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# *THE EFFECT OF DIFFUSION ON THE SCATTERING OF NEUTRONS AND PHOTONS BY CRYSTAL IMPERFECTIONS AND ON THE MÖSSBAUER EFFECT*

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The broadening of the energy distribution of neutrons or photons which are quasi-elastically scattered by crystal defects resulting from diffusion is investigated. The macroscopic approximation is not used and the diffusion mechanism is taken into account explicitly. The broadening may be appreciable in the scattering of neutrons and photons which are emitted without recoil by nuclei in a crystal, and also in certain cases of Rayleigh scattering of light at high temperatures. The analogous broadening should occur for the spectral distribution in the absorption and emission spectra in the Mössbauer effect for the case of high temperatures. The characteristic dependence is found of the broadening on the magnitude and orientation of the wave vector, and this makes it possible in principle to investigate the mechanism of diffusion and the type of defect.

## 1. INTRODUCTION

THE diffuse scattering of neutrons by defects in a crystal at sufficiently low temperatures can be divided into inelastic scattering associated with thermal vibrations and having a continuous energy distribution, and elastic scattering whose energy distribution is described by a $\delta$ function $\delta(E)$ (where $E$ is the change in energy on scattering). At high temperatures, however, defects (atoms injected in interstices, vacancies at lattice sites, etc.) give an appreciable diffusion mobility. A defect moving at random even in the absence of vibration can transfer energy to a neutron, as a result of which the $\delta$ function in the energy distribution of the scattered neutrons is smeared out, and the scattering becomes completely inelastic.

The influence of the diffuse motion of the atoms of a liquid on the scattering of neutrons has been treated by means of the macroscopic approximation in references 1—3. This approximation is applicable for the case of very slow neutrons or small scattering angles. For large differences $q_1$ of the wave vectors of the scattered and incident waves, the results depend essentially on the geometry of the diffusion jumps of the atoms, and the macroscopic approximation ceases to be applicable. In the case of scattering by defects, for each of several possible mechanisms of diffusion the geometry of the diffusion jumps is known, which makes it possible to construct a theory of the energy distribution of scattered neutrons which is also applicable for large $q_1$. As we shall see from the results obtained below, it is just this case which is especially interesting, since the comparison of theory with the experimental data regarding the case of large $q_1$ makes it possible in principle to obtain valuable information concerning the type of defects in the crystal and concerning the mechanism of diffusion. In certain cases, even for small $q_1$, the macroscopic treatment does not allow one to carry out the investigation. In this connection, we shall treat in Sec. 2 the influence of diffusion on the energy distribution of scattered neutrons without using the macroscopic approximation.

It is obvious that the diffusion of defects must give rise to the same sort of broadening of the energy distribution of scattered x rays. But, since the energy of x-ray photons is approximately $10^5$ times greater than the energy of thermal neutrons, while the natural width of x-ray levels is much greater than this broadening, its experimental detection by ordinary methods is impossible. The possibility of such an observation has arisen in connection with the discovery of extremely narrow energy distributions of photons (x rays or $\gamma$ quanta) which are emitted by long-lived excited states of nuclei of certain isotopes in a crystal, and can be studied with high precision by using the resonant nuclear absorption of the photons (the Mössbauer effect).[4] (For reference to other work, we refer to the summary of Belozerskii and Nemilov.[5]) With respect to this we discuss in Sec. 3 the influence of diffuse motion on the energy distribution of such photons.

If the defects can occur only at sites of one type, then for small values of $q_1$ the magnitude of the broadening produced by diffusion falls off like $q_1^2$. For the scattering of light waves in this case, the broadening is approximately $10^7$ times smaller than for the scattering of x rays and is completely insignificant. If, however, the defects may be present at positions of several different types, then, as we shall show later, as $q_1 \to 0$ the broadening tends to a non-zero limit, and may be appreciable for the scattering of light at high temperatures. Therefore in Sec. 3 we also discuss the influence of diffusion on the scattering of light.

Diffusion may also appreciably affect the energy distribution of the emitted radiation if, during the lifetime of the excited state of the radiating atom (nucleus), it succeeds in shifting such a distance that the phase difference between the waves radiated in the initial and final points is comparable with $\pi$. The corresponding broadening of the emission line may become appreciable at high temperatures in the case of the Mössbauer effect and also in the case of no-phonon emission of light, if the radiating defects can be at several different sites. These effects will be treated in Sec. 4.

## 2. THE INFLUENCE OF DIFFUSION OF DEFECTS ON THE SCATTERING OF THERMAL NEUTRONS

The atoms of a crystal carry out motions of two types: oscillations around their equilibrium positions, and diffusion jumps to new equilibrium positions. If the diffusion can be neglected, then there remain only the oscillations of the atoms which lead to a reduction in the amplitude of elastic scattering of the s-th atom by the Debye factor $e^{-M_s}$, where $M_s = \frac{1}{2}\overline{(\mathbf{q}_1\cdot\mathbf{u}_s)^2}$ and the $\mathbf{u}$'s are the thermal displacements of the atoms.

We take account of the diffuse motion for the case where the probability W of diffusion jumps to neighboring positions is considerably less than the effective frequency of oscillation of the atom $\omega_0$. In practice the criterion $W \ll \omega_0$ is always satisfied. We denote by $E = \hbar\omega$ the change in energy of the neutrons during scattering. As will be shown later, diffusion leads to a smearing of the energy distribution of the elastic scattering in the region $\omega \lesssim W$. In the following we shall treat just this region of low values of $\omega$ (corresponding to long times in the time-correlation function). In this case we may treat the oscillations simply by introducing the factor $e^{-M_s}$ into the scattering amplitude.

Suppose that point defects (or defects of finite dimensions) can occupy positions of several types, 1, 2 . . . . , $\nu$, . . . , n. We shall assume that the concentration of defects $c_\nu$ is small ($c_\nu \ll 1$), that they are distributed randomly, and that in the absence of these defects the non-ideality of the crystal can arise only from the presence of isotopes of different types. The detailed distribution of the defects can be characterized by assigning the numbers $c_{r\nu}(t)$, equal to one or zero, if at the time t at the position r of the $\nu$-th type there is or is not a defect. The amplitude of scattering of monochromatic neutrons by a single crystal containing defects, at the time t, is proportional to the sum

$$a(t) = \sum_{r\nu} c_{r\nu}(t) \exp(i\mathbf{q}_1\mathbf{R}_{r\nu}) \Big\{\varphi_\nu + \sum_s{}' [A_s - \overline{A}_s + b_s(\mathbf{s}\mathbf{S}_s)]$$
$$\times \exp(i\mathbf{q}_1\delta\mathbf{R}_{sr\nu}) \exp(i\mathbf{q}_1, \mathbf{R}_s - \mathbf{R}_{r\nu})\Big\}$$
$$+ \sum_s{}'' [A_s - \overline{A}_s + b_s(\mathbf{s}\mathbf{S}_s)] \exp(i\mathbf{q}_1, \mathbf{R}_s + \delta\mathbf{R}_s),$$
$$\varphi_\nu = \sum_s \overline{A}_s \exp(i\mathbf{q}_1\,\delta\mathbf{R}_{sr\nu}) \exp(i\mathbf{q}_1,\ \mathbf{R}_s - \mathbf{R}_{r\nu}). \tag{1}$$

Here $\mathbf{q}_1 = \mathbf{k}_2 - \mathbf{k}_1$ is the difference of the wave vectors of the scattered and incident waves; s numbers the atoms (both those which are at the sites of any sublattice of the ideal crystal, and those belonging to the defects); the summation $\Sigma'$ goes over atoms which move together with the center of the defect $r\nu$ (if the defect is an added atom, then the sum reduces to a term corresponding to this atom); the summation $\Sigma''$ goes over all the other atoms; $A_s$ and $b_s$ are the constants $A_s'$ and $b_s'$ in the expression for the energy of interaction of a neutron with the nucleus s:

$$V_s(\mathbf{r}) = [A_s' + b_s'(\mathbf{s}\mathbf{S}_s)]\,\delta(\mathbf{r} - \mathbf{R}_s)$$

($\mathbf{s}$ and $\mathbf{S}_s$ are the spins of the neutron and the s-th nucleus), multiplied by the Debye factor $e^{-M_s}$; $\overline{A}_s$ is the average value (over the isotopes) of the quantity $A_s$; $\delta\mathbf{R}_{sr\nu}$ is the static displacement of the s-th atom with radius vector $\mathbf{R}_s$, resulting from the influence of the defect at the $\mathbf{r}\nu$ location with radius vector $\mathbf{R}_{r\nu}$; $\delta\mathbf{R}_s = \sum_{r\nu} c_{r\nu}(t)\,\delta\mathbf{R}_{sr\nu}$ is the total displacement of the s-th atom. For small concentrations of defects we may keep in the sum for $\delta\mathbf{R}_s$ just the terms corresponding to the nearest defect. (This point is explicitly taken into account in the formula for $\varphi_\nu$.)

The differential cross section (per unit solid angle and per unit energy range) for the scattering of neutrons is (cf., for example, reference 1) expressible in the form

$$\sigma'(\mathbf{q}_1,\omega)=\frac{m^2}{8\pi^3\hbar^5}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\langle a(t)\,a^*(0)\rangle.$$

Here m is the neutron mass, $\langle\ldots\rangle$ denotes an average over the initial configuration of defects and over the possible types of their diffusion jumps, the bar denotes an averaging over isotopes and over nuclear spins. In the average over isotopes and spins of the product of expressions (1), $a(t)a^*(0)$ is different from zero only for terms of the type

$$[A_s-\bar{A}_s+b_s(\mathbf{sS}_s)]\,[A_{s'}-\bar{A}_{s'}+b_{s'}(\mathbf{sS}_{s'})]$$

with $s = s'$, corresponding to the same atom. As a result of the motion of defects, this atom at various times may be located at different positions (with different $\mathbf{R}_s$). Then for the atoms moving together with the defect [corresponding to $\Sigma'$ in (1)] the change of $\mathbf{R}_s$ is the same as the change of $\mathbf{R}_{r\nu}$, so that $\mathbf{R}_s-\mathbf{R}_{r\nu}$ does not depend on t. The other atoms [corresponding to $\Sigma''$ in (1)] during the motion of the defect (for example, a vacancy) from $r\nu$ to $r'\nu'$ may (in a not completely determined way) move to other sites, which are displaced from the old ones by $\mathbf{R}_s(r\nu r'\nu')$. In the corresponding term in $a(t)a^*(0)$ as a result there appears a factor $\exp[i\mathbf{q}_1\cdot\mathbf{R}_s(r\nu r'\nu')]$, and in these terms we must take an average $\langle\langle\ldots\rangle\rangle$ over the possible types of such displacements of the atoms s.

In calculating $\langle a(t)a^*(0)\rangle$ we shall also take into account that in this case of small concentration, where we neglect configurations of low probability, we may set

$$\exp\Big\{i\mathbf{q}_1\sum_{r\nu}[c_{r\nu}(t)-c_{r\nu}(0)]\,\delta\mathbf{R}_{sr\nu}\Big\}-1$$

$$=\sum_{r\nu r'\nu'}c_{r\nu}(t)\,c_{r'\nu'}(0)\,[\exp(i\mathbf{q}_1,\delta\mathbf{R}_{sr\nu}-\delta\mathbf{R}_{sr'\nu'})-1].$$

Then, substituting (1) in the expression for $\sigma'(\mathbf{q}_1,\omega)$ and subtracting the cross section for scattering by a crystal not containing defects, we find the expression for the change in the scattering cross section $\sigma(\mathbf{q}_1,\omega)$ due to defects:

$$\sigma(\mathbf{q}_1,\omega)=\frac{m^2}{8\pi^3\hbar^5}\frac{k_2}{k_1}\sum_{r\nu r'\nu'}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\langle c_{r\nu}(t)\,c_{r'\nu'}(0)\rangle$$

$$\times[F_{\nu\nu'}\exp(i\mathbf{q}_1,\mathbf{R}_{r\nu}-\mathbf{R}_{r'\nu'})+\Phi_{\nu\nu'}(\mathbf{R}_{r\nu}-\mathbf{R}_{r'\nu'})].\quad(2)$$

Here

$$F_{\nu\nu'}=\varphi_\nu\overset{*}{\varphi}_{\nu'}+\sum_s{}'\,\overline{[(A_s-\bar{A}_s)^2+\overline{B}_s^2]}\exp(i\mathbf{q}_1,\delta\mathbf{R}_{sr\nu}-\delta\mathbf{R}_{sr'\nu'}),\quad(3)$$

$$\Phi_{\nu\nu'}(\mathbf{R}_{r\nu}-\mathbf{R}_{r'\nu'})=\sum_s{}''\,\overline{[(A_s-\bar{A}_s)^2}$$

$$+\overline{B_s^2}]\,[\langle\langle\exp\{i\mathbf{q}_1\mathbf{R}_s(r\nu r'\nu')\}$$

$$\times\exp(i\mathbf{q}_1,\delta\mathbf{R}_{sr\nu}-\delta\mathbf{R}_{sr'\nu'})\rangle\rangle-1],$$

$$B_s^2=b_s^2S_s(S_s+1)/4.\quad(4)$$

Going over in (2) from the quantities $c_{r\nu}$ to their Fourier components

$$c_{\mathbf{k}\nu}(t)=\frac{1}{N}\sum_r c_{r\nu}(t)\exp(i\mathbf{k}\mathbf{R}_{r\nu})\quad(5)$$

(where N is the number of unit cells), we obtain the following expression for the differential cross section for inelastic scattering ($\omega\neq0$):

$$\sigma(\mathbf{q}_1,\omega)=N_g\frac{m^2}{4\pi^2\hbar^5}\frac{k_2}{k_1}\Big\{\sum_{\nu\nu'}[F_{\nu\nu'}\exp(2\pi i\mathbf{K}_n\mathbf{R}_{\nu\nu'})\,f_{\nu\nu'}(\mathbf{q},\omega)$$

$$+\sum_{\mathbf{k}}\Phi_{\nu\nu'\mathbf{k}}f_{\nu\nu'}(\mathbf{k},\omega)]\Big\}.\quad(6)$$

Here

$$f_{\nu\nu'}(\mathbf{q},\omega)=\frac{N^2}{N_g}\frac{1}{2\pi}\int_{-\infty}^{\infty}\langle c_{\mathbf{q}\nu}(t)\,\overset{*}{c}_{\mathbf{q}\nu'}(0)\rangle e^{-i\omega t}dt,$$

$$\Phi_{\nu\nu'}(\mathbf{R}_{r\nu}-\mathbf{R}_{r'\nu'})=\sum_{\mathbf{k}}\Phi_{\nu\nu'\mathbf{k}}\exp(i\mathbf{k},\mathbf{R}_{r\nu}-\mathbf{R}_{r'\nu'}),\quad(7)$$

where $\mathbf{q}=\mathbf{q}_1-2\pi\mathbf{K}_n$, $\mathbf{K}_n$ is the reciprocal lattice vector which is closest to the vector $\mathbf{q}_1/2\pi$, $N_g$ is the number of defects in the crystal, $\mathbf{R}_{\nu\nu'}=\mathbf{R}_{r\nu}-\mathbf{R}_{r\nu'}$. The summation over $\mathbf{k}$ is taken over the values $\mathbf{k}/2\pi$ lying in a cell of the reciprocal lattice.

Thus the problem of determining the energy distribution of neutrons scattered by defects reduces to finding the time correlation function for the Fourier components $c_{\mathbf{q}\nu}$ and $c_{\mathbf{q}\nu'}$. This transition from the quantities $c_{r\nu}$ to their Fourier components greatly simplifies the computation.

First we consider the simplest case, where the defects are located at positions of just one type and move from one position to another, overcoming potential barriers of the same height. We denote by $\rho$ the vector joining the initial and final position in a diffusion jump, and by w the probability of transition of the defect from a given position to a definite neighboring position. If at the time t one of the quantities $c(\mathbf{R}_r)=c_r$ is equal to unity, then at the time $t+dt$ its average value will be

$$1-dt\sum_\rho w=1-zw\,dt$$

(where z is the number of positions to which the diffusion jump can go), while the quantities

$c(\mathbf{R}_r + \rho)$ take the values wdt. As a result, in this case, the quantity $c_{\mathbf{k}}(t)$ satisfies the differential equation

$$dc_{\mathbf{k}}(t)/dt = -w\sum_{\rho}(1 - e^{i\mathbf{k}\rho})\, c_{\mathbf{k}}(t), \tag{8}$$

i.e., $\langle c_{\mathbf{k}}(t)\, c_{\mathbf{k}}^{*}(0)\rangle$ depends exponentially on time:

$$\langle c_{\mathbf{k}}(t)\, \overset{*}{c_{\mathbf{k}}}(0)\rangle = \langle\, |c_{\mathbf{k}}(0)|^2\,\rangle \exp(-\alpha_{\mathbf{k}}\,|\,t\,|),$$

$$\alpha_{\mathbf{k}} = w\sum_{\rho}(1 - \cos \mathbf{k}\rho). \tag{9}$$

Here we make use of the fact that $\langle c_{\mathbf{k}}(t)\, c_{\mathbf{k}}^{*}(0)\rangle$ is an even function of the time (cf., for example, reference 6, Sec. 117). Formula (9) is applicable for long times, where $t \gg 1/\omega_0$.

Taking into account the fact that for low concentration of randomly distributed defects $\langle |c_{\mathbf{k}}(0)|^2\rangle = N_g/N^2$, we obtain from (7) and (9) the following expression for the function $f(\mathbf{q}, \omega)$ (we omit the subscripts $\nu$ and $\nu'$ in this case):

$$f(\mathbf{q}, \omega) = \frac{1}{\pi}\,\frac{\alpha_{\mathbf{q}}}{\alpha_{\mathbf{q}}^2 + \omega^2}. \tag{10}$$

As we see from (10) and (9) for small q the width of the Lorentz curve $f(\mathbf{q}, \omega)$ falls off like $q^2$. The constant w which determines this width is related in this case to the diffusion coefficient D of defects in cubic crystals by the relation

$$D = \tfrac{1}{2}\, w\sum_{\rho}\rho_x^2, \tag{11}$$

i.e., for small q we have $\alpha_{\mathbf{q}} = Dq^2$. In the more general case where the defects, just as in the preceding case, are located only at positions of one type, but can go over from this position to neighboring positions by overcoming potential barriers of various heights, the function $f(\mathbf{q}, \omega)$ can again be calculated from formula (10), but $\alpha_{\mathbf{k}}$ in this formula is now determined not by (9), but by the more general expression $\alpha_{\mathbf{k}} = \sum_{\rho} w_{\rho}(1 - \cos \mathbf{k}\cdot\rho)$, where $w_{\rho}$ is the probability of transition of the defect from the position $\mathbf{R}_r$ to the position $\mathbf{R}_r + \rho$.

We give several examples of the application of the formulas obtained above to defects in cubic crystals of various structures. In all cases we shall assume that during diffusion jumps the defects go to nearest neighbor positions. If the defects are vacancies at the sites of a face-centered cubic lattice, then

$$\alpha_{\mathbf{k}} = 4\frac{D}{a^2}\Big(3 - \cos\frac{k_x a}{2}\cos\frac{k_y a}{2} - \cos\frac{k_x a}{2}\cos\frac{k_z a}{2} - \cos\frac{k_y a}{2}\cos\frac{k_z a}{2}\Big), \tag{12}$$

where a is the length of a side of the cubic unit cell. This expression is also applicable to injected atoms which are located at the octahedral interstices of this lattice (the centers of the cubes and the midpoints of the edges).

In the case of vacancies at the sites of a body-centered cubic lattice

$$\alpha_{\mathbf{k}} = 8\,\frac{D}{a^2}\Big(1 - \cos\frac{k_x a}{2}\cos\frac{k_y a}{2}\cos\frac{k_z a}{2}\Big). \tag{13}$$

For vacancies diffusing through one of the sublattices of a crystal with a lattice of the CsCl type

$$\alpha_{\mathbf{k}} = 2Da^{-2}\,(3 - \cos k_x a - \cos k_y a - \cos k_z a). \tag{14}$$

The expression for $\alpha_{\mathbf{k}}$ in the case of vacancies on one of the sublattices of a crystal of the NaCl type is given by formula (12), in which we must replace a by 2a. For atoms which are injected at the centers of the cubic cells of this lattice, formula (14) can be used.

Formulas (12) — (14) and formula (10) for $f(\mathbf{q}, \omega)$ determine the Lorentz-shaped energy distribution of the scattered neutrons corresponding to the first term in (6). As we see from these formulas, for large q the width of this distribution may differ markedly from the width determined by the phenomenological formula $\alpha_{\mathbf{q}} = Dq^2$. For example, for $q_x = q_y = q_z = \pi/a$, formula (13) gives $\alpha_{\mathbf{q}} = 8D/a^2$, instead of the value $\alpha_{\mathbf{q}} = 3\pi^2 D/a^2$ from the phenomenological theory. From (9), and (12) — (14) we also see that the width $\alpha_{\mathbf{q}}$ of the distribution for large q must depend markedly on the orientation of the vector $\mathbf{q}$ relative to the axes of the single crystal. For example, for the vector $q_x a = \sqrt{3}\,\pi$, $q_y = q_z = 0$, which has the same length as the one given in the preceding example, (13) gives $\alpha_{\mathbf{q}} = 15.3\, D/a^2$, i.e., almost twice the value.

The second terms in (2) or (6) are important only for the case of relatively large incoherent scattering cross sections. The triple integral over k in the second term of formula (6) can be calculated for specific types of defects by using numerical integration. Here in the case of atoms injected into a lattice of Bravais type, the $\Phi_{\nu\nu'\mathbf{k}}$ are proportional to $|\varphi(\mathbf{k})|^2$ where

$$\varphi(\mathbf{k}) = \sum_{s}\exp(i\mathbf{q}_1\,\delta\mathbf{R}_{sr})\exp(-i\mathbf{k}\mathbf{R}_s).$$

The same factor determines the intensity of diffuse scattering of x rays or neutrons by static defects. Therefore it can be obtained from independent experimental data, or from computations of such scattering. In the general case, one can find the frequency dependence of the second term in (6) for small $\omega$. To do this we note that for small k, the functions $\Phi_{\mathbf{k}}$ for arbitrary defects in Bravais lattices with $n = 1$ can be written in the form $\Phi_{\mathbf{k}} = CN^{-1}|\varphi(\mathbf{k})|^2$, where C is the average value (over s) of $\overline{(A_s - \overline{A}_s)^2 + B_s^2}$. Since, in addition, for small k we have $\varphi(\mathbf{k}) = \mathbf{q}_1 \cdot \mathbf{R}_{\mathbf{k}} = \mathbf{q}_1 \cdot \mathbf{e}_{\mathbf{k}} a_{\mathbf{k}}/k$, where $\mathbf{R}_{\mathbf{k}}$ is the Fourier component of $i\delta\mathbf{R}_s$, $\mathbf{e}_{\mathbf{k}}$ is a unit vector, and $a_{\mathbf{k}}$ for small k depends only on the direction (and not on the magnitude) of the vector $\mathbf{k}$ (cf. reference 7), so for small $\omega$, in the sum in the second term in (6) the region of small k predominates, where $\alpha_{\mathbf{k}} \approx Dk^2$. Thus the integration can be carried out in general form and gives for cubic crystals

$$C \frac{v}{48\pi^3 \sqrt{2}} q_1^2 \int d\Omega a_{\mathbf{k}}^2 \frac{1}{\sqrt{D\omega}}$$

(where v is the volume of a cell, $d\Omega$ is the element of solid angle). Thus if the second term in (6) is important, then for small $\omega$ the scattering cross section must increase like $\omega^{-1/2}$ (independent of q).

Now we consider the more general case where the defects may be present at different sites. Then the Fourier components are determined not by (8), but by a system of equations

$$dc_{\mathbf{k}\nu}(t)/dt = -\sum_{\nu'=1}^{n} a_{\nu\nu'}(\mathbf{k})\, c_{\mathbf{k}\nu'}(t), \qquad \nu = 1, 2 \ldots n, \tag{15}$$

where the $a_{\nu\nu'}(\mathbf{k})$ are constants. Remembering that at $t = 0$

$$\langle c_{\mathbf{k}\nu}^{*}(0)\, c_{\mathbf{k}\nu'}(0)\rangle = N_{g\nu} N^{-2} \delta_{\nu\nu'} = x_\nu N_g N^{-2} \delta_{\nu\nu'},$$

where $N_{g\nu}$ is the number of defects at the $\nu$ positions and $x_\nu$ are their relative fractions, we obtain by the usual method (cf. reference 6, Sec. 120) expressions for the functions $f_{\nu\nu'}(\mathbf{q}, \omega)$ defined by formula (7),

$$f_{\nu\nu'}(\mathbf{q}, \omega) = \frac{1}{\pi} \operatorname{Re}\left(\frac{a(\mathbf{q})}{x} + \frac{i\omega}{x}\right)_{\nu\nu'}^{-1} = \sum_{i=1}^{n} \frac{A_i(\mathbf{q})}{\alpha_{\mathbf{q}i}^2 + \omega^2}, \tag{16}$$

where $a(\mathbf{q})/x$ is a matrix with matrix elements $a_{\nu\nu'}(\mathbf{q})/x_\nu$, and the matrix $1/x$ has matrix elements $\delta_{\nu\nu'}/x_\nu$. This last expression is obtained from the preceding by an expansion in elementary fractions. Here the "reciprocal relaxation times" $\alpha_{\mathbf{q}i}$ are determined by the roots $y_i$ of the equation

$$|a_{\nu\nu'} - \delta_{\nu\nu'} y| = 0. \tag{17}$$

In each specific case it is not difficult to carry out the inversion of the matrix $a(\mathbf{q})/x + i\omega/x$ and to find $f_{\nu\nu'}(\mathbf{q}, \omega)$.

As an example we consider the case of atoms injected at the octahedral interstices of a body-centered cubic lattice (the centers of the faces and edges of cubic cells). In this case there are three types of interstices, which have two nearest-neighbor atoms located respectively along the x, y, and z axes. If the injected atoms carry out diffusion jumps to their nearest-neighbor interstices with probability w, then the system of differential equations (15) takes the form

$$dc_{\mathbf{k}\nu}(t)/dt = -4wc_{\mathbf{k}\nu}(t) + \sum_{\nu'=1\,(\nu' \neq \nu)}^{3} C_{\nu''} c_{\mathbf{k}\nu'}(t). \tag{18}$$

Here $\nu'' \neq \nu$ and $\nu'' \neq \nu'$, $C_{\nu''} = 2w \cos \mathbf{k} \cdot \boldsymbol{\rho}_{\nu''}$, where, for example, the vector $\boldsymbol{\rho}_1 = \frac{1}{2} a \mathbf{e}_x$ joins interstices of the second and third types.

Since all the positions are energetically equivalent, $x_\nu = 1/3$. Equation (17), which determines the quantities $\alpha_{\mathbf{q}i}$ in (16), is a cubic equation in this case:

$$D(y) = (y - 4w)^3 - (y - 4w)(C_1^2 + C_2^2 + C_3^2) + 2C_1C_2C_3 = 0. \tag{19}$$

The quantities $f_{\nu\nu'}(\mathbf{q}, \omega)$ are equal in this case [as one finds from (15), (16), and (18)] to

$$f_{11}(\mathbf{q}, \omega) = \frac{1}{3\pi} \operatorname{Re} \frac{(4w + i\omega)^2 - C_1^2}{-D(-i\omega)} \underset{q \to 0}{=} \frac{2}{9\pi} \frac{6w}{36w^2 + \omega^2} + \frac{2}{3\pi} \frac{wa^2q^2}{w^2a^4q^4 + 36\omega^2},$$

$$f_{12}(\mathbf{q}, \omega) = \frac{1}{3\pi} \operatorname{Re} \frac{(4w + i\omega)C_3 + C_1C_2}{-D(-i\omega)} \underset{q \to 0}{=} -\frac{1}{9\pi} \frac{6w}{36w^2 + \omega^2} + \frac{2}{3\pi} \frac{wa^2q^2}{w^2a^4q^4 + 36\omega^2}. \tag{20}$$

The second equalities in (20) are written for small q. The quantity w is related to the coefficient of diffusion of the injected atoms by the relation $w = 6D/a^2$.

As another example, we consider vacancies at the sites of an ordered solid solution of the type of $\beta$ brass (with a lattice of the CsCl type). Suppose that a diffusion jump takes a vacancy from a site of one sublattice to one of the neighboring sites of the other sublattice [the case of the diffusion of vacancies over sites of a single sublattice is described by formulas (10) – (14)]. We shall denote by $w_1/8$ the probability of transition of a vacancy from a site of the first type to sites of the second type, and by $w_2/8$ the probability of the reverse transition. Then the time behavior of $c_{\mathbf{k}1}(t)$ and $c_{\mathbf{k}2}(t)$ is described by (15), in which

$$a_{11} = w_1, \qquad a_{12} = -w_2 C, \qquad a_{21} = -w_1 C, \qquad a_{22} = w_2,$$

$$C = \frac{1}{8} \sum_{\rho} \cos \mathbf{k}\boldsymbol{\rho}, \qquad \boldsymbol{\rho} = \frac{a}{2}(\pm \mathbf{e}_x \pm \mathbf{e}_y \pm \mathbf{e}_z).$$

Noting that

$$x_1 = w_2/(w_1 + w_2), \quad x_2 = w_1/(w_1 + w_2),$$

we obtain from (16)

$$f_{11}(\mathbf{q}, \omega) = \frac{1}{\pi} \frac{w_2}{w_1 + w_2} \operatorname{Re} \frac{w_2 + i\omega}{(w_1 + i\omega)(w_2 + i\omega) - w_1 w_2 C^2}$$

$$\underset{q \to 0}{=} \frac{4}{\pi} \frac{w}{w_1 + w_2} \operatorname{Re} \left[ \frac{1}{w_1 + w_2 + i\omega} + \frac{w_2 / w_1}{w a^2 q^2 + i\omega} \right],$$

$$f_{12}(\mathbf{q}, \omega) = \frac{4wC}{\pi} \operatorname{Re} \frac{1}{(w_1 + i\omega)(w_2 + i\omega) - w_1 w^2 C^2}$$

$$\underset{q \to 0}{=} \frac{4}{\pi} \frac{w}{w_1 + w_2} \operatorname{Re} \left[ -\frac{1}{w_1 + w_2 + i\omega} + \frac{1}{w a^2 q^2 + i\omega} \right],$$

$$w = \frac{1}{4} \frac{w_1 w_2}{w_1 + w_2}. \tag{21}$$

The energy distribution of the scattered neutrons which we have found takes a simpler form for the case where the coefficients $\Phi_{\nu\nu'\mathbf{k}}$ in formula (6) are equal to zero (for example, if the lattice contains only nuclei of one isotope with zero spin, or if we can neglect imperfections). As follows from (16), the energy distribution is then described by a superposition of Lorentz curves. In the two cases considered above, where there are two nonequivalent positions for defects, for small q the function $f(\mathbf{q}, \omega)$ is a sum of two Lorentz functions. One of them is described by a curve with a width proportional to $q^2$ and the coefficient of diffusion of the defects and coincides with the curve obtained from a macroscopic treatment. The width of the curve corresponding to the second function tends to a nonzero limit for $q \to 0$.

If all the quantities

$$F'_{\nu\nu'} = F_{\nu\nu'} \exp(2\pi i \mathbf{K}_n \mathbf{R}_{\nu\nu'})$$

are the same, then these second terms in the sum (6) cancel, and the energy distribution, just as for the case of defects of only one type, is described by a narrow Lorentz curve. In the general case, however, in this sum, in addition to the term corresponding to the narrow curve for small q, there must also be a term corresponding to the broad Lorentz curve and proportional to the differences of the quantities $F'_{\nu\nu'}$. Obviously the appearance of the broad component in the energy distribution cannot be obtained by means of the macroscopic theory which does not take into account the diffusion mechanism.

It is not difficult to show that the broad curve in the energy distribution, in addition to the narrow curve for small q, should be observed in all cases where the defects can go from positions of one type to positions of another type, where the different quantities $F'_{\nu\nu'}$ are not the same. In addition to the examples given above, the defects may also make such transitions between positions of different types in the case of injected atoms at tetrahedral or dodecahedral interstices of body-centered cubic lattices, in the case of atoms of vacancies injected into ordered alloys of different structures, in the case of a pair of vacancies, a pair of injected atoms, or an impurity atom-vacancy pair (where differently oriented pairs may be regarded as defects of different types) etc.

From the results obtained it follows that for each mechanism of diffusion of defects of a given type there should be a characteristic dependence of the width and shape of the energy distribution of scattered neutrons on the magnitude and orientation of the vector $\mathbf{q}$. If the type of defects giving rise to the scattering is known, this makes it possible in principle to make a choice between the various possible mechanisms of diffusion of defects, by comparing the dependence on $\mathbf{q}$ of the width, as calculated for these mechanisms, with the result of experiment. Thus one can, for example, study whether the diffuse jumps of the injected atoms and vacancies to nearest positions occurs as assumed in deriving the formulas given above, or to more remote locations; whether the diffusion in a given crystal occurs by means of vacancies or interstitial atoms. A comparison of calculated and measured energy distributions also makes it possible in principle to choose between various assumptions concerning the type of defects giving rise to the scattering. Thus, for example, the energy distribution, as shown above, is found to be qualitatively different (for small q) for vacancies and for injected atoms in body-centered cubic lattices, for atoms injected at octahedral and tetrahedral holes in face-centered cubic lattices, for isolated vacancies, for pairs of vacancies, etc.

If the coefficients $\Phi_{\nu\nu'\mathbf{k}}$ in formula (6) are different from zero, the analysis of the energy distribution is made more complicated (where for small q the width of the energy distribution of the second sum in (6) always tends to a nonzero value), but can also be carried out in each specific case.

To estimate the order of magnitude of the broadening of the energy distributions, let us consider the case where $D \sim 3 \times 10^{-5}$ cm²/sec (diffusion of vacancies and injected atoms at temperatures close to the melting point; in the case of diffusion of H atoms, D may be 10 — 100 times greater). Setting $a^2 \sim 10^{-15}$ cm², we find that formulas (12), (13), and (20) in this case give a maximum value of the width of the distribution of the order of $(3-6)\times 10^{-4}$ ev. Such a broadening can be detected experimentally. Obviously the difficulty in experimental investigation, aside from the need for obtaining a high resolution in the energy distribution, is related to the presence of an intense elastic scattering resulting from isotopes and spins of nuclei in the crystal, and also the presence of inelastic scattering by thermal vibrations which is especially intense in the case we are considering of high temperature.

The separating out of the scattering by defects from the total cross section for scattering is made easier by the fact that the energy distribution of the isotopic scattering for monochromatic incident neutrons is extremely narrow (its width is proportional to the self-diffusion coefficient which is much smaller than the coefficient of diffusion of the defects), while the energy distribution of the scattering by vibrations, on the other hand, is much broader than the distribution of scattering by defects. Obviously the defect concentration must be sufficiently high. It appears that with present-day technique of experiment the smearing of the energy distribution of neutrons scattered by injected atoms can be studied, for example, in Pd-H solutions. To study the scattering by vacancies, it may be convenient to use substitutional solutions (for example, Co-Al, Ni-Al), where the concentration of "structural" vacancies is high, or to introduce into the crystal impurities to increase the concentration of vacancies.

## 3. INFLUENCE OF DIFFUSION ON SCATTERING OF PHOTONS BY CRYSTAL DEFECTS

The diffusion of defects may lead to a similar broadening of the energy distribution of the elastic scattering of monochromatic photons (x rays or $\gamma$ quanta) as for the case of neutron scattering. Just as before, let us consider the case where $W \ll \omega_0$ and $\omega \lesssim W$ and disregard the scattering by thermal vibrations. Then, in electron units, the intensity of the diffuse scattering of monochromatic photons by defects $I(\mathbf{q}_1, \omega)$, per unit solid angle and per unit frequency range, is given by a formula analogous to formula (6):

$$I(\mathbf{q}_1, \omega) = N_g \sum_{\nu\nu'} \varphi_\nu^* \varphi_{\nu'} \exp(2\pi i \mathbf{K}_n \mathbf{R}_{\nu\nu'}) f_{\nu\nu'}(\mathbf{q}, \omega). \qquad (22)$$

Here $\varphi_\nu$ is given by formula (1), if we make the substitution $\overline{A}_s \to f_s$, where $f_s$ is the atomic scattering factor of the s-th atom multiplied by the Debye attenuation factor $e^{-M_s}$. The functions $f_{\nu\nu'}(\mathbf{q}, \omega)$ in (22) are again determined by formulas (7), (10), and (16) (where it is obvious that in the case of scattering of photons $\Phi_{\nu\nu'\mathbf{k}} = 0$).

Thus the investigation of the function $f(\mathbf{q}, \omega)$ which we carried out above for various specific cases is also applicable for the treatment of scattering of photons. In this case the energy distribution is obtained more simply because of the fact that $\Phi_{\nu\nu'\mathbf{k}} = 0$. As shown above, the magnitude of the broadening associated with diffusion of defects is less than or of the order of $10^{-3}$ ev. Therefore, as already pointed out in Sec. 1, this broadening cannot be observed if one uses ordinary x rays. However, by using the Mössbauer effect one can obtain photons with a very narrow energy distribution, and investigate their scattering by defects of another crystal which is used as a resonance absorption detector. Here the width of the energy distribution may be very small. For example, for $Fe^{57}$ it amounts to approximately $6\times 10^{-9}$ ev. As a result, one can detect and study much smaller broadenings than by using neutrons. Even at low temperatures, where the diffusion coefficient of the defects considered above is $D \sim 10^{-9}$ cm$^2$/sec, the diffusion will give rise to a broadening $\sim 10^{-8}$ ev, which is comparable with the natural width.

If the broadening as a result of diffusion is of the same order as the natural width, then one must take into account the non-monochromatic nature of the incident radiation. Since in the case of monochromatic radiation the energy distribution of the scattered photons is described by a sum of Lorentz functions (16), for the case where the shape of the spectral line of the incident radiation is Lorentzian, the distribution of the scattered radiation will also be described by a sum of Lorentz functions with widths of the corresponding curves, each of which is equal to the sum of $\alpha_{\mathbf{q}i}$ and the width of the line of the incident radiation.

In the same way as for neutron scattering, the study of the dependence of the width of the energy distribution of scattered photons as a function of $\mathbf{q}$ enables one to investigate the mechanism of diffusion and to establish the nature of the defects (cf. Sec. 2). In the case of scattering of photons the analysis of the distribution is somewhat simpler, since $\Phi_{\nu\nu'\mathbf{k}} = 0$. Because of the higher resolution, the separation of the scattering into that by defects and that by vibrations also can be carried out more precisely than for the case of neutrons.

Formula (22) is also applicable to the case of scattering of light waves, but the expressions for the constants $\varphi_\nu$ are then changed ($\varphi_\nu$ will be

$\sim\lambda^2$, where $\lambda$ is the wavelength). If the defects are located at positions of just one type, the width of the energy distribution is $Dq^2 = 16\pi^2 D\lambda^{-2}\sin^2\theta$, and even for the very highest values of D is several orders of magnitude smaller than the width of the spectral distribution of the incident radiation. If, however, the defect can undergo diffusion jumps between positions of different types, and the values of $\varphi_\nu$ for different $\nu$ are different, then there will be a term in the expression for $I(\mathbf{q}, \omega)$ whose graph is a Lorentz curve with a large width independent of $\lambda$. For example, in the case of scattering of light by injected atoms in a body-centered cubic lattice, according to (22) and (20), for $D > 10^{-7}$ cm²/sec, this width is greater than $2 \times 10^{-6}$ ev, i.e., it may be of the order of (or greater than) the width of the spectral distribution of the incident radiation. The intensity of the broad spectral curve in the scattered spectrum should depend in a characteristically strong way on the polarization of the light, but we shall not consider this question here.

## 4. INFLUENCE OF DIFFUSION ON THE MÖSSBAUER EFFECT

The diffuse motion of the atoms may not only lead to a broadening of the spectrum of elastic scattering, but also to a broadening of the absorption and emission spectra. This effect should be observed in the spectra of resonant absorption and emission of photons by nuclei in a crystal which is at high temperature. The intensity of such a recoilless emission of photons is proportional to the Debye attenuation factor $e^{-M_s}$ for $\mathbf{q}_1$ equal to the wave vector of the emitted wave. In various cases where relatively soft photons are emitted, this factor is not very small even at high temperatures, which enables one to investigate the Mössbauer effect at such temperatures. For example, for $Fe^{57}$ (with a photon energy of 14.4 kev) at T = 2000° K, $M_s = 1.4$ if the Debye temperature is equal to 430° K.

Let us first consider the spectral distribution of the emitted (or absorbed) photons for the case where the natural width $\Gamma = 0$ and the emitting nuclei are located at sites of one sublattice. We shall denote by $\omega$ the difference between this frequency and the frequency of the radiation emitted in the absence of diffusion. Since we are considering recoilless radiation, we shall limit ourselves to the range of values $\omega \lesssim W$, where W is the probability of a diffusion jump of an atom. The expression for the spectral distribution of the photons emitted without recoil when we include diffusion of the atoms over sites of their own sublattice is not hard to obtain by using the adiabatic approximation and noting that the inter-nuclear motion is incomparably faster than the motion of the center of gravity of the nucleus. Denoting by $\sigma_p(\mathbf{q}_1)$ the integral cross section (over energy) of the resonance absorption of photons with wave vector $\mathbf{q}_1$ (and a given polarization) by a single nucleus, by $N_p$ the total number of absorbing nuclei at the sites of the given sublattice, and by N the number of sites of the sublattice ($N_p \ll N$), we write the expression for the differential cross section of absorption $\sigma_p(\mathbf{q}_1, \omega)$ (per unit solid angle and per unit frequency range) in the form

$$\sigma_p(\mathbf{q}_1, \omega) = \frac{N^2}{2\pi}\sigma_p(\mathbf{q}_1)\int_{-\infty}^{\infty} dt\, e^{-i\omega t}\langle c_{\mathbf{q}}(t)\, c^*_{\mathbf{q}}(0)\rangle$$
$$= N_p\sigma_p(\mathbf{q}_1)\, f(\mathbf{q}, \omega). \qquad (23)$$

Here $c_{\mathbf{q}}$ is determined by formula (5), in which $c_{\mathbf{r}\nu}$ now refers not to defects, but to nuclei of the absorbing isotope on the $\nu$-th sublattice.

In order to obtain the differential equation describing the time behavior of $c_{\mathbf{q}}(t)$ for the vacancy mechanism of diffusion, we shall choose a "physically infinitesimal" time interval dt, which is much smaller than the interval between two diffusion jumps of an atom and much greater than the interval between two diffusion jumps of a vacancy. Because of the fact that for the vacancy mechanism there is a correlation between successive diffusion jumps of the atoms,[8] there exists a finite probability of transition of an atom during this infinitesimal time interval not only to the neighboring atoms, but also to more remote sites. Therefore our equation has the form

$$\frac{dc_{\mathbf{k}}(t)}{dt} = -\alpha_{\mathbf{k}}c_{\mathbf{k}}(t),$$
$$\alpha_{\mathbf{k}} = w_1\sum_{\boldsymbol{\rho}_1}^{(1)}(1-\cos\mathbf{k}\boldsymbol{\rho}_1) + w_2\sum_{\boldsymbol{\rho}_2}^{(2)}(1-\cos\mathbf{k}\boldsymbol{\rho}_2)$$
$$+\ldots\approx\frac{D_s}{a^2}\sum_{\boldsymbol{\rho}_1}^{(1)}(1-\cos\mathbf{k}\boldsymbol{\rho}_1). \qquad (24)$$

Here the summations are extended over sites of the first, second, etc. coordination spheres, $w_i$ is the probability of transition to a particular site of the i-th sphere. The approximate equation is written for cases of simple, body-centered, and face-centered cubic lattices. In deriving it, we use the fact that the self-diffusion coefficient $D_s$ is equal to

$$D_s = \frac{1}{2}\sum_i w_i\sum_{\rho_i}\rho_{ix}^2$$

and that $w_2 \sim w_1/z^2 \sim 10^{-2}w_1$, so that with a slight error we need keep only the first term in the sum over i.

From (23) and (24) it follows that for $\Gamma = 0$ the spectral distribution is described by the Lorentz function

$$\sigma_p(q_1, \omega) = N_p \sigma_p(q_1)\, \pi^{-1} \alpha_q / (\alpha_q^2 + \omega^2). \qquad (25)$$

For $\Gamma \neq 0$ there is also a Lorentz distribution, but its width is equal to $\alpha_q + \Gamma$.*

From (24), (25), and (12) — (14) it follows that the broadening of the spectral distribution resulting from diffusion at high temperatures may be appreciable. For example, assuming that near the melting point $D_s = 10^{-8}$ cm$^2$/sec and that $a^2 = 10^{-15}$ cm$^2$, we find that for a body-centered cubic lattice for $q_x = q_y = q_z = \pi/a$, the broadening is equal to $10^{-7}$ ev, i.e., much larger than the width $\Gamma$ for Fe$^{57}$. This broadening should depend exponentially on temperature and be strongly dependent on the direction of the vector $\mathbf{q}_1$. It is obvious that the investigation of such a dependence would enable one to establish whether the self-diffusion occurs via a vacancy mechanism or by diffusion jumps to neighboring lattice sites, as was assumed in deriving the formulas given above, or by some other mechanism, (for example, by means of diffusion over interstices).†

In various cases the resonance radiation may be emitted by nuclei which, because of the energy transfer in the preceding radioactive decay, have been ejected from lattice sites and are located in interstices. Then the broadening will be determined by the diffusion coefficient of interstitials, which is several orders of magnitude greater than the self-diffusion coefficient. A significantly larger broadening should therefore occur when the radiating atoms are close to grain boundaries (in a sample consisting of very tiny crystals prepared by diffusion methods at low temperatures) because of the large value of the coefficient of grain boundary diffusion. Apparently a larger broadening than for ordinary crystals should be observed in substitutional alloys. Finally, a large broadening (although much smaller than for gases) should be observed in the case of liquids.

In the absorption and emission of light by crystal defects which can undergo diffusion jumps between non-equivalent positions, there can also occur a diffusion broadening of the spectral curves (cf. Sec. 3). This effect may be appreciable, however, only if the electron-phonon interaction is sufficiently small (so that one can separate a line of a purely electronic transition) and the probability of thermal radiationless transitions from the excited state is small at these high temperatures.

Note added in proof (May 16, 1961): After this paper was sent to press, papers appeared which also consider the influence of diffusion on the Mössbauer effect in solids[9] and in liquids,[10] which obtain results overlapping the results of Sec. 4 of this paper. By using a quasi-classical model, the influence of diffusion on the scattering of neutrons by a liquid has also been treated[11] recently.

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*It is not difficult to see that in a more detailed calculation, which does not use the concept of a "physically infinitesimal" time interval, in the expression for $\sigma_p(q_1, \omega)$ there is an additional small term corresponding to a broad spectral distribution with a width greater than $\alpha_q$ by the factor $D_s/D_v$ (where $D_v$ is the coefficient of diffusion of the vacancies). The ratio of this term to the term considered in (25) is of the order of $N_v/N$, where $N_v$ is the number of vacancies.

†The height of the potential barrier for the transition of an atom from a site to an interstitial position is usually much greater than the barrier height for transition from one interstitial position to another. Therefore if the diffusion occurs via a mechanism in which atoms move through interstices, then $\alpha_{qi}$ does not depend on q and is equal to the probability of transition of an atom from a site to an interstitial position. The temperature dependence of $\alpha_{qi}$ is then different from the temperature dependence of $D_s$.