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Investigation of Anisotropy and Anomaly of Attenuation of Low-Frequency Elastic Oscillations Near the Ferroelastic Curie Point

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The internal friction and the elastic constant features in the vicinity of the phase transition point at frequencies 1Hz in proper ferroelastic crystal $KH_3(SeO_3)_2$ were investigated. The influence of different crystal imperfections (domain boundaries, dislocations, point defects) on the behaviour of complex elasticity near the Curie point for different external forces are discussed.

§1. Introduction

The $KH_3(SeO_3)_2$ crystal (KTS) is a representative of the family of the alkaline trihydrogen-selenite crystals which have different interesting properties. More than ten years ago L. A. Shuvalov *et al.*[1] found out that in the KTS crystal the 2nd-order phase transition takes place at $-62°C$ which accompanied by the appearance of a twin structure at the low temperature phase. Not later than five years ago they proved the KTS crystal to be a proper ferroelastic.[2] Independently but one year later Y. Makita came to the same conclusion.[3] Since the KTS crystal is of particular interest for investigators. In Japan these crystals are studied mainly by Y. Makita and I. Tatsuzaki. In the USSR, Poland, GDR and Yugoslavia these investigations are performed in laboratories which are closely connected with the laboratory of L. A. Shuvalov. Such an interest to the KTS crystal may be explained by the fact that it is an excellent example of the proper ferroelastic and good enough to examine different theories and to develope experimental methods.

In the present paper we speak about elastic and unelastic properties of KTS which were obtained by using the infralow-frequency torsion pendulum. This method is very useful for investigation of ferroelastics because firstly it gives the information about mechanical properties of the crystals (the more important properties of ferroelastics) and secondly it is highly sensitive to different imperfections of the crystal lattice and therefore it gives the possibility to investigate the real crystal structure.

§2. Experimental Technique and Samples

To measure the infralow-frequency internal friction Q^{-1} and the shear modulus G and to write mechanical hysteresis loops a special apparatus has been made on the base of the inverse torsion pendulum.[4] The apparatus permits to make investigations in the temperature range from 80 to 600 K and at the frequency range from 10^{-4} to 50 Hz at the strain amplitude from 10^{-6} to 10^{-1} and the static torsion loads from 0 to 10^7 Pa. The errors for Q^{-1} and G were about 10 and 0.2% respectively. The calculation formulas for Q^{-1}, G and elastic stiffnesses C_{44}, C_{55} and C_{66} are given in ref. 5.

Samples of $2 \times 2 \times 30$ mm were in the form of the rectangular bars whose longer parts were along one of the crystallographic X-, Y-or Z axes of a crystal (X-, Y- and Z-orientation samples).

§3. Results and Discussion

3.1 Anisotropy of internal friction and shear modulus

The investigations of Q^{-1} (T) and $G(T)$ at frequencies 1 Hz have shown that in X-and Z-orientation samples of KTS and DKTS ($D=70-90\%$) in which the external stress σ led to the appearance of the shear strain x_5 the Q^{-1} peaks were observed and $G(T)$ went through the characteristic minimum near T_c (Fig. 1(a), (b)). In the Y-orientation samples of KTS near T_c the G step was observed while the Q^{-1} peak was absent (Fig. 1(c)). But in the DKTS samples the Q^{-1} peak and G minimum appeared. (Fig. 1(d)). The Q^{-1} (T) behaviour in the X- and Z-orientation crystals is due to the anomalous

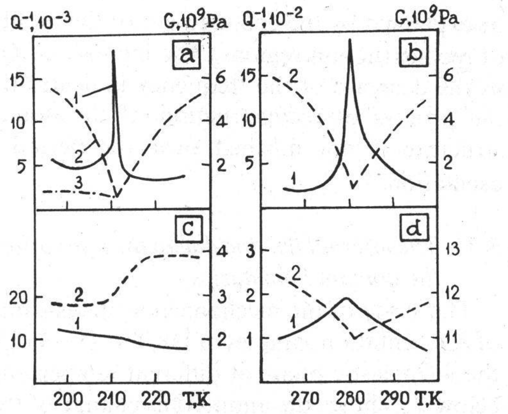

Fig. 1. The temperature dependences of Q^{-1} (1) and G (2, 3) for the X- and Z-orientation samples of KTS (a) and DKTS (D=85P) (b); and for the Y-orientation samples of KTS (c) and DKTS (d).

elastic compliance s_{55} and may be explained by the thermodynamic theory.[6] The Q^{-1} and G behaviours for the Y-orientation samples of DKTS are not clear yet.

It is interesting to note that in single- and polydomain samples with blocked domain walls G is rather higher (Fig. 1(a), curve 2) than that of the samples underwent the preliminary thermocycling or the influence of alternating σ (curve 3).

To make the qualitative analysis of the domain structure influence on the elasticities of the KTS and DKTS crystals the domain boundaries were conditionally taken for equivalent dislocations whose Burgers vectors were defined by the deformations in the bulk of the domain boundaries and the displacements of the domain boundaries. Using well known equations of the dislocation theory[7] we get the formulas[8] which allow us to define the change of elastic permitivity Δs which is due to the domain boundary displacement. From the theoretical analysis[8] it is clear that G of the polydomain crystal may be considerably smaller than that of the single domain one but in the crystal having pinned domain walls G may be larger than that of the crystal having rather mobile domain walls.

3.2 *The Q^{-1} mechanism near T_c at low frequencies*

As it was mentioned above the Q^{-1} peaks were observed near T_c in X- and Z-orientation samples of KTS and DKTS. However a well known Landau-Khalatnikov relaxation loss

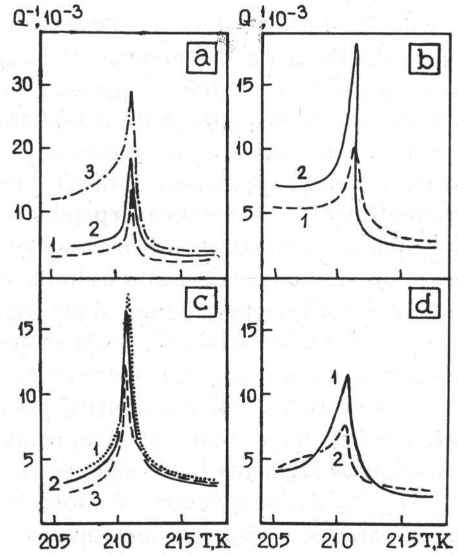

Fig. 2. The temperature dependences of Q^{-1} for the Z-orientation samples of KTS: (a) at the frequency 2Hz and different strain amplitudes $2.5 \cdot 10^{-6}$ (1), $2.5 \cdot 10^{-5}$ (2) and $2.5 \cdot 10^{-4}$ (3); (b) at the strain amplitude $\sim 10^{-5}$ and the frequencies of 2 (1) and 0.1 Hz (2); (c) at the frequency 2 Hz and $\sigma_{=} = 0$ (1), $5 \cdot 10^4$ (2) and 10^5 Pa (3); (d) at the frequency 1 Hz, strain amplitude 10^{-5} for nonirradiated sample (1) and for X-ray irradiated sample, doze 160 Gy (2).

mechanism cannot be used at low frequencies and therefore we propose the influence of dislocations to be taken into account. The influence of the strain amplitude (Fig. 2(a)), the frequency (Fig. 2(b)), the static torsion load (Fig. 2(c)) and the X-ray irradiation (Fig. 2(d)) on the Q^{-1} peaks give the possibility to suggest the following features of the phase transformation taking place in the ferroelastic crystal having the lattice imperfections. The presence of the shear stress component around the dislocation line favours the appearance of the region with order parameter having opposite sign with respect to the order parameter of the bulk of the sample. This region is stretched out along the twinning plane and its sizes depend on the overcooling $\Delta T = T_c - T$. The theoretical analysis shows that the area of the twin S infinitely increases at $\Delta T \to 0$ and therefore near T_c twins initiated by alone dislocations overlap each other and the dislocations would not be considered to be isolated ones. The twin medium is characterized by the whole ensemble of dislocations. Moving away from T_c the isolation of the twin around each dislocation takes place. This process is more intensive at a temperature

ΔT below T_c at which $s \simeq \lambda^{-1}$ (λ-the dislocation density). In this case the number of isolated regions in the twin medium is growing. As a result the crystal becomes more compliant to small $\sigma_{\sim}$. This leads to the decrease of the effective G and the appearance of the Q^{-1} peak. To define the $Q^{-1}(T)$ analytical dependence is a rather diffiicult statistical task because of the random distribution of dislocations in the bulk of the sample. The reconstruction of the domain patterns on both sides of the Q^{-1} peak temperature T_m may be discussed only. Between T_m and T_c the reconstruction of the domain patterns whose sizes are larger than the mean length of the dislocation segments $\lambda^{-1/2}$, takes place. But at $T<T_m$ the reconstruction of more stable domain patterns whose sizes are smaller than $\lambda^{-1/2}$, begins. All mentioned above permits to understand the reason of the decrease of the peak height Q_m^{-1} and its shift to lower temperatures when static $\sigma_=$ are applied to the sample. In this case the reconstruction of the domain structure occuring under the influence of the small $\sigma_{\sim}$, is suppressed but the domain patterns which would be stable in the absence of the $\sigma_=$, begin to reconstruct. Near T_m the number of these patterns is smaller than that in the absence of the $\sigma_=$ and therefore Q_m^{-1} becomes smaller.

The Q_m^{-1} increase vs the amplitude of $\sigma_{\sim}$ may be explained by the enlargement of the number of reconstruction regions. The increase of Q_m^{-1} vs the decrease of the frequency indicates that the process of reconstruction of the domain structure is not finished over the period of oscillation.

3.3 The internal friction due to the relaxation of the domain boundaries

The study of the mechanical hysteresis loops of Z-orientation samples of DKTS ($D=85\%$) in the ferroelastic phase at different temperatures below T_c, shows the anomalous change of their shapes.[9] At $T>260$ K instead of the saturated loops the ellipses whose squares are strongly temperature dependent, are observed (Fig. 3(a)). Assuming that such a behaviour is due to the relaxation loss mechanism we wrote stress-strain loops at different frequencies at a constant temperature near T_c (Fig. 3(b)). At frequencies 10^{-4} to 10^{-1} Hz the Debye type dispersion of the elastic compliance was found. The Cole-Cole diagrams are shown in Fig. 3(c). The activation energy of the relaxation process equals 0.9 ± 0.2 eV and the preexponential factor in Arrhenius equation $\tau_0 = 10^{-14}$s. The relaxation Q^{-1} peak in the ferroelastic phase were also observed in the Z-orientation sample of KTS at strain amplitude $\sim 10^{-5}$. The acti-

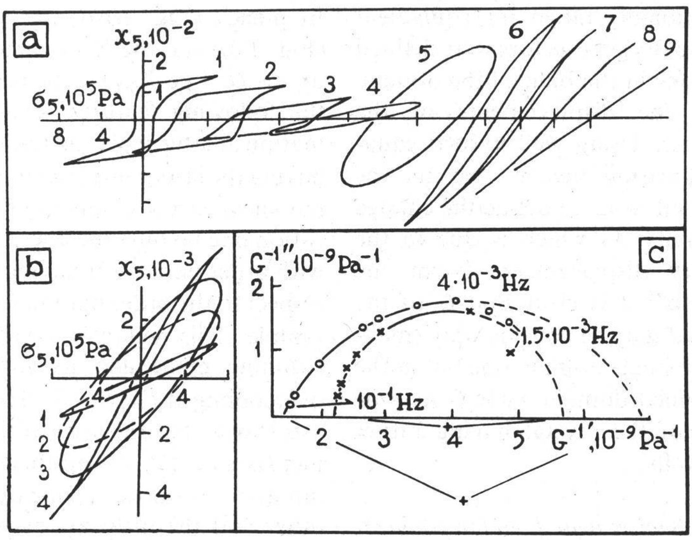

Fig. 3. The mechanical hysteresis loops for Z-orientation samples of DKTS ($D=85\%$): (a) at frequency 10^{-2} Hz and different temperatures 123 (1), 173 (2), 223 (3), 268 (4), 281 (5), 283 (6), 283.5 (7), 284 (8), and 288 K (9); (b) at 281 K and frequencies $1.5\cdot10^{-1}$ (1), $1.5\cdot10^{-2}$ (2), $4\cdot10^{-3}$ (3), $4\cdot10^{-4}$ Hz (4); (c) Cole-Cole plots at temperatures 281 (1) and 282 K (2).

vation energy estimated from T_m shifts vs frequency, equals 0.52 eV and $\tau_0 = 10^{-14}$s. The absence of such relaxation Q^{-1} peaks in the paraelastic phase and noticeable decrease of Q_m^{-1} vs $\sigma_=$ are good reason to believe that the observed relaxation processes are of domain nature and apparently due to the point defect and domain boundary interactions.

3.4 The shape memory effect

In the X- and Z-orientation samples of KTS as in PLZT ceramics[10] near T_c the shape memory effect was found. If at $T > T_c$ we apply $\sigma_=$ to a crystal and keeping $\sigma_=$ cool it through T_c to the ferroelastic phase the strain is changing. The interesting point is that the strain is practically preserved even when $\sigma_=$ is taken off. This shear strain disappeares only when the sample is heated to $T \geqslant T_c$ and it takes its original form. It is clear that in KTS this effct is due to the appearance of the spontaneous strain x_{5s} below T_c and the strength of this effect depends on the character and the state of the domain structure.

§4. Summary

Thus the experimental results show that the anomalous behaviours of Q^{-1} and G of KTS and DKTS in the vicinity of T_c at low frequency are considerably due to the crystal lattice imperfections (domain walls, dislocations, point defects). The low-frequency internal friction is highly effective and in some cases the only technique in investigation of physics of the real ferroelastic crystals.

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