GENERATION OF THE SECOND ACOUSTIC HARMONIC IN SbSi SINGLE CRYSTALS

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Results are described of an experimental investigation of the second harmonic of longitudinal ultrasonic waves with a wave vector along the ferroelectric axis of an SbSI single crystal. The temperature dependence of the amplitude of the second harmonic is obtained in the vicinity of the phase transition. By comparing the results of the direct measurement of the anomalous absorption coefficient at frequencies corresponding to the first and second harmonics, it is possible to evaluate the Grüneisen coefficient as a function of the temperature near the phase transition point for the given SbSI sample. Conclusions can be drawn on the growth of the anharmonism along the direction of the single crystal ferroelectric axis on the basis of the Grüneisen coefficient temperature dependence. This temperature dependence agrees qualitatively with the theoretical results obtained for $KTaO_3$ and $SrTiO_3$.

THE nonlinear effects that appear in the propagation of volume and surface ultrasonic waves (USW) (see, for example,[1-4]) have been studied to a rather large degree in recent years. One of these effects is the nonlinear interaction, which is determined by the anharmonism of the lattice. The experimental investigation of lattice anharmonism in ferroelectrics near the phase transition is of special interest, inasmuch as such an anharmonism leads to the phase transition in particular cases.[5] Unfortunately, there have not yet been any detailed studies so far as we know. Therefore, we have selected for study the ferroelectric-semiconductor SbSI, the acoustical properties of which have been well studied (see, for example,[6-10]). One of the simplest methods of study of nonlinear interactions is the investigation of harmonic generation of the USW. In the present paper we give a description of the experimental investigation of the temperature dependence of the amplitude of the second harmonic of longitudinal USW near a first-order phase transition in the single crystal SbSI.

The ultrasonic measurements were carried out by means of the pulse method.[11] To obtain the corresponding frequencies, we used wave traps. The generator of the radio pulses allowed us to obtain signals with amplitudes up to 1200 V at a frequency of 15 MHz for pulse lengths of about 1 microsec. For generation and detection of the USW, we used X-cut quartz plates with resonant frequencies of 15 and 30 MHz. The single-crystal samples of SbSI with carefully polished surfaces, perpendicular to the ferroelectric axis, had a length of 0.32 cm. To decrease losses we used only one quartz delay line, which was needed to separate the USW pulses and the noise. The detecting plate was attached directly to the face of the specimen. Silicone oil was used as the adhesive. The mechanical system was placed in a thermostatted chamber, the accuracy of the temperature control of which was to within about 0.1°; however, the temperature could be varied smoothly at a rate of 0.4% min. The measurements were during heating of the chamber containing the specimen.

The experiment showed that the harmonic of fre-

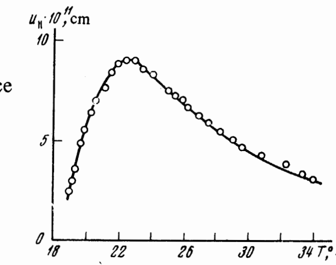

FIG. 1. Temperature dependence of the amplitude of the second harmonic of longitudinal USW, $u_{\parallel}$ (30 MHz) for a voltage of 1000 V applied to the radiator.

quency 30 MHz was generated during passage of the USW into the sample, in addition to the fundamental of 15 MHz. The dependence of the amplitude of the second harmonic on the supply voltage had a quadratic character, independent of the temperature.

Figure 1 shows the temperature dependence of the amplitude of the second harmonic of the longitudinal wave $u_{\parallel} = f(T)$. The measurements were carried out only above the phase transition point, which is equal to 18°C for the sample in question, inasmuch as measurements at the transition point itself are complicated because of the presence of oscillations in the absorption[6,8] and the noise of the receiving circuit. In the ferroelectric phase, the presence of the domain mechanism of USW scattering also greatly complicates the measurements.

As is seen from Fig. 1, a sharply expressed maximum is observed in the $u_{\parallel} = f(T)$ dependence at 22.5°C. It is known that the damping of the USW increases rapidly in the paraphase upon approach to the phase transition.[6-8] Therefore, for a comparison of the theoretical and experimental data, we plotted the amplitude of the second harmonic against the damping coefficient of the fundamental, which could be controlled by disconnecting the wave trap. The dependence $u_{\parallel} = f(\alpha_1)$ is shown in Fig. 2. It is easily seen that the curve reminds one of the $u_{\parallel} - f(l)$ dependence (l is the length of the specimen) obtained by Gedroits and Krasil'nikov[12] for a fixed USW damping coefficient α_1. As is well known $u_{\parallel} = f(\alpha_1, l)$ is expressed theoretically by the formula[13]

$$= -\frac{\beta k^2 u_0^2}{16\alpha_1 c^2}(e^{-2\alpha_1 l} - e^{-4\alpha_1 l}), \qquad (1)$$

where β is the nonlinear parameter, u_0 the initial amplitude of the displacement of the longitudinal USW, k the wave number, α_1 the damping coefficient of the fundamental, and c the speed of the USW. We do not obtain a maximum in the second harmonic with this formula for the curve $u_\parallel = f(\alpha_1)$ under the assumption that the parameters entering into the formula are not temperature-dependent, except α_1, which can change according to the law $\alpha \sim (T - T_C)^{-n}$, where $n \geq 1$.[14,15] The change in the velocity of the longitudinal USW can be neglected. There remains the nonlinear parameter β, for which it is quite natural to expect a temperature dependence near the phase transition. Of course, the coefficient β can be computed from Eq. (1); however, this has the meaning of changing somewhat this formula in such a way as to replace β in it with some parameter frequently used in the theory of ferroelectric phase transitions. We can use the Grüneisen constant as such a parameter (γ_i^3). It should also be noted that the expression (1) is written with account of satisfaction of the law $\alpha \sim \omega^2$ (ω is the USW frequency). However, close to the phase transition this proportionality is violated;[15] therefore, we write (1) in general form, using the data of the work of Hikata, Chick and Elbaum[16] for the case of longitudinal USW propagating in SbSI along the z axis:

$$u_\parallel = \frac{(3c_{33} + C_{333})k^2 u_0^2}{8\rho(\alpha_2 - 2\alpha_1)} \cdot (e^{-2\alpha_1 l} - e^{-\alpha_2 l}), \qquad (2)$$

where c_{33} and C_{333} are the elastic moduli of second and third order, respectively, α_1 and α_2 are the absorption coefficients of the fundamental and the second harmonic, ρ the density of the material. Here β is, in accord with[1],

$$\beta = (3c_{33} + C_{333}) / \rho. \qquad (3)$$

Recognizing that, according to[17],

$$3c_{33} + C_{333} = 2\gamma_i^3 c_{33} \qquad (4)$$

and $c^2 = c_{33}/\rho$, $k = \omega/c$, we get

$$u_\parallel = \frac{\gamma_i^3 \omega^2 u_0^2}{4c^2(\alpha_2 - 2\alpha_1)} \cdot (e^{-2\alpha_1 l} - e^{-\alpha_2 l}). \qquad (5)$$

Thus, we can now, knowing u_0, $u_\parallel$, c, α_1 and α_2, find γ_i^3. The velocity measured by us was $c = 2.7 \times 10^5$ cm/sec. Using the relation[1]

$$u_0^2 = \varkappa P_{em} \lambda^2 / 2\pi^2 \rho c^3 S \qquad (6)$$

(λ is the wavelength of the USW, κ the loss coefficient

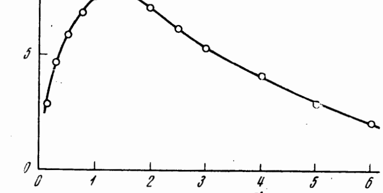

FIG. 2. Dependence of $u_\parallel$ on the damping of the fundamental $u_\parallel = f(\alpha_1)$.

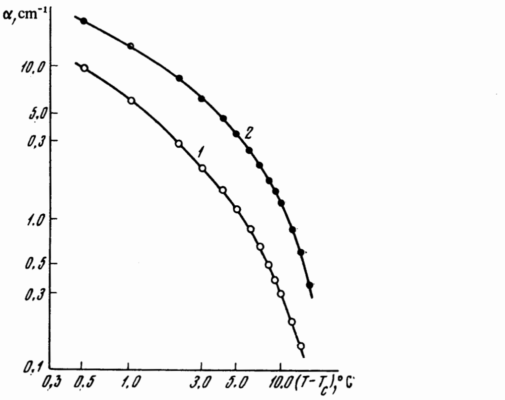

FIG. 3. Temperature dependence of the coefficients α_1 and α_2 of longitudinal USW. USW frequency: 1–15 MHz, 2–30 MHz.

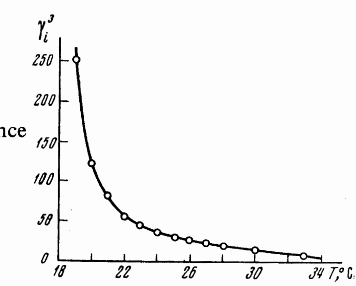

FIG. 4. Temperature dependence of the Grüneisen constant $2\gamma_i^3$ for monocrystalline SbSI.

in the electromechanical transduction, P_{em} the power of the radio pulse at the output of the generator, S the cross sectional area of the acoustic beam) and taking into account the losses from the glue and from reflection, we obtained the value $u_0 = 3.4 \times 10^{-8}$ cm. The measurement of $u_\parallel$ was carried out by means of calibration of the receiving circuit with respect to amplitude, with account of losses in the gluing and in the conversion. The result $u_\parallel = 9.1 \times 10^{11}$ cm was obtained at T = 22.5°C.

The values of α_1 and α_2 at T = 35°C were obtained from a series of short ($\tau = 0.4$ μsec) USW pulses reflected in the sample. These pulses were then summed with the results of the relative α_1, and α_2, and thus the absolute values of the absorption coefficient were obtained. These results are shown in Fig. 3 (for convenience, they are given on a logarithmic scale).

The values of the coefficient γ_i^3 were computed from the results shown in Figs. 1 and 3, and their temperature dependence was determined. The dependence of γ_i^3 on T is shown in Fig. 4.)

It should be noted that we have not taken into account in the calculations the presence and temperature change of the second harmonic in the fused-quartz buffer; however, the curve indicates a rapid increase in the anharmonism, which is generally not expected for fused quartz in the given temperature range.

As we see, γ_i^3 for SbSI increases according to the law $\gamma_i^3 \sim (T - T_C)^{-1}$ as the phase transition point is approached. This qualitatively confirms the theoretical analysis of longitudinal USW in other materials ($KTaO_3$ and $SrTiO_3$), given in[18,19], which shows that γ_i^3 increases in the paraphase according to a similar law, inasmuch as the proportionality $\gamma_i^3 \sim \epsilon_S$ is obtained in these researches (ϵ_S is the static dielectric permittivity).

The experimental study of γ_1^3 in the vicinity of phase transitions is of definite interest, especially in connection with the fact that the theoretical account of the elastic moduli of third order C_{333}, which are responsible for the increase in γ_1^3, is very complicated, let alone the fact that such an investigation of ferroelectrics extends our knowledge of the mechanism of phase transitions.

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