Diffraction of Mössbauer radiation by single-crystal $BaTiO_3$ in the vicinity of the Curie point

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The temperature dependence of the Rayleigh scattering of Mössbauer radiation (MR) in a $BaTiO_3$ single crystal was investigated. Inelastic-scattering peaks were observed for the first time ever on the left and on the right of T_c. An energy analysis of the scattered beam has shown that an appreciable fraction of the inelastic intensity is due to scattering processes with energy transfer on the order of 10^{-8} eV.

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The most complete investigation of lattice dynamics in $BaTiO_3$ near the ferroelectric-transition temperature $T_c = 120\,^\circ C$ was performed by the method of inelastic scattering of neutrons.[1] It was shown in that reference, in particular, that in the vicinity of T_c the soft mode becomes strongly overdamped. For this reason, and also because of the insufficient energy resolution of modern three-crystal neutron spectrometers ($\sim 10^{-5}$ eV), a detailed study of the critical phenomena in $BaTiO_3$ is difficult.

The procedure used by us[2] of electron scattering of *MR* makes it possible to separate in energy the gamma quanta elastically and inelastically scattered by a crystal with accuracy of the order of the width Γ of the *MR* line ($\Gamma \approx 10^{-8}$ eV). It is shown theoretically in Ref. 3 that with the aid of this method it is possible to obtain valuable information on the dynamics of both the soft mode (for example in $BaTiO_3$) and of the central peak ($SrTiO_3$) near T_c, i.e., in those cases when the density of the low-frequency excitations increases strongly in the crystal. Experiments on *MR* scattering by the central peak were made on $SrTiO_3$ crystals[4] and $KMnF_3$ crystals.[5] We present below experimental data that show that the character of the pre-transition phenomena in $BaTiO_3$ is more complicated than it is customarily assumed.

The experiment was performed in the following manner. A collimated beam of *MR* from a Co^{57} source in Cr (250 mCi) was diffracted by a $BaTiO_3$ single crystal mounted on a Mössbauer diffractometer.[6] The sample dimensions were $8\times5\times0.2$ mm. To register the *MR* we used a scintillation detector based on an NaI(Tl) crystal measuring $10\times18\times0.1$ mm. The elastically and inelastically scattered gamma quanta were separated in energy with the aid of a "black" resonant absorber. At each fixed temperature, maintained with accuracy not worse than ±0.1 °C, we measured four intensities $I_{\alpha\beta}$ of the diffracted beam at the Bragg maximum [(002) reflection]. The value $\beta=R$ ($\beta=\infty$) corresponds to the fact that the absorber is at resonance (off resonance) with the *MR* source. The index α is equal to 1 or 2 if the absorber is located between the source and the sample or between the sample and detector. The difference $f_{el}=I_{2\infty}-I_{2R}$ is proportional to the fraction of the pure elastic scattering. The ratio of the intensities of the inelastic scattering to the elastic scattering is $f_{in}/f_{el}=(I_{1\infty}-I_{1R})/I_{2\infty}-I_{2R})-1$ (see Ref. 7).

Figure 1 shows the scattering-intensity temperature dependences obtained in the course of cooling the sample (prior to the measurements, the crystal was annealed for 48 h at $T=250$ °C) The temperature dependence of the total scattering intensity $I_{2\infty}$ is similar to the x-ray data (see, e.g., Ref. 8), the only difference being that the collimation of the *MR* beams is much worse than is usual in the x-ray technique. The characteristic features of $I_{2\infty}$, and particularly of f_{el} near T_c, are determined mainly by the change in the extinction of the crystal. When T_c is approached from above, a realignment of the mosaic structure of the sample takes place[8] (the dimensions of the mosaic blocks decrease), and as a result a jump is observed in the value of f_{el}. What is suppressed here is the small decrease of f_{el} that can be expected on account of the Debye–Waller factor.[9]

A particularly interesting behavior, in our opinion, is exhibited by the temperature dependence of the factor f_{in} of the inelastic scattering of *MR*. It is seen from Fig. 1 that on the right and left of T_c on the f_{in}/f_{el} curve there are maxima at $T\approx150$ °C and $T\approx105$ °C. In the vicinity of T_c, the value of $I_{2\infty}$ is strongly influenced by the prior history of the sample, owing to the change in the mosaic structure. In contrast, the position of the peak on the f_{in}/f_{el} curve depends little on the measurement regime. (Similar results were obtained also when the sample was heated, and also for another $BaTiO_3$ single crystal 0.5 mm thick).

To estimate the energy of the excitations responsible for the onset of the inelastic scattering, we have performed additional temperature investigations of the Mössbauer spectra of the diffracted beam (the absorber was unenriched stainless steel 30 μm thick. Figure 2 shows the results of measurements of this sort for $T=150$ °C. One can see clearly a strong (almost double relative to the room temperature) broadening of the spectrum of the scattered *MR* [Fig. 2(a)]. The narrow line shown for comparison [Fig. 2(b)], obtained when the absorber was placed in front of the sample, is evidence that the observed broadening is determined by the properties of the sample, and not by some other causes. It can therefore be stated that in this temperature range the inelastic scattering of the *MR* in the $BaTiO_3$ takes place with extremely small ($\sim10^{-8}$ eV)

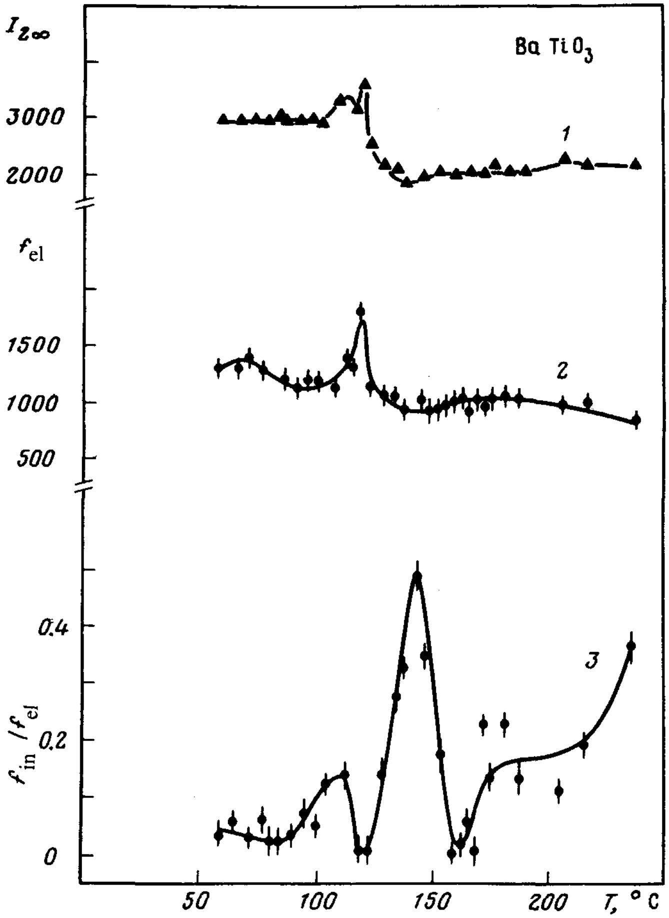

FIG. 1. Temperature dependences (in relative units) of the intensity of the total scattering $I_{2\infty}$ (1), of the fraction of the elastic scattering f_{el} (2), and of the ratio f_{in}/f_{el} (3).

energy transfers. Further experiments have shown that at this temperature the width of the *MR* spectrum changes insignificantly during prolonged measurements (lasting for weeks). The last circumstance evidently indicates that the observed broadening is not connected with the nonequilibrium state of the crystal. No line broadening of the scattered *MR* was observed in the immediate vicinity of T_c. Such small energy transfers are evidence that the observed effects can hardly be attributed to direct scattering of the gamma quanta on the soft mode[10] or by a system of interacting soft optical and acoustic modes.[11] The results indicate that slow relaxation processes with frequencies ~ 5 MHz take place in $BaTiO_3$. It is difficult to point at present to an equivocal cause of these processes. They may be due, for example, to defects in a $\sim 20\,\mu$m surface area of the crystal, the farthest that the *MR* can penetrate. The defects themselves, if their concentrations are reasonable, are weakly scattering, but not too far from T_c they can noticeably influence the lattice dynamics,[12] and the formation and decay of nuclei of a new phase, and this can manifest itself in the *MR* diffraction.[4]

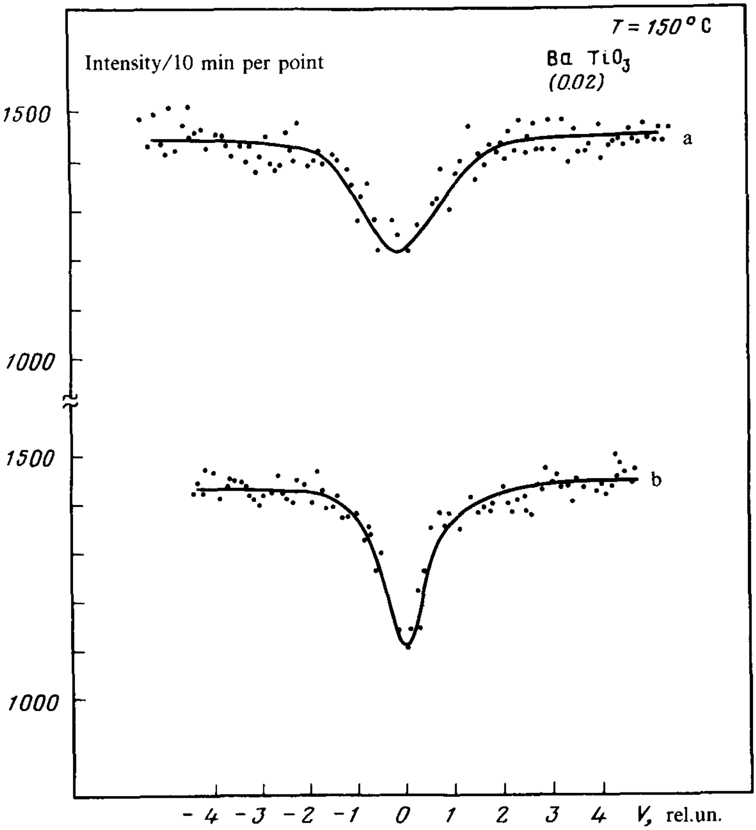

FIG. 2. Mössbauer spectra of diffracted beam: a—absorber behind the sample, absorber in front of the sample.

We note in conclusion that the first measurements of the scattering of *MR* by $BaTiO_3$ (above T_c) were made by O'Connor and Spicer.[13] They obtained a smooth f_{in}/f_{el} dependence that decreases smoothly (without maxima) with decreasing temperature. It is possible that the discrepancy between our results and those obtained in Ref. 13 is due to the fact that O'Connor and Spicer performed the measurements with large intervals between the temperature values, and also with samples that have a different defect structure.

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[1]J. Harada, J.D. Axe, and G. Shirane, Phys. Rev. B **4**, 155 (1971).
[2]N.M. Butt and D.A. O'Connor, Phys. Lett. **7**, 233 (1963).
[3]E.M. Iolin and E.V. Zolotoyabko, Zh. Eksp. Teor. Fiz. **68**, 1331 (1975). [Sov. Phys. JETP **41**, 662 (1975)].
[4]C.N.W. Darlington and D.A. O'Connor, and J. Phys. C **9**, 3561 (1976).
[5]K. Hanisch and M. Drosg, Phys. Lett. **58**, 415 (1976).

[6]E.V. Zolotoyabko, B.V. Kuvaldin, A. Yu. Astapkovich, and E.N. Kozlov, Izv. Akad. Nauk Latv. SSR Ser. Fiz. Tekh. Nauk No. 3, 53 (1977).
[7]E.V. Zolotoyabko, V.N. Gavrilov, and E.M. Iolin, Izv. Akad. Nauk Latv. SSR Ser. Fiz. Tekh. Nauk No. 3, 32 (1978).
[8]V. Ya. Fritsberg and Yu. V. Zvirgzde, Fiz. Tverd. Tela (Leningrad) **19**, 2770 (1977) [Sov. Phys. Solid State **19**, 1621 (1977).
[9]V.V. Sklyarevskiĭ, I.I. Lukashevich, V.P. Romanov, N.I. Filippov, Yu. N. Venevtsev, and A.S. Viskov, Pis'ma Zh. Eksp. Teor. Fiz. **3**, 212 (1966) [JETP Lett. **3**, 135 (1966)].
[10]E.V. Zolotoyabko and E.M. Iolin, Izv. Akad. Nauk Latv. SSR Ser. Fiz. Tekh. Nauk No. **4**, 46 (1975).
[11]N.N. Kristofel' and P.N. Konsin, Fiz. Tverd. Tela (Leningrad) **13**, 2513 (1971) [Sov. Phys. Solid State **13**, 2113 (1971)].
[12]B.I. Halperin and C.N. Varma, Phys. Rev. B **14**, 4030 (1976).
[13]D.A. O'Connor and E.R. Spicer, Phys. Lett. A **29**, 136 (1969).