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Ultrasonic and Dilatometric Study of Phase Transitions in $NaNO_2$

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The ultrasonic velocities and attenuations, and the thermal expansion coefficients of pure and γ-irradiated $NaNO_2$ crystals have been measured in a wide temperature range including the phase transition temperatures T_c and T_N. The observed anomalies near T_N can be satisfactorily described by Landau type thermodynamic potential.

§1. Introduction

$NaNO_2$ crystals undergo two successive phase transitions from disordered (D_{2h}^{25}) phase into ordered incommensurate phase at $T_N \approx 165°C$ and then into commensurate ferroelectric (C_{2v}^{20}) phase at $T_c \approx 164°C$.[1)] Physical properties of $NaNO_2$ crystals at the phase transition region were studied by many researchers.[1-5)] Recently Hatta, Hanami and Hamano[6)] have published the results of their extensive study of ultrasonic properties of these crystals.

Here we report the results of our ultrasonic and dilatometric study of $NaNO_2$ crystals both "pure" and γ-irradiated.

§2. Experimentals

$NaNO_2$ crystals were grown from the melt by the Kyropoulos method. Some of the specimens were irradiated with Co^{60} γ-rays with various doses from 10^6 up to 10^9 R. Ultrasonic velocity and attenuation were measured by conventional pulse-echo method at frequencies 8.16 and 30 MHz at the temperature range from 20 to 180°C. Monodomain samples were measured during heating and cooling.

Thermal expansion coefficients were measured by quartz dilatometer with galvanomagnetic probe[7)] in temperature range from $-190°C$ to 220°C. Sensitivity of dilatometer was $\sim 10^{-7}$ cm.

From Fig. 1–2 one can see for longitudinal waves along a-and b-axes that velocity shows softening on cooling towards T_N. Attenuation increases reaching the maximal value at temperature which is 0.1–0.2°C lower then T_N. Some anomalies of velocity and peaks of attenuation can be observed at temperature T_c also,

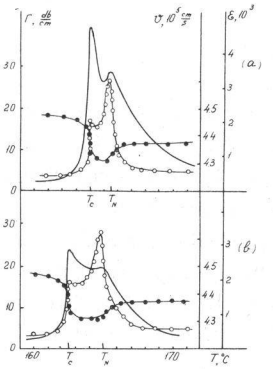

Fig. 1

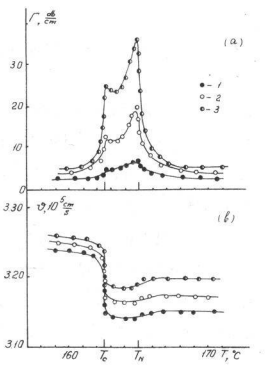

Fig. 2

Fig. 1. Temperature dependences of dielectric constant (solid line), velocity (1) and attenuation (2) of longitudinal waves along b-axis. Frequency 15 MHz
a) "pure" sample ●—1
b) γ-irradiated sample, dose 10^8 R ○—2

Fig. 2. Temperature dependences of attenuation (a) and velocity (b) of longitudinal waves along a-axis in γ-irradiated sample (dose 10^8 R) Frequences: 1–8 MHz, 2–15 MHz, 3–30 MHz.

but the peaks are smaller, then that at the temperature T_N. The results of measurements of nonirradiated and irradiated (Fig. 1(b)) samples are the same, but in the last case the incommensurate phase is wider.

The effect of irradiation doses on T_N, T_c and $(T_N - T_c)$ measured by temperature dependence of dielectric constant are the same as those obtained earlier by Gesi.[8)] As for ultrasonic properties in our experiments they show similar dependence on irradiation doses.

On Fig. 2 temperature dependences of attenuation and velocity are shown for different ultrasonic frequencies. Anomalous part of attenuation in the phase transition region varies

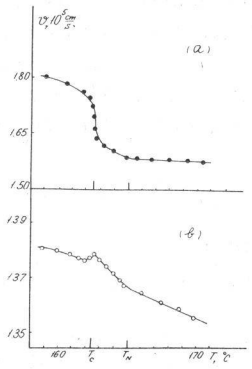

Fig. 3

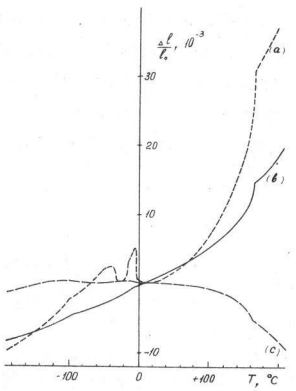

Fig. 4

Fig. 3. Temperature dependence of velocities of shear waves associated with c_{44} (a) and c_{66} (b) in γ-irradiated sample (dose 10^8 *R*). Frequency 30 MH.

Fig. 4. Thermal expansion along *a*-, *b*-, *c*-axes in irradiated samples (dose 10^8 *R*).

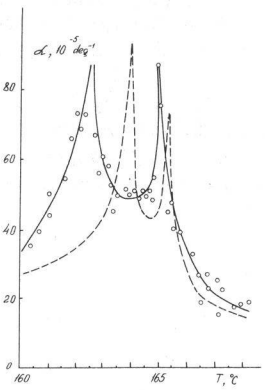

Fig. 5. Thermal expansion coefficient in the phase transition region along b-axis
---"pure" sample, ◦ irradiated sample.

almost linearly with frequency. From Fig. 2b one can see that there is a large dispersion of ultrasonic velocity. This dispersion is not connected with phase transformation, and the nature of it has been explained by Hatta *et al.*[6]

Velocities of shear elastic waves (Fig. 3) show no anomalous behaviour at T_N, but there is a change in the slope of their temperature dependences at T_N.

In Fig. 4–5 experimental results of thermal expansion of "pure" and irradiated crystals are shown. From Fig. 4 one can see that in the temperature range under study the dependences of Δl on T show a number of anomalies along with well known[5] anomalies at T_c and T_N.

§3. Discussion

Characteristic modes for incommensurate phase of $NaNO_2$ are the amplitude and the phase modes.[9] The phase mode has no effect on acoustical properties because the phonon-phason interaction vanishes at small acoustical wavevector.[6,10] By neglecting the wavevector dependence in the expression for amplitude mode frequency we can see that phase transition from disordered phase to the ordered incommensurate phase can be treated as normal phase transition. The Landau type thermodynamic potential density is given as:

$$\Phi=\frac{1}{2}\alpha Q^2+\frac{1}{4}\beta Q^4+(a_1S_1+a_2S_2+a_3S_3)Q^2 +\frac{1}{2}b_{ij}S_iS_jQ^2+\frac{1}{2}c_{ij}S_iS_j \tag{1}$$

where Q is order parameter; S_i is strain; $\alpha=\lambda(T-T_N)$. From eq. (1) one can see the changes of velocity and attenuation of ultrasonic waves due to phase transition. For acoustical waves propagating along *a*-, *b*-, *c*-axes we have:

$$\frac{\Delta v_i}{v_2}=\frac{1}{2\varrho v_i^2}\left(b_iQ_s^2-\frac{1}{1+\Omega^2\tau^2}\frac{2a_i^2}{\beta}\right);$$

$$\Delta\Gamma=\frac{a_i}{\beta}\frac{\Omega\tau}{1+\Omega^2\tau^2} \tag{2}$$

for longitudinal waves ($i=1,2,3$). and for shear waves ($j=4, 5, 6$)

$$\frac{\Delta v_j}{v_j}=\frac{b_j}{2\varrho v_j^2}Q_S;\ \Delta\Gamma_j=0. \tag{3}$$

Here Q_S is spontaneous value of order parameter, $\tau=\mu/M\omega_A^2$ is relaxation time of order parameter, where ω_A is frequency of amplitude mode, μ is viscosity coefficient and M is effective mass. The eqs. (2) and (3) satisfactory describe the experimental results on velocity and attenuation in the vicinity of T_N. According to eq. (3) temperature dependence of shear wave velocity is the same as that of spontaneous value of the order parameter. From eqs. (2) and (3) and experimental results on velocities we obtain:

$$a_1^2/\beta=0.7;\ a_2^2/\beta=8;\ a_2^3/\beta=10^{-2}$$
(in 10^9 erg/cm^3);

and

$$b_4\lambda/\beta=1.2;\ b_5\lambda/\beta\approx b_6\lambda/\beta=0.3$$
(in 10^9 erg/cm^{3}K).

It should be noted that in the temperature dependences of longitudinal wave velocities near T_N there are some continuous changes along with jumps described by the eq. (2). These continuous changes may be attributed to the effect of fluctuations[11] and/or defects.[12]

By the use of eq. (2) and experimental results on attenuation we obtain $\tau = 5 \times 10^{-9}$ s at $(T_N - T) \approx 0.25°C$. As for the temperature dependence of τ we have $\tau \sim (T_N - T)^{-n}$, where n is equal to 0.8 and 0.5 for "pure" and irradiated crystals respectively instead of $n = 1$ which follows from eq. (1).

Using eq. (1) one can deduce the expression for jumps of thermal expansion coefficients at T_N. These jumps are determined by some coefficients in eq. (1), velocity jumps and elastic constants c_{ik}. Taking known experimental values of $\Delta\alpha$, ΔV and c_{ik} we obtain:

$$a_1/\lambda \approx 10 \text{ K}; a_2/\lambda \approx 50 \text{ K}$$

Thus, the behaviour of elastic and thermal properties of $NaNO_2$ crystals near the transition point T_N can be satisfactory described by Landau type thermodinamic potential (I) with amplitude mode as soft mode except of some anomalies due to fluctuations and/or defects.

As for the behaviour of these properties at the transition point T_c one can say only that observed anomalies are due to abrupt change of crystal parameter at the first order phase transition.

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