finite time interval $t > 0$. This amplitude determines the probability to find the system in a certain final state at a certain time—but the details of how or when the system reached that state are not ordinarily accessible to observation.

Of course, one can measure the emitted gamma ray and thus determine that the decay has occurred in a certain interval of time. Furthermore, one can select experiments which detect only those gamma rays emitted in times much shorter than the half-life τ of the nuclear excited state involved ($\tau \sim 10^{-7}$ sec). In resonance scattering such emission processes, however, constitute only a small fraction of those processes which are of experimental relevance. But in selecting such fast processes as those representing the time of momentum transfer in emission *in each single case*, the description of nature is being carried beyond the limits of quantum mechanics.

One should note that the arguments presented above, showing that one can not infer the suddenness of the momentum transfer in a general process from a knowledge of the shape of the incident radiation pulse, do not vitiate the conclusion reached in part (a) with regard to the cloud-chamber example. In that case the suddenness of the momentum transfer could be experimentally verified by observing the sharp bend in the track of the free proton, a type of measurement not available in the case of low energy resonance scattering by nuclei bound in crystals, where it is in general not even possible to determine which particular nucleus received the momentum.

(c) The evaluation of zero-phonon transition probabilities for gamma resonance scattering involves an integration over times of the order of the lifetime of the nuclear state involved, as has been pointed out by Inglis[17] and by Boyle and Hall.[18] This shows that there is no need for a concept of a sudden momentum transfer and that there is sufficient time for the recoil momentum to be transferred to the lattice via the binding forces during the scattering process.

(d) The transfer of the recoil energy to a single nucleus or a few nuclei making up a piece of the crystal can not be measured on account of the zero point energies—as pointed out in Sec. II. Moreover, the times involved in verifying the conservation of energy and momentum by measuring these quantities are long compared to the time of propagation of disturbances through the crystal at the velocity of sound. It therefore is difficult to see how the impulse momentum transfer picture can, from the quantum-mechanical point of view, contribute to an understanding of how momentum is transferred to the crystal.

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It is a pleasure to thank Dr. M. L. Goldberger and Dr. K. M. Watson for a stimulating discussion on the subject matter of Sec. IV. The authors would also like to thank Dr. J. Petzold for several helpful comments.

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[17] D. R. Inglis, in H. Frauenfelder, *The Mössbauer Effect* (W. A. Benjamin, Inc., New York, 1962), p. 169.

[18] A. J. Boyle and H. E. Hall, Rept. Progr. Phys. **25**, 441 (1962).

Lattice Dynamical Aspects of the Resonance Absorption of Gamma Rays by Nuclei Bound in a Crystal

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It is quite common in studies of the resonant emission or absorption of gamma rays by nuclei bound in a crystal that the emitting (or absorbing) nucleus is either an impurity in a host crystal or the crystal is itself imperfect. When this is the case, it is necessary in analyzing the results of such experiments to take into account the modification of the lattice vibrations of the host crystal caused by its departure from ideality. These modifications can give rise to interesting effects in the absorption spectrum of the perfect host crystal and, once the origins of these effects are understood, a proper analysis of experimental results can yield worthwhile information about the dynamics of the host crystal and of the impurity atom.

At the present time there appear to be three dynamical quantities of interest in connection with the resonant absorption of gamma rays by nuclei in crystals. These are the "no-phonon" absorption cross section, the "one-phonon" absorption cross section, and the second-order Doppler shift. The first of these is the cross section for processes in which the resonant nucleus absorbs a gamma-ray photon and no energy is exchanged with the host crystal, that is, the vibrational energy of the host crystal is the same after the absorption takes place as it was before it. This recoilless absorption (or emission) of a gamma-ray photon by a nucleus bound in a crystal is what in fact is called the Mössbauer effect.[1] The second quantity is the cross section for processes in which the gamma-ray photon is absorbed, and the energy of the host crystal increases or decreases by one quantum of vibrational energy. The third effect is the change in the energy of the emitted gamma ray due to the fact that the vibrational energy of the host crystal increases because of the decrease in the mass of the emitting nucleus during the emission process.

If the crystal, whether perfect or containing defects, can be adequately described by the harmonic approximation, then a calculation of the no-phonon spectrum requires essentially the calculation of the mean square amplitude of the resonant nucleus, while the second-order Doppler shift is proportional to its mean square velocity. The one-phonon absorption spectrum is essentially the Fourier transform of the displacement autocorrelation function for the resonant nucleus.

In this survey, among other things, I should like to sketch the theoretical arguments which justify these remarks and show how one can calculate these dynamical properties of the resonant nucleus in the case that it is a substitutional impurity in the host crystal. Since a perfect crystal, that is, one in which the resonant nucleus is one of the atoms of the host crystal, is just a very special case of an imperfect crystal, the results I will obtain contain the corresponding results for a perfect crystal as special or limiting cases. I will illustrate the results of the theoretical analysis with the results of numerical calculations based on them for various models of resonant nuclei in various models for the host crystal. For simplicity, I will assume only Bravais lattices in my discussion, but this is an unessential assumption.

The starting point for a lattice dynamical discussion of the resonance absorption of γ rays by a nucleus bound in a crystal is the Lamb–Mössbauer formula for the cross section for the absorption of a γ ray of energy E by a nucleus in a crystal[1,2]

$$\sigma_a(E) = \tfrac{1}{4}\sigma_0\Gamma^2 \sum_{mn} \frac{e^{-\beta E m}}{Z} \times \frac{\langle m|e^{i(\mathbf{p}/\hbar)\cdot\mathbf{R}(l)}|n\rangle\langle n|e^{-i(\mathbf{p}/\hbar)\cdot\mathbf{R}(l)}|m\rangle}{(E_0 - E + E_n - E_m)^2 + \frac{1}{4}\Gamma^2}\,. \tag{1}$$

In this equation E_0 is the energy difference between the final and initial nuclear states of the absorbing nucleus, E_m and E_n are the energies of the eigenstates $|m\rangle$ and $|n\rangle$ of the crystal, respectively, Γ is the natural width of the excited state of the nucleus, $\mathbf{p}$ is the momentum of the γ ray, $\mathbf{R}(l)$ is the instantaneous position vector of the absorbing nucleus, Z is the crystal's partition function, and σ_0 is the resonance absorption cross section for the absorbing nucleus.

With the aid of an integral representation for the denominator of this expression, we can manipulate Eq. (1) into the form

$$\sigma_a(E) = \tfrac{1}{2}\sigma_0\gamma \int_{-\infty}^{\infty} dt e^{i\omega t - \gamma|t|} \times \langle \exp[-i\mathbf{k}\cdot\mathbf{u}(l;t)] \exp[i\mathbf{k}\cdot\mathbf{u}(l;0)]\rangle\,. \tag{2}$$

In writing this expression we have made use of the fact that in a Bravais crystal the position vector $\mathbf{R}(l)$ can be written as

$$\mathbf{R}(l) = \mathbf{x}(l) + \mathbf{u}(l)\,, \tag{3}$$

where $\mathbf{x}(l)$ is the position vector of the mean position of the absorbing nucleus, while $\mathbf{u}(l)$ is its displacement from the mean position. We have also introduced the notation

$$(1/\hbar)\mathbf{p} = \mathbf{k}\,, \tag{4}$$

$$\hbar\omega = E - E_0\,, \quad \gamma = \Gamma/2\hbar\,, \tag{5}$$

while $\mathbf{u}(l;t)$ denotes the Heisenberg operator

$$\mathbf{u}(l;t) = e^{i(t/\hbar)H}\mathbf{u}(l;0)e^{-i(t/\hbar)H}, \tag{6}$$

and H is the Hamiltonian for a crystal containing a defect. The angular brackets in Eq. (2) denote an average over the canonical ensemble of the crystal.

There are now three steps we must take to rewrite Eq. (2) in a form more suited for actual calculations. For a harmonic crystal it is readily verified that the commutator of $\mathbf{k}\cdot\mathbf{u}(l;t)$ and $\mathbf{k}\cdot\mathbf{u}(l;0)$ is a c number. We can then use a special case of the Baker–Hausdorff formula[3] to write

$$\begin{aligned}\langle \exp[-i\mathbf{k}\cdot\mathbf{u}(l;t)] \exp[i\mathbf{k}\cdot\mathbf{u}(l;0)]\rangle &= \langle \exp[-i\mathbf{k}\cdot[\mathbf{u}(l;t) - \mathbf{u}(l;0)]]\rangle \\ &\quad \times \exp[\tfrac{1}{2}\langle[\mathbf{k}\cdot\mathbf{u}(l;t)\,,\ \mathbf{k}\cdot\mathbf{u}(l;0)]\rangle]\,.\end{aligned} \tag{7}$$

Since we are dealing with a harmonic crystal we can simplify the first thermodynamic average and write it as

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[1] R. L. Mössbauer, Z. Physik **151**, 124 (1958).

[2] W. E. Lamb, Jr., Phys. Rev. **55**, 190 (1939).

[3] H. F. Baker, Proc. London Math. Soc. **3**, 24 (1904); F. Hausdorff, Berichte Sächsischen Akad. Wiss. (Math. Phys. Kl.) Leipzig **58**, 19 (1906); see also, G. H. Weiss and A. A. Maradudin, J. Math. Phys. **3**, 771 (1962).

$$\begin{aligned}\langle \exp [-i\mathbf{k}\cdot[\mathbf{u}(l;t) - \mathbf{u}(l;0)]]\rangle \\ = \exp [-\tfrac{1}{2}\langle\{\mathbf{k}\cdot[\mathbf{u}(l;t) - \mathbf{u}(l;0)]\}^2\rangle] .\end{aligned} \tag{8}$$

This theorem is known in lattice dynamics as Ott's theorem[4] or sometimes as Bloch's theorem.[5] Combining Eqs. (2), (7), and (8) we can write the absorption cross section as

$$\begin{aligned}\sigma_a(E) = \tfrac{1}{2}\sigma_0\gamma e^{-2M}\int_{-\infty}^{\infty} dt \exp(i\omega t - \gamma|t|) \\ \times \exp[\langle\mathbf{k}\cdot\mathbf{u}(l;t)\mathbf{k}\cdot\mathbf{u}(l;0)\rangle] ,\end{aligned} \tag{9}$$

where

$$2M = \tfrac{1}{2}\langle[\mathbf{k}\cdot\mathbf{u}(l;t)]^2\rangle + \tfrac{1}{2}\langle[\mathbf{k}\cdot\mathbf{u}(l;0)]^2\rangle , \tag{10}$$

$$= \langle[\mathbf{k}\cdot\mathbf{u}(l)]^2\rangle . \tag{11}$$

In passing from Eq. (10) to Eq. (11) we have used the assumed time independence of the crystal Hamiltonian. The factor e^{-2M} is called the Debye–Waller factor.[6]

The expression given by Eq. (9) is easier to work with than the one given by Eq. (2) because it contains the simpler correlation function. It is exact for a harmonic crystal, whether it be a perfect crystal or imperfect.

The third step we must take is to expand $u_\alpha(l;t)$ in terms of the normal coordinates of the crystal,

$$u_\alpha(l;t) = \left(\frac{\hbar}{2M_l}\right)^{\frac{1}{2}} \sum_s \frac{B_\alpha^{(s)}(l)}{(\omega_s)^{\frac{1}{2}}} (b_s e^{-i\omega_s t} + b_s^\dagger e^{i\omega_s t}) . \tag{12}$$

In this equation α labels the Cartesian components, M_l is the mass of the lth atom, ω_s is the frequency of the sth normal mode, and $\mathbf{B}^{(s)}(l)$ is the associated unit eigenvector. $b_s^\dagger$ and b_s are the phonon creation and destruction operators for the sth normal mode. By the use of this normal coordinate expansion we can write the exponential of the correlation function appearing in Eq. (9) as

$$\begin{aligned} e^{\langle\mathbf{k}\cdot\mathbf{u}(l;t)\mathbf{k}\cdot\mathbf{u}(l;0)\rangle} &= e^{\sum_s c_s^2\left(\frac{e^{i\omega_s t}}{(\gamma_s)^{\frac{1}{2}}} + (\gamma_s)^{\frac{1}{2}}e^{-i\omega_s t}\right)} \\ &= \prod_s e^{c_s^2\left(\frac{e^{i\omega_s t}}{(\gamma_s)^{\frac{1}{2}}} + (\gamma_s)^{\frac{1}{2}}e^{-i\omega_s t}\right)} \\ &= \prod_s \left[I_0(2c_s^2) + \sum_{n=1}^{\infty} I_n(2c_s^2) \left(\frac{e^{in\omega_s t}}{\gamma_s^{\frac{1}{2}n}} + \gamma_s^{\frac{1}{2}n} e^{-in\omega_s t}\right)\right] ,\end{aligned} \tag{13}$$

where we have put

$$\begin{aligned}\gamma_s &= \frac{n_s + 1}{n_s} = e^{\beta\hbar\omega_s} \\ n_s &= [e^{\beta\hbar\omega_s} - 1]^{-1} \\ c_s^2 &= \frac{\hbar}{2M_l}\frac{[\mathbf{k}\cdot\mathbf{B}^{(s)}(l)]^2}{\omega_s}\frac{e^{\frac{1}{2}\beta\hbar\omega_s}}{e^{\beta\hbar\omega_s} - 1} ,\end{aligned} \tag{14}$$

and have used the generating function for the modified Bessel functions of the first kind, the Bessel functions of pure imaginary argument[7]

$$e^{\frac{1}{2}x(y+y^{-1})} = \sum_{n=-\infty}^{\infty} I_n(x)y^n . \tag{15}$$

n_s is the mean number of phonons in the sth mode at temperature $T = (k\beta)^{-1}$. The Bessel function decomposition of the exponential of the displacement autocorrelation function given by Eq. (13) was first given by Ott,[4] and has subsequently been employed by Pope,[8] Zemach and Glauber,[9] and Kaufman and Lipkin.[10]

When we substitute the result given by Eq. (13) into Eq. (9), the absorption cross section for those processes in which there is no exchange of energy between the resonant nucleus and the host crystal is given by the terms in Eq. (13) which are independent of $e^{i\omega_s t}$ and $e^{-i\omega_s t}$. We therefore obtain the result that

$$\sigma_a^{(0)}(E) = \tfrac{1}{2}\sigma_0\gamma e^{-2M}\prod_s I_0(2c_s^2)\frac{2\gamma}{\gamma^2 + \omega^2} . \tag{16}$$

If we use the fact that the argument of the Bessel functions $2c_s^2$ is of $O(N^{-1})$ for the wavelike or in-band modes of the perturbed crystal, where N is the number of atoms in the crystal, while it is of $O(1)$ for any localized modes that might be present,[11] from the small argument expansion of $I_0(x)$ we can show directly that all factors in the product in Eq. (16) which correspond to wavelike modes reduce to unity in the limit of large N, and the product in Eq. (16) needs to be taken over the localized modes only. If there are no localized modes, the Bessel function factor is absent. This is the case for a perfect crystal or when the resonant nucleus is a heavy impurity.

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[4] H. Ott, Ann. Physik **23**, 169 (1935).

[5] F. Bloch, Z. Physik **74**, 295 (1932).

[6] P. Debye, Ann. Physik **43**, 49 (1914); I. Waller, dissertation, Uppsala, 1925.

[7] This result follows from the substitutions $z = ix$ and $t = -iy$ in the generating function for the ordinary Bessel functions given in G. N. Watson, *Bessel Functions* (Cambridge University Press, Cambridge, 1944), p. 14. The definition of $I_\nu(z)$ given on p. 77 of this reference is also required.

[8] N. K. Pope, Can. J. Phys. **30**, 597 (1952).

[9] R. J. Glauber and A. C. Zemach, Phys. Rev. **101**, 118 (1956).

[10] B. Kaufman and H. J. Lipkin, Ann. Phys. (N.Y.) **18**, 294 (1962).

[11] See, for example, A. A. Maradudin, Westinghouse Research Laboratories Scientific Paper No. 63-129-103-P9 (unpublished).

The function $\sigma_a^{(0)}(E)$ consists of a very sharp peak of width 2γ (the "Mössbauer pip") whose height or intensity is modulated by the product of the Debye–Waller factor and the Bessel functions. The Debye–Waller factor gives the probability of those processes in which the initial and final states of the crystal are identical. The product of Bessel functions represents the contribution to the cross section from processes in which the local mode phonons are excited and de-excited in all possible ways such that the net energy change of the crystal is zero. However, the line shape given by Eq. (16) strictly speaking is not Lorentzian.[12] This is because the frequency of the γ ray, ω, and its wave vector $\mathbf{k}$ are not independent quantities. Quite apart from the Bessel function factors, the line shape is, therefore, a product of a Lorentzian function and a displaced Gaussian, the Debye–Waller factor. In what follows I will refer to the cross section given by Eq. (16) as the "no-phonon" absorption cross section.

In a similar fashion, we can obtain the cross section for all processes in which the resonant nucleus absorbs a gamma-ray photon, recoils, and imparts to or takes up from the crystal one quantum of vibrational energy. This cross section arises from all terms in Eq. (13) which are linear in $e^{i\omega_s t}$ and $e^{-i\omega_s t}$. After some manipulation, substitution of these terms into Eq. (9) and the use of the first line of Eq. (13) yields the following result for this "one-phonon" absorption cross section

$$\sigma_a^{(1)}(E) = \tfrac{1}{2}\sigma_0\gamma e^{-2M} \prod_s{}' I_0(2c_s^2) \times \int_{-\infty}^{\infty} dt e^{i\omega t-\gamma|t|} \langle \mathbf{k}\cdot\mathbf{u}(l;t)\mathbf{k}\cdot\mathbf{u}(l;0)\rangle , \qquad |\omega| < \omega_L \tag{17}$$

$$= \tfrac{1}{2}\sigma_0\gamma e^{-2M} \sum_{\substack{p\\ \text{l.m.}}} \prod_{s\neq p}{}' I_0(2c_s^2) I_1(2c_p^2) \times \left\{ \frac{1}{(\gamma_p)^{\frac{1}{2}}} \frac{2\gamma}{\gamma^2+(\omega+\omega_p)^2} + (\gamma_p)^{\frac{1}{2}} \frac{2\gamma}{\gamma^2+(\omega-\omega_p)^2} \right\}, \qquad |\omega| > \omega_L \tag{18}$$

where ω_L is the maximum frequency of the perfect host crystal. The separation of the cross section into the indicated frequency ranges is possible because the wavelike modes have no frequencies greater than ω_L, while the localized modes have no frequencies smaller than ω_L. From Eq. (18) we see that the localized modes contribute "Lorentzian" peaks of the same width as the Mössbauer pip at γ-ray energies which are equal to $E = E_0 \pm \hbar\omega_p$. The primes on the products in Eqs. (17) and (18) indicate that they extend over the localized modes only, while the initials "l.m." on the sum in Eq. (18) indicate that it extends over only the localized modes also. Since the expression for the localized mode contribution to the one-phonon absorption spectrum has a transparent form I will have comparatively little to say about it in the remainder of this survey.

As it stands, Eq. (17) gives an exact expression for the "in-band" contribution to the one-phonon absorption cross section for a large crystal treated in the harmonic approximation. However, from a purely practical point of view, it is more complicated than it needs to be. If we make a single approximation we can obtain a result which has a remarkably simple form. This approximation consists of letting γ go to zero. This is by now a standard approximation in the calculation of the contributions to the absorption cross section from all processes past the zero phonon processes.[13] It is also a very good approximation. For a popular Mössbauer isotope, Fe^{57}, γ has the value $3.46 \times 10^6\ \mathrm{sec}^{-1}$.[14] A typical value for the maximum frequency of a crystal is of the order of $10^{13}\ \mathrm{sec}^{-1}$. Thus, except for frequencies in the bottom $10^{-5}\%$ of the one-phonon absorption spectrum, the condition $\gamma \ll \omega$ is well satisfied, and setting γ equal to zero in Eq. (17) causes negligible error. I will make this approximation in what follows.

To this approximation, therefore, there are three dynamical quantities which are required for a description of the resonance absorption cross section: the exponent of the Debye–Waller factor, $2M$; the Fourier transform of the displacement autocorrelation function for the resonant, impurity nucleus; and the arguments $2c_s^2$ of the Bessel function factors appearing in the no-phonon and one-phonon cross sections. These quantities are all related, and I now turn to their evaluation.

Theoretical calculations of these properties have been carried out by several workers for a number of different impurity resonant nuclei in a variety of host crystals.[15–21] The number of ways in which these

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[12] I am indebted to Professor R. Barrie for this remark.

[13] K. S. Singwi and A. Sjölander, Phys. Rev. **120**, 1093 (1960).

[14] *The Mössbauer Effect*, edited by H. Frauenfelder (W. A. Benjamin, Inc., New York, 1962), pp. 37 and 47.

[15] Yu. Kagan and Ya. A. Iosilevskii, Zh. Eksperim. i Teor. Fiz. **42**, 259 (1962); **44**, 284 (1962) [English transl.: Soviet Phys.—JETP **15**, 182 (1962); **17**, 195 (1963)].

[16] A. A. Maradudin, in *1962 Brandeis Summer Institute Lectures in Theoretical Physics* [W. A. Benjamin, Inc., New York, to be published], Vol. II.

[17] W. M. Visscher, Phys. Rev. **129**, 28 (1963).

calculations have been performed is approximately equal to the number of these investigators, and some of the techniques used are quite sophisticated. However, as long as we work within the harmonic approximation, a rather simple method, which makes use of the Green's functions of Lifshitz[22] and of Montroll and Potts,[23] suffices for the calculation of the dynamical properties required for a determination of the no-phonon and one-phonon absorption cross sections.

It is convenient to begin a calculation of these dynamical quantities by first obtaining a formal expression for the Fourier transform of the displacement autocorrelation function for the resonant nucleus. If we make use of the normal coordinate transformation, Eq. (12), we can write the correlation function itself as

$$\begin{aligned}&\langle u_\alpha(l;t)u_\beta(l;0)\rangle\\ &\quad=\frac{\hbar}{2M_l}\sum_s \frac{B_\alpha^{(s)}(l)B_\beta^{(s)}(l)}{\omega_s}\left[(n_s+1)e^{-i\omega_s t}+n_s e^{i\omega_s t}\right].\end{aligned}\tag{19}$$

If we now take the Fourier transform of this expression and make use of some simple properties of Dirac's δ function, we obtain the result that

$$\begin{aligned}I_{\alpha\beta}(l;\omega)&=\int_{-\infty}^{\infty}dte^{i\omega t}\langle u_\alpha(l;t)u_\beta(l;0)\rangle=\frac{2\pi\hbar}{M_l}\\ &\times[n(\omega)+1]\operatorname{sgn}\omega\sum_s B_\alpha^{(s)}(l)\delta(\omega^2-\omega_s^2)B_\beta^{(s)}(l)\,,\end{aligned}\tag{20}$$

where

$$n(\omega)=[e^{\beta\hbar\omega}-1]^{-1}\,.\tag{21}$$

As it stands, the result given by Eq. (20) is not very useful because it contains both the normal mode frequencies of the *perturbed* crystal and the associated eigenvectors. While it is possible to calculate these quantities and use them in Eq. (20),[19] it is much easier to eliminate them altogether and to re-express Eq. (20) in a form in which only functions that we know something about appear. We can do this if we make use of a theorem due to Born[24] which in the present context can be expressed by the equation

$$\sum_s B_\alpha^{(s)}(l)f(\omega_s^2)B_\beta^{(s)}(l')=[f(\mathbf{D})]_{\substack{ll'\\ \alpha\beta}}\,.\tag{22}$$

for a wide class of functions $f(x)$. In this equation **D** is the $3N\times 3N$ dynamical matrix for the perturbed crystal; that is, it is the matrix whose eigenvalues are the squares of the normal mode frequencies, and whose eigenvectors normalized to unity are the $\{B_\alpha^{(s)}(l)\}$:

$$\sum_{l'\beta} D_{\alpha\beta}(ll')B_\beta^{(s)}(l')=\omega_s^2 B_\alpha^{(s)}(l)\,.\tag{23}$$

The elements of the matrix **D** are labeled by the index pairs $(l\alpha)$ and $(l'\beta)$, where l and l' label the atoms of the crystal, while α and β label the Cartesian axes. Applied to Eq. (20) this theorem yields the result that

$$I_{\alpha\beta}(l;\omega)=\frac{2\pi\hbar}{M_l}[n(\omega)+1]\operatorname{sgn}\omega[\delta(\omega^2\mathbf{I}-\mathbf{D})]_{\substack{ll\\ \alpha\beta}}\tag{24}$$

where **I** is the $3N\times 3N$ unit matrix.

For computational purposes it is convenient to express the δ-function matrix in the form

$$\delta(\omega^2\mathbf{I}-\mathbf{D})=\frac{1}{\pi}\operatorname{Im}\lim_{\delta\to 0+}[(\omega^2-i\delta)\mathbf{I}-\mathbf{D}]^{-1}\,.\tag{25}$$

The matrix **D** is related to the matrix of the atomic force constants $\mathbf{\Phi}$ by

$$\mathbf{D}=\mathbf{M}^{-\frac{1}{2}}\mathbf{\Phi}\mathbf{M}^{-\frac{1}{2}}\,,\tag{26}$$

where **M** is a diagonal $3N\times 3N$ matrix whose $(l\alpha;l\alpha)$ element is the mass of the lth atom. We can, therefore, write

$$\begin{aligned}[\omega^2\mathbf{I}-\mathbf{D}]^{-1}&=\mathbf{M}^{\frac{1}{2}}[\mathbf{M}\omega^2-\mathbf{\Phi}]^{-1}\mathbf{M}^{\frac{1}{2}}\\ &=\mathbf{M}^{\frac{1}{2}}[\mathbf{M}_0\omega^2-\mathbf{\Phi}_0+\Delta\mathbf{M}\omega^2-\Delta\mathbf{\Phi}]^{-1}\mathbf{M}^{\frac{1}{2}}\\ &=\mathbf{M}^{\frac{1}{2}}[\mathbf{I}+\mathbf{G}(\Delta\mathbf{M}\omega^2-\Delta\mathbf{\Phi})]^{-1}\mathbf{G}\mathbf{M}^{\frac{1}{2}}\\ &\equiv\mathbf{M}^{\frac{1}{2}}\mathbf{U}(\omega^2)\mathbf{M}^{\frac{1}{2}}\,,\end{aligned}\tag{27}$$

where the matrices $\mathbf{M}_0$ and $\mathbf{\Phi}_0$ are the mass and force constant matrices for the unperturbed, perfect crystal, and $\Delta\mathbf{M}$ and $\Delta\mathbf{\Phi}$ express the perturbation due to the defect. The matrix **G** is just the Green's function matrix introduced by Lifshitz[22] and by Montroll and Potts,[23]

$$\mathbf{G}=[\mathbf{M}_0\omega^2-\mathbf{\Phi}_0]^{-1}\,,\tag{28}$$

while the matrix **U** is most conveniently given by the solution of the equation

$$\mathbf{U}=\mathbf{G}-\mathbf{G}(\Delta\mathbf{M}\omega^2-\Delta\mathbf{\Phi})\mathbf{U}\,,\tag{29}$$

and is the Green's function for the perturbed crystal.

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[19] P. G. Dawber and R. J. Elliott, Proc. Roy. Soc. (London) **A273**, 222 (1963).

[20] G. Lehman and R. De Wames, Phys. Rev. **131**, 1008 (1963).

[21] A. A. Maradudin, P. A. Flinn, and J. M. Radcliffe, Ann. Phys. (N.Y.) (to be published).

[22] An extensive bibliography of the work of I. M. Lifshitz and his collaborators is given in I. M. Lifshitz, Suppl. Nuovo Cimento **3**, 716 (1956).

[23] E. W. Montroll and R. B. Potts, Phys. Rev. **100**, 525 (1955); **102**, 72 (1956).

[24] M. Born, Rept. Progr. Phys. **9**, 294 (1942–43).

When we substitute Eqs. (25) and (27) into Eq. (24) we obtain finally

$$I_{\alpha\beta}(l;\omega) = 2\hbar[n(\omega)+1]\operatorname{sgn}\omega\,\operatorname{Im}\lim_{\delta\to0+}U_{\alpha\beta}(ll;\omega^2-i\delta)\,. \tag{30}$$

From the Fourier inversion theorem we obtain for the displacement autocorrelation function

$$\langle u_\alpha(l;t)u_\beta(l;0)\rangle = \frac{\hbar}{\pi}\int_{-\infty}^{\infty}d\omega e^{-i\omega t}\frac{\operatorname{sgn}\omega}{1-e^{-\beta\hbar\omega}} \times\left\{\operatorname{Im}\lim_{\delta\to0+}U_{\alpha\beta}(ll;\omega^2-i\delta)\right\}. \tag{31}$$

Setting $t = 0$ in this expression we obtain a formal result for the exponent of the Debye–Waller factor

$$2M = \operatorname{Im}\lim_{\delta\to0+}\frac{\hbar}{M}\sum_{\alpha\beta}k_\alpha k_\beta\int_{-\infty}^{\infty}d\omega\frac{\operatorname{sgn}\omega}{1-e^{-\beta\hbar\omega}} \times U_{\alpha\beta}(ll;\omega^2-i\delta)\,. \tag{32}$$

To illustrate the results expressed by Eqs. (30)–(32), let me assume that the resonant nucleus is an isotope impurity in a cubic Bravais crystal. With no loss of generality, we can assume that the impurity nucleus is located at the origin of our coordinate system, i.e., at the point $\mathbf{x}(l) = 0$. The matrix $\mathbf{\Delta M}\omega^2 - \mathbf{\Delta\Phi}$ in this case takes the form

$$(\mathbf{\Delta M}\omega^2 - \mathbf{\Delta\Phi})_{\substack{ll'\\ \alpha\beta}} = -\epsilon M\omega^2\delta_{\alpha\beta}\delta_{l0}\delta_{l'0} \tag{33}$$

where the mass defect parameter ϵ is defined in terms of the mass of the impurity M' and the mass of one of the host atoms M by

$$\epsilon = 1 - M'/M\,. \tag{34}$$

The elements of the Green's function matrix $\mathbf{G}$ are given by[25]

$$G_{\alpha\beta}(ll';\omega^2) = \frac{1}{NM}\sum_{\mathbf{k}j}\frac{e_\alpha(\mathbf{k}j)e_\beta(\mathbf{k}j)}{\omega^2-\omega_j^2(\mathbf{k})} \times\exp\left[\{2\pi i\mathbf{k}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]\}\right]. \tag{35}$$

where N is the number of unit cells in the crystal, $\omega_j(\mathbf{k})$ is the frequency of the normal mode of the unperturbed crystal described by the wave vector $\mathbf{k}$ and polarization index j, and $\mathbf{e}(\mathbf{k}j)$ is the corresponding unit polarization vector. The allowed values of $\mathbf{k}$ are uniformly and densely distributed throughout a unit cell of the reciprocal lattice for the host crystal. If we use the fact that the Green's function $G_{\alpha\beta}(00;\omega^2)$ is isotropic for an arbitrary cubic Bravais crystal,[25]

$$\begin{aligned}G_{\alpha\beta}(00;\omega^2) &= \delta_{\alpha\beta}\frac{1}{3NM}\sum_{\mathbf{k}j}\frac{1}{\omega^2-\omega_j^2(\mathbf{k})}\\ &= \delta_{\alpha\beta}G(00;\omega^2)\,,\end{aligned} \tag{36}$$

then the desired matrix element $U_{\alpha\beta}(00;\omega^2)$ is readily found from Eqs. (29) and (33) to be

$$U_{\alpha\beta}(00;\omega^2) = \delta_{\alpha\beta}\frac{G(00;\omega^2)}{1-\epsilon M\omega^2G(00;\omega^2)}\,. \tag{37}$$

Combining Eqs. (30), (36), and (37) we obtain

$$I_{\alpha\beta}(0;\omega) = \delta_{\alpha\beta}\frac{2\pi\hbar}{M}[n(\omega)+1] \times\frac{G_0(\omega^2)\operatorname{sgn}\omega}{[1-\epsilon\omega^2\tilde{G}_0(\omega^2)]^2+\pi^2\epsilon^2\omega^4G_0^2(\omega^2)}\,, \qquad 0<\omega^2<\omega_L^2 \tag{38}$$

$$= \delta_{\alpha\beta}\frac{\pi\hbar}{M}\frac{1}{\epsilon^2\omega_0^3B(\omega_0^2)}\left\{\frac{\delta(\omega+\omega_0)}{e^{\beta\hbar\omega_0}-1}+\frac{\delta(\omega-\omega_0)}{1-e^{-\beta\hbar\omega_0}}\right\}, \qquad \omega^2>\omega_L^2\,. \tag{39}$$

In writing these results I have introduced the functions

$$G_0(\omega^2) = \frac{1}{3N}\sum_{\mathbf{k}j}\delta(\omega^2-\omega_j^2(\mathbf{k})) \tag{40a}$$

$$\tilde{G}_0(\omega^2) = \frac{1}{3N}\sum_{\mathbf{k}j}\frac{1}{(\omega^2-\omega_j^2(\mathbf{k}))_P} \tag{40b}$$

$$B(\omega^2) = \frac{1}{3N}\sum_{\mathbf{k}j}\frac{\omega_j^2(\mathbf{k})}{(\omega^2-\omega_j^2(\mathbf{k}))_P^2}\,, \tag{40c}$$

where $(1/x)_P$ denotes the Cauchy principal value of $(1/x)$. The function $G_0(\omega^2)$ is recognized to be the distribution function for the squares of the normal mode frequencies of the perfect host crystal, while $\tilde{G}_0(\omega^2)$ is its Hilbert transform.

The contribution to $I_{\alpha\beta}(0;\omega)$ given by Eq. (39) arises only when $0 < \epsilon < 1$ and the equation

$$1-\epsilon\omega^2\tilde{G}_0(\omega^2) = 0 \tag{41}$$

has a solution $\omega^2 = \omega_0^2$ for $\omega^2 > \omega_L^2$. It represents the local mode contribution to $I_{\alpha\beta}(l;\omega)$. It is well known now that the localized mode due to a substitutional isotope impurity in a cubic Bravais crystal is triply degenerate.[25] This degeneracy is automatically taken into account in the expression for $I_{\alpha\beta}(0;\omega)$ given by Eq. (39).

The displacement autocorrelation function for the impurity nucleus according to Eq. (31) is given in

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[25] A. A. Maradudin, P. A. Flinn, and S. L. Ruby, Phys. Rev. **126**, 9 (1962).

this case by

$$\langle u_\alpha(l;t)u_\beta(l;0)\rangle = \delta_{\alpha\beta}\frac{\hbar}{M}\int_{-\omega_L}^{\omega_L} d\omega e^{-i\omega t}\frac{\operatorname{sgn}\omega}{1-e^{-\beta\hbar\omega}}$$
$$\times\frac{G_0(\omega^2)}{[1-\epsilon\omega^2\tilde{G}_0(\omega^2)]^2+\pi^2\epsilon^2\omega^4G_0^2(\omega^2)}$$
$$+\delta_{\alpha\beta}\frac{\hbar}{2M}\frac{1}{\epsilon^2\omega_0^3B(\omega_0^2)}\left[\frac{e^{i\omega_0 t}}{e^{\beta\hbar\omega_0}-1}+\frac{e^{-i\omega_0 t}}{1-e^{-\beta\hbar\omega_0}}\right]. \tag{42}$$

The second term on the right of Eq. (42) occurs only when the mass defect gives rise to a localized vibration mode.

Equation (42) provides us with a convenient way of obtaining an expression for the argument of the Bessel function factor appearing in the expression for the no-phonon and one-phonon absorption cross sections. Comparing the first of Eqs. (13) and the local mode contribution to the right side of Eq. (42), we can make the identification

$$2b_0^2 = k^2\frac{\hbar}{M}\frac{1}{\epsilon^2\omega_0^3B(\omega_0^2)}\frac{e^{\frac{1}{2}\beta\hbar\omega_0}}{e^{\beta\hbar\omega_0}-1}. \tag{43}$$

The threefold degeneracy of the localized mode is also automatically included in writing this expression.

Finally, the exponent of the Debye–Waller factor can be obtained by combining Eqs. (32) and (37), or more simply by setting $t = 0$ in Eq. (42). The result is

$$2M = k^2\frac{\hbar}{M}\int_0^{\omega_L} d\omega\coth\tfrac{1}{2}\beta\hbar\omega$$
$$\times\frac{G_0(\omega^2)}{[1-\epsilon\omega^2\tilde{G}_0(\omega^2)]^2+\pi^2\epsilon^2\omega^4G_0^2(\omega^2)}+k^2\frac{\hbar}{2M}$$
$$\times\frac{\coth\frac{1}{2}\beta\hbar\omega_0}{\epsilon^2\omega_0^3B(\omega_0^2)}. \tag{44}$$

The evaluation of the displacement autocorrelation function and of $2M$ can thus be reduced to quadratures when the resonant nucleus is a mass defect in an arbitrary cubic Bravais crystal.

According to Eq. (17) it is only the contribution to $I_{\alpha\beta}(0;\omega)$ given by Eq. (38) that we use in calculating the one-phonon absorption cross section, since the local mode contribution is given by Eq. (18) rather than following from Eq. (39). From Eqs. (17), (18), and (38) we obtain the result that the one phonon absorption cross section is

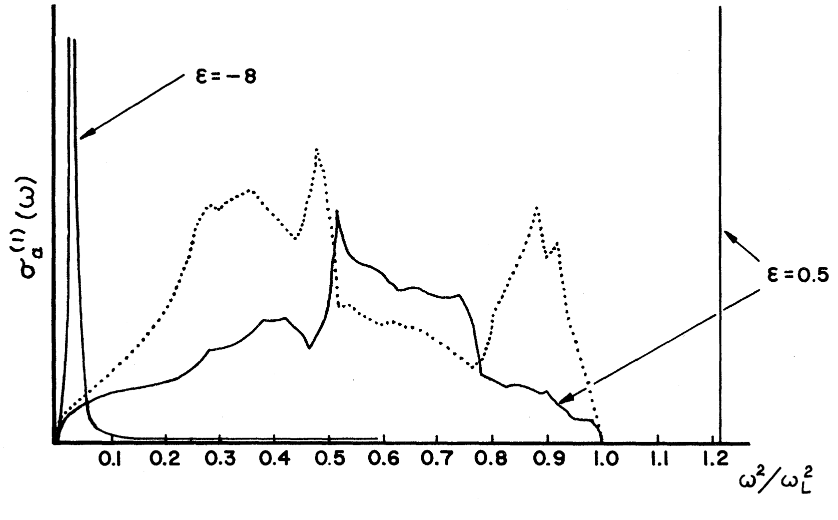
$$\sigma_a^{(1)}(E) = k^2\frac{\pi\hbar}{M}\sigma_0\gamma e^{-2M}I_0(2b_0^2)\frac{\operatorname{sgn}\omega}{1-e^{-\beta\hbar\omega_0}}$$
$$\times\frac{G_0(\omega^2)}{[1-\epsilon\omega^2\tilde{G}_0(\omega^2)]^2+\pi^2\epsilon^2\omega^4G_0^2(\omega^2)},$$
$$0<\omega^2<\omega_L^2 \tag{45}$$
$$=\tfrac{1}{2}\sigma_0\gamma e^{-2M}I_1(2b_0^2)\left\{e^{-\frac{1}{2}\beta\hbar\omega_0}\frac{2\gamma}{\gamma^2+(\omega+\omega_0)^2}\right.$$
$$\left.+e^{\frac{1}{2}\beta\hbar\omega_0}\frac{2\gamma}{\gamma^2+(\omega-\omega_0)^2}\right\},\quad \omega^2>\omega_L^2. \tag{46}$$

In Fig. 1 we have plotted the function

$$\frac{G_0(\omega^2)}{[1-\epsilon\omega^2\tilde{G}_0(\omega^2)]^2+\pi^2\epsilon^2\omega^4G_0^2(\omega^2)} \tag{47}$$

for three different values of ϵ, for a nearest neighbor, central force model of a face-centered cubic host crystal. This function gives the shape of the in-band part of the one-phonon absorption cross section at the absolute zero of temperature. In plotting this function we have used the function $\tilde{G}_0(\omega^2)$ for our model computed by Nardelli and Tettamanzi,[26] who

FIG. 1. The shape of the one phonon spectrum for the resonance absorption of γ rays by a nucleus bound in a crystal for three different values of the mass of the resonant nucleus relative to that of the atoms in the host crystal. The curves are plotted on the basis of a nearest neighbor, central force model of a face centered cubic crystal for the host crystal, and apply only at zero temperature.



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[26] G. F. Nardelli and N. Tettamanzi, Phys. Rev. **126**, 1283 (1962).

used the frequency spectrum $G_0(\omega^2)$ for this model computed previously by Overton and Dent.[27] The curve labeled $\epsilon = 0$ corresponds to a resonant nucleus which is one of the atoms of the host crystal. From (47) we see that it is a plot of $G_0(\omega^2)$ itself, and in this case the one-phonon absorption cross section simply maps out the frequency spectrum of the host crystal. The suggestion that the Mössbauer effect could be used to determine the frequency spectrum of a crystal experimentally was first made by Visscher.[28] The curve labeled $\epsilon = 0.5$ represents the one-phonon absorption cross section when the resonant nucleus is an impurity which is sufficiently light to give rise to a localized vibration mode, which has a frequency $\omega_0^2/\omega_L^2 \cong 1.21$. Finally, the curve labeled $\epsilon = -8$ corresponds to a resonant nucleus whose mass is 9 times that of the atom it replaces. The striking feature of this absorption cross section is that it consists almost entirely of a resonance peak at the low frequency end of the spectrum. The occurrence of such resonances when a heavy mass defect is introduced substitutionally into a crystal was first predicted in another context by Brout and Visscher,[29] and a possible method for observing the resonance experimentally, using the Mössbauer effect, has been suggested by Lehman and Dewames.[30]

For the simple model of an impurity nucleus that we have been considering we see from Eq. (45) that such resonances occur at frequencies in the interval $(-\omega_L, \omega_L)$ for which $1 - \epsilon\omega^2\tilde{G}_0(\omega^2)$ vanishes. Dawber and Elliott[19] have described these frequencies picturesquely as frequencies at which localized modes would like to occur, but because the frequency spectrum $G_0(\omega^2)$ is finite at such frequencies these would-be localized modes acquire a width. It can be shown that such resonances always occur if ϵ is negative and very large in magnitude, i.e., if the resonant nucleus is much heavier than the atom it replaces. Similarly, for more complicated models of impurity atoms, resonances can occur in the one-phonon absorption cross section if the bonds linking the impurity to the host crystal are much softer than they are in the perfect crystal.

Turning now to the Debye–Waller factor for an impurity nucleus, I have plotted in Fig. 2 the Debye–Waller factor for the case of a mass defect in a face-centered tetragonal crystal chosen to represent Fe^{57} in indium.[31] Also plotted are the experimental results of Steyert and Craig[32] for this case. f_x is the Debye–Waller factor for γ rays moving parallel to the x axis, and f_z is the Debye–Waller factor for γ rays moving parallel to the z axis, which has been chosen to be the fourfold rotation axis. That the two functions are unequal is a consequence of the inequivalence of the x and z axes for a tetragonal crystal. The lack of agreement between theory and experiment could be due to the fact that iron in indium may be poorly described by just a mass defect, although it seems unlikely that any simple alteration of the interaction between the impurity and the host crystal would lead to better agreement. The experimental results may indicate the existence of strong anharmonic interactions between the iron impurity and the indium lattice, as suggested by Steyert and Craig. In any case the correct interpretation of the experimental results still leaves room for additional theoretical work.

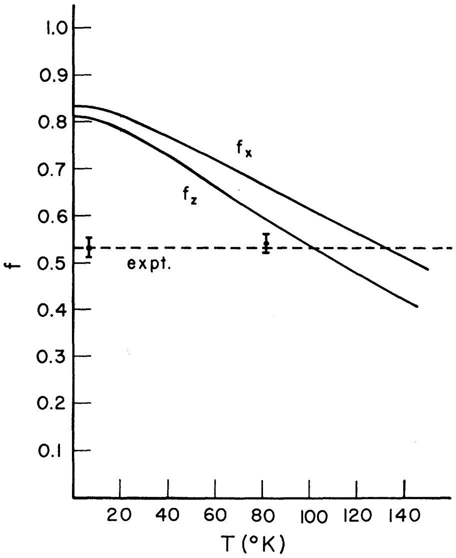

FIG. 2. The Debye–Waller factor for a mass defect in a face-centered tetragonal crystal chosen to represent Fe^{57} in indium. f_x and f_z are the Debye–Waller factors for γ rays moving parallel to the x- and z-axes, respectively, where the z-axis has been chosen to be the fourfold rotation axis.

I have been misleading you slightly up to now. I have obtained the result that the "Mössbauer pip" is centered at $\omega = 0$, i.e., $E = E_0$. In fact, this is not the case.

When a nucleus emits a γ ray of energy E, its mass

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[27] W. C. Overton, Jr., and E. Dent, U. S. Naval Research Laboratory Report 5252, Washington 25, D. C.

[28] W. M. Visscher, Ann. Phys. (N.Y.) 9, 194 (1960).

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

[30] G. Lehman and R. De Wames, Phys. Rev. Letters 9, 344 (1962).

[31] A. A. Maradudin and P. A. Flinn, Bull. Am. Phys. Soc. 8, 42 (1963).

[32] W. A. Steyert and P. P. Craig, Phys. Letters 2, 165 (1962).

changes by $\delta m = -E/c^2$. Because of the change in the mass of the nucleus, the vibrational energy of the crystal changes. This energy change is just the expectation value of the change in the crystal's Hamiltonian, which is just the change in the kinetic energy of the emitting nucleus:

$$\delta E = \langle \Delta H \rangle = -\delta m \left\langle \frac{p^2}{2m^2} \right\rangle = \frac{E}{mc^2} \left\langle \frac{p^2}{2m} \right\rangle . \tag{48}$$

This energy must come from somewhere and is, in fact, drained off from the energy of the γ ray. The result is that the "Mössbauer pip" is not centered at $\omega = 0$ ($E = E_0$) as we have obtained previously, but its center is shifted slightly away from $\omega = 0$, by the amount given by Eq. (48). Thus the relative energy shift is proportional to the mean square momentum of the emitting nucleus,

$$\frac{\delta E}{E} = \frac{1}{2m^2c^2} \langle p^2 \rangle . \tag{49}$$

This relative shift is called the second-order Doppler shift or the velocity shift. It was first predicted theoretically and found experimentally by Pound and Rebka.[33]

The reason that the simple discussion that I have given so far failed to predict this shift is that in making the transformation from the Lamb–Mössbauer expression for the absorption cross section to its expression as the Fourier transform of the correlation function of two exponential operators, I made the assumption ("the usual assumption") that the eigenstate $|m\rangle$, the initial state of the crystal, and the eigenstate $|n\rangle$, the final state of the crystal, are eigenstates of the same crystal Hamiltonian. We know this is not the case. The Hamiltonian for the crystal after the absorption process has taken place differs from the Hamiltonian of the crystal before the absorption in that the mass of the resonant nucleus has increased by the amount $\delta m = +E/c^2$. If this difference is taken into account, the correlation function expression for the absorption cross section takes a slightly different form from the one I showed you earlier, involving as it does two different crystal Hamiltonians. If one carries through the calculation in this way, one finds that the center of the "Mössbauer pip" is shifted away from $\omega = 0$, by the amount given by Eq. (48). A discussion of the second-order Doppler shift along the lines I have just sketched has been given recently by Professor Silsbee,[34] and somewhat earlier by Snyder and Wick.[35] However, the effect is small, and the simple derivation of the magnitude of the shift which I have given, and which is due to Josephson,[36] suffices.

The interest in theoretical calculations of the second-order Doppler shift stems partly from the fact that measurements of the displacement of the center of the "Mössbauer pip" in general yield not only the second-order Doppler shift but also an additional shift, called the isomeric shift.[37] The total shift I will call the "center shift." The isomeric shift arises essentially from the difference between the radius of a nucleus in its excited state and in its ground state, and depends on the electronic charge density at the nucleus. It is of some interest to chemists and to nuclear physicists. In order that the value of the isomeric shift can be obtained from experimental determinations of center shifts, we have to be able to subtract the value of the second-order Doppler shift. In the absence of phase changes, it seems as if it should be a good approximation to regard the isomeric shift as temperature-independent. This fact ultimately provides us with a means for accomplishing this subtraction.[38]

The most useful theoretical result for this purpose is the result that in the classical or high temperature limit the second-order Doppler shift is given by[25]

$$\left(\frac{\delta E}{E} \right) \underset{T\to\infty}{=} \frac{3kT}{2M'c^2} , \tag{50}$$

where M' is the mass of the resonant nucleus. This result is exact. It holds when the force constants of the interaction between the resonant nucleus and the host crystal differ from those in the perfect crystal; it holds when the introduction of the impurity nucleus distorts the host crystal in its vicinity; it holds when anharmonic terms are retained in the expansion of the crystal potential energy in powers of

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

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

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

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

[37] L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters **6**, 98 (1961).

[38] In the discussion following the presentation of this paper Professor Pound emphasized that at constant pressure there are at least two contributions to a temperature dependence of the isomeric shift. One arises from the thermal expansion of the lattice, while the second is an intrinsic temperature dependence of this shift. Although these two effects may tend to cancel each other, it appears that in general they cannot be neglected in very accurate determinations of the values of the isomeric shift and of the second order Doppler shift. Professor Pound has also informed me that on the basis of recent determinations of the temperature dependence of the center shift for Fe^{57} in Fe, it appears that there is an almost exact cancellation between temperature-dependent contributions to the isomeric shift in this case. However, this may be fortuitous, and in any event it is something that as a matter of principle cannot be assumed from the start.

the atomic displacements; it depends only on known quantities. This means that, if measurements of the center shift are made at elevated temperatures and the contribution given by Eq. (50) is subtracted from these results, the remainder gives the isomeric shift. From the temperature independence of the isomeric shift, having obtained it at any elevated temperature, we know it for all other temperatures.[38] We can then turn around and use the value of the isomeric shift obtained in this way to determine the second-order Doppler shift at all other temperatures, and from the latter to draw inferences about the dynamical properties of the resonant nucleus in its particular host crystal environment.

I must interject here that, in practice, the situation is a bit more complicated than I have made it appear here, because experimentally it is possible to measure only the difference between the isomeric shifts and the second-order Doppler shifts when the resonant nucleus is placed in two different host crystals. This is a characteristic difference between nuclear spectroscopy by means of the Mössbauer effect and nuclear spectroscopy carried out by more conventional methods: Only the difference between relative energy shifts for nuclei in different environments can be determined. This circumstance does not invalidate my preceding remarks. It does make the analysis of experimental data more complicated than I have indicated.

At temperatures which are not so high that we are in the classical regime, the second-order Doppler shift has the form[16]

$$\left(\frac{\delta E}{E}\right) = \frac{3kT}{2M'c^2}\left\{1 - \frac{1}{36M'}\left(\frac{\hbar}{kT}\right)^2 \sum_{l\alpha}{}' [\Phi_{\alpha\alpha}(l) + \Delta\Phi_{\alpha\alpha}(l)] + O(T^{-4})\right\} \tag{51}$$

for an impurity resonant nucleus in an arbitrary Bravais host crystal. Here M' is the mass of the resonant nucleus, the $\{\Phi_{\alpha\beta}(ll')\}$ are the atomic force constants of the perfect host crystal and $\{\Delta\Phi_{\alpha\beta}(ll')\}$ are the changes in these force constants due to the introduction of the impurity. From this result we see that if we plot the difference $(\delta E/E) - 3kT/2M'c^2$ against $1/T$ at high temperatures, the slope of the resulting straight line contains information about the perturbed force constants.

This has been done for an Fe^{57} in a stainless steel source, Fe^{57} in Be, and Fe^{57} in stainless steel absorbers and the results are shown in Fig. 3. These results are due to Flinn and Ruby.[25] From the intercepts of these two lines with the vertical axis we can obtain the difference between the isomeric shifts for Fe^{57} in the two absorber materials, which is independent of the source and fully corrected for the second-order Doppler shift. From the slopes of these two lines, which are determined rather less accurately than are the intercepts, one can draw the qualitative conclusion that an iron atom in the beryllium lattice is somewhat more stiffly held than are the beryllium atoms themselves, but quantitative conclusions about the strength of this binding must await more accurate experimental results.

If in some very simple case the change in the atomic force constants due to the introduction of the impurity could be described by a simple parameter, this parameter could be determined from the slopes of the lines in this figure. At the very least, such experimental data can serve as a consistency check on lattice dynamical models of impurity atoms.

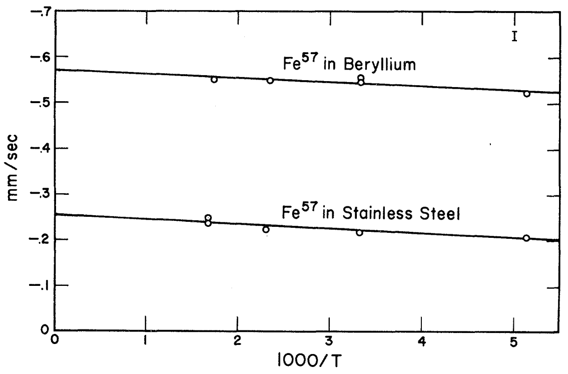

Fig. 3. The variation with temperature of the quantity $s - 3kT/2M'c$, where s is the total observed center shift at high temperatures, and is the sum of the isomeric shift and the second-order Doppler shift between source and absorber.

The formal theory of the second-order Doppler shift is very similar to that given above for the exponent of the Debye–Waller factor, and I won't reproduce the analysis here. The final expression for the second-order Doppler shift due to a resonant impurity nucleus in an arbitrary Bravais crystal is

$$\left(\frac{\delta E}{E}\right) = \frac{\hbar}{2c^2}\,\mathrm{Im}\lim_{\delta\to 0+}\sum_{\alpha}\int_{-\infty}^{\infty} d\omega\,\frac{\omega^2\,\mathrm{sgn}\,\omega}{1-e^{-\beta\hbar\omega}} \times U_{\alpha\alpha}(ll;\omega^2 - i\delta)\,. \tag{52}$$

Numerical calculations of the mean square velocity and the mean square displacement of an impurity atom have now been carried out by a number of different investigators who have used a variety of models for the impurity atom and for the host crystal.[15–21,25,31] A remarkable result of these calculations is the fact that these dynamic properties of an impurity atom appear to be independent of the properties of the host crystal, such as the atomic masses and force constants, and are, in fact, functions only of the mass and force constants associated with the impurity itself.[17,19] The truth or falsity of this result is not readily apparent from the general expressions for $2M$ and $(\delta E/E)$ given by Eqs. (32) and (52), respectively. Lipkin[39] has recently given a perturbation theoretic argument which makes this conclusion plausible in the special case of isotopic impurities in crystals at the absolute zero of temperature. We have also seen that it is rigorously true for the mean square velocity in the high temperature limit. A practical consequence of this peculiarity in the dynamical behavior of impurity atoms is that if, for example, a large value for the intensity of the recoil free transitions is desired, it is the parameters of the impurity nucleus which must be examined, and not those of the host crystal.

Returning now to the one-phonon absorption cross section, we have seen that in the harmonic approximation the localized mode contribution to this cross section consists of Lorentzian peaks of width equal to the width of the excited state of the resonant nucleus centered at the frequencies of the localized modes. In fact, however, the interatomic forces in no crystal are perfectly harmonic, and this fact has the consequence that the peaks contributed to the one-phonon absorption cross section by the localized modes are broadened and shifted relative to their forms in the harmonic approximation. These are anharmonic effects, arising from the terms of third and higher order in the expansion of the crystal potential energy in powers of the displacements of the atoms from their rest positions. The broadening of the local mode peak due to anharmonic effects can be understood if we recall that, in calculating the Fourier transform of the displacement autocorrelation function, we are evaluating matrix elements of phonon creation and destruction operators between the exact eigenstates of our crystal. Unlike the situation in the harmonic approximation, where the application of a phonon creation or destruction operator to one of the exact eigenstates of the crystal leads to another exact eigenstate, in an anharmonic crystal the application of a creation or destruction operator to one of the exact eigenstates of the crystal does not lead to another exact eigenstate. Instead the resulting wave function can be expressed as a superposition of the exact eigenstates. If the anharmonic effects are small the energies of these eigenstates are close to the energy of the exact eigenstate which would result if the anharmonicities were switched off. This distribution or spread of energies about the unperturbed value is the origin of the anharmonic broadening of the local mode peaks. Of course, all of the individual peaks in the one-phonon spectrum associated with the wavelike modes are also broadened by the same mechanism. However, since these peaks are essentially continuously distributed, in the frequency range $(-\omega_L, \omega_L)$, the anharmonic effects on the in-band part of the one-phonon absorption cross section are comparatively less dramatic than they are on the isolated peaks due to the localized modes.

Estimates of the width of the localized mode peaks due to cubic anharmonic terms in the crystal potential energy have been made by Klemens,[40] Mozer,[41] myself,[16] and Visscher.[42] Although different assumptions or approximations were made in each of these calculations, they all agree in predicting a local mode lifetime (that is, the inverse width at half-maximum) of the order of 1000 vibrational periods, under similar conditions of impurity mass, temperature, and strength of anharmonic coupling. This result implies a width for the local mode peaks which is of the order of 1000 to 10 000 times larger than the natural line width of the excited state of the nucleus. This relatively great width for the local mode peaks may pose difficulties for their experimental observation by means of the resonant absorption of gamma rays.

There is yet a second mechanism tending to broaden the localized mode peaks in the one phonon absorption cross section. This mechanism, which is already present even if we treat the crystal in the harmonic approximation, is concentration broadening. All of my discussion up to now has been based on the assumption that there is only a single resonant nucleus present in a host crystal. This assumption is expected to be a reasonable one only as long as the concentration of resonant nuclei in the crystal is so low that the dynamical behavior of any one of these nuclei is not greatly affected by the presence of the remaining resonant nuclei. The range of impurity concentrations for which this is the case depends on the nature of the interaction of the resonant nucleus with the host crystal, and individual cases must be studied separately. For such concentrations the local modes are highly degenerate. However, as the impurity concentration increases, this degeneracy is split and the sharp frequency levels associated with

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[39] H. J. Lipkin, Ann. Phys. (N. Y.) **23**, 28 (1963).

[40] P. G. Klemens, Phys. Rev. **122**, 443 (1961).

[41] B. Mozer (private communication); see also B. Mozer and G. H. Vineyard, Bull. Am. Phys. Soc. **6**, 135 (1961).

[42] W. M. Visscher, Phys. Rev. (to be published).

the localized modes are broadened into impurity bands. An estimate of the concentration broadening of the local mode peaks was made several years ago in another context by Montroll, Weiss, and myself,[43] and more recently Dawber and Elliott[44] and Dinhofer[45] have reconsidered this broadening in the context of impurity-induced optical absorption and resonant absorption of gamma rays, respectively. They find that the width of the local mode peaks due to concentration broadening is of the same order of magnitude as that due to anharmonic broadening.

Up to now I have been concerned with the resonant absorption of gamma rays by a nucleus which is an impurity in an otherwise perfect crystal. I should now like to discuss briefly the converse situation in which the resonant nucleus is essentially one of the atoms in the host crystal, Fe^{57} in Fe, for example, but the crystal as a whole is imperfect. I refer to the situation in which the resonant nucleus is close to or in the surface of a crystal, and regard the free surface of the crystal as a perturbation on the perfectly periodic crystal in which the atomic displacements obey the cyclic boundary condition.

The earliest calculation of a dynamical property of an atom in the surface layers of a crystal, within the context of the resonant absorption of gamma rays by such an atom, was the calculation by Wallis and Gazis[46] of the second-order Doppler shift for a resonant nucleus in a linear chain with free ends. The second-order Doppler shift requires the calculation of the mean square velocity of the resonant nucleus, and Wallis and Gazis found that this quantity is markedly different for an atom at the end of the chain from what it is in the interior, even if as is the case here, the crystal possesses no surface vibration modes. This conclusion was confirmed by the calculations of Rich[47] who studied the Debye–Waller factor and the one-phonon absorption cross section for an atom in the surface layers of a finite simple cubic crystal with nearest neighbor interactions. This model is also incapable of giving rise to surface modes, but it has the virtue that a large part of the calculations can be carried out analytically rather than numerically. Rich found that the mean square amplitude of an atom is rather larger in the surface of a crystal than it is in the interior. This is in contrast with the behavior of the mean square velocity. This quantity is somewhat smaller for a surface atom than for an atom in the interior of a crystal. However, as one proceeds into a crystal from a free surface it is found that the mean square amplitude decays to its bulk or interior value very quickly. By the time the atom is four or five atomic layers deep in the crystal, its mean square amplitude already has essentially the bulk value. Quite recently my colleague, Mr. Melngailis, and I have calculated the variation with distance into the crystal of the mean square amplitude and mean square velocity of an atom.[48] Since these calculations will be described in detail at another point in this conference I will confine myself here to some qualitative remarks about the results. A pair of ideal free surfaces were created in a nearest and next nearest neighbor central force model of a simple cubic crystal by setting equal to zero all interactions crossing the plane $z = \frac{1}{2}a$, where a is the lattice parameter. The perturbation Hamiltonian consisted of the negative of all the interactions crossing the plane $z = \frac{1}{2}a$. Although this is hardly a small perturbation, the fact that the crystal still retains periodicity and translational invariance against displacements parallel to the x- and y-coordinate axes makes the problem tractable. Exact expressions for the mean square amplitude and mean square velocity of an atom at an arbitrary point in the crystal were obtained by the method of double time Green's functions,[49] and were evaluated in the high temperature limit, where they simplify a bit. I should remark that the effects of the surface on such properties of the nucleus as its mean square displacement and velocity are of order unity rather than of the order of the ratio of the surface area to the volume of the crystal, as is the case, for instance, in calculations of the specific heat of a finite crystal.[50] The results for the mean square amplitude are shown in Fig. 4, as functions of the distance into the crystal from the free surface. Note the marked anisotropy of the mean square amplitude. The component of the mean square amplitude for an atom in the surface itself is twice as great as it is in the interior, while the x and y components are about 30% larger than their bulk values. This anisotropy, which is absent in the results obtained by Rich because of the nature of the crystal model used by him, is due to the fact that the introduction of the free surface lowers the initial

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[43] E. W. Montroll, A. A. Maradudin, and G. H. Weiss, *Proceedings of the Stevens Institute Conference on the Many Body Problem* (Interscience Publishers, Inc., New York, 1963).

[44] P. G. Dawber and R. J. Elliott, Proc. Phys. Soc. (London) **81**, 453 (1963).

[45] A. Dinhofer, Phys. Rev. **131**, 535 (1963).

[46] R. F. Wallis and D. C. Gazis, Phys. Rev. **128**, 106 (1962).

[47] M. Rich, Phys. Letters **4**, 153 (1963).

[48] A. A. Maradudin and J. Melngailis, Westinghouse Research Laboratories Scientific Paper No. 63-129-103-P8 (unpublished).

[49] D. N. Zubarev, Uspekhi Fiz. Nauk. **71** (1960) [English transl.: Soviet Phys.—Uspekhi **3**, 320 (1960)].

[50] See, for example, M. Dupuis, R. Mazo, and L. Onsager, J. Chem. Phys. **33**, 1452 (1960).

cubic symmetry of the unperturbed crystal to tetragonal, at least in those regions of the crystal where the perturbation is strongly operative. Note also the rapid decay of the mean square amplitude to its bulk value as one goes into the crystal.

One of the reasons we chose to use this particular crystal model is that it is the simplest cubic crystal model which has the flexibility to allow us to impose the condition of elastic isotropy on the elastic constants derived from it in addition to the Cauchy relation which follows from our assumption of central forces. This is a convenient feature of our model because we can then verify that in the long wavelength limit the displacement–displacement Green's function has a simple pole corresponding to the well-known dispersion curve for Rayleigh surface waves in the theory of elasticity.[51] This result means, in principle, that we could estimate the contribution to the mean square amplitude from the surface modes, but this is a difficult separation to carry out, and we have not attempted it.

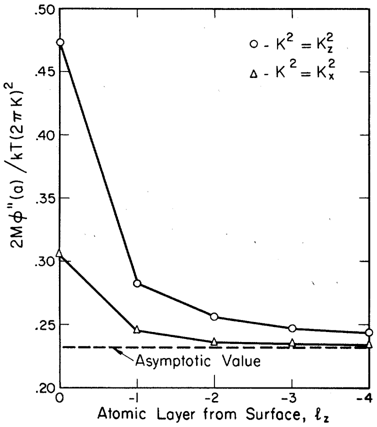

FIG. 4. The exponent $2M$ in the Debye–Waller factor in the high temperature limit as a function of the distance of the resonant nucleus from a free surface of a crystal. $\phi''(a)$ is the second derivative of the interatomic potential evaluated at the nearest neighbor separation; $2\pi\mathbf{K}$ is the wave vector of the γ-ray photon emitted or absorbed by the resonant nucleus.

All the calculations I have just described are highly idealized in their assumption of atomically smooth surfaces, a lack of change of the atomic spacings, and, hence, force constants in the surface layers of a crystal. Even the assumption that the resonant nucleus is one of the atoms of the host crystal has a slightly artificial character. Most of these idealizations can be removed from such calculations, and it is even conceivable that anharmonic effects could be incorporated into the theory, but the required analysis in this case is complicated enough that it would probably keep a graduate student gainfully employed for a couple of months.

One can relate all this to the Mössbauer effect if one can measure the variation with time of the intensity of the recoil free transition or of the second-order Doppler shift of resonant nuclei plated on the surface of a crystal and allowed to diffuse into the interior. Recently, Flinn, Ruby, and Kehl[52] have measured the relative probability of recoilless absorption in different directions in a specially prepared sample of Al_2O_3 of very high specific surface area in which some of the Al ions in surface sites were replaced by trivalent ions of Fe^{57}. They find an anisotropy in the probability of recoilless absorption when the resonant nuclei are in the surface of the Al_2O_3 sample which is absent when the nuclei are in the interior of the sample. The experimental results are not very easy to interpret in the light of the sample theories I have just described, because the experimental conditions depart greatly from the idealized ones assumed in the formulations of the theory. Nevertheless, they have analyzed their data and feel that what they see is in qualitative agreement with the predictions of the simple theories. However, this part of the story is really theirs to tell, and I will not say anymore about it here.

There is a final lattice dynamical aspect to the Mössbauer effect that I should like to mention. This is the pressure dependence of the intensity of the recoil free transitions, of the Debye–Waller factor. Hanks[53] has presented a theoretical calculation of the variation of the Debye–Waller factor with pressure within the framework of the Debye approximation to the frequency spectrum of the host crystal. In this approximation the entire effect comes from the volume dependence of the Debye characteristic temperature for the crystal. Hanks shows that it is possible to increase the value of the Debye–Waller factor by a factor of 2 by the application of pressures of from 5000 to 30 000 atm. to a crystal, but it appears that for such a large change the Debye–Waller factor has to be quite small to begin with. As discussed by Pound,[54] there is also a shift in the position of the recoil free line with pressure, and this effect has been observed experimentally.

From a lattice dynamical standpoint it seems that the pressure dependence of the Mössbauer effect should be of greater interest to nuclear physicists, for example, for inducing the Mössbauer effect in nuclei

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[51] See, for example, A. E. H. Love, *A Treatise on the Mathematical Theory of Elasticity* (Dover Publications, Inc., New York, 1944), pp. 307–309.

[52] P. A. Flinn, S. L. Ruby, and W. L. Kehl, Westinghouse Research Laboratories Scientific Paper No. 63-128-117-P6, private communication.

[53] R. V. Hanks, Phys. Rev. **124**, 1319 (1961).

[54] R. V. Pound, in *The Mössbauer Effect*, edited by D. M. J. Compton and A. H. Schoen (John Wiley & Sons, Inc., New York, 1962), p. 217; R. V. Pound, G. Benedek, and R. W. P. Drever, Phys. Rev. Letters **7**, 405 (1961).

where it is either marginal or nonexistent at zero external pressure. The lattice dynamical information that such pressure experiments can yield seems to be a value for a Grüneisen parameter γ which is a measure also of the thermal expansion of the crystal. This parameter would be a weighted average over the frequency spectrum of the crystal of the Grüneisen γ for each vibration mode. It is, in general, not the same γ as one gets from thermal expansion measurements, in the same way as the equivalent Debye temperature one obtains from the Debye–Waller factor is not the same as one obtains from the specific heat. While such information is worthwhile having, primarily as a consistency check on the results of other calculations, it is neither as interesting nor as useful as the values of the Grüneisen γ's for the individual normal modes, which could be obtained from the results of coherent, one-phonon scattering of neutrons from crystals subjected to hydrostatic pressure.

To conclude, I think it may be appropriate to compare briefly the advantages and disadvantages of the resonant absorption of γ rays by nuclei bound in a crystal relative to other experimental methods now in use for the investigation of the dynamical properties of crystals. The competing methods that I have in mind are the thermal diffuse scattering of x rays, neutron spectroscopy, and infrared optical absorption experiments. In this discussion I will ignore the very considerable experimental difficulties which would arise in carrying out some of the experiments of lattice dynamical interest by means of the resonance absorption of gamma rays. I don't think that this oversight stacks the deck too much in favor of the Mössbauer effect experiments.

Let me consider, first of all, those experiments carried out on essentially perfect crystals, that is, crystals in which the resonant nucleus is one of the atoms of the host crystal, Fe^{57} in Fe or Sn^{119} in Sn, for example. Here, I think that the experiments involving the resonant absorption of gamma rays are at a definite disadvantage compared to the other methods. One can obtain the mean square amplitudes of the atoms comprising the crystal from the intensity of the recoil free transition. However, the same result can be obtained from the temperature dependence of the intensities of the Bragg reflections in x ray diffraction experiments, or better yet, from the inelastic coherent scattering of neutrons from crystals, because here complications arising from the presence of atomic scattering factors in the x-ray case are absent. The chief advantage of the Mössbauer effect for measurements of this kind seems to be that by its use these experiments can be carried out on a laboratory bench; one doesn't need to have a reactor nearby.

From the standpoint of obtaining fundamental lattice dynamical information, I think that no method at present surpasses the coherent, inelastic, one-phonon neutron scattering experiments. These experiments permit one to measure the energies of individual normal modes of a crystal, and, perhaps before much longer, their eigenvectors, and from such data one can obtain, through the intermediary of a crystal model, values of the second-order atomic force constants with a detail and accuracy that no other method can presently match.

While to my knowledge only the measurements of the second-order Doppler shift presently yield the mean square momentum or velocity of an atom in a crystal, the lattice dynamical information contained in this property for a perfect crystal is less detailed than that obtainable from the phonon dispersion curves which neutron spectroscopy yields. Like the mean square amplitude of an atom, the mean square velocity is worthwhile knowing as a check on lattice dynamical models. But its main value for perfect crystals may lie in the fact that its knowledge enables one to obtain values for the isomeric shift in crystals where the second order Doppler shift is large. Even in the study of the atomic vibrations in the vicinity of a free surface in an otherwise perfect crystal, one can argue that other experimental methods are as well suited for these investigations as is the Mössbauer effect. MacRae and Germer[55] have recently scattered very low energy electrons from the surface layers of a nickel single crystal. From the magnitude and temperature dependence of the intensity of the Bragg reflections one can conclude that the mean square amplitude of an atom in the surface is larger than it is for an atom in the interior, in agreement with theoretical predictions. For the determination of the mean square velocity of an atom in the surface layers of a crystal, measurement of the second-order Doppler shift seems to be the only method available at the present time. Analysis of such results with the aid of more detailed theories could yield interesting information about the variation of the atomic force constants in the neighborhood of a crystal surface.

The coherent scattering of neutrons from crystals essentially probes the dynamics of an individual normal mode of a crystal, something which is a property of the crystal as a whole. In contrast, the

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[55] A. U. MacRae and L. H. Germer, Phys. Rev. Letters **8**, 489 (1962).

resonance absorption of gamma rays by a nucleus in a crystal essentially probes the dynamics of that particular nucleus. In this respect, the Mössbauer effect is quite similar to the incoherent, inelastic scattering of neutrons from crystals and leads to similar kinds of results for the one phonon cross section, that is, it yields essentially the frequency spectrum of the host crystal. There are few enough ways at the present time of obtaining the frequency spectrum of a crystal without the intermediate step of constructing a model so that this aspect of the Mössbauer effect, first pointed out by Visscher,[28] deserves to be exploited further. When all the atoms of a crystal are the same there would be few theoretical grounds for preferring one experimental method over the other except that fewer elements scatter neutrons primarily incoherently than display the Mössbauer effect.

It is when we turn to a study of the dynamical properties of impurity atoms in a crystal that the Mössbauer effect as a tool for lattice dynamical research begins to come into its own. There does not seem to be any other way, at the present time, of measuring the mean square amplitude and velocity of an impurity atom in a crystal, and from such determinations it is possible to obtain some information about the force constants of the interaction between the impurity and the host crystal. The fact that the only impurity atoms that can be studied in this way are those which exhibit the Mössbauer effect should not, I think, detract from the interest in such experiments. The one-phonon gamma-ray absorption spectrum associated with an impurity nucleus may be of greater value than the one-phonon incoherent scattering cross section for neutrons for demonstrating the existence of localized vibration modes and the low frequency resonant modes described by Brout and Visscher.[29] This is because very few elements have negative scattering lengths for neutrons, and appreciable concentrations of these nuclei are generally required for alloying with positive scattering length nuclei to yield disordered crystals which scatter neutrons incoherently. The large concentrations of both constituents which are required for the neutron experiments may well smear out or even eliminate such comparatively delicate features in the frequency spectrum as peaks due either to localized or to resonant modes. However, the fact remains that such experiments, by Mozer and his co-workers,[56] have been carried out and show the existence of localized modes. In contrast, with an intense Mössbauer source, only a small concentration of impurity atoms would be required in an absorber to show up the position and strength of these features of the one phonon spectrum by resonance absorption. Correlation of these results with thermal conductivity data would be of great interest. But even here the Mössbauer effect has a competitor for nonmetallic crystals. The experiments of Schaefer[57] and Fritz[58] on the infrared optical absorption spectra of alkali halide crystals with small amounts of hydride and deuteride ions substituting for the halide ions shows that this method is quite capable of showing a great deal of fine structure in the absorption spectra due to defects, for example, peaks associated with localized modes. More recently, following theoretical work of Dawber and Elliott,[44] impurity-induced infrared optical absorption in germanium and silicon has been studied by several groups[59] and promises to be a valuable tool for the study of the interactions, both harmonic and anharmonic, between impurities and the host crystal. Again the fact that such experiments have been and are being carried out, while people are still talking about how hard it is to do the analogous resonance absorption experiments, should not be allowed to detract from the potential interest in the latter type of experiment.

This then completes my comparison of the advantages and disadvantages of resonance absorption experiments versus other kinds of experiments for studying the dynamics of crystal lattices. It was not meant to be a dogmatic discussion but merely a subjective and suggestive one. I have certainly not covered all possible lattice dynamical applications of the Mössbauer effect. For example, it may be that changes in the dynamical behavior of crystals on undergoing the superconducting transition can be studied profitably by means of this effect. In a wilder flight of speculation it may even be possible to modulate the intensity of the Mössbauer line by second sound in solids, if it exists,[60] in analogy to the modulation of its position by ordinary sound in the experiment of Ruby and Bolef.[61] What I have really tried to say is that where there exists the possibility of doing a lattice dynamical experiment using the

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[56] B. Mozer, K. Otnes, and V. W. Myers, Phys. Rev. Letters **8**, 278 (1962).

[57] G. Schaefer, J. Phys. Chem. Solids **12**, 233 (1960).

[58] B. Fritz, J. Phys. Chem. Solids **23**, 375 (1962).

[59] See, for example, M. Balkanski and W. Nazarewicz, J. Phys. Chem. Solids **23**, 573 (1962). See also the papers by the following authors presented at the International Conference on Lattice Dynamics held in Copenhagen, Aug. 5–9, 1963: J. F. Angress and S. D. Smith; R. J. Elliott, W. Hayes, G. V. Jones, and C. T. Sennett; D. G. Montgomery and J. R. Hardy. The proceedings of this conference will be published by Pergamon Press and will appear early in 1964.

[60] E. W. Prohofsky and J. A. Krumhansl, Bull. Am. Phys. Soc. **7**, 219 (1962); M. Chester, Phys. Rev. **131**, 2013 (1963).

[61] S. L. Ruby and D. I. Bolef, Phys. Rev. Letters **5**, 5 (1960).

Mössbauer effect, it is a relevant and a fair question to ask if this is the only way of obtaining the desired information, or even if it is the best way. A good, clever, informative experiment is hard to come by, either by theoreticians or by experimentalists, in any branch of science. The lattice dynamical applications of the Mössbauer effect are no exception. But, as it is often said in other contexts, "it's *got* to be hard to be good!"

ACKNOWLEDGMENT

I should like to thank Professor R. V. Pound for his helpful discussion on the temperature dependence of the isomeric and second-order Doppler shifts.

Optical Analogs of the Mössbauer Effect in Solids

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INTRODUCTION

After most new discoveries in physics there is a period of "digestion" as physicists learn to understand the new effect and in particular to relate it to their previous experience. This digestive process is most fruitful in giving a broader perspective and deeper insight in both the old field of research and the new one. Just such a process has occurred after the discovery by Mössbauer of recoil-free γ-ray transitions in solids. A number of people have been considering problems in solid state optical spectroscopy, a field active for over four decades, in terms of ideas developed in the last four years in the development of solid state γ-ray spectroscopy.[1] The first half of this paper will demonstrate that many of the underlying physical ideas in both fields are essentially the same. The remainder will illustrate this similarity by discussing a number of results of optical experiments in terms of their Mössbauer analogs.

THE ANALOGY

The Mössbauer effect has received a qualitative interpretation from several different points of view.[2] Although the effect is asserted by some to be purely quantum mechanical, a classical description is still instructive. In these terms one thinks of the nucleus held at rest as emitting a classical wave or γ ray of frequency ν_0. If the nucleus is in motion, as it will be in a solid, its "instantaneous frequency" as seen by an observer at rest will vary with time as a result of the Doppler effect and may be written schematically as

$$\nu_n(x,t) = \nu_0 + \frac{\nu_0}{c}\, v(x,t) - \frac{1}{2}\,\frac{\nu_0}{c^2}\, v^2(x,t) + \cdots . \quad \text{(1a)}$$

If the motion of the host crystal is described by the function $\mu(x,t)$ giving the displacement from equilibrium of the atom at position x and time t, the velocity of that atom is simply $\dot{\mu}(x,t)$ and Eq. (1a) may be rewritten

$$\nu_n(x,t) = \nu_0 + \frac{\nu_0}{c}\, \dot{\mu}(x,t) - \frac{1}{2}\,\frac{\nu_0}{c^2}\, [\dot{\mu}(x,t)]^2 + \cdots \quad \text{(1b)}$$

If the function $\exp\,[i \int^t \nu(x,t)\, dt]$ giving the complex amplitude of the classical γ ray is Fourier analyzed, the resultant spectrum has two characteristic features. The first feature is a sharp peak[3] at the frequency $\nu = \nu_0 - \langle \frac{1}{2}\, (\nu_0/c^2)[\dot{\mu}(x,t)]^2 \rangle$; this is the recoilless emission line of γ-ray spectra or the carrier signal of radio frequency engineering. Its strength decreases as the depth of the Doppler-induced frequency modulation increases. The second feature is a continuous spectrum extending over a range of frequencies comparable with or larger than the typical frequencies describing the time variation of the displacement function $\mu(x,t)$. The detailed shape of this broad structure depends on the time dependence of $\mu(x,t)$, while its intensity increases as the mean amplitude of motion of the emitting nucleus increases. This structure is of course the multiphonon

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[1] The relationship between these two fields is either stated or implied in a number of papers. Some of these are: E. O. Kane, Phys. Rev. **119**, 40 (1960); E. D. Trifonov, Doklady Akad. Nauk. SSSR. **147**, 826 (1962) [English transl.: Soviet Phys.—Doklady **7**, 1105 (1963)]; R. Englman and P. Levi, J. Math. Phys. **4**, 105 (1963); See also reference 10. K. K. Rebane and V. V. Khizhnyakov, Optika and Spektroskopiia **14**, 491 (1963) [English transl.; Optics and Spectroscopy **14**, 262 (1963)].

[2] See H. Frauenfelder, *The Mössbauer Effect* (W. A. Benjamin, Inc., New York, 1962) and reprints contained therein.

[3] This peak is strictly a delta function only if the second-order Doppler shift is neglected and if the displacement function, $\mu(x,t)$, has a finite mean square. This second condition is satisfied for a three-dimensional solid in which diffusion is neglected, but not for liquids or one- or two-dimensional "model solids."