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MOSSBAUER EFFECT IN THE FERROELECTRIC $Pb(Fe_{1/2}Nb_{1/2})O_3$

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It was found in [1,2] that the probability of the Mossbauer effect on Sn^{119} impurity nuclei in the systems $Ba(Ti_{0.8}Sn_{0.2})O_3$ and $Ba(Ti_{0.99}Sn_{0.01})O_3$ has a minimum near the temperature T_c of the ferroelectric phase transition. A similar effect was observed in [3] for Co^{57} impurity nuclei in $BaTiO_3$. In the same investigation, singularities in the behavior of the quadrupole splitting and of the position of the symmetry center of the Mossbauer spectrum were also observed at T_c.

We have investigated the variation of the parameters of the Mossbauer absorption spectrum of Fe^{57} nuclei in the ferroelectric $Pb(Fe_{1/2}Nb_{1/2})O_3$ at the ferroelectric phase transition ($T_c = 114°C$) [4]. In our case the Mossbauer nucleus Fe^{57} was a component part of the ferroelectric lattice, unlike the previously investigated impurity nuclei Sn^{119} and Fe^{57} in $BaTiO_3$.

Samples of $Pb(Fe_{1/2}Nb_{1/2})O_3$ absorbers were made by the usual ceramic technology using $Fe^{57}_2O_3$ (60% Fe^{57}). An x-ray analysis has shown that the samples were single-phase and had a well pronounced structure of the perovskite type. The source was Co^{57} in stainless steel. The Mossbauer spectra were measured with apparatus operating at constant speed with a permanent-magnet vibrator [5,6]. The source was mounted on the vibrator and was at room temperature, while the stationary absorber was in an oven. The absorber temperature fluctuation did not exceed 1°.

Figure 1 shows a typical absorption spectrum of $Pb(Fe_{1/2}Nb_{1/2})O_3$ (absorber thickness 5 mg/cm^2; T = 20°C). The isomer shift for this spectrum is 0.52 ± 0.02 mm/sec, corresponding to trivalent iron, and the quadrupole splitting is equal to 0.37 ± 0.02 mm/sec. Figure 2a shows the temperature dependences of the area of the spectrum S(T) (normalized to the area of spectrum at T = 20°C), while Fig. 2b shows the quadrupole splitting $\Delta E_{qu}(T)$ and Fig. 2c shows the position of the symmetry of the spectrum $\delta(T)$. The $\Delta E_{qu}(T)$ and $\delta(T)$ curves were obtained with a 5 mg/cm^2 absorber. The S(T) curve was obtained with a 1 mg/cm^2 $Pb(Fe_{1/2}Nb_{1/2})O_3$ absorber (~0.05 mg/cm^2 Fe^{57}), which can be regarded as thin ($\sigma f' \sim 0.3$ if we assume by way of an estimate that $f' \sim 0.5$ at T = 20°C). The values of ΔE_{qu} and δ were determined by process-

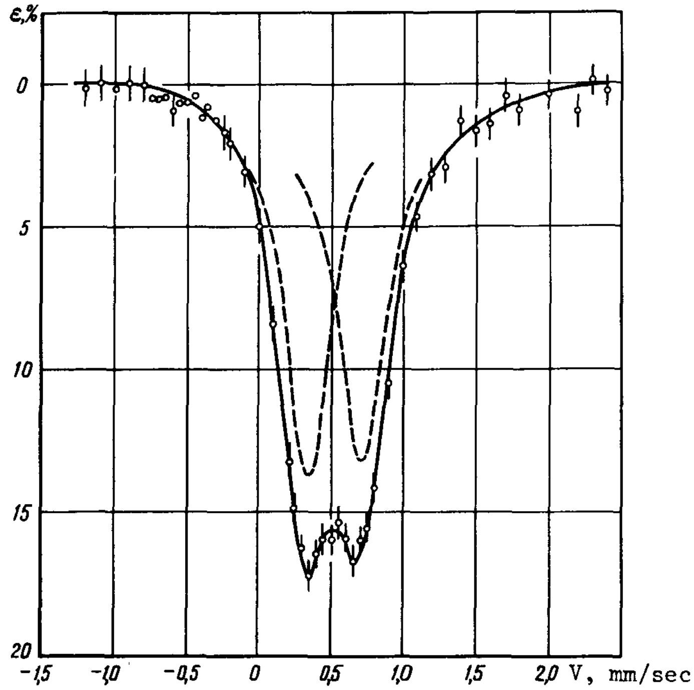

Fig. 1

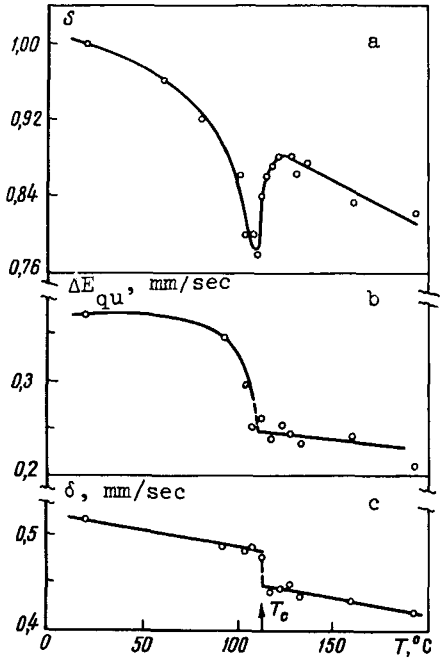

Fig. 2

ing the Mossbauer spectra with an M-20 computer. As seen from Fig. 2, all these spectral parameters have singularities in the vicinity of the Curie point $T_c = 114°C$.

The minimum of S(T) in the vicinity of T_c, i.e., actually in the probability f' of the Mossbauer effect, is apparently connected (like the previously observed minima in the case of $BaTiO_3$) with the fact, as shown in [7-9], that an anomalous decrease in the frequency of one of the transverse optical branches of the lattice, ($\omega^2(T) \sim (T - T_c)$), takes place on approaching the ferroelectric transition point in crystals with perovskite structure. It was shown in [10] that this behavior of the frequency should lead to a change in f near T_c. We note that the width of the minimum of S(T) (~10°C) is much lower than similar curves obtained in [1-3] (~30°C). The S(T) curve for the 5 mg/cm² absorber, which we do not present here, also has a minimum at T_c, but a broader one (~20°C).

The decrease of $\Delta E_{qu}(T)$ with increase of the temperature to T_c is connected with the decrease in the spontaneous polarization. The unit cell of $Pb(Fe_{1/2}Nb_{1/2})O_3$ is weakly rhombohedral-distorted below T_c [11]. With rise in temperature, the degree of distortion of the cell decreases, and the cell is cubic above T_c. The quadrupole splitting remaining when $T > T_c$ is obviously connected with the fact that the symmetry of the environment of these ions is not cubic owing to the statistical distribution of the Fe and Nb ions in the lattice (this is reliably evidenced by magnetic measurements [4]).

It is seen from the δ(T) curve that a jump in the value of δ takes place at T_c, and possibly a small change in the slope of δ(T). Our calculation, based on the assumption that the isomer shift on the sections below and above T_c does not depend on T, has shown that the contribution to the jump of $\delta(T)$ at $T = T_c$ ($\Delta E/E \cong 1.4 \times 10^{-13}$), due to the change in the slope of $\delta(T)$ (i.e., due to the change in the phonon spectrum of the crystal at T_c), does not exceed 3×10^{-14}. Thus, the main contribution to the jump of $\delta(T)$ at $T = T_c$ is introduced by a change in the isomer shift, i.e., by the change in the density of the S-electrons on the nuclei Fe^{57}.

As seen from Fig. 1, the intensities (areas) of the two quadrupole-splitting lines are not equal. We have obtained preliminary results on the temperature dependence of this asymmetry, according to which the magnitude of the asymmetry (the ratio of the areas of two lines) has a minimum in the vicinity of T_c and reverses sign. At the present time there are two known effects that can lead to asymmetry of the quadrupole-splitting lines: anisotropy of the Mossbauer-effect probability [12,13] and relaxation of the electron spins in a ferromagnet [14,15]. An investigation of the temperature variation of the asymmetry can give important information on the dynamics of the realignment of the crystal structure during the ferroelectric transition.

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SUPERCONDUCTIVITY OF La$_3$Te$_4$

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The Americans have recently reported that the chalcogenides of lanthanum, La$_3$Se$_4$ and La$_3$S$_4$, turn into superconductors below 8.6 and 6.5°K respectively [1]. The superconductivity of La$_3$S$_4$ was also reported in another brief note [2].

We show in this paper that the third member of this group of chalcogenides, La$_3$Te$_4$, is also a superconductor of the second kind, and that the superconducting-transition temperature of this substance depends on the technology of its preparation and is possibly connected with some deviation of the composition from stoichiometry.

Lanthanum telluride La$_3$Te$_4$ was synthesized from 99.5% pure lanthanum and tellurium purified by vacuum sublimation and zone melting. A detailed description of the synthesis procedure is given in [3].

We investigated two samples. The first (I) was pressed from previously fused material and annealed at 1450°C for 1.5 hours; the second sample (II) was obtained by melting in a molybdenum crucible. An x-ray diffraction phase analysis has shown that the samples are single-phase and have a structure of the Th$_3$P$_4$ type (a = 9.619 Å). The experimental temperature dependence of the resistivity of the investigated La$_3$Te$_4$ samples, plotted in Fig. 1, indicates that at current density 0.4 A/cm^2 the transition temperature T_{cr} is 2.45°K for sample I and 3.75°K for sample II. The width of the temperature region of these transitions is $\Delta T \approx 0.1$°K.

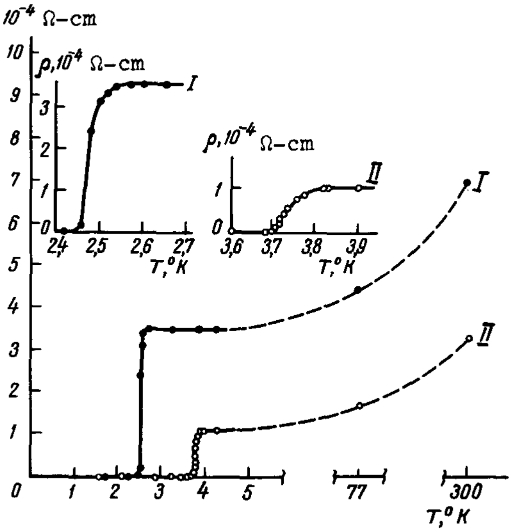

Fig. 1. Temperature dependence of resistivity

The destruction of superconductivity by a transverse magnetic field at T = 1.4°K at the same current density is illustrated in Fig. 2, from which it is seen that the critical fields (H_{c2}) at which normal resistance is restored are 8 and 12.5 kOe for samples I and II respectively.

The magnetic properties of La$_3$Te$_4$ were investigated in a homogeneous constant field by comparing the ballistic deflections produced by succesively introducing into the induction coil the investigated samples and a standard pure-lead sample of the same size (6 x 6 x 20 mm). The plots of