Resonance vibration modes of point defects and the Mössbauer effect

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THIS ARTICLE constitutes the first part of a more extensive study on the influence of sharp resonance modes in the Mössbauer atoms, vibrational frequency spectrum on the recoilless fraction in the case in which the Mössbauer atoms can be regarded as isolated impurities in an arbitrary host lattice; the second part of the paper concerns the case of higher concentrations. The general dependence of the recoilless fraction upon the vibrational resonance width is obtained as a time function which can be measured by means of the coincidence Mössbauer spectroscopy. An experimental determination of the recoil energy transfer time in a gamma emission process is proposed.

Praca stanowi pierwszą część większej całości i dotyczy wpływu ostrych modów rezonansowych w widmie częstości drgań atomu Mössbauera na współczynnik emisji bezodrzutowej w przypadku, gdy atomy mössbauerowskie stanowią domieszkę o niskiej koncentracji (druga część pracy dotyczy przypadku wyższych koncentracji). Macierz dla atomów domieszki jest zupełnie dowolna poza warunkiem tworzenia ostrych rezonansów. Otrzymana została ogólna zależność współczynnika emisji bezodrzutowej od czasu, który upłynął od wzbudzenia mechanicznego atomu, energii wzbudzenia i szerokości linii rezonansowej (wibracyjnej). Poza bezpośrednim zastosowaniem do wyznaczania czasu relaksacji modów rezonansowych zostało omówione zastosowanie otrzymanych wyników do eksperymentalnego określenia czasu trwanie przekazu energii odrzutu przez kwant gamma emitowany przez jądro atomu związanego w krysztale.

Статья является первой частью более обширной работы о влиянии резких резонансных мод в спектре частот колебаний атома Мёссбауэра на коэффициент излучения без отдачи в случае, когда атомы Мёссбауэра составляют примесь с малой концентрацией. Вторая часть работы содержит анализ случая более высоких концентраций. Матрица для атомов примеси является совершенно произвольной и единственным условием, накладываемым на нее, является условие образования резких резонансов. Получена общая зависимость коэффициента излучения без отдачи от времени, истекшего от момента механического возбуждения атома, а также от энергии возбуждения и ширины резонансных (колебательных) полос. Кроме непосредственных приложений к определению времен релаксации резонансных мод обсуждается применение полученных результатов к экспериментальному определению времени переноса энергии отдачи квантом гамма, излучаемым из ядра атома, связанного в кристаллической решетке.

THIS paper presents an application of certain results of the theory of point defects in crystal lattices to the so-called Mössbauer effect. It may also be understood as an attempt at a new experimental research tool in the field of dynamics of such defects.

General characteristics of the main objectives of the paper will be preceded by a qualitative description of the physical situation considered here; it will facilitate precise statement and constitute the necessary introduction to more detailed considerations.

Let us consider a sample of a certain crystal containing Mössbauer-active (for the sake of simplicity called throughout the paper "*M*-active") impurity atoms. Assume the impurity concentration to be very low, thus enabling us to treat its atoms as isolated defects. Dimensions of the host lattice sample are assumed to be sufficiently large that internal defects

only need be considered (the specimen is not a thin layer, for instance). Let us assume moreover, that the choice of the host lattice and impurities is such that in the vibrational frequency spectrum of impurity atoms, sharp resonance modes appear. Such modes occur when the impurity atom is much heavier than the host lattice atoms and/or its coupling parameters with the host lattice atoms are softer than those of the perfect lattice ([1], cf. also [4, 5, 17, 19]). It will be shown later that such a situation is considered favourable in view of the M-nuclides with mass numbers close to two hundred.

Let us consider the phenomenon of recoilless emission for the impurity atoms. It is known to consist in the emitting, by a nucleus of an atom bonded in the crystal lattice, of a gamma quantum in such a manner that the number of lattice phonons before and after emission remains the same. Such emission is a result of the transition of an atomic nucleus from the excited Mössbauer energy state to the ground state. In the cases we are dealing with the M-level is created as a result of another, earlier radiative transition and it should be stressed here that this passage is not recoil-free. Hence we are dealing here with a simultaneous creation of a nuclear M-state and with mechanically excited vibrations of the M-atom due to the gamma recoil from the transition preceding the recoilless emission. Thus the M-emission occurs not from the atomic nucleus whose vibrational state is a state of thermal equilibrium, but from the atom excited to non-stationary vibrations. The mean square of non-stationary component of these vibrations decreases exponentially with time, and the state of the atom approaches the state of equilibrium. Since the parameters characterizing the recoilless emission (we mean here the recoilless fraction f, and the second order Doppler shift) depend on the state of vibration of the atom, it is to be expected that the recoilless emission spectrum is influenced by the mechanical excitation of the atom. It is immediately seen that this influence can be essential only in the case in which the life-time (time of relaxation) of the excited vibrational state is not too short as compared with the life-time of the nuclear M-level. A typical life-time of sharp resonance modes is of the order of 10^{-10}s, while life-times of excited modes of the remaining portion of the atomic vibrational spectrum are still shorter. Thus, e.g., Fe^5 cannot be considered as a suitable M-nuclide (life-time of the M-level $T_M \approx 10^{-7}$s). Many nuclides, however, are characterized by considerably shorter M-level life-times. These are, for instance [6, 7]: Eu^{153}, Gd^{155}, Hf^{177}, Ir^{191}, Pt^{195}, Re^{187}, Tb^{159}, W^{183}, Th^{232}, U^{238} etc., with life-times of M-levels shorter than 10^{-9} s. M-levels of these nuclei are formed as results of radiative transition recoils exciting the vibrations of atoms.

An idea may now be conceived that, in order to evaluate the influence of the excitation upon the recoilless emission process, the delayed coincidence technique might be applied (cf. the classical papers [8, 9], the review paper on the Mössbauer coincidence spectroscopy [10] and [25, 26, 11, 12, 13]). This would make it possible to measure recoilless emission spectrum as a function of time passed from the instant of formation of the M-level and the excited mechanical state. Namely, the gamma quantum resulting from the radiative transition forming the M-level might be used as a signal for the coincidence apparatus. In this manner, it would be possible register the instant of formation of the nuclear M-level and, simultaneously, the moment of excitation of the vibrational state, and next — measure the counts of the spectrometer for various retardation times of the coincidence.

Owing to the fact that the form of time-dependence of the excited states may be determined from the theory of defects, measuring of the time variation of the recoil-free emission spectrum may be used for determination of the influence of mechanical vibrations on the emission parameters.

Two such parameters have already received mention: the recoilless fraction f defined as the ratio of the number of recoilless emissions to the total number of emissions from the M-level (cf. the monograph [14] and review articles [15, 16]) and the second order Doppler shift [5]. The first of them determines the emission line intensity, the second influences the position of its centre. In this paper, we shall deal with the coefficient f only, since here the effects considered can be observed most easily and exceed, at least by one order of magnitude, the variations caused by the second order Doppler shift.

We are now in a position to formulate the principal aims of the present paper. Our objective is to investigate the influence of the existence of sharp resonance lines on the recoilless fraction f as a function of time. It will be shown that $f(t)$, depending in a simple manner on the relaxation time of the resonance mode, furnishes direct information on the width of the resonance λ, is of particular value in the case of mono-atomic crystals in which optical methods must fail. The measuring method proposed would then be a unique method of measurement of λ for low concentration of defects in metals.

In conclusion, another idea of possible application of the $f(t)$-measurement will be discussed; it may be used to solve a certain theoretical problem which arises in connection with the Mössbauer resonance scattering but which falls outside the scope of both the theory of Mössbauer effect and the theory of defects; it concerns the controversy regarding the recoil energy transfer time of a gamma emission by the nucleus of an atom bonded in a crystal lattice, and also the problem of possibility of its being measured.

1. Recoilless fraction f

The recoilless fraction f of an atom being in the state of thermal equilibrium with the crystal may be expressed, in harmonic approximation, by the known formula ([14, 15, 16])

$$(1.1) \qquad f(t) = \exp\{-\varkappa^2 \langle u^2 \rangle_T\},$$

where $\langle . \rangle_T$ is the thermal mean, $\varkappa$ — wave vector of the gamma radiation emitted, u — component of the displacement vector of the emitting atom the direction of $\varkappa$.

Our interest is focused on the situation in which the emitting atom has been knocked off the state of equilibrium at the instant of formation of the nuclear M-level. The starting point of our considerations should then be the definition of the recoilless fraction f without assuming the vibrational state to be stationary. f is namely the probability that the gamma quantum emission will not change the state of energy of the lattice containing the emitting atom. This probability may be written, at any instant, in the form ([14, 15, 16]):

$$(1.2) \qquad f(t) = \sum_L w_L |\langle L| e^{i\varkappa u(t)} |L\rangle|^2 ;$$

Ket $|L\rangle$ is the eigenvector of the Hamiltonian describing the crystal lattice in the state L, w_L is the statistical weight of the L-th energy state of the lattice (lattice temperature is

assumed to be different from zero), u denotes here the displacement operator of the emitting atom in the Heisenberg picture.

The system considered is assumed to be harmonic. Time changes (except the oscillatory term) of the displacement operator u for $t > 0$ (i.e., after excitation) are thus only the results of energy transfer to other atoms of the crystal, without any energy exchange between the normal modes. The Hamiltonian describing the vibrations of each of the normal modes is then independent of time for $t > 0$. In order to determine the time-dependence of f (which makes sense only if $t > 0$) it suffices to know the time-depencence of $u(t)$. Let this assumption be made what splits the problem into two parts: determination of $f(t)$ for arbitrary, known $u(t)$ [subject to the condition that $u(t)$, apart from the high-frequency oscillatory term which does not enter the expectation value, is a slowly varying function as compared with the characteristic frequency of vibration of the atom], and determination of $u(t)$ from the dynamics of the defect itself.

The function u may now be expanded into normal modes [16, 17]: $u = \sum_s \eta_s Q_s$ (with Q_s denoting the normal coordinate of the s-th mode); making use of the fact that L is expressible in terms of the product $\prod_s |n_s\rangle$, $|n_s\rangle$ being the eigenfunction of the Hamiltonian of the harmonic osillator representing vibrations of the s-th mode, we may write

(1.3) $$f(t) = \sum_{n_s} w(n_s) | \prod_s \langle n_s | e^{i\varkappa\eta_s Q_s} | n_s\rangle |^2.$$

$w(n_s)$ is the statistical weight on the n-th energy level of the s-th mode.

Let us assume that the s-th oscillator (normal mode) before excitation was in the state $|m_s\rangle$. If, as a result of excitation, the number of phonons in that mode increased by k_s, then $|n_s\rangle$ may be written in the form $|m_s+k_s\rangle$. Expanding the matrix elements in the Eq. (1.3) into series of the exponent, taking into account the facts that $\eta_s Q_s = 0(N^{-1/2})$ (N denoting the number of elementary cells of the crystal) [17] and that only terms with even powers of Q_s do not vanish, averaging over the distribution $w(n_s)$ and returning to the exponential form, we finally obtain (see, Appendix):

(1.4) $$f(t) = \exp\{-\varkappa^2 \sum_s \eta_s^2 (1+2\langle m_s\rangle_T + 2\langle k_s\rangle_{w(n_s)})\}$$
$$= \exp\{-\varkappa^2 \langle u^2\rangle_T\}_{st} \exp\{-\varkappa^2\langle u^2\rangle_{w(n_s)}\}_{ex}.$$

Here u denotes the stationary part of the displacement operator, u — its excited part. $\langle \cdot \rangle_{w(n_s)}$ is the distribution $w(n_s)$ average. Writig here $\langle u^2\rangle_{w(n_s)} = \langle u^2\rangle_T$ we have made use of the fact that m_s is the distribution before excitation — i.e., the thermal distribution independent of k_s; distribution of the phonon number k_s may, on the other hand, be dependent on m_s, since the probability of excitation of the oscillator by k_s phonons generally depends on the energy level occupied by the oscillator before excitation. It also depends on factors which are external with respect to the s-th oscillator, such as energy of the gamma quantum emitted, form of the frequency spectrum (Fourier transforms) of the recoil forces etc. All factors which enter the relations are contained in the distribution $w(n_s)$,

though explicit presentation — or even knowledge — of them is not necessary thus far. The problem we have to tackle right now consists in the determination of the relation between the mean square of the excited displacement vector and time, which will enable us to find $f(t)$.

Let us now pass to the discussion of dynamics of an emitting Mössbauer atom treated as an isolated defect.

2. M-atom as an isolated defect

It is known that the vibration spectrum of an isolated point defect containing sharp resonance maximum in the low-frequency part of the band models has the form of a line, which may be considered to be a Lorenz line, and a flat background much lower than the line [5, 19, 20]. It should be stressed that we are dealing here with the stationary spectrum of the defect itself, and not with what is called the mean phonon spectrum of the lattice with defects.

The mechanical excitation of defect vibration (i.e., the exciting force) is assumed to be of very short duration as compared with the characteristic period of atomic vibrations — i.e., it is proportional to $\delta(t)$. It turns out that such general information, in the case of isolated defects, suffices to determine the time-dependence of the coefficient f. Let us therefore split the excited contribution of the displacement vector of the defect u_R^{ex} into the resonance part u_R^{ex} and the part due to the background u_B^{ex}, [11, 12]. We may write

(2.1)
$$\langle u^2(t) \rangle_{ex} = \langle u_R^2(t) \rangle_{ex} + \langle u_B^2(t) \rangle_{ex},$$

since $\langle u_R u_B \rangle_{ex\,ex} = 0$, which is immediately seen once u is written in terms of normal modes. Let us recall that the time-dependence of the classical displacement vector and that of the displacement operator in the Heisenberg picture are identical (cf. e.g. [19]).

The relaxation time of $\langle u_B^2 \rangle_{ex}$ is of order 10^{-13} s and thus it may be disregarded in comparison with the excited resonance part with relaxation time greater by three orders of magnitude. More strictly speaking, $\langle u_B^2 \rangle_{ex}$ is disregarded in comparison with the life-time of the nuclear level, which is of the order of the relaxation times of resonance modes, and so $\langle U_B^2 \rangle_{ex}$ "has no time" measurably to influence the coefficient f.

The time dependence of $\langle u_R^2(t) \rangle_{ex}$ for a Lorentz line has the form

(2.2)
$$\langle u_R^2(t) \rangle_{ex} = \langle u_R^2(t=0) \rangle_{ex} e^{-\lambda t},$$

where λ is the resonance line width.

Coefficient f for an isolated impurity atom (with a spectrum containing a sharp resonance line) may then be written as [cf. (1.4)]

(2.3)
$$f(t) = f_{st} \exp\left\{ -\varkappa^2 \langle u_R^2(0) \rangle_{w(n_s)} e^{-\lambda t} \right\}.$$

Here, $f_{st} = \exp\{-\varkappa^2 \langle u^2 \rangle_T\}$ [cf. Eq. (1.1)]. The Eq. (2.3) may also be rewritten in the form:

(2.4)
$$f(t) = f_{st}^{1+\Phi e^{-\lambda t}}.$$

Here

$$\Phi = \langle u_R^2(0) \rangle_{w(n_s)} \cdot \langle u^2 \rangle_T^{-1}.$$
$$\quad\;\; \text{ex} \qquad\qquad\quad \text{st}$$

The measurement of f as a function of time makes it possible to determine the resonance line width λ. The problems arising in connection with the measuring will be discussed in the second part of this paper. For the time being, in order to determine the range of applicability of the Eq. (2.4), let us discuss the assumptions necessary for its derivation. Let us name them consecutively.

1. *Harmonic properties of the system : "impurity atoms—host lattice".* Owing to the prospective measurement of f, we are interested only in crystals at low temperatures. This means, in turn, that we are dealing with systems in which the assumption of harmonicity is most completely satisfied. Let us consider this problem in detail. Harmonic properties are necessary in deriving the Eq. (1.4) for $f(t)$ and in satisfying the Eq. (2.1). They do not intervene, however, in the form of time-dependence of $\langle u_2^R(t) \rangle$: accounting for an-
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \text{ex}$$
harmonicity increases only the width of the resonance line.

Introduction of anharmonic terms into the lattice Hamiltonian leads to energy exchange between the normal modes. Weak anharmonicity corresponds to a soft coupling between the modes. Assuming the equation

(2.5) $$H(t)|L(t)\rangle = E(t)|L(t)\rangle,$$

to be satisfied at any instant (cf. [21], Chapter xvii) (in the formula, the time-dependence of the Hamiltonian of the system $H(t)$ and of its eigenvalues $E(t)$ is treated as dependence on a parameter), a formula analogous to the Eq. (1.3) may be written for each value of t. The solution will be analogous to the Eq. (1.4) except for the fact that, in addition to the damping due to the energy transfer between the atoms within each of the modes, additional damping appears resulting from coupling of the modes; this expressed by a slow dependence of the energy of individual modes on the time. Consequently, the result is of the same form as in the harmonic case except for the necessity to take into account the increased of the width resonance line.

Let us indicate that exact satisfaction of the Eq. (2.1) is not a necessary condition for the Eq. (2.3), which finally appears in our result. It is sufficient to assume that $\langle u_R u_B \rangle$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \text{ex ex}$$
vanishes much faster in time than $\langle u_B^2 \rangle$. This condition is fulfilled since the life-time of
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{ex}$$
$\langle u_R u_B \rangle$ is of the order of the relaxation time $\langle u_B^2 \rangle$ which may be disregarded in further
$$\text{ex ex} \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{ex}$$
considerations.

From the remarks presented it follows that the assumption of harmonicity of the system: "impurity atom—host lattice" may be weakened by allowing for a weak anharmonicity.

2. *Assumption that the excited vibrations frequency spectrum has the same form as the stationary spectrum.* This assumption is reduced to confining the excitations to such as resulting from transitions fast in comparison with the characteristic times of vibration

of the atoms in the lattice (10^{-13}s), since then the exciting recoil force may be assumed in the form $F(t) = \text{const}\,\delta(t)$. It follows that (cf. [19, 20])

$$(2.6) \qquad \underset{\text{ex}}{u(t)} = \int dt'\, G(t-t')\text{const}\,\delta(t') = \text{const}\,G(t),$$

where G is the Green function for a crystal with defect; strictly speaking, it is the function G^{00}, indices denote the lattice sites, $u = u^0$. On the other hand ([19, 22])

$$(2.7) \qquad \text{Im}\,G^{00}(\omega) = \text{const}\,g(\omega^2).$$

Here, $g(\omega^2)$ is the stationary frequency spectrum of the atom in the site 0 (i.e., the spectrum of the M-atom considered), and

$$(2.8) \qquad \text{Re}\,G^{00}(\omega) = HT\{\text{Im}\,G^{00}\}.$$

HT denotes here the Hilbert transform with respect to the variable ω^2. This yields $\underset{\text{ex}}{u^0(t)} =$ $\text{const}\,FT\{g(\omega^2)\}$, and here FT is the Fourier transform.

Let us now relax the assumption that $F(t) \propto \delta(t)$. We select such a reference frame that $F(t) \neq 0$ in the interval $[0, t_F]$. The Eq. (2.6) will take the form:

$$(2.9) \qquad \underset{\text{ex}}{u(t)} = \int_0^{t_F} dt'\, G(t-t')F(t'),$$

or

$$(2.10) \qquad \underset{\text{ex}}{u(t)} = e^{-\lambda t/2} \int_0^{t_F} dt'\, \varphi(t'; t),$$

where the time-dependent exponential term has been excluded from the Green function, the product of the remaining term by $F(t')$ being denoted by $\varphi(t'; t)$. Since $\varphi(t'; t)$ depends on t only through the oscillatory term which does not enter $\underset{\text{ex}}{\langle u^2(t)\rangle}$, from the Eq. (2.10) it is evident that the time of duration of the force does not influence the character of the time-dependence of $\underset{\text{ex}}{\langle u^2(t)\rangle}$.

If it is assumed that the M-level is formed at the instant when $F(t)$ is removed, the assumption of proportionality of $F(t)$ to $\delta(t)$ ceases to be necessary for the fundamental formula (2.4) to hold true; we have to remember, however, that in determining the parameter Φ in Eq. (2.4), $\underset{\text{ex}}{u(t_F)}$ should be used instead of $\underset{\text{ex}}{u(0)}$.

3. Application to the estimation of the recoil energy transfer time in a gamma emission process

Measurements of f as a function of time may serve, in addition to the immediate application for the determination of the relaxation time of impurity atom vibration, to estimation of the recoil energy transfer time in the gamma emission process of the nucleus of an atom bonded in a crystal.

The problem of the time of recoil energy transfer and momentum transfer in such a process was stated in connection with a controversy concerning the mechanism and description of the Mössbauer resonance scattering [23, 24]. MÖSSBAUER and SHARP suggested that the time of duration of an "average" individual process of gamma emission

6*

or absorption cannot be considered as short — i.e., of the order of 10^{-20}s, but that characteristic times of these processes are related to lifetimes of the characteristic nuclear levels. The authors suggested, moreover, that the time of duration of an individual emission or absorption process cannot be measured.

Our present aim is to propose a certain method of estimation of the recoil energy transfer time in the process of gamma emission by a nucleus bonded in a crystal.

Let us start from classical considerations. The point of departure might be the fact that the process of relaxation of atomic vibrations starts simultaneously with the initial instant of their excitation, and thus at the instant t_F, when the force of excitation is removed and the M-level created, a part of the excitation energy has already been transferred to other atoms in the lattice. One should expect the parameter Φ to be dependent on t_F.

Let us consider this problem in detail. The mean recoil energy $\overline{R}$ transferred to the lattice equals

$$(3.1) \qquad \overline{R} = \sum_f p(f,i)(E_f - E_i);$$

f, i labeling the final and initial states of the lattice, with energies E_f and E_i. $\overline{R}$ is independent of t_F [16, 24]. Hence

$$(3.2) \qquad \overline{R} = \overline{E}(t) + \overline{E}(t) = \text{const},$$
$$\qquad\qquad\quad {}_{\text{ex}} \qquad {}_{\text{rl}}$$

where $E(t)$ is the excited energy of M-atom at the instant t, and $E(t)$ — the energy trans-
$\quad{}_{\text{ex}}$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad {}_{\text{rl}}$
ferred to the lattice at the instant t in the process of vibration relaxation. It follows that

$$(3.3) \qquad \overline{u^2(t)} + \overline{u^2(t)} \propto \overline{R},$$
$$\qquad\qquad {}_{\text{ex}} \qquad\;\; {}_{\text{rl}}$$

indices ex and rl having the same meaning as in the Eq. (3.2).

Let us now rewrite the Eq. (2.9) with the Green function in the form $G(t-t') = \gamma(t-t')\exp\{-\lambda(t-t')/2\}$:

$$(3.4) \qquad u(t) = e^{-\lambda t/2} \int_0^{t_F} dt'\, e^{t'/2} \gamma(t-t') F(t').$$
$$\quad {}_{\text{ex}}$$

For $t \geqslant t_F$ it clearly follows that

$$(3.5) \qquad \overline{u^2(t)} + \overline{u^2(t)} = \left\{ \overline{\int_0^{t_F} dt'\, \gamma(t-t') F(t')} \right\}^2$$
$$\qquad\qquad {}_{\text{ex}} \qquad\;\; {}_{\text{rl}}$$

and, in view of the Eq. (3.3), (3.4), that

$$(3.6) \qquad u^2(t) \propto e^{-\lambda t + \lambda \bar{t}} \overline{R}.$$
$$\qquad\quad {}_{\text{ex}}$$

Here, $\bar{t}$ is contained in the interval $[0, t_F]$ and depends on the form of $F(t)$.

The ratio of parameters Φ_1, Φ_2 for two different transitions of excitation (the definition of Φ being employed, cf. Eq. (2.4)) is then

$$(3.7) \qquad \frac{\Phi_1}{\Phi_2} = e^{-\lambda_1 t_{F1} + \lambda_1 \bar{t}_1 + \lambda_2 t_{F2} - \lambda_2 \bar{t}_2} \frac{\overline{R_1}}{\overline{R_2}},$$

since from the Eq. (3.1) it is evident that the mean $\overline{(\,.\,)}$ denotes exactly the same as the mean $\langle\,.\,\rangle_{w(n_s)}$ in the definition of Φ [cf. the Eqs. (2.3), (2.4) and the final remark of Sec. 2].

Knowing the curves $f(t)$ enables us to determine the width of line λ and the parameters Φ [cf. Eq. (2.4) and Appendix]. $\bar{R}$ is known if the energy of the excitation gamma transition is known $(\bar{R} = h^2\varkappa^2/2M$, M — mass of the nucleus, $\varkappa$ — wave vector of the gamma quantum). If, according to our expectations, the force $F(t)$ behaves regularly in $[0, t_F]$, then $\bar{t}$ satisfies the following conditions:

    (i) $\bar{t} < t_F$,

    (ii) $t_F - \bar{t}$ is of the order of t_F.

Thus the Eq. (3.7) indicates that the time differences $t_{F1} - t_{F2}$ could be determined by measuring the curves $f(t)$.

The reasoning leading to the Eq. (3.7) was based on a semi-classical treatment of the excited vibration processes of the atom and their relaxation. Before trying to tackle the problem formulated at the outset, let us first consider the physical situation using the quantum description.

We are dealing here with a nucleus of an atom bonded in a crystal, an atom which is in the state of excitation on the N-th energy level. There is a radiative transition to the M-level (Mössbauer level) and then, in an recoil manner, to the ground state (transitions other than zero-phonon are of no interest to us). The $N \rightarrow M$ transition conveys a certain recoil energy to the atom; thus we have to consider the system "atom-crystal lattice-phonon". Not the entire energy, however, is transferred to the "atom-lattice" system in the form of phonons. A part of the recoil energy is absorbed by the crystal as a rigid structure — by means of the motion of its mass centre. We are interested in that part of energy which is used for the production of phonons — i.e., the part which excites atomic vibrations. It should be noted that the phonons are not the vibration energy quanta of a single atom but the quanta of collective lattice vibrations. This quantization may be performed formally in various, physically equivalent ways. If the lattice vibrations described by the usual normal modes are quantized (cf., e.g., [1, 5, 19]), then the vibrations of a single atom are (in the harmonic approximation) a superposition of normal vibrations with a proper set of coefficients. In a given state of the lattice — i.e., at a given number of phonons in the lattice, the contributions of individual atoms to the energy of each of the modes are determined by coefficients which are c-numbers. Thus, in spite of the fact that the energy of vibration of individual modes possesses a discrete spectrum, the vibration energy of each of the modes can be transferred from one atom to another in a continuous manner. The relaxation of excited atomic vibrations considered here consists mainly in the continuous process of energy transfer from the excited atom to other atoms without any changes in numbers of phonons in the individual modes. Therefore a continuous process of relaxation of the excitation energy according to $\exp(-\lambda t)$ occurs even for individual atoms.

Another, even more important problem consists in replacing the classical description of excitation of atomic vibrations by the force $F(t)$ — with a quantum description.

If the recoil energy transfer time of the gamma quantum is short, then for each of the emitting atoms there exists a probability of excitation of n_s phonons in the s-th mode

the conditional probability of $m_s \neq 0$ phonons at an arbitrary instant later than the instant of excitation of the first $n_s \neq 0$ phonons being equal to zero. It is in this way that the short duration of recoil energy transfer is manifested. If the transfer lasts longer (i.e., say according suggestions of MÖSSBAUER and SHARP, its duration is of the order of the lifetime of nuclear N-level), then the conditional probability of formation of $m_s \neq 0$ phonons at a later instant (with $n_s \neq 0$ initial phonons) is different from zero. This means that phonon excitations occur, with a certain probability, several times within a finite time period which may be called the duration of recoil energy transfer. This time is denoted by t_R.

Let us denote by $p(m_s, t|n_s)$ the conditional probability of excitation in the s-th mode of m_s phonons within the time interval $[t, t+dt]$ provided n_s phonones were excited at $t = 0$. This probability satisfies the following conditions:

(i) $p(m_s, t|n_s) = 0$ for $t \neq 0$ for fast energy transfers,

(ii) $p(m_s, t|n_s) \begin{cases} \neq 0 & \text{for} \quad 0 < t < t_R \\ = 0 & \text{for} \quad 0 < t_R < t \end{cases}$ for slow energy transfers.

Using the probability $p(m_s, t|n_s)$ we may write $\overline{R}$ in the following form [cf. the Eq. (3.3)]:

$$(3.8) \qquad \overline{R} = \eta \int_0^{t_R} dt' \sum_s (n_s + m_s) p(m_s, t'|n_s),$$

η being a certain constant. The mean excitation energy at instant t is, according to that notation, equal to

$$(3.9) \qquad \overline{E}_{\text{ex}}(t) = \eta e^{-\lambda t} \int_0^{t_R} dt' e^{\lambda t'} \sum_s (n_s + m_s) p(m_s, t'|n_s).$$

Thus the ratio of excitations Φ_1/Φ_2 sought for is

$$(3.10) \qquad \frac{\Phi_1}{\Phi_2} = e^{-\lambda_1 t_{R1} + \lambda_2 t_{R2}} \frac{\int_0^{t_{R1}} dt' e^{\lambda_1 t'} \sum_s (n_s + m_s) p(m_s, t'|n_s)}{\int_0^{t_{R2}} dt' e^{\lambda_2 t'} \sum_s (n_s + m_s) p(m_s, t'|n_s)}.$$

The integrals in the Eqs. (3.9), (3.10) may be written in the form:

$$(3.11) \qquad \int_0^{t_R} dt' = e^{\overline{\lambda t}} \overline{R}.$$

Here $0 < \overline{t} < t_R$, since the distribution $p(m_s, t'|n_s)$ is assumed to be different from zero in the finite interval $[0, t_R]$. The Eq. (3.10) then yields finally:

$$(3.12) \qquad \frac{\Phi_1}{\Phi_2} = e^{-\lambda_1(t_{R1} - \overline{t}_1) + \lambda_2(t_{R2} - \overline{t}_2)} \frac{\overline{R}_1}{\overline{R}_2}$$

and may formally be identified with the Eq. (3.7) obtained in the classical considerations, provided the time of action of the classical recoil force is identified with the time (time interval) in which the probability of a repeated excitation of phonones by the recoil energy

of the same gamma quantum is different from zero; the "mean" times $\overline{t}$ should also be identified [cf. the Eqs. (3.4), (3.6), (3.11)].

The formulae (3.7) and (3.12) indicate the limits within which the measurement of $f(t)$ (which in turn serves for the determination of parameters Φ_1, Φ_2 and the relaxation times λ_1^{-1}, λ_2^{-1}) enables to estimation of the times t_R. Namely, it is seen that the difference of times $t_{R1} - t_{R2}$ must be of order λ^{-1} or greater, in order to be manifested in the measurement of $f(t)$. Typical values of λ^{-1} are of order 10^{-10}s. The duration of the gamma recoil energy could then be determined, in principle, with accuracy of 10^{-10}s. Obviously, the entire procedure is limited to the corresponding Mössbauer nuclei with lifetimes of the M-levels being of the order of λ^{-1} (cf. introduction). The energy transfer time can be determined not for the M-level but for the N-level from which the nucleus passes to the M-level. It may be added that the lifetimes of N-levels of the M-nuclides considered here (and presented in the introduction) are practically contained within the limits 0 (that is, $\ll \lambda^{-1}$) and ∞ (cf. [6] and the data of Nuclear Data Sheets).

The controversy concerning the time of duration of the recoil energy transfer in gamma emission processes may now be formulated in the form of the following conclusions.

1. The controversy concerned the emission/absorption of the M-level of the Fe^{57} — nucleus with the lifetime of about 10^{-7}s. The test proposed in this paper makes it possible to register the times of energy transfers from 10^{-10}s up.

2. The experimental data obtained from the measurement of $f(t)$ does not directly refer to the energy transfer time of the radiation emitted from the Mössbauer level, since it concerns the transitions between other nuclear levels. This fact does not seem to be an obstacle to of applying the results of measurement of $f(t)$ to the deduction of the manner in which the process of emission from the M-level occurs, the nuclear processes being independent of the phonon processes (cf. [14, 23]).

Appendix

Transformation of the Eq. (1.3) to Eq. (1.4)

Let us more explicity present the principal stages of the derivation already outlined. The Eq. (1.3) is rewritten (using the notations introduced earlier) in the form

(A.1)
$$f(t) = \sum_{n_s} w(n_s) \left| \prod_s \langle n_s | e^{i\varkappa\eta_s Q_s} | n_s \rangle \right|^2.$$

The matrix element in this equation is equal to

(A.2)
$$\langle || \rangle = 1 - \frac{1}{2} \varkappa^2 \eta_s^2 \langle Q_s^2 \rangle, \quad \langle Q_s^2 \rangle = \langle n_s | Q_s^2 | n_s \rangle,$$

since higher order terms of the expansion may be disregarded in comparison with $\eta_s^2 = 0(N^{-1})$, and the linear term disappears. The absolute value terms in the Eq. (A.1) are real and thus the square of absolute value may be replaced by the ordinary square,

(A.3)
$$\left| \prod_s \langle || \rangle \right|^2 = \prod_s \left(1 - \frac{1}{2} \varkappa^2 \eta_s^2 \langle Q_s^2 \rangle \right)^2 = \prod_s (1 - \varkappa^2 \eta_s^2 \langle Q_s^2 \rangle)$$

still in view of the equality $\eta_s^2 = 0(N^{-1})$. Performing the product in the Eq. (A.3) and putting for ease of writing

$$\chi_s = \varkappa^2 \eta_s \langle Q_s^2 \rangle$$

and $\langle \, . \, \rangle_{w(n_s)} = \langle \, . \, \rangle$ we obtain:

(A.4) $f(t) = \Big\langle 1 - \sum_s \chi_s + \sum_{r<s} \chi_r \chi_s - \sum_{p<r<s} \chi_p \chi_r \chi_s + \dots \Big\rangle$

$$= 1 - \sum_s \langle \chi_s \rangle + \sum_{r<s} \langle \chi_r \rangle \langle \chi_s \rangle - \dots,$$

since χ_r and χ_s are statistically independent for $r \neq s$. The Eq. (A.4) can be rewritten in the form:

(A.5) $f(t) = 1 - N\overline{\langle \chi \rangle} + \dfrac{1}{2!} \, N(N-1) \overline{\langle \chi \rangle} \, \overline{\langle \chi \rangle} - \dots,$

where $\overline{\langle \chi \rangle} = \dfrac{1}{N} \sum_s \chi_s$. Neglecting terms $\leqslant 0 \, (N^{-1})$ the latter equation becomes:

(A.6) $f(t) = 1 - N\overline{\langle \chi \rangle} + \dfrac{1}{2!} \, N^2 (\overline{\langle \chi \rangle})^2 - \dots = e^{-N\overline{\langle \chi \rangle}} = e^{-\varkappa^2 \sum_s \eta_s \langle\langle Q_s^2 \rangle\rangle_{w(n_s)}},$

and the substitution of the explicit form of the matrix element $\langle Q_s^2 \rangle$ leads to the Eq. (1.4), if we can assume

(A.7) $\langle u_R^2(t) \rangle_{w(n_s)} \atop \text{ex} = \langle u_R^2(0) \rangle_{w(n_s)} \atop \text{ex} e^{-\lambda t},$

where $t = 0$ is the moment of the M-level formation. But Eq. (A.7) means that there is no time averaging, i.e., that the energy transfer is fast. We have then to ask whether the use of the Eq. (1.4) is still correct for the investigation of the long energy transfer time case. Note, that if we want to confine ourselves within limits of a pure phenomenological treatment, we cannot say much about the possible time average of the $e^{-\lambda t}$ term. Thus, let us assume the most unfavorable case, namely, that $\langle e^{-\lambda t} \rangle = \dfrac{1}{\lambda t} (1 - e^{-\lambda t})$ which would correspond to a uniform time distribution. It is easy to see, that if one approximates $\langle e^{-\lambda t} \rangle$ by a suitably chosen $e^{-\zeta t}$, the differences between values of ζ for different time windows used in coincidence Mössbauer spectroscopy experiments [10, 25] are relatively small (they differ by a factor ~ 2 for the extremal time windows). Thus, possible time averaging does not matter for the determination of the order of magnitude of t_R and we can conclude that the Eq. (1.4) can be used for the here proposed analysis of the energy transfer time.

Aknowledgement

References

1. A. A. MARADUDIN, *Elementary excitations in solids*, ed. A. A. Maradudin and G. F. Nardelli, Plenum Press, p. 35, 1969.
2. A. J. SIFVERS, Phys. Rev. Letters, **13**, 320, 1964.
3. A. J. SIEVERS, S. TAKENO, Phys. Rev., **140**, A 1030, 1965.
4. J. A. KRUMHANSL, *Localized excitations in solids*, ed. R. F. Wallis, Plenum Press, New York 1968.
5. A. A. MARADUDIN, Solid State Phys., **18**, 272, 1966; **19**, 1, 1966.
6. A. H. MUIR Jr, K. J. ANDO, H. M. COOGAN, *Mössbauer data index* 1958–1965, John Wiley, New York 1966.
7. J. BARA, Proc. of the Conference on the Applications of the Mössbauer Effect, Tihany 1969, ed. I. Dézsi, Akadémiai Kiadó, Budapest 1971.
8. F. J. LYNCH, R. E. HOLLAND and M. HAMERMESH, Phys. Rev., **120**, 513, 1960.
9. C. S. WU, Y. K. LEE, N. BENCZER-KØLLER and P. SIMMS, Phys. Rev. Letters, **5**, 432, 1960.
10. G. R. HOY, D. W. HAMILL, P. P. WINTERSTEINER, *Mössbauer effect methodology*, ed. I. J. Gruverman, Plenum Press, **6**, p. 109, New York 1971.
11. A. SZCZEPAŃSKI, Phys. Stat. Sol. (b), **46**, K 103, 1971.
12. A. SZCZEPAŃSKI, IFTR Reporsts, 15/1971.
13. A. SZCZEPAŃSKI, Sol. State Comm., **10**, 447, 1972.
14. H. FRAUENFELDER, *The Mössbauer effect*, W. A. Benjamin, New York 1962.
15. A. J. BOYLE and H. E. HALL, Rep. Progr. Phys., **25**, 441, 1962.
16. A. MUKERJI and C. ALTON COULTER, *Topics in fields and solids*, ed. C. Alton Coulter and R. A. Shatas, Gordon and Breach, New York 1968.
17. A. A. MARADUDIN, E. W. MONTROLL, G. H. WEISS, *Theory of lattice dynamics in the harmonic approximation*, Academic Press, New York 1963.
18. W. LUDWIG, *Ergebnisse der Exakten Naturwissenschaften*, **35**, Springer-Verlag, p. 1, Berlin 1964.
19. W. LUDWIG, *Recent development in lattice theory*, Springer-Verlag, Berlin 1967.
20. A. A. MARADUDIN, Rep. Progr. Phys., **28**, 331, 1965.
21. A. MESSIAH, *Quantum mechanics*, North-Holland Publ., Amsterdam 1969.
22. E. J. ELLIOT, *Phonons in perfect lattices and in lattices with point imperfections*, ed. R. W. H. Stevenson, Oliver and Boyd, Edinburgh, p. 377, 1966.
23. R. L. MÖSSBAUER and D. H. SHARP, Rev. Mod. Phys., **36**, 410, 1964.
24. H. J. LIPKIN, Ann. Phys., **18**, 182 and 294, 1962.
25. G. P. HOY and P. P. WINTERSTEINER, Phys. Rev. Letters, **28**, 877, 1972.
    As this paper reached the author after his own manuscript had been completed, it is impossible to discuss it here in detail. It may be mentioned, however, that the authors measured $f(t)$ for Fe^{57} secking effects different from those discussed in the present paper. The measurements do not lead to the results expected but, quite the contrary, yield in a certain case a function $f(t)$ which coincides with the ideas of DASH and NUSSBAUM [26] and with our results. Unfortunately, the complex structure of the chemical compound used as the source does not enable prompt orientation in its vibrational structure; thus the results of [25] cannot, for the time being, be interpreted in terms of definite vibration modes.
26. J. G. DASH, R. H. NUSSBAUM, Phys. Rev. Letters, **16**, 567, 1966.

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