value by 0.8%, almost four times the experimental uncertainty in the latter. This discrepancy was noted previously in R1 but, because of uncertainty about the proper interpretation of the experiment, there remained some doubt of its reality at that time.

There seems to be no compelling reason to prefer one value over the other: The two experiments are quite similar in technique and experimental precision, and agreement is found at several points where direct measurements can be compared; the two values of λ result from well-grounded theoretical analyses of the spectra which, in both cases, show a high degree of internal consistency over several molecular levels. We can only conclude that there remains a flaw, undetectable by internal consistency checks, in the theoretical treatment of either the Zeeman effect or the Λ-type doubling. Table VI also shows that the two microwave values of λ, discordant themselves, also fail to agree with the optically measured value. The uncertainty in the optical number, however, is estimated[1] to be as much as 1%; this covers adequately the paramagnetic resonance result, marginally the zero-field microwave result.

Apart from the numerical value of λ and the question of the correct value for the Λ-type doubling frequency of the ${}^2\Pi_{\frac{3}{2}}$, $J=\frac{5}{2}$ level, there are no remaining difficulties in the interpretation of the OH paramagnetic resonance spectra, at least to the precision attained in the present experiments. This precision could perhaps be improved by a factor of ten with moderate effort, but there is little point in doing so without a detailed calculation of relativistic corrections to the molecular Zeeman effect. This is a difficult problem, made more difficult for OH by the apparent seriousness of configuration interaction effects. Although the sort of configuration interaction discussed above does not affect the angular properties of the molecular wavefunctions, and hence cannot perturb the nonrelativistic Zeeman effect, it can enter the relativistic corrections through quantities such as electron kinetic energies which, like the hfs coupling constants, depend on details of the electron distribution.

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Elastic Scattering at Resonance from Bound Nuclei

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The usual Debye-Waller factor, $\langle\exp[-i(\mathbf{k}_f-\mathbf{k}_0)\cdot\mathbf{r}]\rangle$, which when multiplying the fixed-scatterer amplitude gives the nonresonant elastic-scattering amplitude from a bound scatterer, is generally applicable only for fast collisions, i.e., if the "collision time," $\hbar(d/dE)$(scattering phase shift), is much less than a characteristic vibration time, ω_m^{-1}, of the bound scatterer about its mean position. In the opposite extreme case, where the "collision time" is very long compared to ω_m^{-1} (slow collisions), there is negligible correlation between the positions of absorption and subsequence re-emission (for an atom bound in a crystal), and the "Debye-Waller" factor becomes $\langle\exp(-i\mathbf{k}_f\cdot\mathbf{r})\rangle\langle\exp(i\mathbf{k}_0\cdot\mathbf{r})\rangle$. If the scatterers' surroundings exhibit cubic symmetry, the extremes as well as all intermediate cases give the same factor for 90° scattering angle. In the case of medium collisions, collision time $\approx$ vibration time, the elastic scattering amplitude becomes sensitive to the detailed vibrational spectrum of the bound scatterer. For nonresonant scattering the collision times are of the order of transit times (x ray across the atom for Thomson scattering, neutron across the nucleus for neutron potential scattering) and are thus fast collisions.

The inverse characteristic vibration times of atoms in crystals are of the order of their Debye Θ and are a few hundredths of an ev. Slow neutron nuclear resonance widths vary from a few hundredths to a few tenths ev; therefore slow neutron collisions are medium to fast. Gamma-ray resonances for $E_\gamma<100$ kev (Mössbauer), on the other hand, have widths less than 10^{-5} ev, and therefore correspond to slow collisions.

A slight generalization of a formula due to Lamb gives the resonant scattering, and our discussion of the formula is largely a straightforward extension of those of Lamb and Singwi and Sjölander in their discussion of resonance absorption. The total absorption cross section and, in most cases of interest, the inelastic scattering cross section may be obtained from the elastic scattering amplitude.

I. INTRODUCTION

THE waves which are elastically scattered from the various atoms of crystal interfere to give the Laue or Bragg diffraction pattern, and it is from this that their chief interest and usefulness derives.[1] The studies of chemical and magnetic structures of crystals by means of x ray and neutron diffraction techniques are too numerous and well known to require discussion here. It is sufficient to mention that the x-ray scattering is usually mainly given by the Thomson scattering from the atomic electrons, while the neutron scattering is given by the nuclear (potential) scattering and, in the case of magnetic materials, the magnetic electron scattering.

Recently Moon and collaborators[2] have demonstrated

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[1] The elastic scattering also generally has an incoherent part, due to spin effects or crystal imperfections, which contributes a diffuse background between the Bragg peaks. The inelastic scattering, wherein phonons are created or absorbed in the crystal, generally has a coherent component which, however, because of the near continuum of the phonon momentum spectrum, appears as a diffuse background around the Bragg peaks.

[2] P. J. Black and P. B. Moon, Nature **188**, 481 (1960).

the Bragg reflection of the 14.4-kev Mössbauer[3,4] γ rays from an enriched Fe^{57} crystal, the main γ-ray scattering being nuclear resonance scattering, and Peterson and Smith[5] have studied the neutron diffraction pattern of a single crystal of cadmium sulfide for neutron energies in the neighborhood of the 0.18-ev cadmium resonance. Earlier, Brockhouse[6] had determined the resonant neutron scattering cross sections for a number of slow neutron resonances.

The chief interest in diffraction experiments with resonant radiation comes from the usually larger cross sections attainable at resonance, the more rapid energy variation of cross sections (longer collision times), and a negative imaginary component of the scattering amplitude, as compared with the nonresonant interactions.

One may estimate[7] that for the 14-kev γ ray being scattered by an iron crystal containing Fe^{57} the coherent nuclear cross section per crystal site at resonance is $d\sigma/d\Omega \approx F^2 \times 3 \times 10^3$ b/sr, where F is the fractional abundance of Fe^{57}, whereas Thomson scattering by the atomic electrons is $d\sigma/d\Omega \approx 40$ b/sr in the forward direction, and 4 b/sr at 60° scattering angle. The total cross section per site at resonance is $\sigma_T \approx 1 \times F \times 10^6$ b, and so one is limited to the study of superficial (about 10^3 Å) aspects of crystal in this case.[8]

The slow neutron nuclear resonance widths are of the order of 0.1 ev, the low-energy (less than 100 kev) nuclear γ-ray resonance widths are less than about 10^{-5} ev. The Debye temperatures of crystalline materials are commonly of the order 0.01–0.03 ev. During the "collision time" [measured by $(\text{width})^{-1}$] in the case of a slow neutron resonance the nucleus will usually execute only a small (but not very small) fraction of its "crystalline vibration," whereas in the case of the low-energy γ-ray resonance it will execute very many "vibrations" during the collision.

Smith and Peterson have illustrated the use of the imaginary component of the scattering amplitude (resonance) in determining the structure of a noncentrosymmetric unit cell.

Lamb[9] has presented the theory of the resonant absorption of particles by nuclei bound in crystals, and only a slight modification of his theory is necessary to discuss the resonant elastic scattering. We find it useful to transform Lamb's resonance formula from the energy to a time-dependent representation after the mode of procedure utilized by Singwi and Sjölander[10] in their discussion of resonance absorption.[11] This allows us to utilize the elegant methods and results developed by Van Hove[12] in his treatment of the (nonresonant) scattering of neutrons by crystals.

In the following sections formulas governing the elastic scattering of waves from atoms bound in crystals are obtained and discussed.

II. DEVELOPMENT OF PRINCIPAL FORMULAS

In the expression giving the amplitude of the nonresonant elastically scattered waves (of slow neutrons, x rays, etc.) from scatterers which are bound in crystals, the effect of the zero point and temperature motion of the scatterer is contained in a factor which multiplies the fixed scatterer amplitude,[13]

$$\langle \exp[-i(\mathbf{k}_f-\mathbf{k}_0)\cdot\mathbf{r}]\rangle = \exp[-\tfrac{1}{2}\langle[(\mathbf{k}_f-\mathbf{k}_0)\cdot\mathbf{r}]^2\rangle], \quad (1)$$

where $\mathbf{k}_f$ and $\mathbf{k}_0$ are the wave vectors of the scattered and incident waves, respectively, $\mathbf{r}$ is the position of the nucleus of the scatterer relative to its mean position, and the angular brackets indicate the expected value for the crystalline state involved. The equality expressed in Eq. (1) comes from the fact that in the crystal the displacement of a given atom is a result of many small independent displacements (normal modes).[14,15] The left-hand side of Eq. (1) comes immediately upon making the Born approximation in the case of Thomson scattering or the magnetic scattering of neutrons, and, by making use of the Fermi pseudopotential, in the case of nuclear potential scattering of neutrons as well. The elastically scattered waves from the various crystalline sites interfere to give the Bragg reflection, and the factor in Eq. (1) when averaged over a Gibbs

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[3] R. L. Mössbauer, Z. Physik **151**, 124 (1958); Naturwissenschaften **45**, 538 (1958); Z. Naturforsch. **14a**, 211 (1959).

[4] The literature concerning the Mössbauer effect has become very large. An excellent review of experimental and theoretical work, with bibliography, is provided by E. Cotton, J. phys. radium **21**, 263 (1960).

[5] S. W. Peterson and H. G. Smith, Phys. Rev. Letters **6**, 7 (1961).

[6] B. N. Brockhouse, Can. J. Phys. **31**, 432 (1953).

[7] The author, in a paper to appear in the *Proceedings of the International Atomic Energy Agency, Symposium on The Chemical Effects of Nuclear Transformation, October, 1960* considers some theoretical aspects of γ-ray diffraction by resonant nuclei with numerical results estimated for the diffraction of the 14-kev γ ray by Fe^{57}.

[8] Unfortunately, the resonant absorption cross section is usually considerably larger than the scattering cross section. The large absorption cross sections present special problems in the performance and analysis of resonance scattering experiments (see reference 6).

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

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

[11] Effectively this transformation was also made by Lamb[9] but at a later stage in the calculation, and in a manner to somewhat obscure the fact that it was a transformation to a time dependent representation (mainly because he used μ as an integration variable rather than t).

[12] L. Van Hove, Phys. Rev. **95**, 249 (1954); **95**, 1374 (1954).

[13] P. Debye, Ann. phys. **43**, 49 (1914); I. Waller, Z. Physik **17**, 398 (1923); **51**, 213 (1928).

[14] Near crystal imperfections (dislocations, impurity atoms, etc.) the displacement of a given atom may be largely due to a *few* localized vibration modes. Equation (1) will still be true according to Bloch's theorem [F. Bloch, Z. Physik **74**, 295 (1932)] and its discussion by Van Hove,[12] if the angular brackets are interpreted as temperature averages. It is the temperature averaged scattering amplitude which is our principal interest since it determines the coherent elastic scattering from a real crystal.

[15] We consider crystals in thermal equilibrium, excluding cases, e.g., in which the crystal is driven by an ultrasonic generator.

ensemble and squared governs the intensities of the reflections (Debye-Waller factor).

A result of this and succeeding sections will be that Eq. (1) represents an extreme case for which the collision time is very short compared to the time required for the struck scatterer to move an appreciable fraction of a wavelength (of the scattered particle), and that for slow neutron resonant scattering from most crystals at not too elevated temperatures this condition is satisfied to a good approximation. Secondly, that the corresponding factor in case the collision time is very long compared to the "vibration time" of the scatterer in the crystal is

$$\langle e^{-i\mathbf{k}_f\cdot\mathbf{r}}\rangle\langle e^{i\mathbf{k}_0\cdot\mathbf{r}}\rangle=\exp[-\tfrac{1}{2}\langle(\mathbf{k}_f\cdot\mathbf{r})^2+(\mathbf{k}_0\cdot\mathbf{r})^2\rangle], \qquad (2)$$

and that for the resonant scattering of low-energy γ rays from nuclei bound in crystals this condition is satisfied.

According to a formula of Lamb[9] if a wave is incident upon a nucleus with an energy near a resonant energy of the nucleus then the amplitude of the elastically scattered wave is given by[16]

$$f_{\mathrm{R}}=(\Gamma_i/2k_0)\sum_n\frac{\langle\chi_{n_0}|e^{-i\mathbf{k}_f\cdot\mathbf{r}}|\chi_n\rangle\langle\chi_n|e^{i\mathbf{k}_0\cdot\mathbf{r}}|\chi_{n_0}\rangle}{E_{k_0}-E_{\mathrm{R}}-(\epsilon_n-\epsilon_{n_0})+i\Gamma/2}, \qquad (3)$$

times a factor depending on polarizations, multipolarity, etc. In (3) the χ's are the crystal wave functions, the ϵ's are their energy eigenvalues, $E_{\mathrm{R}}-i\Gamma/2$ is the resonance "energy," and Γ_i is the partial width for the incident particle.

The quantity,

$$(\Gamma_i/2k_0)(E_{k_0}-E_{\mathrm{R}}-\epsilon_n+\epsilon_{n_0}+i\Gamma/2)^{-1}, \qquad (4)$$

appearing in (3), is the free-particle resonant scattering length corresponding to an energy (in the c.m. system) $E_{\mathrm{c.m.}}=E_{k_0}-(\epsilon_n-\epsilon_{n_0})$. If there is also a nonresonant term, $\mathcal{R}$, in the free-particle scattering length (e.g., potential scattering term for slow neutron resonances) then it should be added to the resonant term (4), which will result in the addition of

$$f_{\mathrm{N.R.}}=\mathcal{R}\langle\chi_{n_0}|e^{-i(\mathbf{k}_f-\mathbf{k}_0)\cdot\mathbf{r}}|\chi_{n_0}\rangle, \qquad (5)$$

to f_{R}, given by (3) for the scattered amplitude.

Now if $|E_{k_0}-E_{\mathrm{R}}+i\Gamma/2|$ is very large compared to the effective intermediate energy transfers, $\epsilon_n-\epsilon_{n_0}$, then a good approximation to Eq. (3) is (upon the application of closure)

$$f_{\mathrm{R}}\approx(\Gamma_i/2k_0)\frac{\langle\chi_{n_0}|e^{-i(\mathbf{k}_f-\mathbf{k}_0)\cdot\mathbf{r}}|\chi_{n_0}\rangle}{E_{k_0}-E_{\mathrm{R}}+i\Gamma/2}; \text{ (fast collisions)} \qquad (6)$$

whereas, if some average spread of intermediate energy transfer is very large compared to $|E_{k_0}-E_{\mathrm{R}}+i\Gamma/2|$, only $n=n_0$ contributes appreciably to the sum in (3) and one obtains

$$f_{\mathrm{R}}\approx(\Gamma_i/2k_0)\frac{\langle\chi_{n_0}|e^{-i\mathbf{k}_f\cdot\mathbf{r}}|\chi_{n_0}\rangle\langle\chi_{n_0}|e^{i\mathbf{k}_0\cdot\mathbf{r}}|\chi_{n_0}\rangle}{E_{k_0}-E_{\mathrm{R}}+i\Gamma/2}$$

$$\text{(slow collisions)} \qquad (7)$$

The discussion of the region of validity of Eqs. (6) and (7) is facilitated, and a general more lively form is obtained, by transforming the expression (3) for f_{R} into a time-dependent representation,[10,12]

$$f_{\mathrm{R}}=(\Gamma_i/2ik_0)\int_0^\infty dt\, e^{i(E_{k_0}-E_{\mathrm{R}})t}e^{-\Gamma t/2}\times\langle\chi_{n_0}|e^{-i\mathbf{k}_f\cdot\mathbf{r}(t)}e^{i\mathbf{k}_0\cdot\mathbf{r}(0)}|\chi_{n_0}\rangle, \qquad (3')$$

where $\mathbf{r}(t)$ is the nuclear c.m. position operator in the Heisenberg representation. Expressions (6) and (7) now follow from (3′) if in $\mathbf{r}(t)$ we put $t=0$ and $t=\infty$, respectively, and make use of[12]

$$\langle e^{-i\mathbf{k}_f\cdot\mathbf{r}(\infty)}e^{i\mathbf{k}_0\cdot\mathbf{r}(0)}\rangle=\langle e^{-i\mathbf{k}_f\cdot\mathbf{r}}\rangle\langle e^{i\mathbf{k}_0\cdot\mathbf{r}}\rangle, \qquad (8)$$

which is valid for an atom in a crystal.

Equation (3′) is already *anschaulich*, but it leads to the following interesting result. If the incident wave at $r=0$ and time t' is $\int\varphi(E_{k_0})\exp(-iE_kt_0')dE_{k_0}$ then the scattered wave is $\int\varphi(E_{k_0})\,\mathrm{R}^{-1}e^{-ik_0\mathrm{R}}f(E_{k_0},\hat{k}_f,\hat{k}_0)\times\exp(-iE_{k_0}t')dE_{k_0}$, a distance $R\hat{k}_f$ away from the origin. Now if we suppose that over the range in which φf is appreciable the variation of the phase factors (kr) with energy is negligible (the time required for the particle to go from the origin to the scatterer and to R is small compared to the lifetime of the compound nucleus and to the time required for the nucleus to move appreciably), then letting $\varphi=1$, we obtain, $f(t')=(\pi\Gamma_i/2k_0)e^{-iE_{\mathrm{R}}t'-\Gamma t'/2}\langle\chi_{n_0}|e^{-i\mathbf{k}_f\cdot\mathbf{r}(t')}e^{i\mathbf{k}_0\cdot\mathbf{r}(0)}|\chi_{n_0}\rangle$, as the scattered wave amplitude a time t' after the incident particle arrived at the scatterer. Putting $t'=0$ leads to a sum rule on f_{R}.

Again, as in the argument leading to the equalities (1) and (2),

$$\langle\chi_{n_0}|e^{-i\mathbf{k}_f\cdot\mathbf{r}(t)}e^{i\mathbf{k}_0\cdot\mathbf{r}(0)}|\chi_{n_0}\rangle=\exp[-\tfrac{1}{2}\langle(\mathbf{k}_f\cdot\mathbf{r}(t))^2-2(\mathbf{k}_f\cdot\mathbf{r}(t))(\mathbf{k}_0\cdot\mathbf{r}(0))+(\mathbf{k}_0\cdot\mathbf{r}(0))^2\rangle], \qquad (9)$$

in a crystal.

The ordered product in Eq. (9), $(\mathbf{k}_f\cdot\mathbf{r}(t))(\mathbf{k}_0\cdot\mathbf{r}(0))$,

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[16] That the effect of chemical binding is given by Eq. (3) in the case of a γ-ray resonance may be verified by a Wigner-Weisskopf-type treatment or by summing a class of graphs of the S matrix. In the case of a slow neutron resonance, the right-hand side of Eq. (3) should be multiplied by the ratio of the mass of the compound nucleus to that of the target nucleus, the χ_n should be replaced by crystal wave functions in which the mass of the target nucleus is replaced by that of the compound nucleus, and the width, Γ, appearing in the denominator of Eq. (3) should be that of the free particles with a c.m. energy, $E_{k_0}-(\epsilon_n-\epsilon_{n_0})$. Since the slow neutron resonances occur for medium or heavy nuclei and furthermore have relatively small neutron partial widths, Eq. (3) with constant Γ should be sufficiently accurate for practical purposes. The justification of these remarks will be given in a forthcoming letter to The Physical Review.

may be written as the average of the anticommutator, which is real, and the commutator, which is purely imaginary. As Van Hove[12] remarks in a similar context, it is the term containing the commutator which gives rise to specifically quantum effects. The E's and Γ's appearing in (3′) should be divided by $\hbar$ (if t is a time interval), giving frequencies, then (3′) does not involve $\hbar$ explicitly. Equation (3′) then gives the amplitude of the non-frequency-shifted wave scattered from a moving classical resonator if the replacement,

$$\langle \chi_{n_0} | e^{-i\mathbf{k}_f\cdot\mathbf{r}(t)} e^{i\mathbf{k}_0\cdot\mathbf{r}(0)} | \chi_{n_0}\rangle \longrightarrow \langle e^{-i\mathbf{k}_f\cdot\mathbf{r}(t+T)} e^{i\mathbf{k}_0\cdot\mathbf{r}(T)}\rangle_T, \quad (10)$$

is made, where the average over T is implied on the right-hand side of (10). Classical waves (of sufficiently small intensity) do not disturb the c.m. motion of a scatterer, therefore the quantum part of Eq. (9) will contain the effect of an impulse $\hbar k$ imparted to the scatterer during the collision. As is shown below the quantum part of the expression (9) vanishes for $t \longrightarrow \infty$. Then if the major contributions to the integral in Eq. (3′) are from large "t's" (slow collisions), a classical calculation with the replacement (10) will give the correct scattering law.[17]

To evaluate (9) one has from the usual normal mode analysis of the crystal vibrations[18,19]

$$r_i(t) = \sum_{\alpha,\mathbf{q}} \mathbf{e}_{\alpha\mathbf{q}} [\hbar/2MN\omega_{\alpha\mathbf{q}}]^{\frac{1}{2}} [\bar{a}\ _{\mathbf{q}} e^{-i(\mathbf{q}\cdot\mathbf{R}_i - \omega_{\alpha\mathbf{q}}t)} + a_{\alpha\mathbf{q}} e^{i(\mathbf{q}\cdot\mathbf{R}_i - \omega_{\alpha\mathbf{q}}t)}], \quad (11)$$

where $\mathbf{r}_i(t)$ is the displacement of the ith atom from its equilibrium value, $\mathbf{R}_i$, $\mathbf{q}$ is a vector in the first Brillouin zone of reciprocal space, $\mathbf{e}_{\alpha\mathbf{q}}$ is a unit polarization vector, $\alpha = 1, 2, 3$, M is the atomic mass, N is the number of atoms in the crystal, $\omega_{\alpha\mathbf{q}}$ is the angular frequency of the $(\alpha\mathbf{q})$ mode, $\bar{a}$ and a are the usual phonon creation and destruction operators. Making use of Eq. (11), we now obtain

$$\langle \chi_{n_0} | \mathbf{k}_f\cdot\mathbf{r}(t)\mathbf{k}_0\cdot\mathbf{r}(0) | \chi_{n_0}\rangle = (\hbar/MN) \sum_{\alpha\mathbf{q}} \omega_{\alpha\mathbf{q}}^{-1} (\mathbf{k}_f\cdot\mathbf{e}_{\alpha\mathbf{q}})(\mathbf{k}_0\cdot e_{\alpha\mathbf{q}}) \times [(n_{\alpha\mathbf{q}} + \tfrac{1}{2}) \cos\omega_{\alpha\mathbf{q}}t - \tfrac{1}{2}i \sin\omega_{\alpha\mathbf{q}}t], \quad (12)$$

where $n_{\alpha\mathbf{q}}$ is the phonon occupation number of the $(\alpha\mathbf{q})$ mode. The other two terms in the exponent of the right-hand side of Eq. (9) are obtained from Eq. (12) upon putting $t=0$ and replacing $\mathbf{k}_0$ by $\mathbf{k}_f$ or $\mathbf{k}_f$ by $\mathbf{k}_0$.

To this point we have been speaking of the scattering from an atom of a crystal which is assumed to be in a stationary quantum state χ_{n_0} (specified by the numbers $n_{\alpha\mathbf{q}}$). We usually do not have so much information concerning the state of a crystal (except at zero temperature). In order to compute the expected elastic scattering from a macroscopic crystal at a given temperature one should add (with proper phase factors) the contributions [Eq. (3′)] from the various scattering sites. The square of the absolute value of the resultant amplitude should then be averaged (with the usual Boltzman weighting factor) over the crystal states, χ_{n_0}. However, Eqs. (3′), (9), and (12) express the scattering amplitude as a functional of the sum of N small ($\propto 1/N$) independent quantities, so that,

$$\langle | f_\mathrm{R} |^2 \rangle_T = | \langle f_\mathrm{R} \rangle_T |^2 + o(N^{-1}),$$

where the subscript T indicates the thermal average. For a macroscopic perfect crystal, in other words, there is a negligible thermal fluctuation in the elastic scattering amplitude, the stationary states occurring with appreciable probability in the thermal average all yield the same scattered amplitude.[20]

In other words, we may replace stationary-state expectation values in Eqs. (3′), (9), and (12) by temperature averages, if we replace the "$n_{\alpha\mathbf{q}}$'s" in Eq. (12) by their average values in accordance with,

$$\bar{n}(\omega) = (e^{\beta\hbar\omega} - 1)^{-1}, \quad (13)$$

where $\beta = (\kappa T)^{-1}$.

To simplify the formulas somewhat, we specialize to the case that the scattering atoms have a cubic environment. In this case $\langle x_\alpha(t) x_\beta(0)\rangle = \delta_{\alpha\beta}\langle x(t)x(0)\rangle$, where x_α is a Cartesian displacement coordinate of the atom ($\alpha, \beta = 1, 2, 3$), and we obtain,

$$f_{\mathrm{R},T} = \frac{\Gamma_i}{2ik_0} \int_0^\infty dt\, e^{i\Delta t} e^{-\Gamma t/2} \times \exp[-k_0^2 \langle x^2 - \cos\theta\, x(t)x(0)\rangle], \quad (14)$$

where the subscript T and the angular brackets indicate the thermal averaged values, $\Delta = E_{k_0} - E_\mathrm{R}$, $\theta = \sphericalangle(\mathbf{k}_f\mathbf{k}_0)$, and x is a Cartesian coordinate of the displacement of the atom from its equilibrium position.

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[17] The procedure is "semiclassical" rather than classical in that quantum oscillators are replaced by classical oscillators with the same energy (including zero-point contributions), and the disturbance of the scatterers motion by the waves is neglected. Singwi and Sjölander (reference 10) have shown that the intensity of the emitted radiation from a "Mössbauer emitter" is given by an expression similar to that of Eq. (3′) with $\mathbf{k}_f$ replaced by $\mathbf{k}_0$. In this case the "non-Doppler-shifted" component is given correctly by semiclassical considerations, the asymmetry in intensity of the "Doppler-shifted" components of quantum origin.

[18] See, for example, M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954).

[19] We assume for simplicity that there is only one atom per unit crystal cell.

[20] This is manifestly not true for an Einstein model of a crystal, in which the various atoms execute independent oscillations. In this case $\langle |f_\mathrm{el}|^2\rangle_T = |\langle f_\mathrm{el}\rangle_T|^2[1+o(1)]$. Unlike the real perfect crystal, in this case there will be an elastic incoherent scattering component due to (stationary) thermal fluctuations. A small coupling between the oscillators will, however, make the thermal fluctuations nonstationary, and their associated incoherent scattering inelastic. A sufficiently small coupling between the oscillators cannot affect the observed scattering from a crystal in thermal equilibrium; therefore, the formulas developed in the text for the elastic scattering amplitudes from coupled oscillators apply also to the *coherent* elastic scattering amplitudes from uncoupled oscillators. Similar remarks apply to atoms in the vicinity of an imperfection contributing localized vibrational modes to the crystal.

III. DISCUSSION OF EQ. (14)

The imaginary part of $f_{\mathrm{R,T}}$ for $\theta=0$ serves to determine (as is discussed more fully in the next section) the total cross section. The resultant formula obtained from Eq. (14) is, for this special case, the same as that derived and discussed by Singwi and Sjölander[10] and fundamentally the same as that in Lamb's paper.[9] Our discussion of Eq. (14) is mainly a straightforward generalization of those contained in the two cited papers.

The integral in Eq. (14) simplifies in certain regions of the parameters involved.

In the first place for $\theta=90°$ (with our assumption of a cubic crystal) f takes on the simple resonance form,

$$f_{\mathrm{R},T}(\theta=90°)=\frac{[\Gamma_i/(2k_0)]\exp(-k_0^2\langle x^2\rangle)}{\Delta+i\Gamma/2}. \tag{15}$$

For $\cos\theta\, k_0^2\langle x(t)x(0)\rangle$ sufficiently small, an expansion of f as a power series in $\cos\theta\, k_0^2$ is useful, and in any case such an expansion serves to bring out certain general features of Eq. (14).

From Eq. (12) if we perform the temperature average, and assume cubic symmetry, and take N indefinitely large, we obtain

$$\begin{aligned}\langle x(t)x(0)\rangle &= \hbar M^{-1}\int_0^\infty d\omega\, \nu(\omega)\omega^{-1}\\ &\qquad\times[(\bar{n}(\omega)+\tfrac{1}{2})\cos\omega t-(i/2)\sin\omega t],\\ &=\int_{-\infty}^{\infty} g(\omega)e^{-i\omega t}d\omega,\end{aligned} \tag{16}$$

where

$$\begin{aligned} g(\omega)&=\hbar(2M\omega)^{-1}\nu(\omega)[\bar{n}(\omega)+1], && \text{if} \quad \omega\geqslant 0\\ &=\hbar(2M|\omega|)^{-1}\nu(|\omega|)\bar{n}(|\omega|), && \text{if} \quad \omega\leqslant 0.\end{aligned} \tag{17}$$

$d\omega\, \nu(\omega)$ is the fraction of crystal vibration modes with frequencies in the range $(\omega, \omega+d\omega)$, and $\bar{n}(\omega)$ is given by Eq. (13). We might notice that $g(\omega)$ is real and positive. Then $|\mathrm{Re}\langle x(t)x(0)\rangle|\leqslant\langle x^2\rangle$, $|\mathrm{Re}\langle \ddot{x}(t)x(0)\rangle| \leqslant|\mathrm{Re}\langle\ddot{x}(0)x(0)|$, etc.; $|\mathrm{Im}\langle x(t)x(0)\rangle|\leqslant\langle x^2\rangle(T=0)$, etc. Thus the value and curvature of $\mathrm{Re}\langle x(t)x(0)\rangle$ are (not surprisingly) maximum at $t=0$. Some information on the magnitudes of the negative swings of $\mathrm{Re}\langle x(t)x(0)\rangle$ is given by:

$$\mathrm{Re}\int_0^\infty\langle x(t)x(0)\rangle dt=\pi g(0)=\pi C\kappa T/2M,$$

where κ is Boltzman's constant, and C is the constant such that $\nu(\omega)=C\omega^2$ for small ω. Therefore, $\mathrm{Re}\int_0^\infty\langle x(t)x(0)\rangle dt$ is linear in T, whereas $\langle x^2\rangle$ remains finite as $T\rightarrow 0$ (and increases linearly with T for large T's). The proportionality constant C, in fact is given by[18] $C=\frac{4}{3}\pi(2\pi)^{-3}\langle u_1^{-3}+u_2^{-3}+u_3^{-3}\rangle v$, where v is the atomic volume, the u's are the sound velocities of the three polarizations of sound waves propagating in a given direction in the crystal, and the average indicates the average over all propagation directions in the crystal. And this expression is well approximated by[18] $C=3\hbar^3(\kappa\Theta)^{-3}$, where Θ is the empirical Debye temperature of the crystal.

We may now expand $f_{\mathrm{R},T}$, given by Eq. (14), making use of Eqs. (16) and (17), and obtain

$$\begin{aligned} f_{\mathrm{R},T}=\frac{(\Gamma_i/2k_0)\exp(-k_0^2\langle x^2\rangle)}{\Delta+i\Gamma/2}&+\left(\frac{\Gamma_i}{2k_0}\right)\exp(-k_0^2\langle x^2\rangle)\\ &\times\sum_{n=1}^{\infty}\frac{\xi^n}{n!}\int_{-\infty}^{\infty}\frac{p_n(\omega)d\omega}{\Delta-\omega+i\Gamma/2},\end{aligned} \tag{18}$$

where $\xi=k_0^2\cos\theta\langle x^2\rangle$, and

$$p_n(x)=\int_{-\infty}^{\infty}p_1(y)p_{n-1}(x-y)dy, \tag{19}$$

with,

$$p_1(\omega)=(\langle x^2\rangle)^{-1}g(\omega). \tag{20}$$

It follows from Eqs. (16), (17), (19), and (20), that $p_n(\omega)$ is positive and $\int_{-\infty}^{\infty}p_n(\omega)d\omega=1$.

In Eq. (18) the term $\propto\xi^n$ corresponds to n phonons being virtually emitted or absorbed during the scattering process. This expression [Eq. (18)] could, of course, have been obtained directly from Eq. (3) without a transformation to the time representation. The first term in Eq. (18) (no virtual phonons) has a simple pole at $\Delta=-i\Gamma/2$, whereas the succeeding terms correspond to a continuous distribution of poles on the line $\Delta=-i\Gamma/2$. If $(\omega^m)_n=\int_{-\infty}^{\infty}\omega^m p_n(\omega)d\omega$ is the mth moment of the nth distribution, one easily obtains from Eqs. (17), (19), and (20) that

$$(\omega^1)_n=n\hbar/(2M\langle x^2\rangle),$$

and

$$(\omega^2)_n-[(\omega^1)_n]^2=n[M\langle x^2\rangle]^{-1}[\langle\epsilon\rangle-\hbar^2(4M\langle x^2\rangle)^{-1}],$$

where $\langle\epsilon\rangle$ is the energy per degree of freedom of the crystal. For large n, $p_n(\omega)$ becomes the normal distribution function irrespective of the detailed shape of $p_1(\omega)$, the details being smoothed out by reiterations. We may write Eq. (18) as

$$f_{\mathrm{R},T}=\int_{-\infty}^{\infty}\frac{\zeta(\omega)d\omega}{\Delta-\omega+i\Gamma/2}, \tag{18$'$}$$

where $\zeta(\omega)$ is the pole strength density. ζ is real, and for $\cos\theta>0$, ζ is positive. We have for the "total pole strength."

$$\int_{-\infty}^{\infty}\zeta(\omega)d\omega=\left(\frac{\Gamma_i}{2k_0}\right)\exp[-k_0^2\langle x^2\rangle(1-\cos\theta)], \tag{21}$$

and if we define

$$\langle\omega^n\rangle=\left[\int_{-\infty}^{\infty}\zeta(\omega)d\omega\right]^{-1}\int_{-\infty}^{\infty}\omega^n\zeta(\omega)d\omega, \tag{22}$$

then we have for the mean pole position and the mean square "width" of the distribution

$$\langle\omega\rangle = \mathcal{R}\cos\theta/\hbar, \tag{23}$$

and

$$\langle\omega^2\rangle - \langle\omega\rangle^2 = 2\mathcal{R}\cos\theta\langle\epsilon\rangle/\hbar^2, \tag{24}$$

where $\mathcal{R}$ is the so-called recoil energy, $\hbar^2k_0^2/2M$, and $\langle\epsilon\rangle$ is the mean energy per degree of freedom, $\int_0^\infty \nu(\omega)\hbar(\omega)\times[\bar{n}(\omega)+\frac{1}{2}]d\omega$. If $|\Delta+i\Gamma/2|$ is sufficiently large compared to the region of the ω axis where $\zeta(\omega)$ is appreciable, then one may expand (18′) in terms of ω, keep only a few terms, and using the above results obtain $f_{\mathrm{R},T}$ in a form depending only on a few simple properties $(\langle x^2\rangle,\langle\epsilon\rangle)$ of the vibrating nucleus; the scattering being in this case independent of the details of the crystal vibrational spectrum. Also, if ξ is large, the major contributions will be from the large "n" terms in Eq. (18) ($n\cong\xi$) where the $p_n(\omega)$'s are Gaussian, and again (18), or (18′), can be evaluated and depends only on the above simple properties of the vibrating nucleus. Each of these cases may be discussed in a more "*anschaulich*" manner working directly from Eq. (14) (short-collision-time approximation) and we defer their discussion until later.

If ξ is not large, so that just a few terms of Eq. (18) are important (just a few phonons emitted or absorbed), then $f_{\mathrm{R},T}$ may become sensitive to the details of the vibrational spectrum, and this constitutes a method for the experimental investigation of crystal vibrations.

For small ξ, retaining for simplicity only the one-phonon term in Eq. (18), we have

$$f_{\mathrm{R},T} \approx \frac{(\Gamma_i/2k_0)\exp(-k_0^2\langle x^2\rangle)}{\Delta+i\Gamma/2} + k_0^2\langle x^2\rangle\cos\theta(\Gamma_i/2k_0)$$

$$\times\exp(-k_0^2\langle x^2\rangle)\int_{-\infty}^{\infty}\frac{p_1(\omega)d\omega}{\Delta-\omega+i\Gamma/2}. \tag{25}$$

Now, $p_1(\omega)=0$, if $|\omega|>\omega_m$ (maximum crystal vibration frequency). If $\Gamma/2\gg\omega_m$ then again we have the short collision time case, but if $\Gamma/2<\omega_m$, then more detailed knowledge of $p_1(\omega)$ may be obtained by determining experimentally the Δ dependence of the $\cos\theta$ term in $f_{\mathrm{R},T}$. If $\Gamma/2$ becomes small compared to the region in which $p_1(\omega)$ changes appreciably then we obtain

$$f_{\mathrm{R},T} \approx \frac{(\Gamma_i/2k_0)\exp(-k_0^2\langle x^2\rangle)}{\Delta+i\Gamma/2}$$

$$+k_0^2\langle x^2\rangle\cos\theta\exp(-k_0^2\langle x^2\rangle)\Big[-i\pi p_1(\Delta)$$

$$+\mathrm{P.P.}\int_{-\infty}^{\infty}\frac{p_1(\omega)}{\Delta-\omega}d\omega\Big], \tag{25′}$$

but now, aside from the term $k_0^2\langle x^2\rangle\cos\theta$, the second term in Eq. (21′) is of order $|\Delta+i\Gamma/2|\omega_m^{-1}$ relative to the first term. To obtain a measurable effect, then, it would be necessary that $\Gamma/2$ not be *very* small compared to ω_m. In other words, the optimum conditions for determining the vibrational spectrum by means of resonant elastic scattering would be when the life time of the excited state is neither very long nor very short compared to the maximum crystal vibrational frequency. Incidentally, we see from this discussion that if $\Gamma/2$ is sufficiently small the variation of $f_{\mathrm{R},T}$ with Δ for $|\Delta|\ll\omega_m$ is due almost entirely to the first, simple resonance, term in Eq. (25). This is, of course, also true if ξ is not small and we keep higher phonon terms in Eq. (18), since the successive $p_n(\omega)$ become broader and smoother. Strictly speaking these estimates assume that $p_1(\omega)$ is a smooth function, if it should have a "spike" with width $\epsilon\omega_m$, then it would be only when $\Gamma/2\ll\epsilon\omega_m$ that the variation of $f_{\mathrm{R},T}$ with Δ would be independent of the vibrational spectrum for small Δ's. $(\epsilon\omega_m)^{-1}$ determines the time required for the oscillation of $\langle x(t)x(0)\rangle$ to decrease appreciably in amplitude. If $|\Delta+i\Gamma/2|\ll\epsilon\omega_m$ then the first term in Eq. (21) or Eq. (18) represents the contribution to $f_{\mathrm{R},T}$ coming from t's $\gg(\epsilon\omega_m)^{-1}$, whereas the phonon terms represent the contributions from smaller t's (which, incidentally, vanish relative to the no phonon term as $|\Delta+i\Gamma/2|(\epsilon\omega_m)^{-1}$).

The other cases in which Eq. (14) simplifies and becomes independent of the details of the vibration spectrum are when the major contributions to the integral in Eq. (14) come from (a) such small values of t that the first few terms in its Taylor series suffices to approximate $\langle x(t)x(0)\rangle$, or (b), such large values of t that we may set $\langle x(t)x(0)\rangle$ zero.

In order to estimate $f_{\mathrm{R},T}$ in cases where $k_0^2\langle x^2\rangle\cos\theta$ is not necessarily small, we note from Eq. (16) that $\mathrm{Re}\langle x(t)x(0)\rangle$ is maximum at $t=0$, it goes negative at t of the order of ω_m^{-1} (where ω_m is the maximum vibrational frequency of the crystal), usually positive again, etc.; its amplitudes of oscillations, according to Van Hove,[12] eventually going to zero as $t^{-\frac{3}{2}}$.

If $|\Delta+i\Gamma/2|$ is of the order of ω_m one will obtain appreciable contributions to the integral [Eq. (14)] from t's such that nucleus has undergone, perhaps, several oscillations, and $f_{\mathrm{R},T}$ will be sensitive to the details of the crystal vibration spectrum. An exception to this occurs, however, if $k_0^2\langle x^2\rangle\cos\theta$ is sufficiently large and positive, in which case only t's such that $t\ll\omega_m^{-1}$ need be considered as contributing appreciably to the value of $f_{\mathrm{R},T}$.

If $|\Delta+i\Gamma/2|\gg\omega_m$ then only t's $\ll\omega_m^{-1}$ contribute appreciably. An exception to this, however, occurs if for given $|\Delta+i\Gamma/2|$, $k_0^2\langle x^2\rangle\cos\theta$ is sufficiently large and negative, in which case the major contributions to f may come from t's $\approx\omega_m^{-1}$.

If $t<t_1\ll\omega_m^{-1}$ then $\langle x(t)x(0)\rangle$ may be well approximated by the first few terms of its Taylor series; retaining only terms up to t^2 we obtain as an approximation to $f_{\mathrm{R},T}$,[9,10]

$$f_{\mathrm{R},T}\approx(\Gamma_i/2ik_0)\exp[-k_0^2\langle x^2\rangle(1-\cos\theta)]\times\int_0^{t_1}\exp[i(\Delta-\mathcal{R}\cos\theta)t]e^{-\Gamma t/2}\times\exp[-(\mathcal{R}\langle\epsilon\rangle\cos\theta)t^2]dt,\qquad(26)$$

where $\mathcal{R}$ and $\langle\epsilon\rangle$ are defined after Eq. (24).[21]

It is interesting to note that according to Eq. (26) the elastic scattering resonance is shifted to lower energies if $\cos\theta<0$, as if the nucleus were moving toward the incident particle before the collision, which is not surprising.

If $|\Delta+i\Gamma/2|\omega_m^{-1}$ is not small, and, $|i\Delta+\Gamma/2|\omega_m^{-1}+\mathcal{R}\langle\epsilon\rangle\cos\theta\omega_m^{-2}\gg1$, then Eq. (26) is a good approximation to $f_{\mathrm{R},T}$. Under these conditions we may re-express Eq. (26) in the standard form.

$$f_{\mathrm{R},T}\approx(\Gamma_i/2ik_0)\exp[-k_0^2\langle x^2\rangle(1-\cos\theta)]\times\frac{\sqrt{\pi}}{2}(\mathcal{R}\langle\epsilon\rangle\cos\theta)^{-\frac{1}{2}}w(\zeta),\qquad(27)$$

where $\zeta=\frac{1}{2}(\Delta-\mathcal{R}\cos\theta+i\Gamma/2)(\mathcal{R}\langle\epsilon\rangle\cos\theta)^{-\frac{1}{2}}$, and

$$w(x)=(2i/\sqrt{\pi})\exp(-x^2)\int_x^{i\infty}e^{y^2}dy.\qquad(28)$$

$w(x)$ may be expanded for large and small $|x|$ and is tabulated[22] for middle size $|x|$'s. Using[22]

$$w(x)=\frac{i}{\pi}\int_{-\infty}^{\infty}\frac{\exp(-t^2)dt}{x-t}.\qquad(29)$$

Eq. (27) may be put into the forms,

$$f_{\mathrm{R},T}\approx(\Gamma_i/2k_0)\exp[-k_0^2\langle x^2\rangle(1-\cos\theta)]\int_{-\infty}^{\infty}\frac{(4\pi\mathcal{R}\langle\epsilon\rangle\cos\theta)^{-\frac{1}{2}}\exp(-x^2/4\mathcal{R}\langle\epsilon\rangle\cos\theta)}{\Delta-\mathcal{R}\cos\theta-x+i\Gamma/2}dx,\qquad(30)$$

if $\cos\theta>0$, and

$$f_{\mathrm{R},T}\approx(\Gamma_i/2k_0)\exp[-k_0^2\langle x^2\rangle(1-\cos\theta)]\int_{-\infty}^{\infty}\frac{(4\pi\mathcal{R}\langle\epsilon\rangle|\cos\theta|)^{-\frac{1}{2}}\exp(-x^2/4\mathcal{R}\langle\epsilon\rangle|\cos\theta|)}{\Delta-\mathcal{R}\cos\theta+i(\Gamma/2-x)}dx,\qquad(31)$$

if $\cos\theta<0$.

Equation (30) exhibits the familiar form (except for the $\cos\theta$ factor) expressing the effect on the resonance of the distribution of velocities of the scatterer as simple Doppler shifting of the resonance frequencies, this generally has the effect of lowering the maximum scattering amplitude. Equation (31) indicates (for $\cos\theta<0$) a spread of widths, resulting in a larger maximum scattering amplitude than the zero-velocity case. For $\cos\theta>0$ the effective lifetime is decreased due to the scatterer's motion; for $\cos\theta<0$ it is increased.

For large ζ we may approximate Eq. (27) for $f_{\mathrm{R},T}$ by[22]

$$f_{\mathrm{R},T}\approx(\Gamma_i/2k_0)\exp[-k_0^2\langle x^2\rangle(1-\cos\theta)]\times\left[\frac{0.665}{\Delta-\mathcal{R}\cos\theta+i\Gamma/2}+\frac{0.167}{\Delta-\mathcal{R}\cos\theta+i\Gamma/2+x}+\frac{0.167}{\Delta-\mathcal{R}\cos\theta+i\Gamma/2-x}\right],\qquad(32)$$

where $x=2.44[\mathcal{R}\langle\epsilon\rangle\cos\theta]^{\frac{1}{2}}$. If either $(\Delta-\mathcal{R}\cos\theta)\times[\mathcal{R}\langle\epsilon\rangle\cos\theta]^{-\frac{1}{2}}$, or $(\Gamma/2)[\mathcal{R}\langle\epsilon\rangle\cos\theta]^{-\frac{1}{2}}$ is greater than 4, then Eq. (32) represents Eq. (27) with less than 1% error.

Turning now to the long-collision-time case, it is convenient to follow Singwi and Sjölander and rewrite Eq. (14) in the form

$$f_{\mathrm{R},T}=\frac{(\Gamma_i/2k_0)\exp(-k_0^2\langle x^2\rangle)}{\Delta+i\Gamma/2}+(\Gamma_i/2ik_0)\int_0^{\infty}e^{i\Delta t}e^{-\Gamma t/2}\exp(-k_0^2\langle x^2\rangle)\times[\exp[k_0^2\cos\theta\langle x(t)x(0)\rangle]-1]dt.\qquad(33)$$

Now $\langle x(t)x(0)\rangle$ goes to zero as $t^{-\frac{3}{2}}$ as $t\rightarrow\infty$.[23] Let t_2 be such that for $t>t_2$, $|k_0^2\cos\theta\langle x(t)x(0)\rangle|\ll1$. Now if $|\Delta+i\Gamma/2|t_2\ll1$ the first, simple resonance, term in Eq. (33) represents the contribution to Eq. (14) of t's$>t_2$, whereas the second term represents the contribution of t's$<t_2$. In the second term $|\Delta+i\Gamma/2|$ may be set zero (neglecting term of relative order $|\Delta+i\Gamma/2|t_2$),

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[21] G. H. Vineyard, Phys. Rev. **110**, 999 (1958).

[22] V. N. Faddeyeva and N. M. Terentev, *Mathematical Table Series* (Pergamon Press, New York, 1960), Vol. II.

[23] We have ignored the effect of anharmonic terms in the crystalline potential energy on the crystal vibrations, as did Van Hove in his derivation of the $t^{-\frac{3}{2}}$ law (reference 12). The effect of these terms, which lead to a "finite phonon lifetime, will be an eventual exponential decay of the correlation function, $\langle x(t)x(0)\rangle\sim e^{-\alpha t}$. A crude estimate of α is $\alpha\approx$(atomic displacement÷interatomic distance)$\times\omega_m\approx$a few percent of ω_m at room temperature. Now α may be ignored if $\Gamma\gg\alpha$, of course, or generally in the short-collision-time case; but even if Γ is comparable to or smaller than α only the value of the integral in Eqs. (33) and (34) is affected, and for long collision times this integral is small compared to the simple resonance term. In a crude approximation the effect on the integral may be estimated by the replacement $\omega\rightarrow\omega-in\alpha$ in the denominators of Eq. (18), which gives a small effect so long as $p_n(\omega)$ varies relatively little in $\Delta\omega\approx n\alpha$.

and we obtain,

$$f_{\mathrm{R},T}\approx\frac{(\Gamma_i/2k_0)\exp(-k_0^2\langle x^2\rangle)}{\Delta+i\Gamma/2}+(\Gamma_i/2ik_0)\int_0^\infty \exp(-k_0^2\langle x^2\rangle)\times[\exp[k_0^2\cos\theta\langle x(t)x(0)\rangle]-1]dt,\quad(34)$$

for $|\Delta+i\Gamma/2|t_2\ll 1$. The second (nonresonant term) is or order, $|\Delta+i\Gamma/2|t_2$ relative to the first term, and is then negligible for sufficiently long collision times.[24] If we keep $(\Gamma/2)t_2\ll 1$ but vary Δ, then as Δ becomes of the order of t_2^{-1} the variation with Δ of the second term in Eq. (33) may become as important as that of the first, $f_{\mathrm{R},T}$ in this region becoming a complicated function of Δ depending on the details of the crystal vibrations. For sufficiently large Δ, or sufficiently large $k_0^2\cos\theta\langle x^2\rangle$, such that the conditions leading to Eq. (27) (deleting the condition $|\Delta+i\Gamma/2|\omega_m^{-1}$ not being small) are satisfied, then Eq. (27) may be used to represent the integral in Eq. (33).

For a simple monatomic crystal t_2 may be taken as a few times $\omega_m^{-1}\approx[\kappa\Theta]^{-1}$, but for a molecular crystal there may be modes of vibration of a single molecule which decrease in amplitude with a characteristic time much longer than ω_m^{-1}, i.e., in $\nu(\omega)$ there may be "spikes" with widths much less than ω_m. We might have a situation in which $t_2^{-1}\ll\omega_m$ is satisfied. In order to gain some insight into the effect of such spikes, we evaluate Eq. (14) assuming $\nu(\omega)=\delta(\omega-\omega_0)$, i.e., we take an Einstein model for the solid. In this case we obtain

$$f_{\mathrm{R},T}=(\Gamma_i/2k_0)\exp(-k_0^2\langle x^2\rangle)\times\sum_{m=-\infty}^{\infty}\left(\frac{p}{q}\right)^{m/2}\frac{I_m(2(pq)^{\frac{1}{2}}\xi)}{\Delta-m\omega_0+i\Gamma/2},\quad(35)$$

where

$$p=[\bar{n}(\omega_0)+1][2\bar{n}(\omega_0)+1]^{-1},\quad q=\bar{n}(\omega_0)[2\bar{n}(\omega_0)+1]^{-1},\quad \xi=k_0^2\cos\theta\langle x^2\rangle,$$

and

$$I_m(2z)=z^{|m|}\sum_{n=0}^{\infty}\frac{z^{2n}}{n!(n+|m|)!}=e^{-im\pi/2}J_m(2iz)\quad(36)$$

is the modified Bessel function.

IV. TOTAL CROSS SECTION, INELASTIC SCATTERING

Our discussion to this point has been concentrated upon the elastic scattering amplitude, but of course the amplitude of the elastically scattered wave (more exactly the coherent part of it) in the forward direction determines the total cross section, in accordance with

$$\sigma_T=-4\pi k_0^{-1}\,\mathrm{Im}f(\mathbf{k}_f=\mathbf{k}_0).\quad(37)$$

Inserting the expression obtained in the preceding sections for $f_{\mathrm{R},T}$ into Eq. (37), one finds the expressions for σ_T obtained by Lamb[9] and Singwi and Sjölander.[10] Along with Lamb we have neglected the dependence of the lifetime of the compound nucleus on the crystal binding, and the dependence of the resonance width on the energy of the incident particle. Furthermore, in the preceding sections we have computed $f_{\mathrm{R},T}$ for a single scatterer. Inserting such a value of f into Eq. (37) cannot properly represent the effect of interference of the waves from the various scatterers on the total effective cross section. If $\mathbf{k}_0$ is not at a Bragg angle of a single crystal there is no coherent elastic scattering, and then inserting $f_{\mathrm{R},T}$ into Eq. (37) will overestimate the total cross section; whereas if $\mathbf{k}_0$ is at a Bragg angle we would get an underestimate of the total cross section. For a powdered crystal these effects tend to compensate each other. In addition, since at a non-Bragg angle there is no coherent elastic scattering the effective width of the resonance is decreased, at a Bragg angle, increased. So long as $\Gamma_i/\Gamma\ll 1$ these effects are of little importance and may be neglected.[25] In order to take them properly into account one must consider multiple scattering of the waves.

In addition to the total cross section one may obtain the total differential inelastic scattering from the elastic differential cross section in most cases of practical interest (the velocity of the incident particle large compared to that of the target nucleus).

One has for the differential scattering cross section,

$$\frac{d\sigma}{d\Omega}=\sum_{n_f}\left|\sum_n\frac{\langle\chi_{n_f}|e^{-i\mathbf{k}_f\cdot\mathbf{r}}|\chi_n\rangle\langle\chi_n|e^{i\mathbf{k}_0\cdot\mathbf{r}}|\chi_{n_0}\rangle}{E_{k_0}-E_R-(\epsilon_n-\epsilon_{n_0})+i\Gamma/2}\right|^2\left(\frac{\Gamma_i}{2k_0}\right)^2\approx\left|\sum_n\frac{\langle\chi_n|e^{-i\mathbf{k}_0\cdot\mathbf{r}}|\chi_{n_0}\rangle}{E_{k_0}-E_R-(\epsilon_n-\epsilon_{n_0})+i\Gamma/2}\right|^2\left(\frac{\Gamma_i}{2k_0}\right)^2=(\sigma_T/4\pi)(\Gamma_i/\Gamma),\quad(38)$$

where in the second line we have assumed that we could neglect the variation of k_f in the sum over states. Thus, in this case, the elastic plus inelastic differential scattering cross section is independent of scattering angle, and knowledge of the total cross section and the differential elastic cross section allows us to obtain the total differential inelastic cross section.

V. CONCLUSION AND EXAMPLES

If the collision time, $|\Delta+i\Gamma/2|^{-1}$, is very short compared to the time required for the struck nucleus to move appreciably [for $\langle\mathbf{k}_f\cdot\mathbf{r}(t)\mathbf{k}_0\cdot\mathbf{r}(0)\rangle$ to change

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[24] A rough overestimate of its relative magnitude is
$$|\Delta+i\Gamma/2|\omega_m^{-1}\exp(k_0^2|\cos\theta|\langle x^2\rangle).$$

[25] Such coherence effects are dealt with by the author in reference 7 and M. I. Podgonetskii and I. I. Raizen, J. Exptl. Theoret. Phys. (U.S.S.R.) **39**, 1473 (1960) [translation: Soviet Phys.—JETP **12**, 1023 (1961)].

TABLE I. Mean square atomic displacements.

	A	Θ	$(2\pi\times10^8)^2\langle x^2\rangle_0$	$(2\pi\times10^8)^2\langle x^2\rangle_{300}$
Fe	57	355	0.07	0.25
Cd	112	165	0.078	0.51
Au	197	164	0.04	0.32
Pu	240	200	0.027	0.13

appreciably from $\langle \mathbf{k}_f\cdot\mathbf{r}\mathbf{k}_0\cdot\mathbf{r}\rangle]$, then the elastic scattering amplitude near resonance is just the usual Breit-Wigner expression multiplied by, $\exp[-\frac{1}{2}\langle(\mathbf{k}_f\cdot\mathbf{r})^2+(\mathbf{k}_0\cdot\mathbf{r})^2-2(\mathbf{k}_f\cdot\mathbf{r})(\mathbf{k}_0\cdot\mathbf{r})\rangle]$. If the collision time is long compared to the time required for $\langle\mathbf{k}_f\cdot\mathbf{r}(t)\mathbf{k}_0\cdot\mathbf{r}(0)\rangle$ to become negligible, the multiplying factor is got from the above by leaving out the $\langle\mathbf{k}_f\cdot\mathbf{r}\mathbf{k}_0\cdot\mathbf{r}\rangle$ term, there being no correlation between the places of absorption and subsequent re-emission. Assuming, for simplicity, that the nuclear vibrations in three perpendicular directions are independent and equal in amplitude (cubic symmetry) the multiplying factors simplify, becoming $\exp[-k_0^2\langle x^2\rangle(1-\cos\theta)]$, for fast collisions, and, $\exp(-k_0^2\langle x^2\rangle)$, for slow collisions.

In the slow-collision case the elastic cross section becomes negligible rapidly as, $k_0^2\langle x^2\rangle$, becomes larger than one. In the fast-collision case, on the other hand, the multiplying factor is always one in the forward direction, and the total elastic scattering cross section decreases just as $[k_0^2\langle x^2\rangle]^{-1}$ as $k_0^2\langle x^2\rangle$ becomes large.

In Table I[26] we give the values of $\langle x^2\rangle$, estimated using the Debye model[27] of a solid, for a few metals. We give $(2\pi\times10^8)^2\langle x^2\rangle$; to obtain $k_0^2\langle x^2\rangle$, one must multiply by $[E(\text{kev})/12.3]^2$ in the case of γ-ray scattering, and $[E(\text{ev})/0.07]$, for neutron scattering. It is seen that for 1 Å radiation the Debye-Waller factor is near one even at room temperature, whereas for 0.1 Å radiation, even at low temperatures the factor will be small.

The widths of nuclear levels less than about 100 kev above the ground state are less than about 10^{-5} ev. Since the vibration frequencies in solids correspond to a $\hbar\omega_m=\kappa\Theta=$a few hundredths of an ev, γ-ray resonances resulting in appreciable elastic scattering will correspond to slow collisions. For the slow neutron resonances, on the other hand, one has an excitation energy of the compound nucleus of about 10 Mev and level widths ranging from several hundredths to a few tenths of an ev, corresponding to medium to short collision times.

As a first numerical example we consider the scattering of 14.4-kev γ rays by Fe^{57}. $\Gamma/2=2.3\times10^{-9}$ (ev),[4] and, from the table, $k_0^2\langle x^2\rangle_{300}\approx0.34$. In Eq. (25′) the second term is only about 10^{-7} as large as the first term if Δ is of the order of $\Gamma/2$, and may be ignored. If the Fe^{57} is in a magnetically-ordered crystal, then the Zeeman splittings of the ground and excited states are somewhat larger than Γ. Taking account of the fact that the transition is a magnetic dipole transition, we have

$$f=\sum_\mu \tfrac{3}{2}D_{\mu m'}{}^{(1)*}(\hat{k}_f,\hat{z})D_{\mu m}{}^{(1)}(\hat{k}_0,\hat{z})C^2(j_0 1 j_1;m_0\mu)\times(\Gamma_i/2k_0)\frac{\exp(-k_0^2\langle x^2\rangle)}{[E_{k_0}-E_R(m_0,m_0+\mu)+i\Gamma/2]},\quad(39)$$

where f is the amplitude of the elastically scattered wave in the $\hat{k}_f$ direction with polarization m' (±1 for right- or left-hand circularly polarized waves), if a photon of energy E_{k_0}, polarization m, is incident in the $\hat{k}_0$ direction on a nucleus which has a magnetic quantum number m_0 along the z axis. j_0 and j_1 are the spin of the ground state and the excited state, respectively. The notation for the rotation matrixes (D) and the vector addition coefficients (C) are those of Rose.[28] $\mu=\pm1$ correspond to right- and left-hand "circular" oscillators, $\mu=0$, to a linear oscillator along the z axis. The C^2 factor gives the oscillator strength, the $E_R(m_0,m_0+\mu)$ the oscillator frequency, and the D's the usual angle-dependent excitation and emission factors for these oscillators. The coherent amplitude is obtained from Eq. (39) by averaging over the initial spin states, m_0, and if we assume negligible nuclear polarization we obtain

$$f_{\text{coh}}=(2j_0+1)^{-1}\textstyle\sum_{m_0} f,\quad(40)$$

where f is the right-hand side of Eq. (39). Equation (40) simplifies if the splittings are negligible compared to Γ (magnetically disordered state, e.g., Fe in stainless steel); replacing all $E_R(m_0,m_0+\mu)$ by E_R, we obtain[28]

$$f_{\text{coh}}=\frac{3}{2}\frac{2j_1+1}{3(2j_0+1)}d_{mm'}{}^{(1)}(\hat{k}_f\cdot\hat{k}_0)\times\frac{\Gamma_i\exp(-k_0^2\langle x^2\rangle)}{2k_0[E_{k_0}-E_R+i\Gamma/2]}.\quad(41)$$

If we square Eq. (41), integrate over angles, and sum over m', we obtain,

$$\sigma_{\text{coh}}=\frac{2\pi}{3}\left(\frac{2j_1+1}{2j_0+1}\right)^2\left|\frac{\Gamma_i\exp(-k_0^2\langle x^2\rangle)}{2k_0[E_{k_0}-E_R+i\Gamma/2]}\right|^2.\quad(42)$$

Also, from Eq. (41) and the optical theorem [Eq. (37)], we have for the total cross section,

$$\sigma_T=2\pi\left(\frac{2j_1+1}{2j_0+1}\right)\frac{\Gamma_i\Gamma\exp(-k_0^2\langle x^2\rangle)}{4k_0^2|E_{k_0}-E_R+i\Gamma/2|^2}.\quad(43)$$

Inserting numerical values for Fe^{57} ($j_0=\frac{1}{2}$, $j_1=\frac{3}{2}$, $\Gamma_i/\Gamma=(1+\alpha)^{-1}=15^{-1}$, $\alpha=$interval conversion coeffi-

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[26] The values of the Debye Θ are taken from the *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957) except that the value for Pu was taken to be the same as that listed for U, a value of Θ for Pu not being found listed.

[27] For a review together with curves to aid in the computation of $\langle x^2\rangle$ see, for example, E. Cotton, reference (4).

[28] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957), pp. 32, 48.

cient), we obtain $\sigma_{\mathrm{coh}}=3\times10^4$ b, and $\sigma_T=10^6$ b at resonance.

As a second example we consider the 77-kev level in Au^{197} $[\Gamma/2=1.1\times10^{-7}$ ev, $(\Gamma_i/\Gamma)=0.22]$. At zero temperature we have $k_0^2\langle x^2\rangle=1.6$, at room temperature it is some eight times larger, so appreciable scattering will occur only for $T\ll164°$. At these low temperatures the corrections to Eq. (39) are still only of the order of $e^{1.6}\times10^{-5}\approx10^{-4}$ of the resonant value of Eq. (39), and thus may be neglected, near resonance, at low temperatures. Assuming that the $(\frac{3}{2}+)\rightarrow(\frac{1}{2}+)$ transition is predominantly $M1$, Eqs. (41) and (42) will also apply to this case. Inserting numbers into Eqs. (42) and (43) we obtain $\sigma_{\mathrm{coh}}=200$ b, and $\sigma_T=3\times10^4$ b, at resonance.

Turning now to neutron resonances it is only necessary to multiply $f_{R,T}$ by $[(2j_1+1)/2(2j_0+1)]$ to obtain the coherent scattering amplitude (unpolarized neutrons, unpolarized nuclei).

As a first example we consider the 4.9-ev neutron resonance in Au^{197}. These neutrons have a little shorter (3/4) wavelength than the 77-kev γ ray. We have[29] $\Gamma/2=0.07$ ev, $\Gamma_n/2=0.008$ ev, $j_0=\frac{3}{2}$, $j_1=2$, and, from the table, $k_0^2\langle x^2\rangle=2.9$, at low temperatures. Now, $\hbar\omega_m\approx\kappa\Theta\approx0.014$ ev, and so the conditions (short collision time) leading to the validity of Eq. (24) are met. We have $\mathcal{R}=4.9/197=0.025$ ev and $\langle\epsilon\rangle\approx\frac{1}{2}\hbar\omega_m$ at low temperatures (in the Debye approximation $\langle\epsilon\rangle=\frac{3}{8}\hbar\omega_m=0.005$ ev). Approximating Eq. (27) by Eq. (32), we have

$$f_{\mathrm{coh}}\approx\frac{510^{-3}}{k_0}e^{-2.9(1-\cos\theta)}\left[\frac{0.665}{\Delta-0.025\cos\theta+0.07i}+\frac{0.167}{\Delta-0.025\cos\theta+0.07i+0.027(\cos\theta)^{\frac{1}{2}}}+\frac{0.167}{\Delta-0.025\cos\theta+0.07i-0.027(\cos\theta)^{\frac{1}{2}}}\right].\quad(44)$$

The corrections to the resonance denominator of the simple fixed-nucleus Breit-Wigner formula are small, but not completely negligible. Equation (44) when squared yields a maximum, $d\sigma_{\mathrm{coh}}/d\Omega\approx200e^{-2.9\theta^2}$ b/sr, for small θ.

As our last example we consider the 1-ev resonance in Pu^{240}. This resonance is given as having the remarkably small width, $\Gamma/2=0.017$ ev, $\Gamma_n/2=0.001$ ev.[29] According to our estimate of Θ for Pu, $\hbar\omega_m\approx0.02$ ev. Consequently, the coherent scattering amplitude, and therefore the total cross section, will be rather sensitive to the details of the phonon spectrum (during the scattering process the nucleus will execute a vibration or so). According to the table the Debye-Waller factor is not small even at room temperature. The scattering amplitude will, then, not be very small in the region for which Eq. (25) is valid, and an experimental study of the coherent scattering could give detailed information concerning the crystal vibrational spectrum.

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[29] *Newton Cross Sections*, completed by D. J. Hughes and R. Schwartz, Brookhaven Natural Laboratory Report BNL-325 (Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. 1958), 2nd ed.

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Nuclear Magnetic Relaxation of a Three-Spin Asymmetric Molecule in a Liquid*

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The semiclassical density-matrix theory of relaxation is employed to calculate the relaxation of the z component of nuclear magnetization of molecules in a liquid for the case in which three identical nuclei of spin $\frac{1}{2}$ are arranged at the vertices of an isosceles triangle whose angles are 30°, 30°, and 120°. It is found that, if the initial state of the spin systems is characterized by a spin temperature, the relaxation consists of the sum of seven terms which decay exponentially with different time constants. It is also found that even though the z component of the magnetization is a function of seven distinct time constants, a plot of $\ln(M_z-M_{eq})$ can be approximated by a single straight line for regions of experimental interest. The time constant for this straight line differs less than 1% from the average relaxation time calculated from the formulas of Gutowsky and Woessner.

I. INTRODUCTION

THE semiclassical density-matrix theory of relaxation was employed by P. S. Hubbard[1] to calculate the relaxation of the z component of nuclear magnetization for a system of identical nuclei of spin $\frac{1}{2}$ arranged, respectively, at the corners of an equilateral triangle or a regular tetrahedron. Hubbard showed, for the former case, that, although the z component of the magnetization relaxed with two distinct relaxation times, the relaxation was dominated by a single relaxation time. This relaxation time differed less than 1% from the one calculated using the method of Gutowsky and Woessner[2]

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[1] P. S. Hubbard, Phys. Rev. **109**, 4 (1958).

[2] H. S. Gutowsky and D. E. Woessner, Phys. Rev. **104**, 843 (1956).