Broadening of the Mössbauer Line*

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The thermal excitation of the solid which leads to a temperature-dependent shift of the Mössbauer line could conceivably cause a broadening of this line. We show here through a quantum-mechanical treatment, that for a perfect crystalline solid such a broadening does not occur.

IT has been pointed out[1,2] that the energy of recoil-free γ rays emitted or absorbed by solids (Mössbauer line) is subject to a small temperature-dependent shift to lower energy, which has been described as a second-order Doppler effect[1] or alternatively[2] as a result of the small change in the vibrational energy of the lattice system, which must accompany the emission of the γ ray, owing to the decrease in mass $\delta M = E_\gamma/c^2$ of the emitting nucleus.

Our purpose here is to discuss some finer points connected with this effect, namely the existence or nonexistence of a minute broadening of the Mössbauer line, associated with the mechanism which produces the temperature shift.

From a classical point of view, one is tempted to discuss the problem as an ordinary frequency-modulation effect, corresponding to the assumption that at any time t the wave emitted by the nucleus has an instantaneous circular frequency

$$\omega(t) = \omega - \tfrac{1}{2}\omega v^2(t) c^{-2}, \tag{1}$$

where $v(t)$ is the instantaneous velocity of the nucleus.[3] It is then convenient to separate the small frequency-modulating term into a constant part, and a variable part whose time average is zero. The integrated phase of the emitted wave is then of the form

$$\int^t \omega(t')dt' = \omega t - \tfrac{1}{2}\omega t\langle v^2/c^2\rangle + \phi(t), \tag{1'}$$

where $\langle\cdots\rangle$ represents a time average and $\phi(t)$ is a rapidly variable term which remains finite as $t \to +\infty$ or at least increases more slowly than t. If we neglect $\phi(t)$, we get of course a sharp line, which exhibits a small Doppler shift relative to ω, corresponding to the expectation value of v^2. The existence of $\phi(t)$ leads in principle to a broadening of the line; the structure and width of the ensuing spectrum could be treated by the familiar stochastic methods, which have been applied to other linewidth problems[4]; qualitatively it is easy to conclude in this way that the broadening due to $\phi(t)$ is exceedingly small.

The only objection we have to this treatment is that it makes use of classical approximations and statistical assumptions, which are wholly unnecessary in the present case (in the more complicated cases of paramagnetic and nuclear resonance, on the other hand, they may well be unavoidable).

We prefer therefore to follow a straightforward quantum-mechanical treatment, along lines somewhat similar to Josephson's. By definition recoil-free γ emission is a transition in which none of the quantum numbers $n_1, n_2, n_3, \cdots n_s, \cdots$ of the various oscillating modes of the crystal changes; the energy of the lattice

$$E_n \equiv \textstyle\sum_s \hbar\omega_s(n_s+\frac{1}{2}), \tag{2}$$

will change slightly, however, because of the slight increase $\delta\omega_s$ in the frequencies ω_s produced by the decrease in mass δM of the emitting nucleus. An increase of E_n after the emission of the γ ray, must appear, by energy conservation, as a decrease in the energy of the γ ray. These frequency changes $\delta\omega_s$ are analogous to the impurity and isotope effects, which have been studied by various authors.[5] In general, the changes $\delta\omega_s$ are small of the order $1/N$, if N is the number of atoms in the crystal. The exceptions to this statement will be mentioned later; at any rate they are of rather academic interest. Furthermore, since the relative mass change $\delta M/M$ is extremely small, the changes are linear in δM. Let us write therefore

$$\delta\omega_s = (1/N)(\delta M/M) f_s, \tag{3}$$

$$\delta E_n = \frac{\delta M}{M} \sum_s (1/N)\hbar f_s(n_s+\tfrac{1}{2}), \tag{3'}$$

where the quantities f_s remain finite when $N \to \infty$.

Equation (3') determines δE_n when the quantum numbers $n_1, n_2, \cdots$ are given. In the actual case, of course, the state of the system is only determined macroscopically, i.e., only the total energy or the tem-

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[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] At this point we may point out as a curiosity that also the linear Doppler effect could be included in a similar way by means of a term $\omega v_{||}(t)/c$, where $v_{||}$ is the velocity component parallel to the direction of emission of the γ ray, and that such a treatment would, in fact, reproduce in a remarkable fashion the most outstanding features of the correct quantum mechanical treatment.

[4] See for example: P. W. Anderson and P. R. Weiss, Revs. Modern Phys. **25**, 269 (1953); P. W. Anderson, J. Phys. Soc. Japan **9**, 316 (1954); and also N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

[5] See for example: M. Lifshitz, Suppl. Nuovo cimento **3**, 716 (1956); E. W. Montroll and R. B. Potts, Phys. Rev. **100**, 525 (1955); **102**, 72 (1956).

perature T is given. Hence each term in (3′) may fluctuate widely. Nevertheless δE_n, being the sum of a large number ($3N$) of statistical variables (each term in the sum being small of order $1/N$), will fluctuate only in a negligible way. Thus we see that the Mössbauer line, as defined above, will remain completely sharp for all practical purposes.

Specifically, writing $\epsilon(\omega)=\exp(\hbar\omega/kT)$, $\epsilon_s=\epsilon(\omega_s)$, we have for the expectation value and fluctuation of n_s, respectively,

$$\langle n_s\rangle=[\epsilon_s-1]^{-1} \tag{4}$$
$$\langle n_s^2\rangle-\langle n_s\rangle^2=\epsilon_s[\epsilon_s-1]^{-2}.$$

If $g(\omega)$ is the frequency spectrum of the lattice we can write $\sum_s\cdots\rightarrow N\int g(\omega)d\omega\cdots$, $f_s\rightarrow f(\omega_s)$, and finally

$$\langle\delta E\rangle=\delta M\int d\omega\, g(\omega)\hbar f(\omega)[\epsilon\omega)-1]^{-1}, \tag{5}$$

$$\langle\delta E^2\rangle-\langle\delta E\rangle^2=\frac{1}{N}(\delta M)^2 \times\int d\omega\, g(\omega)\hbar^2 f^2(\omega)\epsilon(\omega)[\epsilon(\omega)-1]^{-2}. \tag{6}$$

The rms deviation of δE from the expectation value (5) is therefore of the order $N^{-\frac{1}{2}}$, i.e., negligible for a macroscopic crystal.

The connection between (3′) and the specific heat can be obtained as follows. Let us assume that the N nuclei in the lattice are identical and occupy equivalent positions. The change $\delta\omega_s$ will be independent of the particular nucleus to which the mass change δM is applied (we must, of course, neglect surface effects). If we were to apply the mass change δM to all nuclei simultaneously, the frequency change (to first order in δM) would then be N times as large. Inspection of the secular equation which determines ω_s shows that we must have

$$M\omega_s^2=(M-\delta M)(\omega_s+N\delta\omega_s)^2,$$
i.e.,
$$\delta\omega_s=+(1/2N)\omega_s\delta M/M \quad\text{or}\quad f_s=+\tfrac{1}{2}\omega_s. \tag{7}$$

We see that in this case the energy shift of the γ ray

$$\delta E_\gamma=-\delta E_n=-\tfrac{1}{2}(\delta M/M)N^{-1}E, \tag{8}$$

depends only on the total energy E of the crystal, or more precisely on the energy per atom E/N. E is of course given by $E_0+\int C_v dT$, where E_0 is the zero-point energy.[6]

It should be emphasized that the simple formula (8) only holds under the special assumption made above. If, for example, the lattice contains two different species of atoms, the derivative of ω_s with respect to the mass of one species cannot be computed so simply. A simple result may be still shown to obtain at high temperatures, when all degrees of freedom contribute fully to the specific heat, but this will not be demonstrated here as it is not of great interest.

[6] In the case when Eq. (8) holds, the fluctuation is obviously zero, if E is fixed.

ADDITIONAL REMARKS

We now turn our attention to some examples in which the fluctuation of the shift, i.e., the line broadening, does not vanish. These examples are probably not of great practical interest; they are mainly mentioned to show that the question is not entirely trivial and that some proof such as the one given above is necessary. Let us first notice that the conclusion that (6) is $O(N^{-1})$ is essentially dependent on the assumption that the contribution of every oscillation "mode" to the total energy of the lattice is distributed over the whole crystal. If there are "localized modes" the energy of which is shared amongst a few atoms only (amongst which is the emitting atom) the sum (3′) will contain, in general, a dominant term, not of order $1/N$, whose fluctuation will not be negligible.

An extreme example of such a situation is the Einstein model, where each atom in the crystal is such a localized mode. In this case (3′) consists of a single term,

$$\delta E=\tfrac{1}{2}(\delta M/M)\hbar\omega_1(n+\tfrac{3}{2}),$$

where ω_1 is the frequency of the Einstein oscillator and $n=n_x+n_y+n_z$ is the total oscillation quantum number of the three-dimensional oscillator. Application of (4) gives for the deviation of δE

$$\tfrac{1}{2}\sqrt{3}(\delta M/M)\hbar\omega_1\epsilon^{\frac{1}{2}}(\omega_1)[\epsilon(\omega_1)-1]^{-1},$$

which at high temperatures is comparable to $\langle\delta E\rangle$ itself.

There is, of course, no crystal for which the Einstein model is a good approximation. A slightly more realistic example is that in which the radioactive atoms are embedded as impurities in a lattice of radically different atoms. If there are localized modes associated with these impurities, then these modes will contribute a fluctuating term of δE and something similar to the result for an Einstein oscillator will obtain.

Incidentally, the possibility of localized modes raises a question that we must dispose of. Since it is known that changing the mass of an atom in the lattice may give rise to a localized mode, one can ask whether the very change of mass due to the γ transition may not produce this effect. In this case Eq. (7) would not be valid. It is easy to see, however, that such a breakdown of perturbation theory can only occur in a one-dimensional lattice. In three dimensions an appreciable change in mass is necessary to produce a localized mode,[5] and it is clear that $\delta M=E_\gamma/c^2$ is much too small in practice to produce such an effect.

Finally, one should mention a possible small broadening of the Mössbauer line, which will occur when the mass of the atoms surrounding the emitting atom is subject to fluctuations, as in the case of an isotope mixture. Roughly speaking this will have the same effect as a random variation in the Debye temperature, of the order $\Delta\theta/\theta\approx\Delta M/2M$ if ΔM is the variation in mass of the neighbors. This is a very small effect, but in view of the recent detection of the very sharp Mössbauer line of Zn^{67} it is possible that even broadenings of this order may have to be taken into account.