Inelastic scattering of Mössbauer γ rays by crystals near the temperature of a structural phase transition

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It is shown that as a result of the amplification of low-frequency fluctuations at a structural phase transition an appreciable fraction of the phonons excited in inelastic scattering of γ rays have an energy of the order of the Mössbauer line width, and this is manifested in the spectrum of the scattered radiation. The determination of the fractions of elastically and inelastically scattered γ rays by means of a Mössbauer filter makes it possible to obtain information on the dispersion of the soft optical mode.

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It has been shown in a number of theoretical papers[1] that inelastic scattering of Mössbauer radiation (MR) enables us to obtain a wealth of information on the dynamics of a crystal lattice. However, a number of difficulties have been encountered on the road to realizing this idea experimentally, the chief of which is evidently the small width Γ of the Mössbauer line compared with such characteristic quantities of the phonon spectrum as the Debye frequency and the inverse lifetime of the phonons.

Below we treat theoretically the inelastic scattering of MR near the temperature of a structural phase transition (SPT), i.e., in the case when the role of low-frequency excitations in the crystal dynamics is increasing sharply. It is shown that study of the energy spectrum of the scattered MR gives information on excitations with energy $\sim\Gamma\sim 10^{-8}$ eV, while the determination of the fraction of inelastically scattered γ quanta enables us to obtain data on the "soft-mode" phonons with energy greater than Γ. For definiteness, the calculations pertaining to both these problems are carried out for the scattering of Co^{57} MR (E_γ = 14.4 keV) by monocrystals of $SrTiO_3$ and $BaTiO_3$ respectively, for $T > T_c$ (T_c is the SPT temperature).

1. EFFECT OF RELAXATION PROCESSES NEAR THE SPT ON THE LINESHAPE OF THE SCATTERED MÖSSBAUER γ-RADIATION

In the second-order SPT in $SrTiO_3$ ($T_c \approx 106$ K) the symmetry of the crystal lattice changes (cubic-tetragonal). A model of the SPT for this crystal was proposed in the paper[2] of Unoki and Sakudo. For $T > T_c$ there is no long-range order in the angles of rotation of the TiO_6 octahedra about the C_4 axis, and the transition is a consequence of the instability of the phonon mode at the R-point of the Brillouin zone. In the tetragonal phase ($T < T_c$) the oxygen octahedra are rotated relative to each other through an angle $\pm\varphi$, long-range order appears and as a result of the doubling of the lattice constants the unstable mode is now situated at the center of the zone. In the inelastic neutron-scattering experiments of[3,4], besides the doublet associated with the creation and absorption of the soft-mode phonons, a quasi-elastic "central peak" caused by scattering by fluctuations of the order parameter (which in this case is the angle of rotation of the TiO_6 octahedron) was also observed. For $T - T_c < 1$ K, this peak begins to dominate the scattering spectrum[5], and its energy-width decreases like $\Gamma_{cp} \sim \epsilon^\beta$ as the SPT temperature is approached ($\epsilon = (T - T_c)/T_c$; β is a critical exponent).

Suppose that MR undergoes diffuse[1)], one-phonon[2)] scattering near the R-point of the Brillouin zone of $SrTiO_3$, and is then studied using a resonance absorber characterized by a chemical shift δ and Doppler shift v with respect to the source and also by cross-sections σ_M and σ_e for resonance nuclear and electronic absorption. Near the SPT the most important scattering is that at the central peak, the probability $f(\omega, \mathbf{q})$ of which[6] (omitting such factors as the structure factor, etc.) is determined by the expression

$$f(\omega, \mathbf{q}) \sim \{\omega^2 + B^2[\mathbf{q}^2 - (1-\Delta)q_z^2 + k^2]^{2-\eta}\}^{-1}, \tag{1}$$

where ω and $\mathbf{q}$ are the energy and momentum of the fluctuations, Δ is the anisotropy parameter of the fluctuation spectrum, $k = k_0\epsilon^\nu$ is the inverse correlation length, B and k_0 are dimensional constants, and η, ν are critical exponents ($\eta \ll 1$; e.g., for the three-dimensional Ising model, $\eta \approx 0.04$[7]). Formula (1) is, of course, approximate. However, it gives a fairly good description of the experimental data on the SPT[6,8,9] and can be justified qualitatively in dynamic scaling theory.

The fractions of MR absorbed resonantly (N_M) and nonresonantly (N_e) in the filter have the following form:

$$N_M = \frac{1}{\pi}\iint_{-\infty}^{\infty} \frac{\Gamma/2}{(x-v)^2+(\Gamma/2)^2} f(\omega,\mathbf{q}) \frac{(\Gamma/2)^2\sigma_M\xi\,dx\,d\omega}{(x+\omega-\delta)^2+(\Gamma/2)^2}\int_\tau d^3\mathbf{q} = \frac{\pi}{2}\sigma_M\xi\Gamma\int_\tau d^3\mathbf{q} \tag{2}$$

$$\times\frac{B[\mathbf{q}^2-(1-\Delta)q_z^2+k^2]^{1-\eta/2}+\Gamma}{B[\mathbf{q}^2-(1-\Delta)q_z^2+k^2]^{1-\eta/2}\{(v-\delta)^2+[B(\mathbf{q}^2-(1-\Delta)q_z^2+k^2)^{1-\eta/2}+\Gamma]^2\}}$$

$$N_e = \sigma_e\int_{-\infty}^{\infty} d\omega\int_\tau f(\mathbf{q},\omega)\,d^3\mathbf{q}, \tag{3}$$

where τ is the volume of the region of integration in the space of the phonon momenta about $\mathbf{q} = \mathbf{q}_R$, determined by the collimation conditions for the MR beams, and ξ is the relative content of Fe^{57} atoms in the absorber.

Inasmuch as the integral (2) converges rapidly at large q, for weak collimation (the corresponding criterion will be given below) the integration can be extended to an infinite region. For anisotropic, but three-dimensional fluctuations of the order parameter, taking into account that $\eta \ll 1$, we obtain[3)]

$$N_M \approx \frac{\pi^3\sigma_M\xi\Gamma^{3/(2-\eta)-1}}{\Delta^{1/2}B^{3/(2-\eta)}[1+(a-b)^2]}\{-K+2^{-1/2}[\sqrt{(a-b)^2+(1+K^2)^2}+1+K^2]^{1/2}$$
$$+2^{-1/2}|a-b|[\sqrt{(a-b)^2+(1+K^2)^2}-(1+K^2)]^{1/2}\}, \tag{4}$$
$$K = k\left(\frac{B}{\Gamma}\right)^{1/(2-\eta)}, \quad a = \frac{v}{\Gamma}, \quad b = \frac{\delta}{\Gamma}.$$

For $K^2 \gg 1$, i.e., far from the SPT,

$$N_M \approx \frac{\pi^3 \sigma_M \xi \Gamma^{3/(2-\eta)-1}}{2\Delta^{1/2} B^{3/(2-\eta)} K} \left[1 - \frac{1}{4K^2} + \frac{1}{8K^4}(1-(a-b)^2)\right]. \qquad (5)$$

It follows from (5) that in this case the N_M absorption linewidth is $\sim K^2$. As the SPT is approached the central-peak width Γ_{cp} decreases and its intensity increases[8]. Analogous changes also occur in the absorption lineshape (cf. (4), (5) and the Figure).

Starting from $K^2 \lesssim 1$, the N_M absorption linewidth ceases to narrow rapidly, and, at $T = T_c$, being non-Lorentzian, has the equivalent width $\sim 5\Gamma$. Using the experimental data of[5,9] ($k_0 \approx 0.2$ Å^{-1}, $\nu = 0.65$, $\Gamma_{cp} \approx 0.6 \times 10^8$ sec^{-1} at $T = T_c + 2$ K), we find that for $SrTiO_3$ $B = 1.5 \times 10^{-5}$ cm^2/sec, so that the condition $K^2 = 1$, corresponds to $T = T_c + 0.75$ K. As $T \to T_c$ the quantity $\Gamma_{cp} \to 0$. However, N_M has in this case a width $\sim 5\Gamma$ in place of the two natural widths characteristic of elastic scattering of MR. This circumstance is due to the fact that the MR beam was assumed in (4) to be weakly collimated. To estimate the role of the collimation we shall confine ourselves in (2) to the integration-region τ of a sphere of radius q_m. For $q_m \lesssim (\Gamma/B)^{1/2(-\eta)}$ the N_M width tends to 2Γ as T_c is approached. In our case $(\Gamma/B)^{1/(2-\eta)} \approx 10^6$ cm^{-1}, which corresponds to MR collimations of the order of 10′. Next we shall compare the magnitude of N_M at resonance ($a = b$) with the nonresonant absorption N_e for an isotropic fluctuation spectrum ($\Delta = 1$):

$$N_e \approx \frac{4\pi^2 \sigma_e k^{1+\eta}}{B}\left(\frac{q_m}{k} - \operatorname{arctg}\frac{q_m}{k}\right). \qquad (6)$$

For collimation such that the phonon wavelength is greater than the correlation length ($q_m < k$) and far from the SPT temperature ($K^2 \gg 1$), the ratio

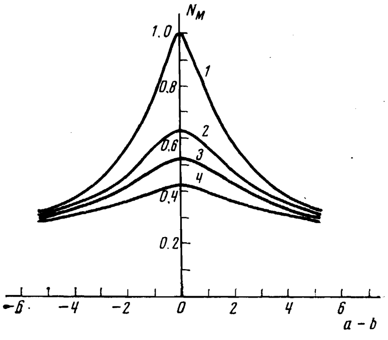
$$P_1 = \frac{N_M}{N_e}\bigg|_{a=b} \approx \frac{\sigma_M \xi}{2\sigma_e} \frac{\Gamma}{Bk^{2-\eta}}, \qquad (7)$$

i.e., P_1 is small, since the broad line (of width $\sim Bk^{2-\eta}$) arising in the scattering by $SrTiO_3$ is "overlooked" by the filter with resonant-absorption bandwidth Γ.

As T_c is approached a slowing-down of the order-parameter fluctuations occurs and, therefore, more and more scattered γ-quanta are resonantly absorbed by the filter. For $K^2 \ll 1$ and weak collimation (4) the ratio

$$P_2 = \frac{N_M}{N_e}\bigg|_{a=b} \approx \frac{\pi}{4} \frac{1}{q_m} \frac{\sigma_M}{\sigma_e} \xi \left(\frac{\Gamma}{B}\right)^{3/(2-\eta)-1}. \qquad (8)$$

It is interesting to note that, unlike in ordinary one-phonon scattering of MR (e.g., by optical or acoustic phonons), which is proportional to Γ, there appears in



Velocity dependence of N_M (in relative units). Curve 1 corresponds to the value $K^2 = 0$, curve 2—$K^2 = 0.25$, curve 3—$K^2 = 0.5$, curve 4—$K^2 = 1$.

P_2 the much larger, though small quantity $\Gamma^{3/(2-\eta)-1} \sim \Gamma^{1/2}$. Because of this, for $SrTiO_3$ at $T - T_c \approx 0.75$ K and for collimation $\approx 2 \times 10^7$ cm^{-1}, which is realistic for observing inelastic scattering[10], $P_2 \approx 0.2\,\sigma_M \xi/\sigma_e$, i.e., is of a quite appreciable size.

2. EFFECT OF THE SOFT OPTICAL PHONONS ON THE INELASTIC-SCATTERING INTENSITY OF THE MÖSSBAUER RADIATION

The intensity I of one-phonon scattering of MR near a Bragg reflection $\mathbf{H} \equiv (hkl)$ is given by the expression

$$I = \frac{1}{2}\sum_j \int_\tau \frac{2n_j(\mathbf{q})+1}{\omega_j(\mathbf{q})} \left|\sum_\alpha f_\alpha e^{-W_\alpha} \frac{\mathbf{q}_1 \mathbf{e}_\alpha}{\sqrt{m_\alpha}} \exp(2\pi i \mathbf{H}\mathbf{R}_\alpha)\right|^2 d\tau, \qquad (9)$$

where $\omega_j(\mathbf{q})$ and $n_j(\mathbf{q})$ are the energy and occupation numbers of phonons of the j-th branch with momentum $\mathbf{q}$; $\mathbf{q}_1$ is the photon scattering vector; f_α, m_α, $\mathbf{e}_\alpha$, W_α and $\mathbf{R}_\alpha$ are the atomic factor, mass. polarization vector, Debye-Waller factor and position of the α-th atom in the unit cell.

The use of a Mössbauer filter enabled Albanese et al.[10] to determine I for crystals of Si and Al. Their results are explained by the scattering of the MR by acoustic phonons (because of the large excitation energies, the contribution of the optical branches, by the estimates of[10], amounted to less than 5%). The ferroelectric SPT of the displacement type in $BaTiO_3$ ($T_c = 120°$C) is accompanied by softening of the optical mode at $q = 0$. We shall show that this leads to an appreciable increase in the intensity I_{opt} of the scattering by optical phonons as compared with the scattering I_{ac} by the acoustic vibrations.

Taking into account that in the long-wave acoustic vibrations the entire unit cell is displaced as a whole, and assuming (in accordance with[10]) that the region of integration in (9) is a sphere of radius q_m, we find

$$I_{ac} \approx \frac{8}{3M}|M_{ac}|^2 \left(\frac{\sin\theta}{\lambda}\right)^2 T\left(\frac{1}{v_l^2} + \frac{2}{v_t^2}\right) q_m,$$
$$M_{ac} = f_{Ba} e^{-W_{Ba}} + f_{Ti} e^{-W_{Ti}} \exp i\pi(h+k+l) \qquad (10)$$
$$+ f_O e^{-W_O}[\exp i\pi(h+k) + \exp i\pi(k+l) + \exp i\pi(h+l)],$$

where M is the mass of the unit cell, θ is the Bragg angle, λ is the wavelength of the γ quanta, and v_l, v_t are the longitudinal and transverse sound velocities.

We shall take it that only the rigid oxygen skeleton and the Ti atom take part in the long-wave soft-mode vibrations in $BaTiO_3$, and that they move in opposition[11]. Taking into account the soft-mode dispersion law

$$\omega_j^2(\mathbf{q}) = \omega_0^2 + \Lambda_j(\mathbf{q}/q)\mathbf{q}^2, \qquad (11)$$

where $\omega_0 \sim (T - T_c)^{1/2}$ and $\Lambda_j(\mathbf{q}/q)$ is the anisotropy parameter, the cubic symmetry of the crystal for $T > T_c$ and the spherical shape of the integration region τ, we find for $q_m\sqrt{\lambda_b} \gg 1$

$$I_{opt} \approx \frac{8}{3M}\left(\frac{\sin\theta}{\lambda}\right)^2 |M_{opt}|^2 \frac{T[q_m\sqrt{\lambda_g} - 0{,}9\operatorname{arctg}(q_m\sqrt{\lambda_b})]}{\omega_0^2 \lambda_g^{1/2}},$$
$$\mu = m_{Ti} + 3m_O,$$
$$M_{opt} = f_{Ti} e^{-W_{Ti}} (3m_O/m_{Ti})^{1/2} \exp i\pi(h+k+l) \qquad (12)$$
$$- f_O e^{-W_O}\left(\frac{m_{Ti}}{3m_O}\right)^{1/2}[\exp i\pi(h+k) + \exp i\pi(k+l) + \exp i\pi(h+l)],$$
$$\lambda_g = \Lambda_{100}/\omega_0^2, \quad \lambda_b = \Lambda_{111}/\omega_0^2,$$

where Λ_{100} and Λ_{111} are the constants given in the paper[12] by Harada et al.

Since, because of the strong anisotropy of the spectrum (11), the main contribution to I_{opt} is made by phonons with momenta lying in planes of the (100) type, to find (12) the cumbersome integral (9) was calculated by the method of steepest descents near these planes.

When the collimation of the incident and reflected MR beams is poor ($q_m\sqrt{\lambda_b} \gg 1$), I_{opt} depends weakly on ω_0 and, consequently, on T for $T \sim T_c$. In this case, in a substantial range of phonon momenta the soft mode has the dispersion law $\omega_j(\mathbf{q}) \sim \sqrt{\Lambda_j}|\mathbf{q}|$ (11). For good collimation ($q_m\sqrt{\lambda_b} \ll 1$), $I_{opt} \sim \omega_0^{-2} \sim (T - T_c)^{-1}$, i.e., depends strongly on T.

It is interesting to note that the criterion for poor or good collimation has a relative character and depends on the proximity to the SPT. Thus, the ratio I_{opt}/I_{ac} has a peak at $T = T_c$, and its temperature width depends on the collimation of the MR beams.

By choosing different reflections, it is possible to change I_{opt} substantially relative to I_{ac}. This is connected with the fact that the displacements of the oxygen skeleton and Ti atom participating in the soft mode are in opposite directions, while the displacements of the atoms that give rise to the acoustic phonons have the same sign. From the point of view of the relative increase of I_{opt}/I_{ac} the best reflections are those for which $h + k + l$ is odd and $h + k$, $k + l$, $h + l$ are even. Using the numerical values of ω_0 and Λ_{100}, Λ_{111}, measured at $t = 150^\circ C$, and the atomic factors from (13), and assuming that $v_l = 7 \times 10^5$ cm/sec, $v_t = 5 \times 10^5$ cm/sec, and that the angular dimensions of the MR beams are $\sim 4^\circ$[10], we obtain that the ratio I_{opt}/I_{ac} at 150°C for the (100), (111) and (333) reflections are respectively equal to 9, 30 and 23%.

3. CONCLUSION

Near a SPT intense pumping of excitations into the low-frequency part of the spectrum occurs. Because of this process, an appreciable fraction of the phonons excited (absorbed) in the inelastic scattering of MR have energies falling in the absorption band Γ of the Mössbauer filter. It should be noted that this also occurs in the case when, because of weak collimation of the MR beams, the phonons being excited (absorbed) can have energies much greater than Γ. The role of SPT in this can be illustrated by the following considerations. In principle, the γ-ray spectrum also possesses a resonance character in scattering by ordinary acoustic phonons. However, to observe this effect a MR collimation $\sim q_m \sim \Gamma/v_t \sim 10^2\ \mathrm{cm}^{-1}$ is necessary, and this is evidently not very realistic from the point of view of the counting intensity. For reasonable collimations, as a calculation shows, because of the linear dispersion law only the scattering by the zeroth vibrations, the probability of which is 10—12 orders of magnitude smaller than N_M (4), possesses a resonance spectrum.

The use of a Mössbauer filter to separate inelastic and elastic scatterings (with an energy resolution of $\sim 10^{-8}$ eV) gives the possibility, in principle, of obtaining information (from the temperature dependence of the ratio I_{opt}/I_{ac}) on the soft-mode parameters (12), supplementing in a number of cases the results obtained by other methods.

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[1)] For $T > T_c$ elastic scattering at the R-point is forbidden.

[2)] The influence of multiphonon processes can be neglected at the temperatures considered.

[3)] Since Γ is very small, η is retained in the factor preceding the curly brackets in (4).

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