THEORY OF THE TEMPERATURE RED SHIFT AND THE BROADENING OF THE MÖSSBAUER LINE

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The problem of the broadening of the Mössbauer line accompanying the temperature red shift is considered. The shape of the line is found and the value of the resulting width is determined in both ideal crystals and for cases where the radiating atom is an impurity. The restrictions on temperature in the case of supernarrow lines are examined. A relation is established between the probability of the effect when T = 0 and the temperature dependence of the Mössbauer line shift.

1. INTRODUCTION

IT is known that the change in the mass of the radiating atom in a crystal by the amount $\Delta m = E_\gamma/c^2$ results in a shift of the Mössbauer emission line toward lower frequencies, and that this shift is temperature dependent.[1,2] This phenomenon, first observed in iron,[1] was seen later by many experimenters on a variety of compounds. The question arises whether, together with the line shift, there is a broadening of the line, which naturally also depends on the temperature.

This problem was first treated in a paper of Snyder and Wick.[3] By relating the broadening to the fluctuation of the energy of the individual nucleus in the crystal, which the authors determined by taking the energy of the whole crystal per nucleus, Snyder and Wick concluded that in a regular crystal there will be no broadening on a macroscopic scale. Unfortunately their result is incorrect. Actually the temperature shift of the line is proportional to the average value of the operator $\hat{P}_0^2$ (where $\hat{P}_0$ is the momentum operator for the radiating nucleus). One can show directly that the fluctuation of this quantity in the crystal is large, with a dispersion

$$[\langle(\hat{P}_0^2)^2\rangle - (\langle\hat{P}_0^2\rangle)^2]^{1/2},$$

which is comparable in order of magnitude with $\langle\hat{P}_0^2\rangle$, and does not vanish even for T = 0. Thus we arrive at a statement which is diametrically opposite to that of Snyder and Wick.

But even having found the value of the dispersion over the whole temperature range, we still have not solved the problem. The reason for this is that in general it is incorrect to relate the line width with the statistical fluctuations of the corresponding quantities.

In Sec. 2 we give a general treatment of the problem, which makes it possible to obtain the line shape in a consistent fashion. A detailed analysis is given of the broadening of the Mössbauer line due to the change in mass of the nucleus resulting from radiation of the γ quantum, which in particular enables us to analyze what limits are imposed on the possible widths of supernarrow lines. Some of the results of this section have been given previously.[4]

In connection with the question treated here, we should call attention to the work of Silsbee,[5] who attempted an analysis of the problem of broadening using the relatively crude method of moments.

The problem of the line shift in an arbitrary crystal is treated in Sec. 3. It should be stated that in the papers of Pound and Rebka [1] and Josephson [2] the value of the shift was properly related to the crystal energy per atom, and the temperature derivative of the frequency to the specific heat. But this result is valid only for an ideal crystal. For polyatomic lattices and when the radiator is a foreign atom in a host lattice, the temperature red shift of the Mössbauer line already depends in a complicated way on the parameters of the crystal. This problem was treated for the whole temperature range in conference reports by the author.[4,6] Maradudin, and Flinn [7] independently analyzed the temperature shift in the classical domain. The results given in Sec. 3 coincide with those reported in [4,6].

In this same section we give the connection between the probability of the Mössbauer effect at T = 0 and the temperature shift of the line as a function of T for a radiating atom in an arbitrary crystal.[6] Thus it becomes possible to relate W(T = 0) to a quantity whose experimental determination has a purely resonant character.

2. BROADENING OF THE MÖSSBAUER LINE

Let us consider an arbitrary crystal, and suppose that the atom labelled 0 emits a γ quantum. We first assume that the natural line width is negligibly small. (Taking account of the finite width under the usual assumptions is trivial. Below we shall give the appropriate final formulas.) For the probability that a γ quantum of energy E is emitted in the decay, we have the usual expression

$$W(E) = \sum_{i,f} \rho_i |\langle f' | e^{i\mathbf{k}\mathbf{u}_0} | i \rangle|^2 \delta(E^0 + \varepsilon_i - \varepsilon_{f'} - E). \quad (2.1)$$

Here the subscripts i and f' denote eigenfunctions referring respectively to the Hamiltonian $\hat{H}$ of the crystal before the decay and $\hat{H}'$ after the decay:

$$\hat{H}' = \hat{H} + \hat{V}, \qquad \hat{V} = (E_\gamma/2m_0c^2)\hat{\mathbf{P}}_0{}^2/m_0; \quad (2.2)$$

ϵ_i and $\epsilon_{f'}$ are the crystal energies before and after emission of the γ quantum; E^0 is the energy of the nuclear level; $\mathbf{k}$ is the wave vector of the γ quantum; ρ is the density matrix corresponding to thermal equilibrium.

We go over to the time formalism. We then find for (2.1):

$$W(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, e^{i(E^0-E)t}$$

$$\times \sum_{i,f'} \rho_i \langle i | e^{i\hat{H}t} e^{-i\mathbf{k}\mathbf{u}_0} e^{-i\hat{H}'t} | f' \rangle \langle f' | e^{i\mathbf{k}\mathbf{u}_0} | i \rangle \quad (2.3)$$

(throughout, $\hbar = 1$). According to the well known transformations,

$$e^{-i\hat{H}'t} = e^{-i\hat{H}t - i\langle V \rangle t}\hat{S}(t), \qquad \hat{S}(t) = T \exp\left\{-\int_0^t \tilde{V}(t_1)\,dt_1\right\},$$

$$\tilde{V}(t) = e^{i\hat{H}t}(\hat{V} - \langle V \rangle)e^{-i\hat{H}t} \quad (2.4)$$

where we have used the notation

$$\langle A \rangle = \mathrm{Sp}(\hat{\rho}\hat{A}). \quad (2.5)$$

We make a unitary transformation from the eigenfunctions of the Hamiltonian H'(f') to the eigenfunctions of the Hamiltonian H(f). We then find

$$W(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, e^{i(E^0-E-\langle V \rangle)t}$$

$$\times \sum_{i,f} \rho_i \langle i | e^{-i\mathbf{k}\mathbf{u}_0(t)}\hat{S}(t) | f \rangle \langle f | e^{i\mathbf{k}\mathbf{u}_0(0)} | i \rangle$$

or

$$W(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, e^{i(E^0-E-\langle V \rangle)t} \mathrm{Sp}\{\hat{\rho}e^{-i\mathbf{k}\mathbf{u}_0(t)}\hat{S}(t)\,e^{i\mathbf{k}\mathbf{u}_0(0)}\}. \quad (2.6)$$

We are interested in the shape of the line at distances $E - (E^0 - \langle V \rangle)$ of the order of its

width, and consequently in the value of the integrand in (2.6) at large times t_0 of the order of the reciprocal width. We make the obvious assumption that the total width Γ_0 (including the natural width) is small compared with all the energy parameters of the phonon system. (Among such parameters are the characteristic frequency ω_0 of the spectrum, the width of narrow optical branches Δ_{opt}, and the widths of local levels Δ_d, in a crystal containing an isolated impurity atom, which arise from anharmonicity and concentration broadening.) Then the average of the product of operators in (2.6) which are separated by a time interval of order t_0 splits into a product of averages.

On the other hand, considering the negligible phase space corresponding to an energy interval of order Γ_0, we can keep only the diagonal elements under the trace in the expression

$$\mathrm{Sp}\,(\hat{\rho}e^{-i\mathbf{k}\mathbf{u}_0(t)}\hat{S}\,(t)). \quad (2.7)$$

But

$$\langle i | e^{-i\mathbf{k}\mathbf{u}_0(t)} | i \rangle = \langle i | e^{-i\mathbf{k}\mathbf{u}_0(0)} | i \rangle,$$

and for a time of order t_0, expression (2.7) in turn splits into a product of averages. The final expression for W(E) thus has the following form:

$$W(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(E^0-E-\langle V \rangle)t} |\langle e^{i\mathbf{k}\mathbf{u}_0} \rangle|^2 \langle S(t) \rangle \quad (2.8)$$

[cf. the notation (2.5)]. The factor

$$W^0 = |\langle e^{i\mathbf{k}\mathbf{u}_0} \rangle|^2 \quad (2.9)$$

is simply the probability for the Mössbauer effect, and this quantity is independent of the time. Thus the line shape is completely determined by $\langle S(t) \rangle$.

Let us express $\hat{V}$ in terms of normal coordinates. If in place of $\mathbf{u}_m{}^i$ (where m labels the atoms) we introduce

$$w^i_m = \sqrt{m_n}\,u^i_n$$

and make the standard unitary orthogonal transformation from the displacements of the individual atoms to the normal coordinates q_β:

$$q_\beta = \sum_n L^i(\beta, n)w_n{}^i, \qquad w_n{}^i = \sum_\beta L^i(\beta, n)q_\beta, \quad (2.10)$$

then

$$\frac{\partial}{\partial w_0{}^i} = \sum_\beta L^i(\beta, 0)\frac{\partial}{\partial q_\beta}, \qquad \hat{V} = \sum_{\beta,\beta_1} D_{\beta\beta_1}\hat{p}_\beta\hat{p}_{\beta_1}. \quad (2.11)$$

Here $\hat{p}_\beta$ is the momentum operator of the normal oscillator β and

$$D_{\beta\beta_1} = (E_\gamma/2m_0c^2)L^i(\beta, 0)L^i(\beta_1, 0). \quad (2.11')$$

In the harmonic approximation the line shift is then given by the following expression:

$$\langle V \rangle = \sum_\beta D_{\beta\beta} \, \omega_\beta \, (\bar{n}_\beta + {}^1/_2) \qquad (2.12)$$

(where $\bar{n}_\beta$ are the average values of the occupation numbers).

Now let us determine the quantity

$$\langle S(t) \rangle = \mathrm{Sp} \left\{ \rho T \exp \left[- \int_0^t \widetilde{V}(t_1) \, dt_1 \right] \right\}. \qquad (2.13)$$

At first we leave out of consideration those cases where there are local frequencies in the vibration spectrum. We expand the exponential in (2.13) in series. Using (2.4), the second term of the expansion vanishes. In the harmonic approximation the third term is

$$- \sum_{\beta_1, \, \beta_2, \, \beta_3, \, \beta_4} D_{\beta_1\beta_2} D_{\beta_3\beta_4} \int_0^t dt_1 \int_0^{t_1} dt_2$$

$$\times \langle (\hat{p}_{\beta_1}(t_1) \, \hat{p}_{\beta_2}(t_1) - \omega_{\beta_1}(\bar{n}_{\beta_1} + {}^1/_2) \delta_{\beta_1\beta_2}) (\hat{p}_{\beta_3}(t_2) \, \hat{p}_{\beta_4}(t_2)$$

$$- \omega_{\beta_3}(\bar{n}_{\beta_3} + {}^1/_2) \delta_{\beta_3\beta_4}) \rangle,$$

$$\hat{p}_\beta(t) = e^{i\hat{H}_\beta t} \hat{p}_\beta e^{-i\hat{H}_\beta t},$$

where $\hat{H}_\beta$ is the Hamiltonian for the normal oscillator β. Obviously in this expression the only nonzero terms are those in which the indices are equal in pairs. Only operators referring to different times should have their indices paired.

Remembering that the commutator

$$[\hat{p}_{\beta_1}(t_1) \, \hat{p}_{\beta_2}(t_2)] = 0, \qquad \beta_1 \neq \beta_2, \qquad (2.14)$$

we find, after integration, for values of t of the order of t_0,

$$2 \sum_{\beta, \gamma} \sum_{h=\pm 1, \, k=\pm 1} (D_{\beta\gamma})^2 \overline{|\langle n_\beta | \hat{p}_\beta | n_\beta + h \rangle|^2} \, \overline{|\langle n_\gamma | \hat{p}_\gamma | n_\gamma + k \rangle|^2}$$

$$\times [it/\Omega_{\beta\gamma}^{hk} - \pi |t| \delta (\Omega_{\beta\gamma}^{hk})]. \qquad (2.15)$$

Here we have introduced the notation

$$\Omega_{\beta\gamma}^{hk} = h\omega_\beta + k\omega_\gamma \qquad (2.16)$$

(where the bar denotes a temperature average of the occupation numbers). Let us consider the next even term in $\hat{V}$ in the expansion, which we write as

$$\frac{1}{4!} \sum_{\substack{\beta_1 \neq \beta_2, \, \beta_3 \neq \beta_4 \\ \beta_5 \neq \beta_6, \, \beta_7 \neq \beta_8}} D_{\beta_1\beta_2} D_{\beta_3\beta_4} D_{\beta_5\beta_6} D_{\beta_7\beta_8} T \int_0^t dt_1 \int_0^t dt_2 \int_0^t dt_3 \int_0^t dt_4$$

$$\times \langle \hat{p}_{\beta_1}(t_1) \, \hat{p}_{\beta_2}(t_1) \, \hat{p}_{\beta_3}(t_2) \, \hat{p}_{\beta_4}(t_2) \, \hat{p}_{\beta_5}(t_3) \, \hat{p}_{\beta_6}(t_3) \, \hat{p}_{\beta_7}(t_4) \, \hat{p}_{\beta_8}(t_4) \rangle.$$

$$(2.17)$$

First let us consider a pairing of indices such that each pair of indices at one time is paired off with the corresponding pair of indices at the other time. There are twelve of these. It is not difficult to show using (2.14) that we then get one half the

square of (2.15). Similarly, if we take the $(2m+1)$-st term in the expansion of the exponential in (2.13), choosing the terms with the same pairing of indices leads to an expression which is the m'th power of (2.15), divided by m!

If we analyze other pairings of indices in (2.17), we find that the corresponding terms increase with time no faster than the first power of t. But if we consider that each factor $D_{\beta_1\beta_2}$ contains the small parameter E_γ/m_0c^2, it is clear that these terms give a negligible correction to (2.15) and can be dropped. A completely similar situation exists for the odd terms of any order. Thus in the $(2m+1)$-st term of the expansion, after selecting the terms with pairing described above, the remaining terms increase with time no faster than $m-1$ and are actually small corrections to the terms of lower order. It is easily shown that the even terms (odd in $\hat{V}$) in the expansion of the exponential in (2.13) of order 2m increase with time no faster than t^{m-1}, but contain the factor $(E_\gamma/m_0c^2)^{2m-1}$. They can also be neglected, remembering that the main terms in the $(2m-1)$-st term of the expansion are proportional to $t^{m-1} \times (E_\gamma/m_0c^2)^{2m-2}$.

It is not difficult to show that the sum of the remaining terms gives the following expression.

$$\langle S(t) \rangle = \exp \{ -{}^1/_2 \Gamma_1 |t| + iV_1 t \}, \qquad (2.18)$$

where (cf. (2.15))

$$\Gamma_1 = \pi \sum_{\beta, \gamma} \sum_{h=\pm 1, \, k=\pm 1} (D_{\beta\gamma})^2 \, \omega_\beta \omega_\gamma (\bar{n}_\beta + {}^1/_2 + {}^1/_2 h)$$

$$\times (\bar{n}_\gamma + {}^1/_2 + {}^1/_2 k) \, \delta (\Omega_{\beta\gamma}^{hk}), \qquad (2.19)$$

while V_1 is gotten from (2.19) by replacing $\delta (\Omega_{\beta\gamma}^{hk})$ by $1/\pi\Omega_{\beta\gamma}^{hk}$. The final expression for $W(E)$ starting from (2.8) is

$$W(E) = W^0 \frac{(\Gamma + \Gamma_1)}{2\pi [(E^0 - E - \langle V \rangle + V_1)^2 + (\Gamma + \Gamma_1)^2/4]}.$$

$$(2.20)$$

We have given this relation in the form which would be gotten if the natural width Γ were taken into account right from the start. The quantity V_1 in (2.20) determines a small correction of order E_γ/m_0c^2 to the Mössbauer line shift (2.12), while Γ_1 is the resulting line width. This last is obviously the quantity of principal interest.

First we consider an ideal crystal lattice and assume that the j-th atom in the unit cell emits a γ quantum. Then in accordance with (2.11'), (2.10) and, for example,[8], we have

$$\Gamma_{1j} = 2\pi \left(\frac{E_\gamma}{2m_j c^2} \right)^2 \frac{V_0^2}{(2\pi)^6} \sum_{\alpha, \, \alpha'} \int \int d^3f \, d^3f' \, v_j^i$$

$$\times (\mathbf{f},\,\alpha)\,v_j{}^{k*}(\mathbf{f},\,\alpha)\,v_j{}^i(\mathbf{f}',\,\alpha')\,v_j{}^{k*}(\mathbf{f}'\alpha')\,\omega(\mathbf{f},\,\alpha)\,\omega(\mathbf{f}',\,\alpha')$$

$$\times [\bar{n}(\mathbf{f}',\,\alpha')+1]\,\bar{n}(\mathbf{f}',\,\alpha')\,\delta[\omega(\mathbf{f},\,\alpha)--\omega(\mathbf{f}',\,\alpha')]. \quad (2.21)$$

Here V_0 is the volume of the unit cell; $v_j^i(\mathbf{f},\,\alpha)$ are the complex polarization vectors corresponding to the wave vector $\mathbf{f}$ and branch number α; they satisfy the following orthonormality condition:

$$\sum_\alpha v_j{}^i(\mathbf{f},\,\alpha)\,v_{j'}{}^{k*}(\mathbf{f},\,\alpha)=\delta^{ik}\delta_{jj'}. \quad (2.21')$$

Let us assume for simplicity that the position of the j-th atom is one of cubic symmetry. Then introducing the normalized function

$$\Psi_j(\omega)=\frac{1}{3}\frac{v_0}{(2\pi)^3}\sum_\alpha \int \frac{|\mathbf{v}_j(\mathbf{f},\,\alpha)|^2}{|\nabla\omega(\mathbf{f},\,\alpha)|}\,dS_\omega \quad (2.22)$$

(where the integration is taken over a surface of constant energy), we find

$$\Gamma_{1j}=6\pi\left(\frac{E_\gamma}{2m_jc^2}\right)^2\int d\omega\,\Psi_j{}^2(\omega)\,\omega^2\bar{n}(\omega)\,[\bar{n}(\omega)+1]. \quad (2.23)$$

From (2.21) and (2.23) it follows that the temperature red shift in an ideal crystal is accompanied by a finite broadening. This broadening is always small compared to the shift (2.12), since (2.21) or (2.23) contains the square of the small parameter E_γ/m_0c^2. But Γ_{1j} is not related to the value of Γ. Thus the ratio of these quantities is arbitrary, and this is what determines the change in the probability for the Mössbauer effect.

Let us estimate the quantity Γ_{ij} (2.23). For $T\to 0$, we have $\Gamma_{ij}\to 0$, where it is easy to see that for $T\ll\omega_{max}$,

$$\Gamma_{1j}\sim T^7. \quad (2.24)$$

In the classical limit, for $T\gtrsim\omega_{max}$

$$\Gamma_{1j}\sim T^2. \quad (2.24')$$

First we consider a monatomic lattice and use the Debye approximation. Then in the classical limit

$$\Gamma_1=\frac{54}{5}\pi\left(\frac{E_\gamma}{2mc^2}\right)^2\frac{T}{\Theta}\,T \quad (2.25)$$

(where we have used energy units for the temperature). To evaluate (2.25) we take as an example the case of Ag^{107} ($E_\gamma=93.5$ keV, $\Gamma\approx 10^{-17}$ eV). At room temperature

$$\Gamma_1\sim 10^{-13}\text{ eV}. \quad (2.25')$$

Consequently the resulting width is 10^4 times as large as the natural width of the nuclear line! Thus we see that even in the usual case of a regular lattice the temperature broadening of the line imposes sharp restrictions on the value of the temperature at which one can observe the Möss-

bauer effect for very narrow lines. This is of fundamental importance for all experiments on nuclei having such narrow lines, in particular for experiments of the type recently carried out by Bizina, Beda, Burgov, and Davydov [9] (using the isotope Ag^{107}).

We note that because of the large coefficient appearing in the expression for the low temperature limit,

$$\Gamma_1=\frac{288\pi^7}{7}\left(\frac{E_\gamma}{2mc^2}\right)^2\left(\frac{T}{\Theta}\right)^6 T, \quad (2.26)$$

the critical temperature is shifted to quite low values, even though $\Gamma_1\sim T^7$.

Now let us consider a crystal with optical branches. If the widths of the optical branches are of the same order as the acoustical branch widths, all the results are qualitatively unchanged. If however the spectrum of vibrations contains a narrow optical band with a characteristic width Δ_{opt} and if the radiating atom preferentially oscillates at these optical frequencies, i.e., if the values of $|\mathbf{v}_j(\mathbf{f},\,\alpha)|^2$ for the corresponding values of α are large in the integrand of (2.22), the situation is essentially changed. (Under these conditions, as a rule the probability for the Mössbauer effect is quite large; for more details cf. [10,11].) In fact, taking account of the normalization of the function $\Psi_j(\omega)$ (2.22), we find for the classical limit, from (2.23),

$$\Gamma_{1j}\approx 6\pi\beta\left(\frac{E_\gamma}{2m_jc^2}\right)^2\frac{T}{\Delta_{opt}}\,T \quad (2.27)$$

(where β is a numerical coefficient of order unity).

Thus the broadening is increased by a factor Θ/Δ_{opt}. We note that at low temperatures, Γ_{1j} will behave similarly to (2.26), but with a much smaller numerical coefficient.

We now proceed to treat the case where the crystal spectrum contains local frequencies, and we shall assume as before that while the width Δ_γ of these levels is small, nevertheless $\Delta_\gamma\gg\Gamma$. We shall then have to go to formula (2.13) and analyze the whole transition from (2.13) to (2.18) and (2.19), now taking account of the local levels.

The finite width of the local levels enables us to perform an integration over all transitions to which there correspond different values of the energy within Δ_γ, and in this sense we have a situation similar to a band in the quasicontinuous spectrum. On the other hand, the total probability for emission or absorption of a quantum of the vibration ω_γ, corresponding to a local frequency,

has the same value when $\Delta_\gamma/\omega_\gamma \ll 1$ as in the case of zero width.

Taking these remarks into account and assuming a Lorentz shape (with half-width equal to Δ_γ) for the spectral density over the region of smearing of the local level, we easily find the contribution to (2.15) because of the presence of the local frequencies in the spectrum (we give only the real part):

$$- 2|t| \sum_\gamma{}' \frac{(D_{\gamma\gamma})^2}{\Delta_\gamma} \overline{|\langle n_\gamma | \hat{p}_\gamma | n_\gamma + 1 \rangle|^2} \, \overline{|\langle n_\gamma | \hat{p}_\gamma | n_\gamma - 1 \rangle|^2} \tag{2.15'}$$

(where we sum over local frequencies). All the other arguments remain valid, and we arrive at (2.18) and (2.20), but we have to add to Γ_1 in (2.19) the term

$$\Gamma_{1d} = \sum_\gamma{}' \frac{(D_{\gamma\gamma})^2}{\Delta_\gamma} \omega_\gamma{}^2 (\bar{n}_\gamma + 1) \bar{n}_\gamma. \tag{2.28}$$

We consider an arbitrary crystal with isolated impurity atoms and assume, as usual, that the change in the force constants is negligible. Suppose an impurity atom of mass m_0 replaces the t-th atom of the unit cell. Then using the results of [12-14] one can find the explicit expression for $D_{\beta\beta}$ in (2.11):

$$D_{\beta\beta_1} = \frac{E_\gamma}{2m_0c^2} \mathbf{j}_\beta \mathbf{j}_{\beta_1} (1 - \varepsilon_t) \left(\frac{d \ln \omega_\beta{}^2}{d\varepsilon_t} \right)^{1/2} \left(\frac{d \ln \omega_\beta{}^2}{d\varepsilon_t} \right)^{1/2}, \tag{2.29}$$

where $\epsilon_t = 1 - m_0/m_t$ (the notation is the same as in [10-12]).

Suppose first that the mass of the impurity atom is greater than the mass of the atoms of the host lattice, i.e., $\epsilon_t < 0$, and consequently there are no free local frequencies. We restrict our treatment to crystals whose symmetry is no lower than rhombic. Then the unit vectors $\mathbf{j}_\beta$ will be along the principal axes of the crystal. We use the explicit form of $d \ln \omega_\beta^2/d\epsilon_t$ to determine (2.29). Then changing from summation to integration in (2.19) (cf. [12-14]), we find

$$\Gamma_1 = 4\pi \left(\frac{E_\gamma}{2m_0c^2} \right)^2 \sum_{\sigma=x,\,y,\,z}$$
$$\times \int_0^{\omega_0{}^2{}_{max}} d\omega^2 \cdot \omega^3 (G_t{}^{(\sigma)}(\omega^2))^2 [\bar{n}(\omega) + 1] \bar{n}(\omega). \tag{2.30}$$

Here the function

$$G_t{}^{(\sigma)}(\omega^2) = (1 - \varepsilon_t) g_t{}^{(\sigma)}(\omega^2)$$
$$\times \left\{ \left[1 - \varepsilon_t \int_0^{\omega_0{}^2{}_{max}} \frac{g_t{}^{(\sigma)}(\omega_0{}^2) \, d\omega_0{}^2}{\omega^2 - \omega_0{}^2} \right]^2 + [\pi\varepsilon_t\omega^2 g_t{}^{(\sigma)}(\omega^2)]^2 \right\}^{-1} \tag{2.31}$$

is normalized by the condition

$$\int_0^\infty G_t{}^{(\sigma)}(\omega^2) \, d\omega^2 = 1, \tag{2.31'}$$

$$g_t{}^{(\sigma)}(\omega^2) = \frac{v_0}{(2\pi)^3} \sum_\alpha \int \frac{|v_t{}^\sigma(\mathbf{f}, \alpha)|^2}{|\nabla\omega_0{}^2(\mathbf{f}, \alpha)|} \, dS_\omega. \tag{2.32}$$

If m_0 is not very different from m_t, the behavior of (2.30) is quite similar to the case of the regular crystal. But the picture changes drastically if $m_0 \gg m$. It is known [12-15] that in this case the spectral density of the square displacement of the impurity atom in a given direction, which is given by the function $G_t{}^{(\sigma)}(\omega^2)$ of (2.31), has a marked resonance character and is localized near the frequencies

$$\omega_{*\sigma} = |\varepsilon_t|^{-1/2} (\langle \omega^{-2}\rangle_t{}^{(\sigma)})^{-1/2} \ll \omega_{max} \tag{2.33}$$

[where $\langle \ldots \rangle_t{}^{(\sigma)}$ denotes averaging with the function (2.32)]. This enables us to integrate (2.30) explicitly. The result is

$$\Gamma_1 \cong 2 \left(\frac{E_\gamma}{2m_0c^2} \right)^2 \sum_\sigma \frac{\omega_0{}^3{}_{max}}{\pi d_t{}^{(\sigma)}} \langle \omega^{-2}\rangle_t{}^{(\sigma)} [\bar{n}(\omega_{*\sigma}) + 1] \bar{n}(\omega_{*\sigma}), \tag{2.34}$$

(where $d_t{}^{(\sigma)}$ is the numerical coefficient in the low frequency expansion

$$g_t{}^{(\sigma)}(\omega^2) = d_t{}^{(\sigma)} \sqrt{\omega^2}/\omega_0{}^3{}_{max};$$

Equation (2.34) is valid for all temperatures except the narrow range $T \ll \omega_{*\sigma}$). The expression (2.34) already has a value corresponding to the classical limit even at relatively low temperatures $T \gtrsim \omega_{*\sigma}$. For a cubic, monatomic crystal, using the Debye approximation for the phonon spectrum of the host, we get

$$\Gamma_1 \cong \frac{36}{\pi} |\varepsilon| \left(\frac{E_\gamma}{2m_0c^2} \right)^2 \frac{T}{\Theta} T. \tag{2.35}$$

Let us compare this result with the one for a regular lattice (2.25). If we are dealing with the same Mössbauer nucleus, it is easy to see that when $|\epsilon| \gg 1$ (2.35) may be much greater than (2.25), and that in the impurity case Γ_1 increases steadily with increasing m_0/m_t. We should make a special note that the transition to the dependence (2.35) occurs at temperatures $T \ll \Theta$, and the region where the temperature dependence of (2.24) is valid is shifted quite markedly toward low temperatures. Thus both the value of Γ_1 and the temperature behavior may differ markedly in the case of a heavy impurity atom from their appearance in the case of a regular lattice.

Suppose now that $\epsilon_t > 0$. As is well known, there may be discrete frequencies in the perturbed vibration spectrum when $m_0 < m_t$. In this case Γ_1 is given as before by (2.30), but we must now add to this expression the quantity Γ_{1d} of (2.28) with the values $D_{\gamma\gamma}$ of (2.29), determined for the local levels. Using the results of [12-14],

we find immediately

$$\Gamma_{1d} = \left(\frac{E_\gamma}{2m_0 c^2}\right)^2 (1 - \varepsilon_t) \sum_\nu \left(\frac{d \ln \omega_{d\nu}^2}{d\varepsilon_t}\right)^2 \frac{\omega_{d\nu}^2}{\Delta_\nu}$$

$$\times [\bar{n}(\omega_{d\nu}) + 1] \bar{n}(\omega_{d\nu}), \qquad (2.36)$$

$$\frac{d \ln \omega_{d\nu}^2}{d\varepsilon_t} = \left\{\varepsilon_t^2 \omega_{d\nu}^4 \int_0^{\omega_{0max}^2} \frac{g_t^{(\sigma)}(\omega_0^2) d\omega_0^2}{(\omega_{d\nu}^2 - \omega_0^2)^2} - \varepsilon_t\right\}^{-1}. \qquad (2.36')$$

Here $\omega_{d\nu}^2$ are the values of the discrete frequencies which are the solutions of the equations

$$1 - \varepsilon_t \omega^2 \int_0^{\omega_{0max}^2} \frac{g_t^{(\sigma)}(\omega_0^2) d\omega_0^2}{\omega^2 - \omega_0^2} = 1 \qquad (2.36'')$$

for the three values of σ.

Consider the limiting value of (2.36) when $m_0 \ll m_t$. For simplicity we limit ourselves to the case of a monatomic lattice with cubic symmetry. Then (2.36) becomes much simpler:

$$\Gamma_{1d} \cong 3 \left(\frac{E_\gamma}{2m_0 c^2}\right)^2 \frac{\omega_d^2}{\Delta} [\bar{n}(\omega_d) + 1] \bar{n}(\omega_d). \qquad (2.37)$$

In the classical limit

$$\Gamma_{1d} \cong 3 \left(\frac{E_\gamma}{2m_0 c^2}\right)^2 \frac{T}{\Delta} T. \qquad (2.37')$$

From these results it follows that Γ_{1d} contains Δ in the denominator, and not ω_d or ω_{0max}, and therefore the broadening in this case may be much greater than Γ_1 for a regular lattice. Available estimates for the width of local levels make it reasonable to assume that Γ_{1d} may exceed (2.23) by a factor $10 - 10^2$. If we recall the estimate (2.25'), it follows that such a broadening approaches the natural width of lines like that in Zn^{67}.

We note, in conclusion, that our results contradict those of Snyder and Wick[3] and Silsbee,[5] who did not take into account the finite width of the discrete levels, which is practically always many times greater than the natural width of the Mössbauer line.

3. TEMPERATURE RED SHIFT OF THE MÖSSBAUER LINE

A. The shift of the Mössbauer line in first order in the parameter $E_\gamma/m_0 c^2$ is given by (2.12). The magnitude of the shift at low temperatures depends strongly on the nature of the system, but this dependence disappears completely at high temperatures. Thus when $T > \omega_{max}$ (cf. (2.11'))

$$\langle V \rangle = \frac{E_\gamma T}{2m_0 c^2} \sum_\beta L^i(\beta, 0) L^i(\beta, 0) = \frac{E_\gamma}{2m_0 c^2} 3T. \qquad (3.1)$$

[The last equality is a consequence of the orthogonality of the transformation (2.10).] The result of (3.1) is well known (cf., for example, [7]), and requires no special discussion. But we will be principally interested in the value of the shift of the Mössbauer line at low temperatures.

Let us first consider a regular crystal with an arbitrary unit cell, and assume the radiator is the j-th atom in the cell. Then using the appropriate value for $L^i(\beta, 0)$ in (2.11'), we find

$$\langle V_j \rangle = \frac{E_\gamma}{2m_j c^2} \frac{v_0}{(2\pi)^3} \sum_\alpha \int |\mathbf{v}_j(\mathbf{f}, \alpha)|^2 \omega(\mathbf{f}, \alpha)$$

$$\times \left[\bar{n}(\mathbf{f}, \alpha) + \frac{1}{2}\right] d^3 f. \qquad (3.2)$$

From (2.21') we easily get the following relation:

$$\frac{1}{3} \frac{v_0}{(2\pi)^3} \int |\mathbf{v}_j(\mathbf{f}, \alpha)|^2 d^3 f = 1.$$

It then follows from (3.2) that when $T = 0$ the shift is given by the average over phase space and the frequency branches of the frequency $\omega(\mathbf{f}, \alpha)$, where the probability density is the quantity $\frac{1}{3} |\mathbf{v}_j(\mathbf{f}, \alpha)|^2$. Thus the greater the relative value of the amplitudes of oscillation in the high lying optical branches in the main part of the phase space, the greater the shift. In particular we can state that if we compare a monatomic and a polyatomic crystal with similar characteristic acoustic frequencies and the same radiator, the shift of the Mössbauer line in the polyatomic crystal will always be the larger.

The temperature dependence of the shift in the transition region is also fundamentally related to the character of the vibration of the j-th atom. If this atom vibrates preferentially in the acoustic branches, the characteristic temperature for the transition to the classical limit (3.1), as in the case of a monatomic crystal, is close to the Debye temperature Θ. But if the high lying optical branches play an important part in the vibrations of the j-th atom, the increase of the shift with temperature is slowed down markedly, and the transition to the limit (3.1) occurs at much higher temperatures.

It should be mentioned that the anomalous behavior of the probability for the Mössbauer effect in crystals having optical branches [10] and the peculiarities in the temperature shift which were mentioned above have, of course, a common origin. Thus in all cases where, because of the optical branches, there is a large probability for the Mössbauer effect which decreases anomalously slowly with temperature, there will simultaneously be a large shift when $T = 0$ and a noticeably

gradual transition with temperature to the classical limit.

The presence of the polarization vectors in the integrand in (3.8) has the consequence that in a polyatomic crystal, in contrast to the monatomic case, [1,2] the temperature shift and the lattice energy per unit volume (the derivative of the shift with respect to temperature and the specific heat) are no longer uniquely related to one another. This relation is reestablished for trivial reasons only in the classical limit.

B. We shall now determine the temperature shift for isolated impurity atoms, replacing the t-th atom of the unit cell in an arbitrary crystal, assuming that the force constants remain unchanged. Then taking account of (2.12), (2.11'), and (2.29) and making the usual change from summation to integration, we find

$$\langle V \rangle = \frac{E_\gamma}{2m_0c^2}(1 - \epsilon_t) \sum_\beta \frac{d \ln \omega_\beta{}^2}{d\epsilon_t} \omega_\beta \left(\bar{n}_\beta + \frac{1}{2} \right)$$

$$= \frac{E_\gamma}{2m_0c^2} \sum_{\sigma=x,\,y,\,z} \int_0^\infty d\omega^2 G_t^{(\sigma)}(\omega^2) \omega \left[\bar{n}(\omega) + \frac{1}{2} \right]. \quad (3.3)$$

The functions $G_t^{(\sigma)}(\omega^2)$ are defined in accordance with (2.31).

The extension of the integration in (3.3) to infinity enables one to include discrete levels automatically. This is easily seen by considering that the discrete levels are the roots of Eq. (2.36") and appear in the frequency region where $g_t^{(\sigma)}(\omega^2) = 0$.

The value of the shift (3.3) is obviously completely determined by the functions $G_t^{(\sigma)}(\omega^2)$. The behavior of these functions is treated in detail in [12-14], so we shall limit ourselves to some brief remarks.

Suppose $m_0 > m_t$. Then the spectral density for the square amplitude of the impurity atom, $G_t^{(\sigma)}(\omega^2)$, is shifted toward low frequencies compared to $g_t^{(\sigma)}(\omega^2)$. As a result there is a reduction in the shift for T = 0 and a more rapid transition to the classical limit compared to the corresponding value for the t-th atom in the ideal lattice. In the limiting case of a very heavy impurity atom, when $| \epsilon_t | \gg 1$, the sharp localization of $G_t^{(\sigma)}(\omega^2)$ in the narrow frequency range (2.33) enables us to integrate (3.3) explicitly

$$\langle V \rangle = \frac{E_\gamma}{2m_0c^2} \sum_\sigma \frac{\omega_{*\sigma}}{2} \operatorname{cth} \frac{\omega_{*\sigma}}{2T}. \quad (3.4)*$$

The transition to the classical limit now already occurs at low frequencies $T \gtrsim \omega_{*\sigma}$.

*cth = coth.

When $m_0 < m_t$ the spectral density $G_t^{(\sigma)}(\omega^2)$ is shifted toward higher frequencies compared to $g_t^{(\sigma)}(\omega^2)$, and with the appearance of local frequencies above ω_{max} there is a partial shift of the spectral density to these frequencies. Then the amount of the temperature shift is increased relative to the regular lattice, and the transition to the classical limit is displaced toward higher temperatures.

We give the limiting value corresponding to the case where $1 - \epsilon_t \ll 1$:

$$\langle V \rangle = \frac{E_\gamma}{2m_0c^2} \sum_{\nu=1}^3 \frac{\omega_{d\nu}}{2} \operatorname{cth} \frac{\omega_{d\nu}}{2T}, \quad (3.5)$$

where $\omega_{d\nu}$ is the solution of Eq. (2.36"). Formula (3.5) demonstrates the large value of the shift and the slow increase with temperature. The transition to the classical limit occurs at temperatures determined by the frequencies of the local levels.

C. There is an interesting relation between the temperature shift of the line and the probability W of the Mössbauer effect at T = 0. The general expression for W has the form

$$W = e^{-z}, \quad (3.6)$$

where, in accordance with the definition (2.10),

$$Z = R_0 \sum_\beta \frac{(\mathbf{q}\mathbf{L}(\beta, 0))^2}{\omega_\beta} [2\bar{n}_\beta + 1]. \quad (3.6')$$

Here $\mathbf{q}$ is a unit vector along the direction of emergence of the γ quantum; $R_0 = E_\gamma^2/2m_0c^2$.

We introduce the quantity $\bar{Z}$, the average of (3.6') over three mutually perpendicular directions for the vector $\mathbf{q}$:

$$\bar{Z} = \frac{R_0}{3} \sum_\beta \frac{(\mathbf{L}(\beta, 0))^2}{\omega_\beta} [2\bar{n}_\beta + 1]. \quad (3.7)$$

There is a general relation between $\bar{Z}(T = 0)$ and $\langle V \rangle$ which is valid for Mössbauer nuclei in any regular or irregular harmonic lattice. It is easy to show directly that

$$\bar{Z}(T = 0) = \frac{4}{\pi^2} E_\gamma \int_0^\infty [\langle V \rangle_T - \langle V \rangle_{T=0}] \frac{dT}{T^3}. \quad (3.8)$$

We note that the integrand behaves like $1/T^2$ at high temperatures and like T at low temperatures, so that there are no basic difficulties in performing the integration.

The quantity $\bar{Z}(T = 0)$ is directly related to the probability of the Mössbauer effect. In the case of a cubic crystal, $\bar{Z}$ is simply equal to Z. In an anisotropic crystal, if, as is often the case, $Z(T = 0)$ is small compared to unity, it is easy to show that in a polycrystalline sample

$$W(T = 0) = \exp\{-\bar{Z}(T = 0)\}.$$

In the general case, in an anisotropic single crystal $\overline{Z}$ is related only to the average value of ln W, determined for three mutually perpendicular directions of emergence of the γ quantum.

We emphasize the interesting point that (3.8) actually relates the probability for the Mössbauer effect to the temperature red shift, which is a resonantly determined quantity.

[1] R. V. Pound and G. A. Rebka, Phys. Rev. Letters 4, 274 (1960).

[2] B. D. Josephson, Phys. Rev. Letters, 4, 341 (1960).

[3] H. S. Snyder and G. C. Wick, Phys. Rev. 120, 128 (1960).

[4] Yu. Kagan, Report to the All-Union Conference on Low Temperature Physics, Leningrad, June, 1962); cf. UFN 80, 331 (1963), Soviet Phys. Uspekhi 6, 459 (1963).

[5] R. H. Silsbee, Phys. Rev. 128, 1726 (1962).

[6] Yu. Kagan, Report to the Conference on the Mössbauer Effect, Dubna, July, 1962 (cf. preprint JINR p-1231, p. 112).

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

[8] Yu. Kagan, JETP 40, 312 (1961), Soviet Phys. JETP 13, 211 (1961).

[9] Bizina, Beda, Burgov and Davydov, JETP 45, 1408 (1963), Soviet Phys. JETP 18, 973 (1964).

[10] Yu. Kagan, JETP 41, 659 (1961), Soviet Phys. JETP 14, 472 (1962).

[11] Yu. Kagan and V. A. Maslov, JETP 41, 1296 (1961), Soviet Phys. JETP 14, 922 (1962).

[12] Yu. Kagan and Ya. A. Iosilevskiĭ, JETP 42, 259 (1962), Soviet Phys. JETP 15, 182 (1962).

[13] Yu. Kagan and Ya. A. Iosilevskiĭ, JETP 44, 284 (1963), Soviet Phys. JETP 17, 195 (1963).

[14] Ya. A. Iosilevskiĭ and Yu. Kagan, JETP 46, 2165 (1964), Soviet Phys. JETP 19, 1462 (1964).

[15] R. Brout and W. Visscher, Phys. Rev. Letters 9, 54 (1962).