscillations assumes in lieu of (2.1) the form

$$\tilde{\omega}^2_{p\mu}\tilde{\Psi}^i_{p\mu}(\mathbf{r}_\mathbf{n}, j) = \sum_{n'j'}(m_{\mathbf{n}j}m_{\mathbf{n}'j'})^{-1/2} A^{ii'}_{0jj'}(\mathbf{r}_\mathbf{n} - \mathbf{r}_{\mathbf{n}'})\tilde{\Psi}^{i'}_{p\mu}(\mathbf{r}_{\mathbf{n}'}, j') + \gamma\sum_{\mathbf{n}'j'}(m_{\mathbf{n}j}m_{\mathbf{n}'j'})^{-1/2}\Lambda^{ii'}_{(0,t)}(\mathbf{r}_\mathbf{n}, j; \mathbf{r}_{\mathbf{n}'}, j')\tilde{\Psi}^{i'}_{p\mu}(\mathbf{r}_{\mathbf{n}'}, j'). \tag{A1.2}$$

Here and below, the tilde over a letter denotes that the corresponding quantity pertains to the system described by Eq. (A1.2).

If we assume that m'/m_t is arbitrary and that the change in the force constants is small, then, taking as the zeroth approximation the solutions of (A1.2) for $\gamma = 0$ [i.e., the solutions of (2.1)] and using usual perturbation theory, we can calculate the corrections to expressions for the Mössbauer-effect probability and the infrared absorption obtained in Secs. 2 and 3 and linear in γ (analogous calculations for single-atom crystals can be found in II, Sec. 3).

In the case under consideration, the expression for the probability of the Mössbauer effect can be written in the form (see II)

$$\tilde{W}_t = \exp(-\tilde{Z}_t),$$

$$\tilde{Z}_t = R'\sum_{p\mu}\frac{(\varkappa\tilde{\Psi}_{p\mu}(0, t))^2}{\hbar\tilde{\omega}_{p\mu}}\operatorname{cth}\frac{\hbar\tilde{\omega}_{p\mu}}{2T}, \tag{A1.3}$$

which is valid for any γ. For small γ, to calculate (A1.3) in the required approximation it is sufficient to calculate the linear (in γ) corrections to $\Psi^i_{p\mu}(0, t)$ and ω_p (actually only to ω^2_p, since the corrections to the frequencies of the quasicontinuous spectrum are proportional to N^{-1}). It is important that in this case there is no need for using other solutions of (2.1) except (2.7), for only the latter differ from zero in the site $(0, t)$.

When $\gamma = 0$ each level p degenerate in the ideal crystal splits into at most three frequencies, which are solutions of Eq. (2.13) and to which the functions (2.7) correspond. As a result of the symmetry, two or all three frequencies may coincide. In this case we can always choose, by means of an orthogonal transformation, linear combinations of the functions $\Phi^i_{p\nu}(\mathbf{r}_\mathbf{n}, j)$ —the functions $\Psi^i_{p\mu}(\mathbf{r}_\mathbf{n}, j)$ ($\nu, \mu = 1, 2$ or $1, 2, 3$ —depending on the degree of degeneracy), such as to cause the vanishing of the matrix elements of the operator $\hat{\Lambda}$, corresponding to the transitions between the degenerate levels. We shall use as the unperturbed functions the set of functions $\Psi^i_{p\mu}(\mathbf{r}_\mathbf{n}, j)$.

We seek the solution of (A1.2) in the form

$$\tilde{\Psi}^i_{p\mu}(\mathbf{r}_\mathbf{n}, j) = \Psi^i_{p\mu}(\mathbf{r}_\mathbf{n}, j) + \gamma\Psi'^i_{p\mu}(\mathbf{r}_\mathbf{n}, j),$$

$$\tilde{\omega}^2_{p\mu} = \omega^2_{p\mu} + \gamma\omega'^2_{p\mu}. \tag{A1.4}$$

Using ordinary perturbation theory we readily obtain

$$\Psi'^i_{p\mu}(0, t) = \sum_{p'\mu'}{}' \frac{\Lambda_{p'\mu', p\mu}}{\omega^2_{p\mu} - \omega^2_{p'\mu'}}\Psi^i_{p'\mu'}(0, t), \tag{A1.5}$$

$$\Lambda_{p'\mu', p\mu} = \sum_{\mathbf{n}'j'\mathbf{n}j}\Psi^{i'}_{p'\mu'}(\mathbf{r}_{\mathbf{n}'}, j')\frac{\Lambda^{i'i}_{(0,t)}(\mathbf{r}_{\mathbf{n}'}, j'; \mathbf{r}_\mathbf{n}, j)}{\sqrt{m_{\mathbf{n}'j'}m_{\mathbf{n}j}}}\Psi^i_{p\mu}(\mathbf{r}_\mathbf{n}, j). \tag{A1.6}$$

In (A1.5) the summation is over all the (p', μ') which are not equal to (p, μ). Let us substitute (A1.4)–(A1.6) in (A1.3). As a result we obtain

$$\tilde{Z}_t = Z_t + \gamma Z'_t. \tag{A1.7}$$

$$Z_t = R'\sum_{p\mu}\frac{(\varkappa\Psi_{p\mu}(0, t))^2}{\hbar\omega_{p\mu}}\operatorname{cth}\frac{\hbar\omega_{p\mu}}{2T} = R'\sum_{p\nu}\frac{(\varkappa\Phi_{p\nu}(0, t))^2}{\hbar\omega_{p\nu}}\operatorname{cth}\frac{\hbar\omega_{p\nu}}{2T}, \tag{A1.8}$$

$$Z'_t = R'\varkappa^i\varkappa^{i'}\frac{1}{\hbar}\sum_{p\mu p'\mu'}\Psi^i_{p\mu}(0, t)\,\Psi^{i'}_{p'\mu'}(0, t) \times\frac{\Lambda_{p'\mu', p\mu}}{\omega^2_{p\mu} - \omega^2_{p'\mu'}}\left(\frac{1}{\omega_{p\mu}}\operatorname{cth}\frac{\hbar\omega_{p\mu}}{2T} - \frac{1}{\omega_{p'\mu'}}\operatorname{cth}\frac{\hbar\omega_{p'\mu'}}{2T}\right)$$
$$= R'\varkappa^i\varkappa^{i'}\frac{1}{\hbar}\sum_{p\nu p'\nu'}\Phi^i_{p\nu}(0, t)\,\Phi^{i'}_{p'\nu'}(0, t) \times\frac{\Lambda_{p'\nu', p\nu}}{\omega^2_{p\nu} - \omega^2_{p'\nu'}}\left(\frac{1}{\omega_{p\nu}}\operatorname{cth}\frac{\hbar\omega_{p\nu}}{2T} - \frac{1}{\omega_{p'\nu'}}\operatorname{cth}\frac{\hbar\omega_{p'\nu'}}{2T}\right). \tag{A1.9}$$

The second equality in (A1.8) and (A1.9) is a direct consequence of the orthogonality of the transformation from the functions $\Phi^i_{p\nu}(\mathbf{r}_\mathbf{n}, j)$ into the functions $\Psi^i_{p\mu}(\mathbf{r}_\mathbf{n}, j)$ [$\Lambda_{p'\nu', p\nu}$ is determined by expression (A1.6) if we replace in it the functions $\Psi^i_{p\mu}(\mathbf{r}_\mathbf{n}, j)$ by $\Phi^i_{p\nu}(\mathbf{r}_\mathbf{n}, j)$]. The final expression in (A1.8) then simply coincides with (3.2).

At high temperatures $T > \hbar\omega_{\max}$ expression (A1.9) is transformed into

$$Z_t' = -2TR'\varkappa^i\varkappa^{i'}\hbar^{-2}\sum_{p\nu}\sum_{p'\nu'}\frac{\Phi^i_{p\nu}(0,t)\,\Lambda_{p'\nu',p\nu}\Phi^{i'}_{p'\nu'}(0,t)}{\omega^2_{p\nu}\,\omega^2_{p'\nu'}}. \tag{A1.10}$$

It must be noted that at high temperatures we can obtain for $\widetilde{Z}_t$ a certain general expression (see II)

$$\widetilde{Z}_t = 2TR'm'\,[A^{-1}(0,t;0,t)]^{ii'}\varkappa^i\varkappa^{i'}. \tag{A1.11}$$

Thus, the problem actually reduces to finding a matrix which is the reciprocal of the matrix (A1.1). At relatively small γ, this problem can be solved in the usual fashion, and the final solution is represented in the form of a perturbation-theory series

$$\hat{A}^{-1} = \hat{A}_0^{-1}\sum_{m=0}^{\infty}(-\gamma)^m(\hat{\Lambda}\hat{A}_0^{-1})^m. \tag{A1.12}$$

To find the quantities of the type $[A^{-1}_{0jj'}(\mathbf{r}_n - \mathbf{r}_n)]^{kk'}$, which are contained in (A1.12), we multiply both sides of the equation for the ideal lattice [(2.1) with $\epsilon_t = 0$]

$$\omega_0^2(\mathbf{f},\alpha)\,\varphi^i{}_{\mathbf{f}\alpha}(\mathbf{r}_1,p) = \sum_{\mathbf{l}'p'}(m_pm_{p'})^{-1/2}A^{ii'}_{0pp'}(\mathbf{r}_1 - \mathbf{r}_{\mathbf{l}'})\varphi^{i'}{}_{\mathbf{f}\alpha}(\mathbf{r}_{\mathbf{l}'},p')$$

by

$$m_p^{1/2}\omega_0^{-2}(\mathbf{f},\alpha)\,\varphi^{k*}_{\mathbf{f}\alpha}(\mathbf{r}_{\mathbf{n}'},j')\,[A^{-1}_{0jp}(\mathbf{r}_\mathbf{n} - \mathbf{r}_\mathbf{l})]^{ki}$$

and sum over **l**, p, i, **f**, and α. As a result, using the explicit form (2.3) for the functions $\varphi^i_{\mathbf{f}\alpha}(\mathbf{r}_\mathbf{n}, j)$, we have

$$[A^{-1}_{0jj'}(\mathbf{r}_\mathbf{n} - \mathbf{r}_{\mathbf{n}'})]^{kk'} = \frac{1}{(m_jm_{j'})^{1/2}}\,\frac{1}{N}\sum_{\mathbf{f}\alpha}\frac{e_j^k(\mathbf{f},\alpha)\,e_{j'}^{k'*}(\mathbf{f},\alpha)}{\omega_0^2(\mathbf{f},\alpha)}$$
$$\times\exp[i\mathbf{f}(\mathbf{r}_\mathbf{n} - \mathbf{r}_{\mathbf{n}'})]. \tag{A1.13}$$

Finally, using (A1.11)—(A1.13), we find

$$\widetilde{Z}_t = \frac{2TR_t}{\hbar^2}\varkappa^i\varkappa^{i'}\sum_{m=0}^{\infty}(-\gamma)^m\left[\frac{v_0}{(2\pi)^3}\right]^{m+1}$$
$$\times\sum_{\alpha_1\alpha_2\ldots\alpha_{m+1}}\int\cdots\int d^3f_1\,d^3f_2\ldots d^3f_{m+1}$$
$$\times\frac{e_t^i(\mathbf{f}_1,\alpha_1)\,\Lambda_{\mathbf{f}_1\alpha_1,\,\mathbf{f}_2\alpha_2}\Lambda_{\mathbf{f}_2\alpha_2,\,\mathbf{f}_3\alpha_3}\cdots\Lambda_{\mathbf{f}_m\alpha_m,\,\mathbf{f}_{m+1}\alpha_{m+1}}e_t^{i'*}(\mathbf{f}_{m+1},\alpha_{m+1})}{\omega_0^2(\mathbf{f}_1,\alpha_1)\,\omega_0^2(\mathbf{f}_2,\alpha_2)\cdots\omega_0^2(\mathbf{f}_{m+1},\alpha_{m+1})}, \tag{A1.14}$$

where

$$\Lambda_{\mathbf{f}\alpha,\,\mathbf{f}'\alpha'} = \sum_{\mathbf{n}j}\sum_{\mathbf{n}'j'}(m_jm_{j'})^{-1/2}\Lambda^{ii'}_{(0,t)}(\mathbf{r}_\mathbf{n},j;\mathbf{r}_{\mathbf{n}'},j')\,e_j^{i*}(\mathbf{f},\alpha)\,e_{j'}^{i'}(\mathbf{f}',\alpha')$$
$$\times\exp[-i\mathbf{f}\mathbf{r}_n + i\mathbf{f}'\mathbf{r}_{\mathbf{n}'}]. \tag{A1.15}$$

The term m = 0 in (A1.14) does not contain $\hat{\Lambda}$ and corresponds to the case of invariant force constants, whereas the term m = 1 coincides exactly with (A1.10). To verify this, we transform the sum contained in (A1.10) into

$$\sum_{p\nu,\,p'\nu'}\Phi_{p\nu}{}^i(0,t)\,\Phi^{i'}_{p'\nu'}(0,t)\sum_{\substack{\mathbf{nn'mm'}\\ jj'ss'}}\Phi^k_{p\nu}(\mathbf{r}_\mathbf{n},j)\sqrt{m_{\mathbf{n}j}m_{\mathbf{n}'j'}}$$
$$\times[A^{-1}_{0jj'}(\mathbf{r}_\mathbf{n} - \mathbf{r}_{\mathbf{n}'})]^{kk}(m_{\mathbf{n}'j'}m_{\mathbf{m}'s'})^{-1/2}\,\Lambda^{k'l'}_{(0,t)}(\mathbf{r}_{\mathbf{n}'},j',\mathbf{r}_{m'},s')$$
$$\times\sqrt{m_{\mathbf{m}'s'}m_{\mathbf{m}s}}\,[A^{-1}_{0ss'},(\mathbf{r}_{\mathbf{m}'} - \mathbf{r}_\mathbf{m})]^{l'l}\,\Phi^l_{p'\nu'}(\mathbf{r}_\mathbf{m},s)$$
$$= m'(\hat{A}_0^{-1}\hat{\Lambda}\hat{A}_0^{-1})^{ii'}_{\substack{\mathbf{r}_\mathbf{n}=\mathbf{r}_{\mathbf{n}'}=0\\ j=j'=t}},$$

q.e.d. (see (A1.11)—(A1.12)).

APPENDIX 2

Leaving out the indices t and ν from (2.16) and (2.17) so as to simplify the notation, and going over to the dimensionless frequency x (2.20), we consider the integral

$$J_n = \int_0^\infty G(x)\frac{dx}{x^n}, \qquad n = 0.1; \tag{A2.1}$$

$$G(x) = (1-\varepsilon)\,g(x)\left\{\left[1 - \varepsilon x\int_{\{X_i\}}\frac{g(x')\,dx'}{x-x'}\right]^2 + [\pi\varepsilon x g(x)]^2\right\}^{-1}. \tag{A2.2}$$

The integration in (A2.2) is carried out over all the segments $X_1 = (0, x_1')$, $X_2 = (x_2x_2')$, . . . , $X_\sigma = (x_\sigma, 1)$ which correspond to the quasicontinuous bands of the ideal crystal ($\sigma < 3s$, inasmuch as some of the bands overlap, as is customarily the case), and which define the only region where the function g(x) differs from zero.

With respect to the function g(x) which is normalized to unity

$$\int_{\{X_i\}} g(x)\,dx = 1,$$

we can show, using the results of van Hove[16], that in the closed intervals $X_1, X_2, \ldots, X_\sigma$ it satisfies the Lipschitz condition with exponent $1/2$. Then, as is well known, the improper integral contained in (A2.2) exists and defines in the closed intervals $X_1, X_2, \ldots, X_\sigma$ a function of x satisfying the Lipschitz condition with the same exponent $1/2$; consequently the integral (A2.1) exists for both indicated values of n.

Let us transform the expression (A2.2) for the function G(x), recasting it in the form

$$G(x) = -\frac{1-\varepsilon}{2\pi i\varepsilon}\frac{1}{x}\left\{\left[1 - \varepsilon x\int\frac{g(x')\,dx'}{x-x'} + i\pi\varepsilon x g(x)\right]^{-1}\right.$$
$$\left.-\left[1 - \varepsilon x\int\frac{g(x')\,dx'}{x-x'} - i\pi\varepsilon x g(x)\right]^{-1}\right\}$$
$$= -\frac{1-\varepsilon}{2\pi i\varepsilon}\frac{1}{x}\lim_{\delta\to+0}\left\{\left[1 - \varepsilon x\int\frac{g(x')\,dx'}{x-x'+i\delta}\right]^{-1}\right.$$
$$\left.-\left[1 - \varepsilon x\int\frac{g(x')\,dx'}{x-x'-i\delta}\right]^{-1}\right\}. \tag{A2.3}$$

Inasmuch as the integrand in (A2.1) does not have any singularities at all (n = 0), or has an integrable singularity (n = 1), we can, after first shifting the lower limit of integration to the point $x = \rho$ ($\rho \to +0$), break up the integral (A2.1) into two parts corresponding to the two terms in (A2.3). In the first of the integrals resulting from this splitting we can slightly deform the path of integration from the real axis into the upper half-plane (this is equivalent to introducing an integration variable $z = x + i\delta$), while in the second we can deform the path to the lower half plane ($z = x - i\delta$). We thus have

$$J_n = -\frac{1-\varepsilon}{2\pi i\varepsilon}\lim_{\rho,\,\delta\to+0}\int_L F_n(z)\,dz, \qquad \text{(A2.4)}$$

where

$$F_n(z) = z^{-(n+1)}\left[1-\varepsilon z\int_{\{X_i\}}\frac{g(x)\,dx}{z-x}\right]^{-1}, \qquad \text{(A2.5)}$$

and the integration in (A2.4) is carried out along two horizontal lines—from $\rho + i\delta$ to $\infty + i\delta$ in the upper half plane and from $\infty - i\delta$ to $\rho - i\delta$ in the lower half plane.

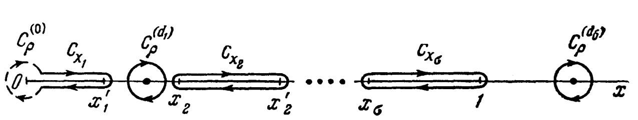
The Cauchy-type integral in (A2.5), as is well known, defines a regular function of the variable z outside the segments $X_1, X_2, \ldots, X$ even under the most general assumptions with respect to the function d(x) (the latter need merely be continuous on the segments $\{X_i\}$). Therefore the function $F_n(z)$ is analytic in the entire plane of the complex variable z, with the exception of the segments $\{X_i\}$ of the real axis, and perhaps also the poles $z = x_d$ corresponding to the roots of the equation

$$1-\varepsilon z\int_{\{X_i\}}\frac{g(x)\,dx}{z-x} = 0, \qquad \text{(A2.6)}$$

which coincides with the equation (2.19′) for the determination of the discrete frequencies (corresponding to the indices t and ν, which are omitted here). Therefore, the integrals taken in the opposite directions along the straight-line segments $(\rho + i\delta, \infty + i\delta)$ and $(\infty - i\delta, \rho - i\delta)$ (where $g(x) \equiv 0$ and, consequently $F_n(z)$ is analytic) cancel each other and the integration can be carried out over the contour

$$L = \sum_{i=1}^{\sigma} C_{X_i} + \sum_i C_\rho^{(d_i)},$$

shown by the solid line in the figure; this is indicated in (A2.4) by the corresponding symbol on the integral sign. The integration over the circles $C_\rho^{(d_i)}$ with small radius ρ is carried out only near the discrete frequencies ("gap" and "free") which actually exist for the given ε.



Let us consider the integral

$$K_n = -\frac{1-\varepsilon}{2\pi i\varepsilon}\int_{L+C_\rho^{(0)}+C} F_n(z)\,dz, \qquad \text{(A2.7)}$$

where the integration is carried out over the combined contour made up of L and the small-radius circle $C^{(0)}$ with center at the point x = 0, circuited in the clockwise direction (shown dashed in the figure), and also over the circle C_R of radius $R \to \infty$ in the counterclockwise direction. It is obvious that

$$J_n = K_n + \frac{1-\varepsilon}{2\pi i\varepsilon}\int_{C_\rho^{(0)}} F_n(z)\,dz + \frac{1-\varepsilon}{2\pi i\varepsilon}\int_{C_R} F_n(z)\,dz. \qquad \text{(A2.8)}$$

On the other hand, it is also obvious that inasmuch as the function $F_n(z)$ is analytic in the region contained between the contour $L + C^{(0)}$ and the circle C_R, the integral assumes the value

$$K_n = 0. \qquad \text{(A2.9)}$$

When $|z| \ll 1$, as can be readily seen, the function $F_n(z)$ can be represented in the form

$$F_n(z) = \frac{1}{z^{n+1}}\left\{1 + z\left[\frac{d}{dz}\left(1-\varepsilon z\int\frac{g(x)\,dx}{z-x}\right)^{-1}\right]_{z=0}\right\}$$
$$= \frac{(1 - z\varepsilon\langle x^{-1}\rangle)}{z^{n+1}},$$

where we introduce the usual notation

$$\langle x^{-1}\rangle \equiv \int x^{-1}g(x)\,dx.$$

Thus, we have

$$\frac{1-\varepsilon}{2\pi i\varepsilon}\int_{C_\rho^{(0)}} F_0(z)\,dz = \frac{1-\varepsilon}{2\pi i\varepsilon}\int_{C_\rho^{(0)}}\frac{dz}{z} = -\frac{1-\varepsilon}{\varepsilon},$$

$$\frac{1-\varepsilon}{2\pi i\varepsilon}\int_{C_\rho^{(0)}} F_1(z)\,dz = \frac{1-\varepsilon}{2\pi i\varepsilon}\int_{C_\rho^{(0)}} dz\left(\frac{1}{z^2}-\frac{1}{z}\varepsilon\left\langle\frac{1}{x}\right\rangle\right)$$
$$= (1-\varepsilon)\left\langle\frac{1}{x}\right\rangle. \qquad \text{(A2.10)}$$

Finally

$$\frac{1-\varepsilon}{2\pi i\varepsilon}\int_{C_R} F_n(z)\,dz = \begin{cases}\varepsilon^{-1} & \text{for } n=0\\ 0 & \text{for } n=1\end{cases}. \qquad \text{(A2.11)}$$

Taking (A.8)—(A2.11) into consideration, we obtain ultimately

$$J_0 = \int_0^\infty G(x)\,dx = 1, \quad J_1 = \int_0^\infty G(x)\frac{dx}{x} = (1-\varepsilon)\left\langle\frac{1}{x}\right\rangle. \qquad \text{(A2.12)}$$

The first of these relations obviously coincides with (2.15), whereas the second corresponds to the classical limit for Z_t (3.5).

The result (A2.12) is of interest also from the mathematical point of view. We see that a rather complicated functional such as J_0 turns out to be utterly independent of ϵ or of the concrete form of the normalized function g(x). The final expression for J_1 turns out to depend on ϵ and on the concrete form of the function g(x), but it is striking because of the universality of this dependence and because of its extraordinary simplicity.

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Translated by J. G. Adashko
321