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ABSORPTION OF SOUND IN SINGLE-CRYSTAL NH_4Cl DURING ITS PHASE TRANSFORMATION

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Submitted 28 September 1966
JETP Pis'ma 5, No. 1, 6-9, 1 January 1967

The phase transition occurring in ammonium chloride at -31°C is of the order-disorder type and is close to the critical Curie point. The investigated crystal belongs to the cubic system, class T_d, below the phase-transition temperature, in the asymmetric phase, and to class O_h above the transformation point. In the asymmetric phase, the NH_4 groups are bound in orientation to a single system of the body diagonals of the cubic cell of the crystal. In the symmetric phase, the orientation of the NH_4 group relative to both possible systems of body diagonals of the unit cell becomes equally probable [1,2]. A group-theoretical analysis of the investigated phase transition of the NH_4Cl crystal has shown that only longitudinal acoustic waves can be anomalously absorbed during the phase transition.

We have measured the absorption of longitudinal acoustic waves propagating along the edge of the crystal cubic lattice. The measurements were made at 5 and 15 MHz by a method described earlier [3]. Particular attention was paid to the thermal conditions of the experiments. The investigated crystal samples, measuring 10 x 10 x 3 mm, were in acoustic contact with a metallic thermostat-controlled delay line. This entire system was placed in turn in a massive copper thermostat isothermal with the delay line. Our measurement results for 15 MHz are shown in Figs. 1 and 2, where the abscissas are the experimental temperatures $t - \theta$ reckoned from the maximum sound-absorption temperature, and the ordinates are the differences of the absorption coefficient, $\kappa_t - \kappa_{-28°C}$ in cm^{-1}. Figure 1 corresponds to heating of the crystal and Fig. 2 to cooling. Similar results were obtained for the absorption coefficient of sound waves at 5 MHz, but the maximum absorption was one-fourth that for 15 MHz.

During the performance of our measurements, we have learned of a research close in scope to ours, by C. W. Garland and J. S. Jones [4], who observed a smaller absorption of sound in NH_4Cl than we did. Namely, in [4] the maximum sound-absorption coefficient is only 1.6 cm^{-1}, while we obtained $\kappa_{max} - \kappa_{-28°C} = 4.6$ cm^{-1}, which likewise may not be the final value. A possible explanation for the difference is the appreciable length (more than 10 mm) of the crystal samples used by Garland and Jones, whereas the working length of our crystal did not exceed 3 mm. In long samples, even at minimal temperature gradients, it is difficult to expect the region of the direct phase transition of the crystal to extend over the entire path of the acoustic signal in the crystal. Yet failure to satisfy this condition leads to

undervalued κ_{max}. We note, in addition, that Garland and Jones did not register the slight over- and underheating of the NH_4Cl crystal, which were observed in our case, as can be deduced from the difference between our plots in Figs. 1 and 2. We have been unable to es-

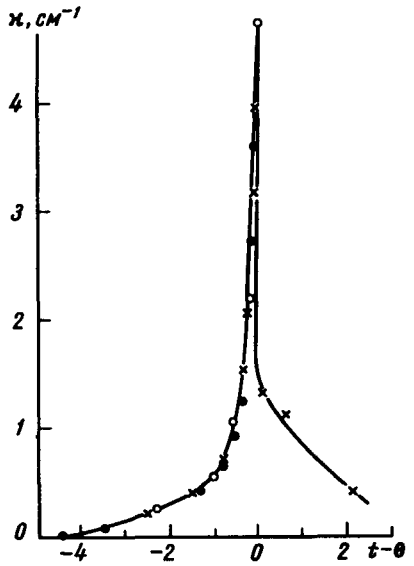

Fig. 1

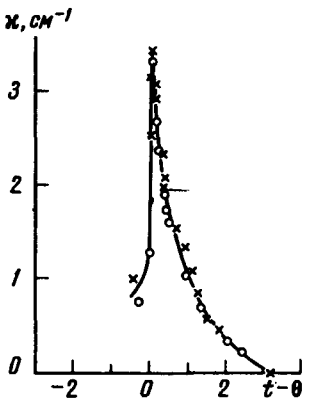

Fig. 2

tablish the reason for the absence of these slight effects in [4], since that paper, unfortunately, does not describe details of the experimental thermal conditions.

The theory of sound absorption during phase transitions in crystals was created by L. D. Landau and I. M. Khalatnikov [5]. According to Landau, in the asymmetric phase of a non-ferroelectric crystal, near the transformation temperature θ, the elastic-constant tensor $\mu_{ik\ell m}$, which relates the deformation U_{ik} with the stresses $\sigma_{\ell m}$ ($U_{ik} = \mu_{ik\ell m}\sigma_{\ell m}$) takes the form

$$\mu_{iklm} = \mu^{\circ}_{iklm} + \frac{\Delta C_p}{\theta}\frac{\partial\theta}{\partial\sigma_{ik}}\frac{\partial\theta}{\partial\sigma_{lm}}\frac{i\omega\tau}{1-i\omega\tau}. \qquad (1)$$

Here ΔC_p is the jump of the specific heat of the crystal during the phase transition, ω the cyclic frequency of the sound, $\tau = \gamma/(\theta - T)$ is the temperature-dependent relaxation time of the nonequilibrium states of the medium. When $[(\Delta C_p/\theta)(\partial\theta/\partial\sigma_{ik})][(\partial\theta/\partial\sigma_{\ell m})] \ll \mu_{ik\ell m}$, we obtain for the amplitude sound absorption coefficient κ per unit length the approximate expression

$$\kappa = \frac{\sqrt{\rho}}{\sqrt{\mu^{\circ}_{iklm}}}\frac{\Delta C_p}{2\theta}\frac{\partial\theta}{\partial\sigma_{in}}\frac{\partial\theta}{\partial\sigma_{lm}}\frac{\omega^2\tau}{1+\omega^2\tau^2}, \qquad (2)$$

where ρ is the crystal density. This expression has a maximum at a temperature T satisfying

the condition $\theta - T = \omega\gamma$. The functional dependence of κ on τ and ω in (2) is not unexpected [5], but it is important that (2) contains in explicit form the dependence of κ on the thermodynamic parameters of the crystal.

The reduction of our data for the absorption of sound in the asymmetric phase of the NH_4Cl crystal yields $\tau = 1 \times 10^{-9}/(\theta - T)$ sec, which agrees in order of magnitude with the value of τ obtained in [4]. Using the Landau relation (2), we were able to obtain for the first time the value of $d\theta/dp$ from acoustic measurements. The values of ΔC_p and $\mu_{zzzz} = 1/E$ needed for this calculation were taken from [6,7], and we used the value of κ from our measurements for sound of 15 MHz frequency. We obtained $d\theta/d\sigma = 3 \times 10^{-9}$ deg-cm^2/dyne, whereas direct static measurements of the dependence of the phase-transition temperature θ on the pressure p yield 9×10^{-9} deg-cm^2/dyne [6,8]. Recognizing that $d\theta/dp = 3(\partial\theta/\partial\sigma)$, the agreement between values of $d\theta/dp$ obtained by entirely different methods can be regarded as convincing confirmation of Landau's formula (2).

We are deeply grateful to L. A. Shcherbakova and G. K. Chirkin for growing the highly perfect NH_4Cl crystals and kindly furnishing them for our optical [9] and acoustic measurements.

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SEMICONDUCTING PROPERTIES OF FERROELECTRICS

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Submitted 29 September 1966
ZhETF Pis'ma 5, No. 1, 9-12, 1 January 1967

Following [1], we assume that the spontaneous induction in $BaTiO_3$ is screened by free carriers flowing from within the crystal. It is shown in [1] that the spontaneous induction of a c-domain $BaTiO_3$ plate can be represented as in Fig. 1. Since the charge density of the free carriers is determined from the equation $divD = 4\pi\rho$, the free-carrier distribution over the thickness of the plate takes the form shown in Fig. 2. Thus, the $BaTiO_3$ crystal in question is similar to a p-n junction (see [2]) in which the regions of high free-carrier density (n and p regions) are separated by a broad dielectric gap. We shall estimate the