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DYNAMICS OF SEPARATE ATOMS AND THE MOSSBAUER EFFECT IN A COMPLEX MULTICOMPONENT SYSTEM. EFFECTIVE DEBYE FREQUENCY

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Spectral functions are introduced describing the oscillations of separate atoms in an arbitrary macroscopically uniform system of harmonically interacting particles (an amorphous body, solid solution, ideal polyatomic crystal), and their properties are discussed. Several general results are obtained characterizing the probability of the Mossbauer effect, and the shift and shape of the phononless line in such a system.

1. INTRODUCTOIN

THE purpose of the present paper is to consider a number of general results pertaining to the vibration spectrum of individual atoms, the Debye factor, and the temperature shift of the Mossbauer line in solid solutions and in ideal multicomponent crystals; these quantities do not depend essentially on either the concentration of the components or the details of the microstructure, and they can be expressed in terms of other independently defined quantities (e.g., the mass of the active atom and the Debye frequency of the system). In this connection, we discuss the question of effective Debye frequencies for an individual atom and the Mossbauer effect on this atom.

2. VIBRATION SPECTRUM OF INDIVIDUAL ATOMS

A. General Formulas

Let us consider the problem of natural vibrations of an arbitrary macroscopic multicomponent system of harmonically-interacting particles:

$$M_{\mathbf{n}}\omega_\beta^2\psi_\beta^i(\mathbf{x}_\mathbf{n}) = \sum_{\mathbf{n}'} A^{ik}(\mathbf{x}_\mathbf{n}, \mathbf{x}_{\mathbf{n}'})\psi_\beta^k(\mathbf{x}_{\mathbf{n}'}),$$

$$\sum_{\mathbf{n}} M_{\mathbf{n}}\psi_\beta^i(\mathbf{x}_\mathbf{n})\psi_{\beta'}^i(\mathbf{x}_\mathbf{n}) = \delta_{\beta\beta'}, \tag{2.1}$$

$$\sum_{\beta} \psi_\beta^{i*}(\mathbf{x}_\mathbf{n})\psi_\beta^{i'}(\mathbf{x}_{\mathbf{n}'}) = \frac{1}{M_\mathbf{n}}\delta^{ii'}\delta_{\mathbf{n}\mathbf{n}'} \tag{2.2}$$

and introduce the quantities

$$g^{ik}(\omega^2, \mathbf{x}_\mathbf{n}) = M_\mathbf{n}\sum_{\beta}\psi_\beta^{i*}(\mathbf{x}_\mathbf{n})\psi_\beta^k(\mathbf{x}_\mathbf{n})\delta(\omega^2 - \omega_\beta^2),$$

$$g(\omega^2, \mathbf{x}_\mathbf{n}) = {}^1\!/_3 g^{ii}(\omega^2, \mathbf{x}_\mathbf{n}); \tag{2.3}$$

$$\int_0^{\omega_m^2} g^{ik}(\omega^2, \mathbf{x}_\mathbf{n})\,d\omega^2 = \delta^{ik}, \qquad \int_0^{\omega_m^2} g(\omega^2, \mathbf{x}_\mathbf{n})\,d\omega^2 = 1, \tag{2.4}$$

which describe the distribution, with respect to the frequencies, of the squares of the reduced amplitudes of the vibrations of the **n**-th atom; $\psi_\beta^i(\mathbf{x}_\mathbf{n})$ and ω_β denote respectively the eigenfunction and frequency of the normal vibration of the species β[1]. The normalized conditions (2.4) follow directly from the second relation of (2.2) at $\mathbf{n} = \mathbf{n}'$ (ω_m = maximum vibration frequency).

As to the particle system itself, we shall only assume that it is macroscopically homogeneous, in equilibrium, and free of internal stresses, and we shall regard $\mathbf{x}_\mathbf{n}$ as the fixed equilibrium positions of the particles. This means that the matrix of the force constants satisfies the necessary invariance conditions[1] and admits of a transition from Eqs. (2.1) to the usual theory of elasticity at low frequencies. We shall deal concretely either with a solid solution (substitution of interstitial, disordered or partially ordered) with the indicated equilibrium properties, or an ideal polyatomic crystal. However, all the general results pertain also to an amorphous body, provided the latter can be regarded microscopically as a harmonic system and macroscopically as an internally unstressed elastic continuum. In the case of a solid solution, the quantities $M_\mathbf{n}$ in (2.1) are regarded as random, assuming t values M_a, $a = 1, 2, \ldots, t$, corresponding to the masses of atoms of t species (the index a denotes the species of the particle). In the case of an ideal r-atomic t-component crystal, Eq. (2.1) has known solutions in the form of plane waves; in this case $M_\mathbf{n} = M_\mathrm{j}$ and $\beta = (\mathbf{f}, \sigma)$, where $\mathrm{j} = 1, 2, \ldots, \mathrm{r}$ is the number of the atom in the unit cell, $\mathbf{f}$ is the wave vector, and $\sigma = 1, 2, \ldots, 3\mathrm{r}$ is the number of the branch. Expressions (2.3) now define the functions $\mathrm{g}^{\mathrm{ik}}(\omega^2, \mathrm{j})$ and $\mathrm{g}(\omega^2, \mathrm{j})$, which are the same for all atoms of the same sublattice.

B. Low Frequencies

For concreteness we shall speak of a solid solution. With respect to low frequencies, i.e., long waves, such a solution is a homogeneous continuous body. Therefore, setting aside the important question of the connection of its elastic constants $\mathrm{C}^{\mathrm{ik}l\mathrm{m}}$ with the matrix of the force constants (which generally speaking is random), we can nonetheless state quite rigorously that the solutions of (2.1) should be determined in the low-frequency region by the usual Cristoffel equation of elasticity theory:

$$\rho c^2(\mathbf{q}, s)e^i(\mathbf{q}, s) = C^{iklm}q^k q^m e^l(\mathbf{q}, s),$$

$$e^i(\mathbf{q}, s)e^i(\mathbf{q}, s') = \delta_{ss'}, \qquad \sum_{s=1}^{3} e^i(\mathbf{q}, s)e^{i'}(\mathbf{q}, s) = \delta^{ii'}, \tag{2.5}$$

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[1] Since the matrix of the force constants $\mathrm{A}^{\mathrm{ik}}(\mathrm{x}_\mathrm{n}, \mathrm{x}_{\mathrm{n}'})$ is real, the function $\mathrm{g}^{\mathrm{ik}}(\omega^2, \mathrm{x}_\mathrm{n})$ is real and is symmetrical with respect to permutation of the indices. For the same reason, the functions $\psi_\beta^\mathrm{i}(\mathrm{x}_\mathrm{n})$ can also be chosen to be real.

and are of the form $(\beta = (\mathbf{f}, s))$

$$\psi^{i}_{\mathbf{f}s}(\mathbf{x_n}) = (\overline{M}N)^{-1/2} e^{i}(\mathbf{q}, s)\, e^{i\mathbf{f}\mathbf{x_n}}, \quad \omega^2(\mathbf{f}, s) = c^2(\mathbf{q}, s) f^2. \tag{2.6}$$

To this end, the wavelength λ should be large compared with the average distance between atoms of one species, i.e.,

$$\lambda \gg \eta_a^{-1/3} \bar{d} \quad \text{or} \quad \omega \ll 2\pi\eta_a^{1/3} \bar{c}\bar{d}^{-1} \sim \omega_m \eta_a^{1/3} \tag{2.7}$$

for all $a = 1, 2, \ldots, t$. In (2.5) and (2.6) we use the following notation: $c(\mathbf{q}, s)$, $e(\mathbf{q}, s)$, and $\mathbf{q} = \mathbf{f}/f$ are respectively the phase velocity, the polarization vector, and the unit vector in the propagation direction of the sound wave (the index $s = 1, 2, 3$ corresponds to three polarizations); $\bar{c}$ is a certain average sound speed; $\bar{d}$ is the average interatomic distance; $\rho = \overline{M}/v_0$ is the density of the medium, $\overline{M}$ and v_0 is the average mass and the average volume per atom,

$$\overline{M} = \frac{1}{N} \sum_{\mathbf{n}} M_{\mathbf{n}} = \sum_{a=1}^{t} \eta_a M_a, \qquad v_0 = \frac{V}{N},$$

N is the total number of particles in the system, and η_a is the relative concentration of the a-th component, so that $\sum\limits_{a=1}^{t} = 1$. The normalization factor $(MN)^{-1/2}$ in (2.6) is chosen such as to satisfy the first relation in (2.2) (to satisfy the second relation in (2.2) it is necessary to know all the solutions of the dynamic problem (2.1), and not only those corresponding to the acoustic waves of elasticity theory). The boundary conditions for the problem (2.1), owing to the macroscopic dimensions of the system in question, can be arbitrary and, in particular, periodic. Then, as usual, $f^i = 2\pi n^i/L_i$, where n^i are integers and L_i are the linear dimensions of the periodicity volume $V = L_1L_2L_3$.

We substitute (2.6) in (2.3) and go over from summation over f to integration. Introducing then the spherical coordinates $(f, \mathbf{q})$ of the vector $\mathbf{f}$, we finally obtain after integration with respect to f

$$g^{ik}(\omega^2, \mathbf{x_n}) = \frac{3M_{\mathbf{n}}}{2\overline{M}} (\hat{\Omega}^{-3})^{ik} \sqrt{\omega^2}, \quad g(\omega^2, \mathbf{x_n}) = \frac{3M_{\mathbf{n}}}{2\overline{M}\Omega^3} \sqrt{\omega^2}, \tag{2.8}$$

where, by definition,

$$(\hat{\Omega}^{-3})^{ik} \equiv \frac{v_0}{3(2\pi)^3} \sum_{s=1}^{3} \int \frac{e^i(\mathbf{q}, s)\, e^k(\mathbf{q}, s)\, dS_{\mathbf{q}}}{c^3(\mathbf{q}, s)}, \qquad \Omega^{-3} \equiv \frac{1}{3} (\hat{\Omega}^{-3})^{ii} \tag{2.9}$$

(the integration is over the total solid angle).

The constant symmetric tensor $(\hat{\Omega}^{-3})^{ik}$ has a certain fixed system of principal axes in a macroscopically homogeneous medium of any symmetry:

$$(\hat{\Omega}^{-3})^{ik} j_\alpha^k = \Omega^{(\alpha)-3} j_\alpha^i, \quad j_\alpha^i j_{\alpha'}^i = \delta_{\alpha\alpha'}, \quad \sum_{\alpha=1}^{3} j_\alpha^i j_\alpha^{i'} = \delta^{ii'}, \tag{2.10}$$

so that $\mathbf{j}_\alpha$ and $\Omega^{(\alpha)-3}$ are the eigenvectors and the eigenvalues of this tensor. At the same time, the functions $g^{ik}(\omega^2, \mathbf{x_n})$ (2.8) are also diagonalized in the coordinate system with unit vectors $\mathbf{j}_\alpha$. In crystals with symmetry not lower than rhombic, the vectors $\mathbf{j}_\alpha$ are directed along the principal crystallographic axes. In particular, if the system has cubic symmetry, then

$$(\hat{\Omega}^{-3})^{ik} = \Omega^{-3}\delta^{ik}. \tag{2.11}$$

Expressions (2.8) give the true values (accurate to quantities of higher order of smallness in $\omega/\Omega^{(\alpha)}$) of the spectral functions in the region of low frequencies. In their derivation we have, obviously, neglected the relative displacement of the atoms situated at a distance smaller than $\eta_{-a}^{1/3}$p with respect to one another, compared with their absolute displacement during the vibration process. If we average the quantity $g(\omega^2, \mathbf{x_n})$ (2.3) over all the atoms of the system, we obtain the complete spectrum in its usual definition. Accordingly, Ω in (2.9) is the usual Debye frequency, which determines the low-temperature specific heat. In the general case, the low-frequency oscillations of an anisotropic crystal are described by the inverse tensor of the cubes of the "Debye frequencies" $(\hat{\Omega}^{-3})^{ik}$ (2.9) or by the three "Debye frequencies" $\Omega^{(\alpha)}$ (2.10). As seen from (2.8), the initial section of the spectrum for an atom of a given species a depends only on its mass $M_{\mathrm{n}} = M_a$, and not on the lattice site at which it is situated, and can be described in terms of the reciprocal tensor of the cube of the effective "Debye frequencies":

$$(\hat{\Omega}_a^{-3})^{ik} = (M_a / \overline{M}) (\hat{\Omega}^{-3})^{ik} \tag{2.12}$$

or effective "Debye frequencies"

$$\Omega_a^{(\alpha)} = (\overline{M}/M_a)^{1/3} \Omega^{(\alpha)}, \qquad \Omega_a = (\overline{M}/M_a)^{1/3} \Omega. \tag{2.13}$$

In conclusion we note that the tensor $(\hat{\Omega}^{-3})^{ik}$ determines the density of the phonon states near the lower boundary of the acoustic vibrations, and this sense it is analogous to the effective-mass tensor for "inertial" elementary excitations in a solid (e.g., carriers).

C. Impurity atom

The results obtained above apply in particular, also to impurity atoms, the possible change in the force constants being included in the "Debye frequencies" $\Omega^{(\alpha)}$, which are characteristics of the entire crystal. As a consequence we find that in the case of asymptotically small concentration, the spectrum of the impurity-atom vibrations at the lowest frequencies is determined only by their mass and by the "Debye frequencies" of the matrix (which in general has many components). Indeed, let the atoms of species 1 $(a = 1)$ be the impurity atoms, with $\eta_1 \ll 1$. Then, obviously, $\Omega^{(\alpha)} = \Omega_0^{(\alpha)} + \Delta\Omega^{(\alpha)}(\eta_1)$ and $\overline{M} = \overline{M}_0 + \Delta\overline{M}(\eta_1)$, where $\Omega_0^{(\alpha)}$ and $\overline{M}_0$ are the "Debye frequencies" and the average mass of the matrix atoms, and $\Delta\Omega^{(\alpha)}(\eta_1)$ and $\Delta\overline{M}(\eta_1)$ tend to zero when $\eta_1 \to 0$. Consequently, in accordance with (2.8), the spectrum of the vibrations of the isolated impurity atoms is of the form

$$g_1^{ik}(\omega^2) = \frac{3M_1}{2\overline{M}_0} (\hat{\Omega}_0^{-3})^{ik} \sqrt{\omega^2}, \qquad g_1(\omega^2) = \frac{3M_1}{2\overline{M}_0\Omega_0^3} \sqrt{\omega^2}. \tag{2.14}$$

These formulas were obtained here for frequencies satisfying the condition (2.7) at $a = 1$. However, the region of their applicability is much broader: in the limit as $\eta_1 \to 0$ they should remain valid independently of the value of η_1, provided

$$\omega \ll \tilde{\omega}_1, \qquad \lambda \gg d_1, \tag{2.15}$$

where $\tilde{\omega}_1$ is a certain characteristic frequency of oscillations of the impurity atom (near this frequency the functions (2.3) reach a maximum for $a = 1$), and d_1 is a characteristic linear dimension of the region around the impurity, in which the force constants greatly differ from the initial ones. Obviously, $\tilde{\omega}_1 \sim \sqrt{\gamma_1/M_1}$, where γ_1 is the characteristic magnitude of the force constants corresponding to the impurity atom. The foregoing is connected with the fact that the elastic waves with frequencies satisfying (2.15) are practically not scattered by the impurity. We note also that the last condition of (2.15) does not differ essentially from the general condition for the applicability of elasticity theory, inasmuch as $d_1 \sim \bar{d}$.

The result (2.14) does not depend on whether the stiffness of the "springs" coupling the impurity with its neighbors changes or not[2]. Physically this is caused by the fact that these "springs" strongly change the picture of the vibrations of the impurity atom only if they "operate" effectively during the vibration process, and consequently the phases of the vibrations of the impurity atom and of its neighbors differ greatly from one another. But a strong phase shift in the displacement of neighboring atoms corresponds to normal vibrations with sufficiently short wavelengths, and, consequently, with sufficiently high frequencies (on the order of $\tilde{\omega}_1$). It is precisely such a dephasing which causes, in particular, the resonant form of the spectrum for relatively heavy and relatively light atoms (quasilocal and local vibrations) with a maximum at the frequency (see[2-4])

$$\tilde{\omega}_1^{(\alpha)} \sim \Omega_0^{(\alpha)} (\bar{M}_0/M_1)^{1/2}. \tag{2.16}$$

We note also that the exact analytic expressions obtained in[2-4] within the framework of the simple force model of the type (2.20) (see below), for the spectrum of the impurity atom (see, e.g., (2.16) in[4]) at low frequencies agree fully with the general result (2.14).

D. Ideal Polyatomic Crystal

All the relations of Sec. C remain in force also in the case of an ideal polyatomic crystal, apart from the need for substituting $x_n \to j$ in (2.8). This case is of special interest, since the connection between the dynamic lattice theory and elasticity theory can be traced here in detail by well tried methods[1]. In particular, the relative displacement of the sublattices in the acoustic vibrations at small values of f turns out to be smaller by a factor fd_m (d_m - length of the largest period) than the amplitudes of the absolute displacement of the atoms, as should be the case. The main and perfectly natural result is now that the low-frequency spectrum of the vibrations of atoms of a given species depends only on its mass, but not on the sublattice to which it belongs.

E. Moments

One more result can be obtained quite simply, namely, the moments of the functions (2.3), which we shall express in terms of the matrix of the force constants. We define, as usual, the l-th even moment of the function $g^{ik}(\omega^2, x_n)$ by the relation

$$\langle \omega^{2l} \rangle_n^{ik} = \int_0^{\omega_m^2} \omega^{2l} g^{ik}(\omega^2, x_n)\, d\omega^2, \qquad l = -1, 0, 1, 2, \ldots \tag{2.17}$$

and analogously the moments of the function $g(\omega^2, x_n)$. Replacing in (2.1) n by n_l and i by i_l, and then multiplying it by

$$(M_{n_2} M_{n_3} \ldots M_{n_l})^{-1} \psi_\beta^{i*}(x_n) A^{i'i_2}(x_n, x_{n_2}) A^{i_2 i_3}(x_{n_2}, x_{n_3}) \ldots A^{i_{l-1} i_l}(x_{n_{l-1}}, x_{n_l}),$$

we obtain after summation over $n_2, n_3, \ldots, n_l, i_2, i_3, \ldots, i_l$ and, with allowance for (2.2),

$$\begin{aligned} \langle \omega^{2l} \rangle_n^{ii'} &\equiv M_n \sum_\beta \psi_\beta^{i*}(x_n) \psi_\beta^{i'}(x_n) \omega_\beta^{2l} \\ &= \frac{1}{M_n} \sum_{n_2, n_3, \ldots, n_l} \frac{1}{M_{n_2} M_{n_3} \ldots M_{n_l}} A^{i'i_2}(x_n, x_{n_2}) \cdot \\ &\quad \cdot A^{i_2 i_3}(x_{n_2}, x_{n_3}) \ldots A^{i_l i}(x_{n_l}, x_n), \qquad l = 1, 2, \ldots \end{aligned} \tag{2.18}$$

Multiplication of (2.1) by $\omega_\beta^2 \psi_\beta^{i*}(x_n) [\hat{A}^{-1}(x_n, x_{n_1})]^{i'i_1}$ after making the substitutions $n \to n_1$ and $i \to i_1$, with subsequent summation over n_1, i_1, and β, yields

$$\langle \omega^{-2} \rangle_n^{ii'} = M_n [A^{-1}(x_n, x_n)]^{ii'} \tag{2.19}$$

(all the tensor moments are symmetrical with respect to permutation of the indices, see footnote[1]).

F. Simple Force Model

Particular interest attaches to the case when the matrix

$$A^{ik}(x_n, x_{n'}) = A^{ik}(x_n - x_{n'}) \tag{2.20}$$

depends only on the difference between the radius vectors of the atoms in the system, and the x_n themselves form a regular fixed lattice (the dynamics of ideal two-component superstructures AB_{r-1} with a force interaction of the type (2.20) was considered in[5,6]). Such an assumption is quite satisfactory for many substitutional solutions, particularly for solutions of metals belonging to the same group of the periodic system and having identical structure (the elastic constants and the interatomic distances of such metals differ as a rule much less than the masses of the atoms). Let us introduce the concept of a "standard" crystal X_{st}, which is constructed on the basis of the force matrix (2.20) by filling all the sites with identical atoms with a certain "standard" mass M_{st}. By way of M_{st} it is convenient to choose here $\bar{M}$ or M_a. Then, by virtue of the equation

$$M_{эт}\, \omega_{эт}^2(f, s)\, e^i(f, s) = \Big(\sum_n A^{ik}(x_n) e^{-ifx_n} \Big) e^k(f, s), \tag{2.21}$$

the oscillation frequencies $\bar{\omega}(f, s)$ and $\omega_a(f, s)$ corresponding to the "standard" crystals $\bar{X}$ and X_a are connected by the relation

$$\bar{M}\bar{\omega}^2(f, s) = M_a \omega_a^2(f, s) \tag{2.22}$$

(the system of orthonormal eigenvectors e(f, s) for such crystals is the same), whence

$$\Omega_{0a}^{(\alpha)} = \left(\frac{\bar{M}}{M_a} \right)^{1/2} \Omega^{(\alpha)} \quad \text{or} \quad \Omega^{(\alpha)-2} = \sum_{a=1}^{t} \eta_a \Omega_{0a}^{(\alpha)-2}, \tag{2.23}$$

where $\Omega^{(\alpha)}$ and $\Omega_{0a}^{(\alpha)}$ are the "Debye frequencies" corresponding to these crystals. The last relation in (2.23) expresses the "Debye frequencies" of a solid solution in terms of the "Debye frequencies" of the pure components (see[7]).

Comparing expressions (2.18) and (2.19), in which (2.20) is taken into account, with the analogous expressions for the "standard" crystal, we obtain directly that for the atom of species a in the solution, regard-

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[2] Formulas (2.14) give the low-frequency spectrum of the vibrations of the impurity atoms proper in the zeroth approximation in their concentration. In calculating the values of $\Omega^{(\alpha)}$ or the spectral functions (2.8) at $a \neq 1$ ($M_n = M_a$) in the approximation linear in η_1, of course, it is necessary to take into account both the change of the mass and the stiffness of the "springs" connected with the impurity atoms.

less of the number of the site **n** at which it is situated, the following relations hold:

$$\langle\omega^2\rangle_{\mathbf{n}}^{ik}=\frac{\bar{M}}{M_a}\langle\bar{\omega}^2\rangle^{ik}=\langle\omega_a{}^2\rangle^{ik},\ \langle\omega^{-2}\rangle_{\mathbf{n}}^{ik}=\frac{M_a}{\bar{M}}\langle\bar{\omega}^{-2}\rangle^{ik}=\langle\omega_a{}^{-2}\rangle^{ik}, \tag{2.24}$$

where, by definition,

$$\langle\omega_{\text{эт}}^{2l}\rangle^{ik}\equiv\int\limits_0^{\omega^2_{m\,\text{эт}}} g_{\text{эт}}^{ik}(\omega^2)\,\omega^{2l}\,d\omega^2,\qquad l=-1,0,1,2,\ldots,$$

$$g_{\text{эт}}^{i\cdot}(\omega^2)\equiv\frac{v_0}{(2\pi)^3}\sum_{s=1}^{3}\int d^3\mathbf{f}\,e^i(\mathbf{f},s)\,e^k(\mathbf{f},s)\,\delta(\omega^2-\omega^2(\mathbf{f},s)), \tag{2.25}$$

and the "standard" crystal is chosen to be, in succession, $\overline{\mathrm{X}}$ and X_a ($\omega_{\mathrm{m.st}}$ is the maximum frequency of the vibrations of the "standard" crystal; the integration in (2.25) with respect to **f** is within the limits of the Brillouin zone).

Particular interest attaches to the final results in Eqs. (2.24), pertaining to the crystal X_a. They mean that the moments $\langle\omega^{\pm 2}\rangle_{\mathrm{n}}^{\mathrm{ik}}$ for atoms of species a, located in the solid solution with force interaction (2.20), coincide exactly with the corresponding moments in an ideal crystal consisting only of atoms a. The dependence of the masses of the atoms of the other components, on their concentration, or on their distribution over the sites becomes manifest only in moments of higher order, starting with $l = 2$. Calculating the eigenvalues $\langle\omega_a^{\pm 2}\rangle^{(\alpha)}$ of the indicated moments (the latter are diagonalized in the crystallographic system of coordinates if the crystal symmetry is not lower than rhombic, see (2.10)) and $\langle\omega_a^{\pm 2}\rangle$ in the Debye approximation,

$$\langle\omega_a{}^m\rangle^{(\alpha)}=\frac{3}{3+m}\,\Omega_{0a}^{(\alpha)m},\qquad\langle\omega_a{}^m\rangle=\frac{3}{3+m}\,\Omega_{0a},$$

we see that $\langle\omega^{\pm 2}\rangle_{\mathrm{n}}^{(\alpha)}$ and $\langle\omega^{\pm 2}\rangle_{\mathrm{n}}$ can be interpreted in terms of the "Debye frequencies" Ω_{0a} and $\Omega_{0a}^{(\alpha)}$ ($\Omega_{0a} = (1/3)\,\Sigma_{\alpha=1}\Omega_{0a}^{(\alpha)}$) of the pure "standard" crystal X_a. At the same time, the low-frequency vibration spectra of the individual atoms in the solution is described as before by the effective "Debye frequencies" (2.13) which, as can be seen, greatly differ from $\Omega_{0a}^{(\alpha)}$ (2.23) and Ω_{0a} in their dependence on M_a.

3. THE MOSSBAUER EFFECT

We now use our results to consider the Mossbauer effect. The normalized intensity of the phononless emission (absorption) $\mathrm{P}_a^{(0)}(\kappa, \mathrm{E})$ of a γ quantum with energy E in a direction of the unit vector κ by the nucleus of species a in a complex system can be written, with allowance for the definitions (2.3), in the form

$$P_a^{(0)}(\varkappa,E)=\frac{1}{\eta_a N}\sum_{\mathbf{n}}\tau_a(\mathbf{x_n})\,W(\varkappa,\mathbf{x_n})\,\delta(E-E_0\pm\delta E_{\mathbf{n}}'\pm\delta E_{\mathbf{n}}''), \tag{3.1}$$

where

$$W(\varkappa,\mathbf{x_n})=\exp\{-Z_{\mathrm{n}}(\varkappa)\}, \tag{3.2}$$

$$Z_{\mathrm{n}}(\varkappa)=\varkappa^i\varkappa^k R_{\mathrm{n}}\int\limits_0^{\omega_m{}^2} d\omega^2\,g^{ik}(\omega^2,\mathbf{x_n})\,(\hbar\omega)^{-1}\,\mathrm{cth}\,\frac{\hbar\omega}{2T} \tag{3.3}$$

is the probability of recoilless emission (absorption)[3,4,8],

$$\delta E_{\mathbf{n}}'=\frac{3E_0}{4M_{\mathrm{n}}c^2}\int\limits_0^{\omega_m^2} d\omega^2 g(\omega^2,\mathbf{x_n})\,\hbar\omega\,\mathrm{cth}\,\frac{\hbar\omega}{2T} \tag{3.4}$$

is the temperature shift[9], and

$$\delta E_{\mathrm{n}}''\infty(\rho_{\mathrm{n}}'-\rho_{\mathrm{n}})\,|\Psi_{\mathbf{n}}(0)|^2 \tag{3.5}$$

is the temperature-independent isomeric shift[10] of the phononless line for the **n**-th atom. Accordingly

$$W_a(\varkappa)=\int\limits_0^{\infty}P_a^{(0)}(\varkappa,E)\,dE=\frac{1}{\eta_a N}\sum_{\mathbf{n}}\tau_a(\mathbf{x_n})\,W(\varkappa,\mathbf{x_n}) \tag{3.6}$$

is the total (integral) probability of the Mossbauer effect for atoms of species a.

In (3.1)–(3.6) we use the following notation: $\mathrm{R_n} = \mathrm{E}_0^2/2\mathrm{M_n}c^2$ is the recoil energy of the free nucleus, E_0 is the energy of the excited nuclear level, $|\Psi_{\mathrm{n}}(0)|^2$ is the density of the electrons in the region of the **n**-th nucleus. ρ_{n}' and ρ_{n} are the average radii of the distribution of the electric charge of the **n**-th nucleus in the excited and in the ground states. The quantity $\tau_a(\mathrm{x_n})$ is equal to unity if the site **n** is occupied by an atom of species a, and to zero in all other cases. In (3.1), obviously, no account was taken of the finite width of the photonless line, and it is assumed that there are magnetic or quadrupole interactions. The upper sign in the argument of the δ-function corresponds to emission and the lower to absorption of a γ quantum. In the case of an ideal polyatomic crystal, it is sufficient to replace in all these formulas $\mathrm{x_n}$ by j and $\tau_a(\mathrm{x_n})$ by the quantity $\tau_a(\mathrm{j})$, which equals unity if the j-th sublattice is populated by atoms of species a, and zero in all other cases. Here $\eta_a \equiv \mathrm{r}_a/\mathrm{r}$, where r_a is the number of sublattices made up of atoms of species a.

Let us analyze expressions (3.1)–(3.6).

Low temperatures. In the case $\mathrm{T} \ll \hbar \min\{\Omega^{(\alpha)}\}$, expression (3.1) is transformed into

$$P_a^{(0)}(\varkappa,E)=\exp\{-Z_T(\varkappa)\}\frac{1}{\eta_a N}\sum_{\mathbf{n}}\tau_a(\mathbf{x_n})\exp\{-Z_{0\mathrm{n}}(\varkappa)\}\cdot$$
$$\cdot\delta(E-E_0\pm\delta E_T'\pm\delta E_{0\mathrm{n}}'\pm\delta E_{\mathrm{n}}''), \tag{3.7}$$

with

$$Z_{\mathrm{n}}(\varkappa)=Z_{0\mathrm{n}}(\varkappa)+Z_T(\varkappa),\qquad\delta E_{\mathrm{n}}'=\delta E_{0\mathrm{n}}'+\delta E_T';$$

$$Z_{0\mathrm{n}}(\varkappa)=\varkappa^i\varkappa^k R_{\mathrm{n}}\int\limits_0^{\omega_m{}^2} d\omega^2\,g^{ik}(\omega^2,\mathbf{x_n})\,(\hbar\omega)^{-1}, \tag{3.8}$$

$$Z_T(\varkappa)=\pi^2T^2\bar{R}\sum_{\alpha=1}^{3}(\varkappa\mathrm{j}_\alpha)^2(\hbar\Omega^{(\alpha)})^{-3}; \tag{3.9}$$

$$\delta E_{0\mathrm{n}}'=\frac{3E_0}{4M_{\mathrm{n}}c^2}\int\limits_0^{\omega_m{}^2} d\omega^2\,g(\omega^2,\mathbf{x_n})\,\hbar\omega,\qquad\delta E_T'=\frac{3\pi^4T^4E_0}{10\hbar^3\Omega^3\bar{M}c^2}, \tag{3.10}$$

where $\mathrm{Z_{0n}}(\kappa)$ and $\delta\mathrm{E}_{0\mathrm{n}}'$ determine the probability of the effect and the measured shift at T = 0, and $\overline{\mathrm{R}} \equiv \mathrm{E}_0^2/2\overline{\mathrm{M}}c^2$. This result can be obtained directly by substituting $\coth x = 1 + 2(e^{2x} - 1)^{-1}$ ($x \equiv \hbar\omega/2\mathrm{T}$) in (3.3) and (3.4), and by using in the calculation of the temperature-dependent terms the expressions (2.8) and (2.10), extending the integration with respect to ω^2 to infinity (as is done in calculating the low-temperature specific heat). If the anisotropy of the effect is immaterial, then

$$Z_{0\mathrm{n}}=R_{\mathrm{n}}\int\limits_0^{\omega_m{}^2} d\omega^2\,g(\omega^2,\mathbf{x_n})\,(\hbar\omega)^{-1},\qquad Z_T=\pi^2T^2\bar{R}(\hbar\Omega)^{-3}. \tag{3.9'}$$

The relations obtained allow us to draw certain conclusions concerning the form of the phononless line and its temperature dependence at small values of T in different complicated systems.

1. In the case of disordered solid solutions, expression (3.7) signifies that the "concentration" broadening of the phononless line does not depend on the temperature. (Many aspects connected with "concentration" broadening are considered in[11].) This becomes obvious if one chooses as the null of the energy scale the quantity $E_0 \pm \delta E_T'$, which does not depend on **n**. It should be noted that when retaining the δ-function in (3.7) we presuppose that the "concentration" broadening greatly exceeds the natural line width.

2. In the case when the Mossbauer atoms of one species occupy a finite discrete series of non-equivalent positions in the system, the Mossbauer line splits into as many components as there are such non-equivalent positions[12]. Considering for simplicity an ideal polyatomic crystal, let us replace x_n in (3.7) by j. The result is that at low temperatures the splitting of the phononless line is determined by the quantity $\delta E_{0j}' + \delta E_j''$ for different j, and does not depend on T. When T increases from zero, the "comb" of lines corresponding to T = 0 shifts as a whole (this shift is determined by the quantity $\delta E_T'$) and the decrease of their intensity is determined by the same factor $\exp\{-Z_T(\kappa)\}$.

3. The quantity

$$\frac{d\delta E_n'}{dT} = \frac{6\pi^4 T^3 E_0}{5\hbar^3\Omega^3 \overline{M} c^2} = c_L \frac{E_0}{2\overline{M}c^2} \tag{3.10'}$$

is proportional to the low-temperature lattice specific heat of the system c_L, but unlike the ideal monatomic crystal[13], the proportionality coefficient contains the average mass and not the true mass of the active atom.

4. In the case when the anisotropy of the effect is insignificant and Z_n is determined by formulas (3.8) and (3.9′), the ratio

$$\frac{d\delta E_n'}{dT} \Big/ \frac{dZ_n}{dT} = \frac{6\pi^2 T^2}{5E_0}, \tag{3.11}$$

which connects the temperature variations of $\delta E_n'$ and Z_n, depends neither on n nor on the properties of the system in general.

5. The quantities $Z_T(\kappa)$ (3.9) and $\delta E_T'$ (3.10) can be described in terms of the effective "Debye frequencies" (2.13), if we introduce in them in place of $\overline{R}$ and $\overline{M}$ the quantities $R_a = E_0^2/2M_a c^2$ and M_a, corresponding to the actual recoil energy and mass of the active atom.

6. Measurements of the temperature dependence of $W_a(\kappa)$ (3.6) at $\kappa = j\alpha$, $\alpha = 1, 2, 3$ (or in general for any three non-complanar values of κ) makes it possible to find the "Debye frequencies" $\Omega^{(\alpha)}$. As a consequence, we can determine from this directly also Ω (see (2.9)). The quantities $Z_{0n}(\kappa)$ and $\delta E_{0n}'$ should be regarded as experimentally determined parameters, which in the general case cannot be interpreted with the aid of the "Debye frequencies."

High temperatures. In the case of sufficiently high temperatures

$$T \gtrsim \frac{\hbar}{2\pi} \max\{\Omega^{(\alpha)}\},$$

when

$$\operatorname{cth} x = \frac{1}{x} + \frac{x}{3} - \frac{x^3}{45} + \dots \qquad (0 < x < \pi),$$

we have

$$Z_n(\varkappa) = 2R_n T\hbar^{-2}\varkappa^i\varkappa^k\langle\omega^{-2}\rangle_n{}^{ik} + \frac{R_n}{6T} - \frac{R_n\hbar^2}{360T^3}\varkappa^i\varkappa^k\langle\omega^2\rangle_n{}^{ik} + \dots, \tag{3.12}$$

$$\delta E_n' = \frac{3E_0T}{2M_nc^2}\left(1 + \frac{\hbar^2}{12T^2}\langle\omega^2\rangle_n - \dots\right) \tag{3.13}$$

in lieu of the general expressions (3.3) and (3.4). All the moments are defined in Sec. 2E.

From (5.18), in the zeroth approximation in 1/T, we obtain for the atom of species *a*

$$\frac{d\delta E_a'}{dT} = c_L\frac{E_0^2}{2M_ac^2}, \tag{3.14}$$

where $c_L \equiv 3$ is the high-temperature lattice specific heat (in units of the Boltzmann constant k). This formula differs from the corresponding low-temperature expression (3.10) only in a numerical coefficient, namely, it contains not $\overline{M}$ but the actual mass M_a of the active atom.

Within the framework of approximation (2.20), formulas (3.12) and (3.13) take the form

$$Z_n(\varkappa) = Z_a(\varkappa) + O(T^{-5}), \quad \delta E_n' = \delta E_a' + O(T^{-3}), \tag{3.15}$$

$$Z_a(\varkappa) = 2R_aT\hbar^{-2}\sum_{\alpha=1}^{3}(\varkappa\mathbf{j}_\alpha)^2\langle\omega_a^{-2}\rangle^{(\alpha)} + \frac{R_a}{6T} - \frac{R_a\hbar^2}{360T^3}\sum_{\alpha=1}^{3}(\varkappa\mathbf{j}_\alpha)^2\langle\omega_a^2\rangle^{(\alpha)}, \tag{3.16}$$

$$\delta E_a' = \frac{3E_0T}{2M_ac^2}\left(1 + \frac{\hbar^2}{12T^2}\langle\omega_a^2\rangle\right). \tag{3.17}$$

These expressions depend neither on n nor on the concrete structure of the system (such a dependence is observed only in the next higher terms of the expansion, which are not written out explicitly in (3.15)), and coincide with the corresponding expressions in the pure "standard" crystal X_a (in the Debye approximation they can be interpreted in terms of "Debye frequencies" $\Omega_{0a}^{(\alpha)}$ (2.23)). In this approximation, as can be seen from (3.17), there is no pure temperature line splitting. The obtained relations are analogous in a considerable degree to those considered earlier for impurity atoms[14,15,3] and for the case of superstructures[16,17].

4. CONCLUSION

1. All the results, with the exception of the results of Sec. 2F and formulas (3.15)–(3.17), which are based on the simple force model (2.20), are perfectly general and are not connected with additional model assumptions.

2. In the case of a single-component (but not necessarily a monoatomic) crystal, one can hope that the modified interpolation formulas

$$Z(\varkappa) = 3R\sum_{\alpha=1}^{3}\frac{(\varkappa\mathbf{j}_\alpha)^2}{\hbar\Omega^{(\alpha)3}}\int_0^{\Omega^{(\alpha)}}\omega\operatorname{cth}\frac{\hbar\omega}{2T}\,d\omega,$$

$$\delta E' = \frac{3E_0\hbar}{4Mc^2}\sum_{\alpha=1}^{3}\frac{1}{\Omega^{(\alpha)3}}\int_0^{\Omega^{(\alpha)}}\omega^3\operatorname{cth}\frac{\hbar\omega}{2T}\,d\omega,$$

which are obtained from (3.3) and (3.4) by substituting (2.8) in lieu of $g^{ik}(\omega^2, x_n)$ and $g(\omega^2, x_n)$, satisfactorily describe the effect and, in particular, its anisotropy (we exclude "anomalous" cases similar to that considered in[18]). In cubic crystals they coincide with those customarily used (see[19]).

3. In connection with the results obtained in Sec. 3, we call attention to the following circumstance. In the case of two-component superstructures AB_{r-1}, and particularly in the case of impurity atoms ($r \gg 1$), when the atoms A and B differ greatly in mass, the vibration spectrum of the atoms *A*, as shown in[2,5] (see also[3,4,6]) has a resonant character with a maximum at the frequencies $\omega^2 \approx \langle \omega_A^{-2} \rangle^{(\alpha)-1}$ when $M_A \gg M_B$, and $\omega^2 \approx \langle \omega_A^2 \rangle^{(\alpha)}$ when $M_A \ll M_B$ (a = A, B). The approximate formulas obtained in this case for the Mossbauer effect (see, e.g., (26), (27), and (37) in[16]) are frequently interpreted entirely in terms of the effective "Debye frequencies" $\Omega_{0A}^{(\alpha)} = \Omega_{0B}^{(\alpha)} \sqrt{M_B/M_A}$ (see (2.23) and also[20]). Such an interpretation is quite arbitrary, however, even regardless of model assumptions (of the type (2.20)). The indicated formulas have an "Einstein" form and describe correctly the temperature variation of the effect only at sufficiently high temperatures ($T \gtrsim \hbar\Omega_{0A}$). At low temperatures they give the magnitude of the effect only accurate to temperature-dependent terms (which fortunately are small). The dependence of the effect on the temperature is described correctly by the general formulas (3.8)—(3.10) (i.e., in terms of the effective "Debye frequencies" $\Omega_A^{(\alpha)} = (M_B/M_A)^{1/3} \Omega_{0B}^{(\alpha)}$, see (2.13)), where now Z_{0A} and $\delta E'_{0A}$ (n is replaced by A) can be estimated with allowance for the resonant character of the spectrum, as was done in[2-4,16,17].

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[1] A. Maradudin, E. Montroll, and J. Weiss, Solid State Physics (F. Seitz and F. Turnbull, eds), Suppl. 3, Academic Press.

[2] Yu. Kagan and Ya. A. Iosilevskiĭ, Zh. Eksp. Teor. Fiz. 42, 259 (1962) [Sov. Phys.-JETP **15**, 182 (1962)].

[3] Yu. Kagan and Ya. A. Iosilevskiĭ, ibid. **44**, 284 (1963) [17, 195 (1963)].

[4] Ya. A. Iosilevskiĭ and Yu. Kagan, ibid. **46**, 2165 (1964) [19, 1462 (1964)].

[5] Ya. A. Iosilevskiĭ, Fiz. Tverd. Tela 8, 2025 (1966) [Sov. Phys.-Solid State 8, 1611 (1967)].

[6] Ya. A. Iosilevskiĭ, Zh. Eksp. Teor. Fiz. **51**, 201 (1966) [Sov. Phys.-JETP 24, 136 (1966)].

[7] Ya. A. Iosilevskiĭ, Fiz. Tverd, Tela 9, 2661 (1967) [Sov. Phsy.-Solid State 9, 2090 (1968)].

[8] M. A. Krivoglaz, Zh. Eksp. Teor. Fiz. **46**, 637 (1964) [Sov. Phys.-JETP 19, 432 (1964)].

[9] Yu. Kagan, ibid. 47, 366 (1964) [20, 243 (1964)].

[10] A. R. Bodmer, Nucl. Phys. **21**, 347 (1961).

[11] M. A. Krivoglaz, Zh. Eksp. Teor. Fiz. **41**, 765 (1961) [Sov. Phys.-JETP **14**, 552 (1962)].

[12] Ya. A. Iosilevskiĭ, Fiz. Tverd. Tela 8, 1314 (1966) [Sov. Phys.-Solid State 8, 1055 (1966)].

[13] B. D. Josephson, Phys. Rev. Lett. 4, 274 (1960).

[14] A. A. Maradudin and P. A. Flinn, Phys. Rev. 126, 2059 (1962).

[15] A. A. Maradudin, P. A. Flinn, and S. Ruby, ibid. **126**, 9 (1962).

[16] Ya. A. Iosilevskiĭ, Fiz. Tverd. Tela 8, 3032 (1966) [Sov. Phys.-Solid State 8, 2421 (1967)].

[17] Ya. A. Iosilevskiĭ, Phys. Stat. Sol. 16, 633 (1966).

[18] E. G. Brovman and Yu. Kagan, Fiz. Tverd. Tela 8, 1402 (1966) [Sov. Phys.-Solid State 8, 1120 (1966)].

[19] G. K. Wertheim, Mossbauer Effect, Academic Press, 1964.

[20] A. A. Maradudin, Sol. State Physics, ed. F. Seitz and D. Turnbull 18, Academic Press, 1966, p. 273.

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