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THE ACOUSTIC DISPERSION NEAR THE INCOMMENSURATE PHASE TRANSITION IN $[N(CH_3)_4]_2MnCl_4$ [1]

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The temperature dependence of the anomalous ultrasonic attenuation in $[N(CH_3)_4]_2MnCl_4$ has been measured in the frequency range 12.7 - 71 MHz around the normal-incommensurate phase transition at T_i = 292.3 K. Shift of the attenuation peaks towards the lower temperature side with increasing frequency has been observed. The relaxation time of the amplitudon $\tau_{A0} = 4 \times 10^{-10}$ sK has been determined.

I. INTRODUCTION

The ultrasonic measurements near the phase transitions (PT) represent an important tool for gaining information about both the static and dynamic behavior of PT due to the fact that the elastic properties are sensitively affected by the structural changes in the crystals [1]. The important role plays here the coupling between the strain and the order parameter.

From the ultrasonic data one can evaluate the development of the order parameter, which is by its nature a static quantity, as well as the relaxation time of the decay of the order parameter fluctuations. An interesting feature of ultrasonic measurements in some systems with an incommensurate (IC) phase is the frequency dispersion of some of the elastic constants around the normal-incommensurate phase transition temperature T_i [2]. This can be caused by interaction between acoustic phonons and some other low frequency excitations. In IC systems this can be either the phasons or the amplitudons.

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We report here on experimental results of the velocity and attenuation of the ultrasonic longitudinal waves near T_i in tetramethylammonium tetrachloromanganate $[N(CH_3)_4]_2MnCl_4$ (TMATC-Mn), which undergoes at atmospheric pressure at $T_i = 292.3$ K the transition from the paraelastic "normal" phase with the space symmetry group Pman to an IC phase [3-5] with the ordering wave vector $\mathbf{q_0} = (1 - \delta)\ \mathbf{a^*}/2$, where δ is the incommensurability parameter. (The crystalografic axes are labeled in agreement with international standards ($c < a < b$) so that a=12.3 Å, b=15.6 Å and c=9.1 Å.) At $T_c = 291.7$ K the ordering wave vector locks in at $\mathbf{q_0} = \mathbf{a^*}/2$ and an improper ferroelastic monoclinic commensurate phase $P112_1/a$ develops with a 2a superstructure. The acoustic dispersion was observed near the normal-incommensurate phase transition in the sound attenuation data.

II. EXPERIMENTAL PROCEDURE

Single crystals of TMATC-Mn were grown by slow evaporation from an aqueous solution of the compounds $N(CH_3)_4Cl$ and $MnCl_2.4H_2O$. The crystals of good optical quality were cut with a diamond saw. The orientation of the samples was roughly done according to natural faces of the crystals (TMATC-Mn crystals are mainly prism-like pillars elongated along the a axes, cleaving along the b plane) and then more accurately using a polarizing microscope by orientation of the index ellipsoid parallel to the main crystal faces. Samples were prepared by grinding with Al_2O_3 powder of size 12.5, 5 and 3 μm. The sample dimensions were about $4 \times 4 \times 4$ mm^3. The density of the samples was determined to be 1327 kgm^{-3} by the Archimedes' method.

Overtone polished 10 MHz Y-cut $LiNbO_3$ transducers (diameter 0.125") from Valpey Fisher were bonded to the (100) faces by using glycerin. The measurements were performed on increasing or decreasing the temperature at a rate of about 0.05 K/min . The pulse echo overlap method [6] with one transducer was used to determine the velocity of sound. The ultrasonic attenuation coefficient was measured together with the velocity in the frequency range 12.7-71 MHz by using the exponential comparator method [7]. In the very vicinity of T_i for higher frequencies, where only the first echo was observed, the attenuation was determined from the relative changes of the height of this first echo.

III. RESULTS AND DISCUSSION

Recently we have measured the complete set of elastic constants of TMATC-Mn and have found that all longitudinal elastic constants show similar behavior near T_i [8]. In order to gain a more detailed picture of this transition and to determine the role of amplitudons we have carefully measured the ultrasonic velocity and the attenuation as a function of frequency (12.7-71 MHz) and temperature (280-310 K) which we report here.

As one can see from the temperature dependence of the elastic constant c_{11} measured at 12.7 MHz (Fig.1) there is a step-like change of c_{11} only at the transition temperature T_c and no change at the lock-in temperature T_i. This is consistent with the Landau theory of these phase transitions [8, 9].

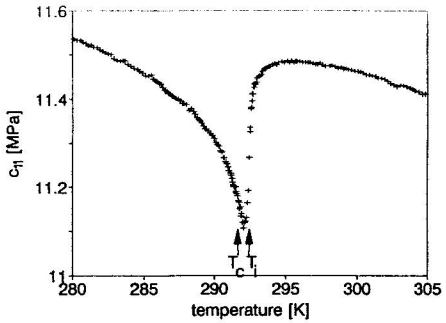

Fig. 1. Temperature dependence of the elastic constant c_{11} at 12.7 MHz around the normal-incommensurate phase transition.

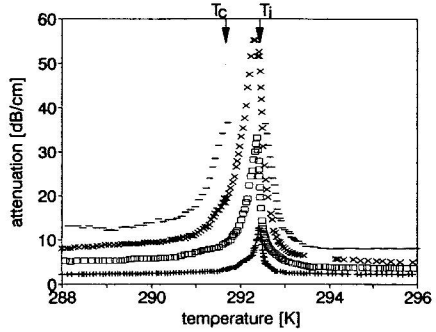

Fig. 2. Temperature dependence of the sound attenuation α for a longitudinal wave propagating along the [100] direction for various frequencies: +, 12.7 MHz; □, 31 MHz; ×, 51 MHz; -, 71 MHz.

The temperature and the frequency dependence (12.7-71 MHz) of the attenuation α of the c_{11} mode near the IC phase transition is shown in Fig.2. Here one can see a shift of attenuation peaks towards lower temperatures with increasing frequency. The frequency dependence of the temperature of the attenuation maximum is shown in Fig.3. The phase transition temperature $T_i = 292.45$ K was obtained by extrapolating the straight line to zero frequency as seen in Fig.3. The lock-in temperature T_c in Fig.1, 2, and 4 has been then determined from the T_i value and the fact that the IC phase in TMATC-Mn is 0.6 K wide [3].

In order to extract only the attenuation associated with the PT, the anomalous part of the attenuation, the so called critical attenuation α_{crit}, has been obtained by subtracting the temperature independent background α_0 which was taken from the attenuation coefficients at much higher temperatures. The values of α_0 were 1.8, 3.5, 4.5 and 6.5 dB/cm for 12.7, 31, 51 and 71 MHz, respectively. The measured data will be further discussed on the basis of the Landau-Levanyuk theory [10].

Starting from the free energy expansion, which includes the corresponding interaction terms between strain and order parameter one can derive the relations

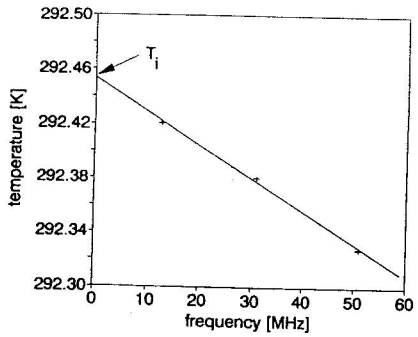

Fig. 3. The frequency dependence of the temperature of maximum attenuation.

for the change of the velocity and attenuation of the longitudinal waves near the T_i point [8, 9]

$$\Delta v_{ii} = \frac{1}{2\rho v_{ii}} \left(b_{ii}\rho_0^2 - \frac{2a_{ii}^2\rho_0^2}{\omega_A^2(1+\Omega^2\tau_A^2)} \right), \qquad (1)$$

$$\Delta\alpha_{ii} = \frac{1}{\rho v_{ii}^2} \frac{a_{ii}^2\rho_0^2}{\omega_A^2(1+\Omega^2\tau_A^2)} \Omega^2\tau_A, \qquad (2)$$

where $\omega_A^2 = 2A(T_i - T) + hq^2$, and $\tau_A = \Gamma_Q/\omega_A^2$ are the frequency and the relaxation time of the amplitudon, $\rho_0^2 = A(T_i - T)/B$, $\Omega = qv_{ii}$ is the ultrasonic frequency, ρ is the density of crystal and A, B, a_{ii} and b_{ii} are constants (i=1,2,3).

The equations (1) and (2) are mean-field results and describe the change of the elastic constant due to the relaxation processes of the order parameter (and its coupling to the strain). Nevertheless to gain the correct description of the PT one has to add the fluctuation contribution to the change of the elastic constant. This affects the results both below and above T_i contrary to the relaxation part which is effective only below T_i. The fluctuation contribution is usually smaller than the relaxation one (also here, see Fig.2) and its influence for Δv and $\Delta\alpha$ below T_i is often neglected [11]. Strictly speaking we should subtract this part before the beginning of the processing of our data, but we did not do this here being satisfied with the first approximation results only. This is sufficient for demonstration of the qualitative character of our results.

Thus proceeding in evaluation of our data according to the equations (1) and (2) one can easily calculate the relaxation time of the amplitudons τ_A. The position of the attenuation maximum is determined by the condition $\Omega\tau_A = 1$ where $\tau_A = \tau_{A0}/(T_i - T)$. From the shift of the attenuation maximum (Fig.3) one obtains $\tau_{A0} = 4 \times 10^{-10}$ sK.

The relaxation time τ_A is big enough to manifest itself in the dispersion of the attenuation as one can see from Fig.4, which shows the temperature dependence of the critical part of the attenuation divided by the square of the frequency α_{crit}/f^2. Here we note that the condition $\Omega\tau_A << 1$ fails for $T_i - T < 0.5$ K and the dispersion manifests itself not only in the shift of attenuation maximum (which is in fact

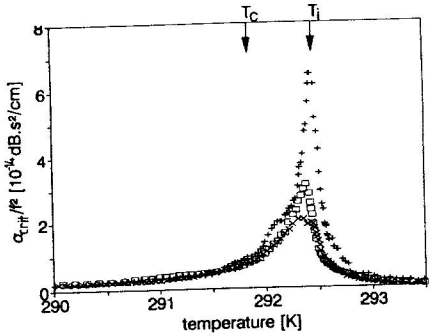

Fig. 4. The temperature dependence of the critical attenuation α_{crit}/f^2 near the normal-incommensurate phase transition for various frequencies: +, 12.7 MHz; □, 31 MHz; ×, 51 MHz; –, 71 MHz.

not very impressive) but also in the different height of this critical part of attenuation. These results are consistent with the theoretical description according to the

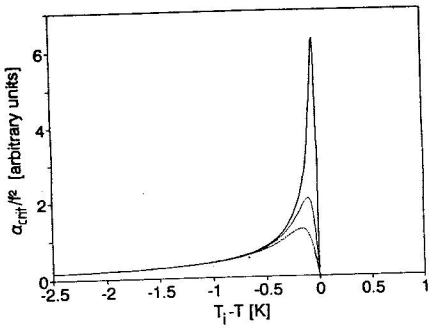

Fig. 5. The theoretical behavior of the relaxational part of critical attenuation α_{crit}/f^2 near the normal-incommensurate phase transition calculated from equation (2) for $\tau_{A0} = 4 \times 10^{-10}$ sK for various frequencies: full line: 12.7 MHz; dots: 31 MHz; dashed line: 51 MHz.

equation (2) which is shown in Fig.5. Here we have taken $\tau_{AO} = 4 \times 10^{-10}$ sK. Analogously the dispersion should have been observed also for the ultrasonic velocity, but we were not able to measure the velocity very close to T_i for higher frequencies because of the high attenuation of the signal. The situation here is different from that in NH_4LiSO_4 [12] which we studied earlier, where we did not observe dispersion. To compare our results to those in similar materials [2, 11, 13-15] we note that the relaxation time is nearly the same as in Rb_2ZnCl_4 or TMATC-Zn. However in TMATC-Zn [13] the authors did not observe dispersion because they were not able to measure the attenuation for higher frequencies close to T_i. Some more results on acoustic investigations of phase transitions in TMATC-Mn including the influence of fluctuation, shear wave investigations and a detailed thermodynamic

theory of the phase transitions will be presented elsewhere [8].

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