Internal friction and dielectric loss related to domain walls

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The internal friction in potassium dihydrogen phosphate (KDP) crystal and the dielectric loss in KDP and triglycine sulfate (TGS) crystals are measured near T_c in the kHz frequency range. An internalfriction peak (P_{M2}) and a dielectric loss peak (P_{D2}) appear at about several degrees below T_c , which are found to be associated with the viscous movement of domain walls. With the temperature dependence of the density and the viscosity of domain walls, the order parameter, and the interaction among the domain walls taken into account, the internal friction and the dielectric loss due to the viscous movement of domain walls are calculated and compared with the experimental data.

I. INTRODUCTION

There is an internal-friction peak (P_2) due to the movement of domain walls which reveals thermal hysteresis at a few degrees below T_c in materials with second-order or weak first-order phase transitions¹ such as $La_{1-x}Nd_xP_5O_{14}$ (LNPP),^{2,3} A 15 alloys,⁴ and trigly-cine sulfate (TGS).⁵ Wang *et al.*^{2,3} have experimentally confirmed that this peak is caused by the movement of domain walls and attributed the formation of the P_2 peak to the variation of the number of domain walls with temperature and to the increase of the repulsive force among the domain walls with decreasing distance between them, but an expression of the internal friction was not given. Snead and Welch⁴ have proposed a theory of internal friction due to martensitic transformation in A15 alloys on the basis of the movement of domain walls and concluded that the internal friction is proportional to the tetragonal deformation $(1-c/a)^2$. This result is in agreement with the experimental data for pure A15 alloys, but it disagrees with the experimental results for deuterated and irradiated samples. Aside from there, no other experimental data on the dependence of the internal friction on the frequency are available for comparison with theory. This discrepancy may be due to their neglect of the interaction among domain walls and the variation of the density of domain walls with temperature. To study further the microscopic mechanism of the energy loss caused by domains, it is preferable to make simultaneous internal-friction and dielectric measurements because it is much easier to change the frequency in the latter than in the internal-friction experiment. As we know, KDP crystals undergo both ferroelastic and ferroelectric phase transition at T_c ; ferroelastic domain walls are also ferroelectric domain walls and they can be driven in motion by an external stress in the internal-friction measurement and by an external electric field in the dielectric measurements. If the microscopic origin of both energy losses is ascribed to the movement of ferroelastic-ferroelectric domain walls, the mechanisms of the internal friction and the dielectric loss are expected to be the same over a certain frequency and temperature range. In the present paper, both the internal friction and the dielectric loss are investigated for potassium dihydrogen phosphate (KDP) crystals and only the dielectric loss for TGS is studied.

II. EXPERIMENTAL METHODS

The two-node-clamped reed vibration with electrostatic drive and detection method is used to measure the internal friction with resonant frequency about 1.7, 2.2, and 4.1 kHz in KDP crystals with the normal of the thin plate along the *c*-direction, i.e., the polarization direction and the strain amplitude is about 10^{-6} . The dielectric loss and the dielectric constant are measured on a GR1615-A capacitance bridge. The sample size of the crystal dielectric measurements KDP for is $a \times b \times c = 10 \times 10 \times 1 \text{ mm}^3$ with the alternative electric field of measurements applied along the c direction. The sample sizes of TGS and triglycine sulfate (LATGS) doped with α -alanine (Ref. 3) crystals are $a \times b \times c = 10 \times 1 \times 10$ mm³, with the electric fields along the *b* direction, which is the polarization direction.

III. EXPERIMENTAL RESULTS

The results of the internal friction in KDP show that there are three peaks $(P_{M1}, P_{M2}, \text{ and } P_{M3})$ in the temperature range from 90 to 130 K, as shown in Fig. 1. The P_{M1}



FIG. 1. The internal friction (Q^{-1}) on heating (\bigcirc) and cooling (\triangle) processes and the resonant frequency (f) on heating (\bullet) for KDP as a function of temperature (T).

46 3290



FIG. 2. The dielectric loss (D) vs temperature of KDP on heating (\bigcirc) and cooling (\bullet) processes.

peak always appears at T_c whether measured in cooling or heating and is attributed to the ferroelastic and ferroelectric transition.^{2,3} The P_{M2} peak appears about 5 °C below T_c , which exhibits a thermal hysteresis for heating and cooling processes, similar to that of LNPP (Refs. 2 and 3) and TGS (Ref. 5) which have been confirmed to be caused by the movement of domain walls. The P_{M3} peak emerges at about 96 K, which has been ascribed to the freezing effect.⁶

Two dielectric loss peaks (P_{D1}, P_{D2}) also appear near T_c in the KDP crystal. P_{D1} appears exactly at T_c . P_{D2} emerges at about 5 °C below T_c , indicating a hysteresis for the heating and cooling processes (Fig. 2) as does P_{M2} . The result of the dielectric loss of TGS is similar to that of KDP (see below). In order to verify that the P_{D2} peak for multiple-domain crystals is due to the movement of domain walls, the dielectric loss of the monodomain ferroelectric crystal LATGS is studied and shows that there is hardly any dielectric loss peak below T_c and the value of dielectric loss is about 10^2 times smaller than that of



FIG. 3. The internal friction (Q^{-1}) vs temperature of KDP for different frequencies. Experimental data for f = 1.7 kHz (\odot), f = 2.2 kHz (\bullet), and f = 4.1 kHz (\triangle). Theoretical curves (---) with $A_0 = 5.4 \times 10^{-3}$ s, $h_3 = 2 \times 10^{-4}$.



FIG. 4. The dielectric loss (D) vs temperature of KDP for different frequencies. Experimental data for f = 1.2 kHz (\odot), f = 2 kHZ (\bullet), and f = 3 kHz (\triangle). Theoretical curves (---) with $A_0 = 1.3 \times 10^{-2}$ s, $h_1 = 0.19$ K⁻¹.

the multiple-domain crystal TGS. Consequently, the P_2 peak definitely originates from domains.

In order to get more information about the mechanism of the P_{M2} and P_{D2} peaks, the dependence of both the internal friction and the dielectric loss on the frequency is also surveyed. It is discovered that the high-temperature sides of the P_{M2} and P_{D2} peaks are almost independent of frequency, but the low-temperature sides are obviously frequency dependent and the positions of the P_{M2} and P_{D2} peaks move to higher temperature as the frequency increases (Figs. 3-5), but the relaxation time does not obey the Arrhenius relation, i.e., $\log \omega_p$ vs $-1/T_p$ is not a linear relation (Fig. 6), where ω_p , and T_p are the frequency and the temperature at the position of the peak. These are quite different from the behaviors of the thermally activated relaxation peak. From all the results mentioned above, the P_{M2} and P_{D2} peaks may be considered to be a kind of peak related to a complicated viscous movement of domain walls.



FIG. 5. The dielectric loss (D) vs temperature of TGS for different frequencies. Experimental data for f = 1.5 kHz (\odot), f = 3 kHz (\odot), and f = 5 kHz (\triangle). Theoretical curves (---) with $A_0 = 1.1 \times 10^{-2}$ s, $h_1 = 0.185$ K⁻¹.



FIG. 6. $\log(f_p)$ vs $-1/T_p$. (•) for the internal friction of KDP (from Fig. 3), (\triangle) for the dielectric losses of KDP (from Fig. 4), and (\bigcirc) for TGS (from Fig. 5).

IV. THE THEORY OF THE INTERNAL FRICTION AND THE DIELECTRIC LOSS DUE TO THE VISCOUS MOVEMENT OF DOMAIN WALLS

A. The interaction force (F^{I}) among domain walls in LNPP, KDP, and TGS

The domain walls in LNPP (Refs. 2 and 3) and KDP (Refs. 7-9) are planes crossing transversely the whole sample and they have interaction among themselves.^{2,3} They will be equally spaced when the density of domains is high enough. Let the distance between two walls be d, the number of domain walls per unit length N, and the spontaneous shear stain $\varepsilon_{st}^{(s)}$ ($s \neq t$). The interaction between the nearest-neighbor domain walls will be discussed here. The configuration of the walls is shown in Fig. 7 when the displacement of the domain walls is x, where $\varepsilon_{st}^{(2)}$ are the shear strains of negative and



FIG. 7. Dashed and solid lines express the schematic configurations before and after the walls have a displacement x, respectively.

positive domains, respectively. When $x \ll d$,

$$\varepsilon_{st}^{(i)} = \varepsilon_{st}^{(s)} d / (d + x) = \varepsilon_{st}^{(s)} (1 - x / d) ,$$
 (4.1)

$$\varepsilon_{st}^{(2)} = \varepsilon_{st}^{(s)} d / (d - x) = \varepsilon_{st}^{(s)} (1 + x / d) , \qquad (4.2)$$

the change of elastic energy is

$$U = C_{stst} [(\varepsilon_{st}^{(2)} - \varepsilon_{st}^{(s)})^2 (d - x) + (\varepsilon_{st}^{(1)} - \varepsilon_{st}^{(s)})^2 (d + x)]/2 ,$$
(4.3)

where C_{stst} is the shear modulus. The force acting on the walls per unit area is

$$F^{I} = -dU/dx = -2C_{stst}N\varepsilon_{st}^{(s)2}x \quad . \tag{4.4}$$

Although there is not any spontaneous shear strain in TGS, the antipiezoelectric effect^{10,11} will induce shear strain $\varepsilon_{13}^{(i)}$.

$$\varepsilon_{13}^{(i)} = d_{213}E_2 = -8\pi d_{213}p_s \quad , \tag{4.5}$$

where d_{213} is the piezoelectric coefficient and P_s is the spontaneous polarization vector. Then the interaction among the domain walls in TGS will be similar to that of LNPP and KDP because of the nonzero value of $\varepsilon_{13}^{(i)}$.

B. The configuration force acting on ferroelastic domain walls in an external stress field

The configuration of the domains is schematically shown in Fig. 8 when an external shear stress σ_{st} is applied to the multiple-domain crystals. Under the condition of small stress amplitude, $x \ll d$,

$$\varepsilon_{st}^{(2)} = (\varepsilon_{st}^{(s)}d - y)/(d - x) - J_{stst}\sigma_{st} , \qquad (4.6)$$

$$\varepsilon_{st}^{(1)} = (2\varepsilon_{st}^{(t)}d - 2J_{stst}\sigma_{std} + \varepsilon_{st}^{(s)}d - y)/(d + x) + J_{stst}\sigma_{st} , \qquad (4.7)$$

where y is the displacement as shown in Fig. 8, J_{stst} is the compliance of the single crystal, and $\varepsilon_{st}^{(t)}$ is the total shear



FIG. 8. Dashed and solid lines express the schematic configurations before and after the stress was applied, respectively.

strain of the sample. The change of elastic energy equals

$$U = C_{stst} [(\varepsilon_{st}^{(2)} - \varepsilon_{st}^{(S)})^2 (d - x) + (\varepsilon_{st}^{(1)} - \varepsilon_{st}^{(s)})^2 (d + x)]/2 - \varepsilon_{st}^{(1)} \sigma_{st} (d + x) + \varepsilon_{st}^{(2)} \sigma_{st} (d - x)$$
(4.8)

because the walls move along the orbit with minimum value of U,

$$\partial U/\partial x = 0, \quad \partial U/\partial y = 0, \quad \partial U/\partial \varepsilon_{st}^{(t)} = 0.$$
 (4.9)

We get, from (4.6) - (4.9),

$$\begin{aligned} \varepsilon_{st}^{(2)} &= \varepsilon_{st}^{(s)} - J_{stst} \sigma_{st} , \qquad (4.10) \\ \varepsilon_{st}^{(1)} &= \varepsilon_{st}^{(s)} + J_{stst} \sigma_{st} , \qquad (4.11) \end{aligned}$$

$$\begin{aligned} \varepsilon_{st}^{(t)} &= [\varepsilon_{st}^{(1)}(d+x) - \varepsilon_{st}^{(2)}(d-x)]/2d \\ &= \varepsilon_{st}^{(s)} x/d + J_{stst} \sigma_{st} \\ &= \varepsilon_{st}^{(d)} + J_{stst} \sigma_{st} , \end{aligned}$$
(4.12)

where $\varepsilon_{st}^{(d)}$ is the nonelastic strain due to the movement of domain walls. Let $F(\sigma_{st})$ be the configuration force acted on the walls per unit area by the external stress, then

$$F(\sigma_{st}) = -\frac{\partial}{\partial x} \left[-\varepsilon_{st}^{(1)} \sigma_{st} (d+x) + \varepsilon_{st}^{(2)} \sigma_{st} (d-x) \right]$$
$$= 2\varepsilon_{st}^{(s)} \sigma_{st} . \qquad (4.13)$$

C. The internal friction and the dielectric loss due to the viscous movement of domain walls

When an external longitudinal stress (σ_{mm}) is applied to the multiple-domain crystals, there will be six components of stress acting on the crystals for the coordinate system as shown in Fig. 8:

$$\sigma_{ij} = a_{mi} \partial_{mj} \sigma mm , \qquad (4.14)$$

where *i* and j = 1, 2, or 3 and a_{mi} are the direction cosines between the *m*th direction and the crystal *i* axis. Then the elastic strain ε_{st} of single domains is

$$\varepsilon_{st} = \sum_{i,j} J_{stij} \sigma_{ij} \tag{4.15}$$

and the effective shear stress which will drive the domain walls to move can be written as

$$\sigma_{st}^* = C_{stst} \varepsilon_{st} = \sum_{l,j} C_{stst} J_{stij} \sigma_{ij}$$
$$= \sum_{i,j} a_{mi} a_{mj} C_{stst} J_{siij} \sigma_{mm} . \qquad (4.16)$$

So there will be five forces acting on domain walls: (1) the configuration force $F(\sigma_{st}^*)$ by the external stress, (2) the interaction F^I among the walls, (3) the viscous force $-\Gamma \dot{x}$ (Ref. 12) due to the scattering of the lattice as the walls move in the crystals, where Γ is the viscous constant, (4) the recovering force $-k_0 x$ by the defects where k_0 is the force constant, and (5) the Peierls force.^{5,12}

The domain walls are considered to be quasiparticles with effective mass M per unit area and the Peierls force can be neglected,¹² the equation of motion of domain walls is

$$M\ddot{x} + \Gamma \dot{x} + k_0 x - F^I = F(\sigma_{st}^*) . \qquad (4.17)$$

Let $\sigma_{mm} = \sigma_0 e^{i\omega t}$, from (4.10), (4.12), and (4.17) when $\omega^2 \ll (k_0 + 2C_{stst} N \varepsilon_{st}^{(s)2})/M$; it can be obtained that the nonelastic strain $\varepsilon_{st}^{(d)}$ due to the movement of domain walls is

$$\varepsilon_{st}^{(d)} = \left[\frac{2N\varepsilon_{st}^{(s)2}}{k} \frac{1}{1+\omega^2\tau^2} - i\frac{2N\varepsilon_{st}^{(s)2}}{k} \frac{\omega\tau}{1+\omega^2\tau^2} \right] \sigma_{st}^* , \qquad (4.18)$$

so the complex strain equals

$$\begin{aligned} \varepsilon_{mm} &= \varepsilon'_{mm} - i \varepsilon''_{mm} \\ &= \sum_{k,l} a_{mk} a_{ml} \varepsilon_{kl} + a_{ms} a_{mt} \varepsilon_{st}^{(d)} \\ &= J' \sigma_{mm} + C' \frac{2N \varepsilon_{st}^{(s)2}}{k} \left[\frac{1}{1 + \omega^2 \tau^2} - i \frac{\omega \tau}{1 + \omega^2 \tau^2} \right] \sigma_{mm} , \end{aligned}$$

$$(4.19)$$

where

$$J' = \sum_{i,j,k,l} (2 - \delta_{ij})(2 - \delta_{kl}) a_{mk} a_{ml} a_{mi} a_{mj} J_{klij}$$
$$C' = \sum_{i,j} (2 - \delta_{ij}) a_{ms} a_{ml} a_{mi} a_{mj} C_{stst} J_{stij} ,$$

so the internal friction due to the viscous movement of domain walls is

$$Q^{-1} = \frac{C'}{J'} \frac{2N\varepsilon_{st}^{(s)2}}{k} \frac{\omega\tau}{1+\omega^2\tau^2}$$
(4.20)

and the dynamic modulus equals

$$E = \frac{1}{J'} - \frac{C'}{J'^2} \frac{2N\varepsilon_{st}^{(s)2}}{k} \frac{1}{1+\omega^2\tau^2} , \qquad (4.21)$$

where $\tau = \Gamma / (k_0 + 2C_{stst} N \varepsilon_{st}^{(s)2})$, $k = k_0 + 2C_{stst} N \varepsilon_{st}^{(s)2}$, and J_{klij} are the components of a compliance.

For the multiple-domain crystal KDP below T_c , s = 1and t = 2, $^{9-11}$

$$C' = 2a_{m1}^2 a_{m2}^2 C_{1212} J_{1212} + (a_{m1}^3 a_{m2} + a_{m1} a_{m2}^3) C_{1212} J_{1211} .$$
(4.22)

Let the electric field of the dielectric measurement be $E_m = E_0 e^{i\omega t}$, which is applied along the direction of the spontaneous polarization *m* direction and similar to that of (4.10) and (4.12), the polarization vector $P_m = \chi_{mm} E_m + 2P_s x/d$,¹³ and the force acted on the domain walls per unit area is $F(E_m) = 2P_s E_m$,¹³ where P_s is the spontaneous polarization vector. Under the condition of $\omega^2 \ll (k_0 + 2C_{stst} N \varepsilon_{st}^{(s)2})/M$, it is obtained that the dielectric loss equals

$$D = \frac{2NP_s^2/k}{[\chi_{mm}(\chi_{mm} + 2NP_s^2/k)]^{1/2}} \frac{\omega\tau_0}{1 + \omega^2\tau_0^2} , \qquad (4.23)$$

and the dielectric constant is

$$\varepsilon_{mm} = \chi_{mm} + \frac{2NP_s^2}{k} \frac{1}{1 + \omega^2 \tau^2},$$
 (4.24)

where $\tau_0^2 = \tau^2 \chi_{mm} / (\chi_{mm} + 2NP_s^2/k)$, χ_{mm} is the dielectric constant of monodomain crystals along the spontaneous polarization direction.

D. Results of calculation, comparison with experimental data

The existence of domains in crystals can decrease the elastic energy of the crystals but it increases the interface energy on the other hand, so there is a definite number of domain walls in the crystals at each temperature. When $T \rightarrow T_c$, the interface energy $\rightarrow 0$ (Refs. 5, 14, and 15) for the order parameter $\rightarrow 0$,¹⁶⁻²⁰ so the density of the domain walls $N \rightarrow \infty$, Wang *et al.*^{2,3} have detailed the relation between N and the temperature as

$$N = N_0 / (T_c - T) , \qquad (4.25)$$

where N_0 is a constant independent of temperature.

When $T \rightarrow T_c$, the order parameter $\rightarrow 0$, so the difference between the domain wall and the domain interior becomes unclear, which leads to the scattering by the phonons to the domain walls $\rightarrow 0$ and then the viscous coefficient Γ of the movement of domain walls in the crystals $\rightarrow 0$. Combs and Yip¹² got the expression for the viscous coefficient by computer simulation,

$$\Gamma = A e^{-B/(T_c - T)}, \qquad (4.26)$$

where A and B are constants independent of temperature.

Taking account of the dependence of the density of domain walls N and the viscous coefficient Γ on the temperature in addition to the well-known relations $P_s^2 = P_0^2(T_c - T)$, $^{17-20}$, $\chi_{mm} = C/(T_c - T)$, $^5 \varepsilon_{st}^{(s)2} = \varepsilon_0^2(T_c - T)$, $^{16} C_{stst} = C_0 g(T_c - T)/[1 + g(T_c - T)]$, 16 where k_0 , N_0 , P_0 , C, ε_0 , C_0 , and g are constants independent of temperature, we get for $g \ll 1$, 16 and when Q^{-1} (and D) $\ll 1$,

$$\tau = \tau_0 = A_0 e^{-B/(T_c - T)} , \qquad (4.27)$$

$$Q^{-1} = h_3 \frac{\omega \tau}{1 + \omega^2 \tau^2} , \qquad (4.28)$$

$$D = h_1 (T_c - T) \frac{\omega \tau_0}{1 + \omega^2 \tau_0^2} , \qquad (4.29)$$

where $A_0 = A/k_0$, $h_1 = 2N_0P_0^2/(Ck_0)$, $h_3 = 2N_0\varepsilon_0^2C'/J'k_0$.

The calculated results and experimental data of the internal friction and the dielectric loss are shown in Figs. 3-5 and the results are fairly coincident with the experimental data, where B = 9.8 and 9.5 K for TGS and KDP, respectively.

V. DISCUSSIONS AND CONCLUSIONS

The experimental results of the present paper show that there is a loss peak (Q^{-1}, D) related to the movement of domain walls at a few degrees below T_c in the range of audio frequency for the ferroelectric and/or ferroelastic polydomain crystals KDP, TGS, and it is not found to be a simple thermal activation relaxation peak because the relaxation times does not obey the Arrhenius relation. Taking account of the rapid change of order parameter, domain-wall density, the mobility of domain walls, and the interaction among walls with temperature below T_c , the peak can be explained successfully.

For the materials with second- or weak first-order ferroelectric phase transition, such as RbH_2PO_3 ,²¹ CsH_2PO₄,²¹ RbH_2AsO₄,21 Sr_{0.4}(Na_{0.5}Bi_{0.5})TiO₃,²² Ba(Ti_{1-x}M_x)O₃ (M=Zr, Fe, or Mn),²³ PbZrO₃,^{24,25} CdNa₂O₇,^{26,27} (1-x)Pb(Mg_{1/3}M_{2/3})O_{3-x}PbTiO₃ (1-x)Pb $(Mg_{1/3}M_{2/3})O_{3-x}$ PbTiO₃ $[M = Nb^{'}(\text{Ref. 28}) \text{ or } \text{Ta} (\text{Ref. 29}), Sn_2P_2^{'}(Se_xS_{1-x})_6^{'30}$ PbIn_{0.5}Nb_{0.5}O₃,³¹ LiKSO₄,³² and Pb(Sc_{1/2}Ta_{1/2})O₃,³³ etc., there is also a dielectric loss peak at a few degrees below T_c in the audio frequency range similar to our results, and most authors of the references cited above suggested that it is due to the movement of domain walls. So, it can be concluded that this kind of peak is universal for the materials with second- or weak first-order ferroelectric and/or ferroelastic phase transitions. This universality is found to originate from the continuous change of order parameter, i.e., the spontaneous polarization vector (P_s) or the spontaneous shear strain $(\varepsilon_{st}^{(s)})$ with temperatures below T_c which result in the fast variation of domain-wall density, the viscous coefficient of domain walls, and the interaction among domain walls with temperature. In this way, the loss peak can be explained using the theory proposed in this work uniformly. The comparison between the experimental data of some crystals mentioned above and the theory has been made as shown in Fig. 9.

The calculated results also indicate that the energy loss due to the viscous movement of domain walls is very small when the frequency is higher than 10 kHz, but Wang *et al.*^{2,3} and Liu *et al.*⁵ still observed an internal



FIG. 9. The comparison between the theory and the experimental data for (1) RbH₂AsO₄ (Ref. 21) (\odot), (2) BaTiO₃ (Ref. 23) (\blacktriangle), (3) PbZrO₃ (Ref. 24) (\bigtriangleup), and (4) Pb(Sc_{0.5}Ta_{0.5})O₃ (Ref. 33) (\odot) at 1 kHz. The solid lines express the computed results. For (1): $A_0 = 1.3 \times 10^{-2}$ s, $h_1 = 3.5 \times 10^{-2}$ K⁻¹, B = 12.8 K. For (2): $A_0 = 1.9 \times 10^{-2}$ s, $h_1 = 3 \times 10^{-3}$ K⁻¹, B = 17.7 K. For (3): $A_0 = 2.9 \times 10^{-2}$ s, $h_1 = 2.1 \times 10^{-2}$ K⁻¹, B = 9.7 K. For (4): $A_0 = 1.7 \times 10^{-2}$ s, $h_1 = 6.5 \times 10^{-3}$ K⁻¹, B = 19.2 K.

friction peak related to domain walls at 10° below T_c around 100 kHz and the position of the peak hardly moves as frequency changes, which exhibits the static hysteresis character. Why such peak has not been detected in the lower kHz frequency range may be due to the strain amplitude of the electrostatic drive method being too small.³⁴

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