Domain freezing in potassium dihydrogen phosphate, triglycine sulfate, and CuAlZnNi

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The temperature dependence of the dielectric constant and dissipation in potassium dihydrogen phosphate (KDP), its deuterated compound (DKDP), triglycine sulfate (TGS), and TGS doped with α-alanine (LATGS) has been studied at various frequencies. It is found that the relaxation time of domain freezing in KDP and DKDP in the kHz range can be described by the Vogel-Fulcher relation. Evidence of domain freezing in TGS is presented through an analysis of relaxation time related to domain walls and a comparison between TGS and LATGS. Studies of internal friction and compliance show preliminary evidence of domain freezing in CuAlZnNi alloy. A domain-freezing model is proposed based upon the collective pinning of randomly distributed pinning centers to domain walls. Some key experiments related to domain freezing, such as (1) the Vogel-Fulcher relation for relaxation time; (2) the size effect of domain freezing; (3) two kinds of relaxation in low- and high-frequency ranges, respectively; and (4) the dependence of T_F on defect density and applied field, etc., are explained. [S0163-1829(97)01323-4]

I. INTRODUCTION

Dielectric studies in potassium dihydrogen phosphate (KDP)-type crystals have shown that, in a certain temperature range down from Curie temperature T_C, the dielectric constant ϵ' exhibits an anomalously high value as compared to that predicted by the phenomenological Landau theory, showing a plateaulike temperature dependence. Then at a temperature T_F, ϵ' abruptly falls down to its phenomenological value. This feature looks like a ''kink'' and a dissipation ϵ'' peak appears within the range of the ''kink.'' The large ϵ' between $T_F<T<T_C$ (a so called ''plateau'' region) is believed to be due to the motion of domain walls (DW's). The abrupt decrease of ϵ' is then attributed to the freezing of DW motion or domain freezing,[1–14] and T_F is defined as a freezing temperature.

Domain freezing has been known for a long time since being first discussed by Barkla and Finlayson[1] in 1953. This phenomenon has been intensively studied in recent years, and at least three representative models have been put forward to describe it.

(1) Bornarel[2] proposed a model in 1972: because of quasidislocations of the edge type in DW's, there is a critical shear stress σ_c necessary to move the quasidislocations in their glide plane, which decreases with increasing temperature and becomes zero when DW's disappear at T_C. Then T_F corresponds to the temperature where applied field F_A equals σ_c, i.e., DW's cannot be driven below T_F (domain freezing state) for $F_A<\sigma_c$, and they are movable above T_F for $F_A>\sigma_c$. Obviously, $T_F\rightarrow T_C$ when $F_A\rightarrow 0$ according to this model.

(2) Another model was proposed by Fedsov and Sidorkin[3] in 1977, which takes the short-range interactions of pseudospins with their neighbors into account, with tunneling effects and interaction via the subsystem of heavy ions. This model gives two possible configurations of DW's corresponding to two minimum energies in different temperature intervals, and T_F corresponds to the temperature at which the two configurations invert themselves between the ground state and the saddle one. This induces modifications in the lattice-energy barrier and then in the wall mobility.

(3) Kuramoto[4] proposed a model in 1987: dipole reversal in DW's will lead to violation of the ice rule of proton configuration, so there exists cooperative reorientation between the dipoles and ions in order to get a minor violation of the ice rule, i.e., a certain size of cooperative region in DW's (two-dimensional clusters) will be formed, and the restriction on dipole reversal becomes severe as spontaneous polarization reaches its saturated value. Therefore, the relaxation time τ of dipole reversal increases remarkably as temperature decreases and becomes infinite at a certain temperature at which the configuration entropy reaches a limiting value. At the same time, thermal motion of DW's diminishes because of the abrupt increase of the relaxation time, i.e., freezing of DW mobility or domain freezing.

Although the above models can explain some experimental results, there are still some questions. For example, when the measurement field $\rightarrow 0$, $T_F\rightarrow T_C$ according to Bornarel's model as mentioned above, but this is not consistent with the experimental results of Nakamura,[5] which show that T_F is

about 20 K below T_C when the field tends to zero. As Bornarel[6] and Bornarel and Torche[7] point out, it seems difficult to imagine that Fedsov and Sidorkin's model with only short-range interaction being taken into account can explain the size effect of domain freezing, i.e., the dependence of T_F on the sample thickness d. This effect is not considered by Kuramoto[4] in their model either. In KDP doped with potassium hydroxide (KOH), T_C is the same as that of pure KDP, which implies that the parameter for proton tunneling does not change, while T_F changes with varying the defect density. So, Nakamura and Kuramoto[8] stressed that this fact implies that domain freezing in the KDP family is not a phase transition governed by proton tunneling, as suggested by Fedsov and Sidorkin because T_F is only dependent on proton tunneling according to their model. In short, as Kubinec *et al.*[14] pointed out (1995): ''Although the domain-freezing phenomenon has been known for a long time and was intensively studied in recent years, the problem has not been solved yet.'' In one part of this paper, a domain-freezing model is proposed based upon the collective pinning of randomly distributed pinning centers to DW's, and some key experiments related to domain freezing are explained.

Up to now, the method of frequency scanning is usually used to measure the complex dielectric constant $\epsilon=\epsilon'-i\epsilon''$.[4,5,8,10,12–14] It is found that near T_F, ϵ related to domain freezing is nearly independent on frequencies f in the kHz range, but shows relaxation features in the 10^8 Hz region with its relaxation time in accordance with the Vogel-Fulcher relation

$$\left[\tau=\tau_0\exp\left(\frac{U}{T-T_{\mathrm{VF}}}\right)\right]$$

for the tetragonal KDP family.[4,5,8,10,13,14] But in monoclinic CsH_2PO_4 (CDP) and both in the kHz and 10^8 Hz frequency ranges,[12] the ϵ' reveals relaxation characters with their relaxation times being all of the Vogel-Fulcher type. An obvious difference between the relaxation spectra is that there is a piezoelectric resonance of a crystal plate that is related to the movement of DW's around 10^5 Hz in the tetragonal KDP family, but not in CDP.[4,5,8,10,12–14] So it is speculated that the relaxation feature in the kHz range may be smeared by the resonance in the KDP family. Although the method of temperature scanning, which can minimize the influence at a certain level, has been used to study domain freezing, the dependence of ϵ on frequencies has not been obtained yet.[9] In one part of this paper, the method of temperature scanning at a fixed frequency f in a cooling and heating cycle with f being changed in succeeding cycles in the kHz range is used to measure the dielectric constant $\epsilon'$and dissipation ϵ''in KDP and DKDP. Experimental results indicate that the positions of the ''kink'' in ϵ' and ϵ'' peak both shift to high temperature weakly with increasing frequencies f, and the relaxation time during domain freezing is consistent with the Vogel-Fulcher relation.

On the other hand, domain freezing is only confirmed in the KDP family.[1,2,4–14] The existence in other crystals, such as standard ferroelectrics triglycine sulfate (TGS) (Refs. 15–18) and ferroelastics CuAlZnNi (Ref. 19) will be questioned. Although a preliminary observation of domain freezing at low temperature in TGS has been made by Trybula *et al.*,[17] they propose that the low-temperature anomaly of the complex dielectric constant results from the formation of a rotational glass involving synchronous reorientation of glycine-I and rotation of NH_3 groups. Motegi, Ibaraki, and Nakamura[16] discovered that this anomaly is a relaxation with its relaxation time in accordance with the Arrhenius relation

$$\left[\tau=\tau_0\exp\left(\frac{U}{T}\right)\right].$$

This result suggests that the anomaly is just a thermal activation process and does not involve any transition.[20] So, further studies are required to clear the mechanisms of this phenomenon. One part of this paper is that the ϵ' and ϵ'' related to the anomaly are studied in TGS, and evidence of domain freezing is presented. In addition, studies of internal friction Q^{-1} and compliance J' show preliminary evidence of domain freezing in CuAlZnNi.

II. EXPERIMENT

Triglycine sulfate $(NH_2CH_2COOH)_3H_2SO_4$ (TGS) (Refs. 15–18), triglycine sulfate doped with α-alanine (LATGS),[21–24] potassium dihydrogen phosphate KH_2PO_4 (KDP),[4–10] and its deuterated compound KD_2PO_4 (DKDP)[6,25] single crystals were obtained from aqueous solution by slow evaporation.

Ferro-paraelectric transitions of second order take place at 322 K, 323 K in TGS (Refs. 15–18), and LATGS (Refs. 21–24), respectively. There are 180° polydomains in the ferroelectric phase in TGS, and the shape of the domain walls is an elliptic cylinder. Ratio of the long- and short axes of the ellipse perpendicular to spontaneous polarization direction (b axis of crystal coordinate) is $\sim$5.[5,26] Doping α-alanine in TGS (LATGS) induces an internal electric field that polarizes crystals to a monodomain state, but its influence on the Curie temperature T_C is little, and T_C shifts to higher temperature by only $\sim$1 K.[15–18] All TGS and LATGS samples used in dielectric measurements are prepared as platelets with sizes being $a\times b\times c=5\times 0.6\times 5\ \mathrm{mm}^3$, and each b surface was coated with silver by evaporation.

Ferroelectric/ferroelastic to paraelectric/paraelastic transitions are weak first order in both KDP (Refs. 4–10) and DKDP (Refs. 5 and 25) and their T_C's are 122 and 213 K, respectively. Domain walls are parallel planes and spontaneous polarization directions are along the c axis of crystal coordinate in both KDP and DKDP.[4–10,25] KDP and DKDP samples in dielectric measurements are platelets with sizes being $a\times b\times c=5\times 5\times 0.5\ \mathrm{mm}^3$, and each c surface was evaporated with silver. Sizes of DKDP samples used in internal friction measurements are about $0.3\times 2.5\times 28\ \mathrm{mm}^3$.

CuAlZnNi (Cu-28.76 at. % Al-4.76 at. % Zn-2.33 at. % Ni) single crystals[19] were obtained by the vacuum induction melting method and homogenized at 970 °C for 5 hours. Sample sizes for internal friction measurements are $\sim 0.25\times 3\times 30\ \mathrm{mm}^3$. Before measurements, the samples were kept at 830 °C for 10 min, followed by water quenching to room temperature. The starting temperature of the martensitic transformation is about 270 K.

Some information concerning the samples used here is shown in Table I.

TABLE I. Some information on samples used here.

Samples	T_C or M_S	Domain states in ferroelectric and/or ferroelastic phases	Shape of domain walls
TGS	T_C=322 K	180° polyferroelectric domains	elliptic cylinder
LATGS	T_C=323 K	Mono domain	
KDP	T_C=122 K	180° polyferroelectric and ferroelastic domains	plane
DKDP	T_C=213 K	180° polyferroelectric and ferroelastic domains	plane
CuAlZnNi	$M_S \approx 270$ K	180° polyferroelastic domains	plane

Complex dielectric constant $\epsilon = \epsilon' - i\epsilon''$ was measured from 10 Hz to 100 kHz by a GA-1615 A capacitance electric bridge. Here ϵ' is the dielectric constant and ϵ'' is the dissipation. A method of temperature scanning at a fixed frequency f in a cooling and heating cycle was used, and f is changed in succeeding cycles. The scanning rate is ~1 K/min.

Internal friction Q^{-1} and compliance J' were measured by a one-node-clamped reed vibration device with electrostatic driving and detection of the cooling or heating rate ~1.5 K/min.

In order to avoid the aging effect of measurements in ferroelectric and/or ferroelastic phases,[17] the samples were heated to a temperature about 20 K above T_C before measurements every time, and data on cooling were used.

III. RESULTS

Shown in Figs. 1 and 2 is the temperature dependence of the dielectric constant ϵ' and dissipation ϵ'' in KDP and DKDP for different frequencies f.Same as the previous results,[1–14] there is a λ-shaped peak of dielectric constant ϵ' just at T_C, and in a certain temperature region down from T_C, ϵ' reveals an anomalously high ''plateau'' region as compared to that predicted by the phenomenological Landau theory (about two orders). Then at a temperature T_F, ϵ' abruptly falls down to its phenomenological value. A new result is that the ''kink'' position shifts to high temperatures with increasing f.

The dissipation ϵ'' in KDP and DKDP is also shown in Figs. 1 and 2, respectively. There are three peaks (P_1, P_2, and P_3) in the measuring temperature range. The narrow P_1 peak appears just at T_C: the reason why it was not observed some times may be from its narrow width. This peak has been attributed to field-induced preferred orientation of the dynamic-phase domains reported by Wang and co-workers.[27–30] The P_2 peak is located at 5–10 K below T_C, and the high-temperature side goes to zero when temperature tends to T_C. By taking into account the temperature dependence of the density and the viscosity of domain walls, as well as the interaction between domain walls, Huang and co-workers have given a successful explanation.[29,30]

Within the temperature range of the ''kink'' (Figs. 1 and 2), a dissipation peak P_3 emerges, and its peak position T_P

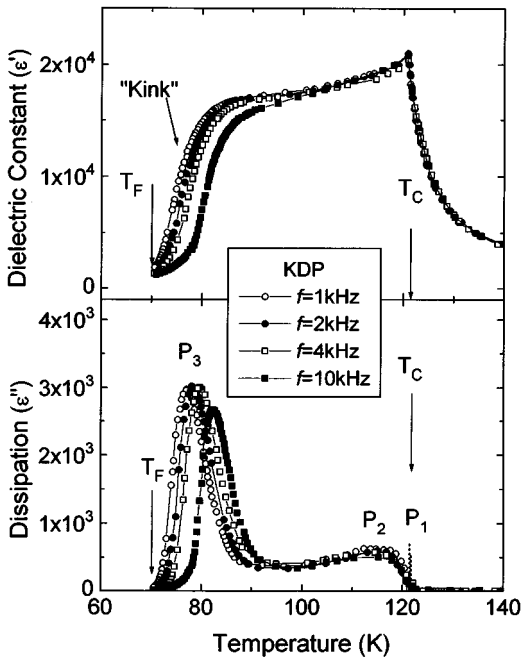

FIG. 1. Dielectric constant ϵ' and dissipation ϵ'' of KDP versus temperature and frequency f.

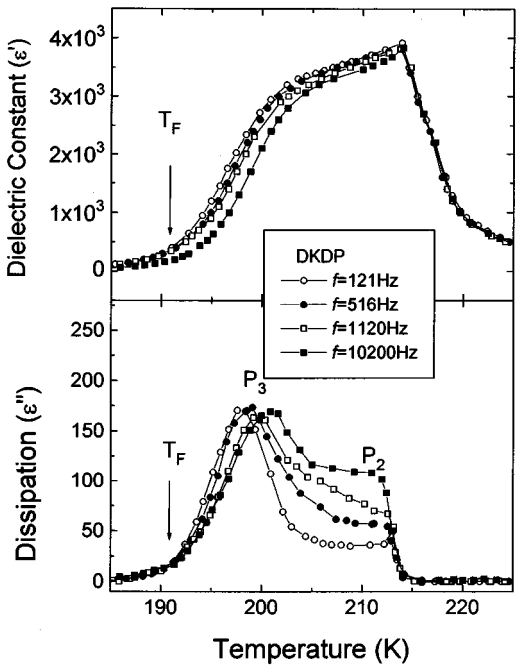

FIG. 2. Dielectric constant ϵ' and dissipation ϵ'' of DKDP versus temperature and frequency f.

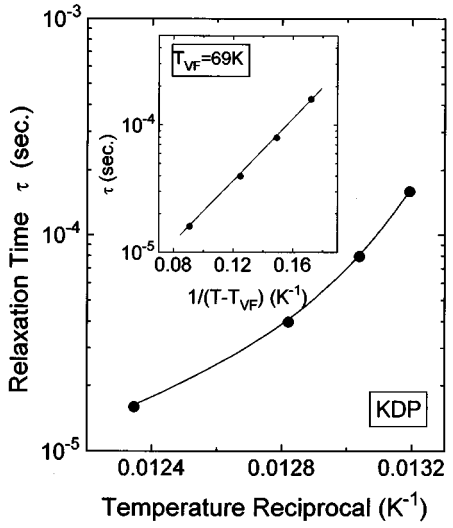

FIG. 3. Relaxation time τ related to domain freezing in KDP versus temperature reciprocal in the kHz range. Inset: relaxation time τ versus reciprocal of T-T_{VF} with T_{VF} being 69 K.

moves to higher temperature with increasing f. According to standard relaxation theory:[20] the relation between the relaxation time τ at T_P and f is that $2\pi f\tau(T_P)=1$, i.e.,$\tau(T_P)=1/2\pi f$. So, temperature dependence of τ can be obtained from the frequency dependence of T_P and has been shown in Figs. 3 and 4. Obviously, τ is not consistent with the Arrhenius relation [$\tau=\tau_0\exp(U/T)$] because there is a linear relation between the logarithm τ and the inverse temperature according to this relation,[20] but can be described by the Vogel-Fulcher formula[31,32] in both KDP and DKDP (inset of Figs. 3 and 4):

$$\tau=\tau_0\exp\left(\frac{U}{T-T_{\mathrm{VF}}}\right), \tag{1}$$

where T_{VF} is the Vogel-Fulcher temperature and its physical meaning will be discussed in the following.

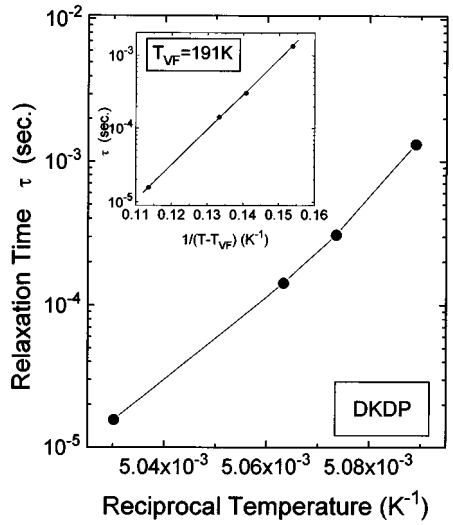

FIG. 4. Relaxation time τ related to domain freezing in DKDP versus temperature reciprocal in the kHz range. Inset: relaxation time τ versus reciprocal of T-T_{VF} with T_{VF} being 191 K.

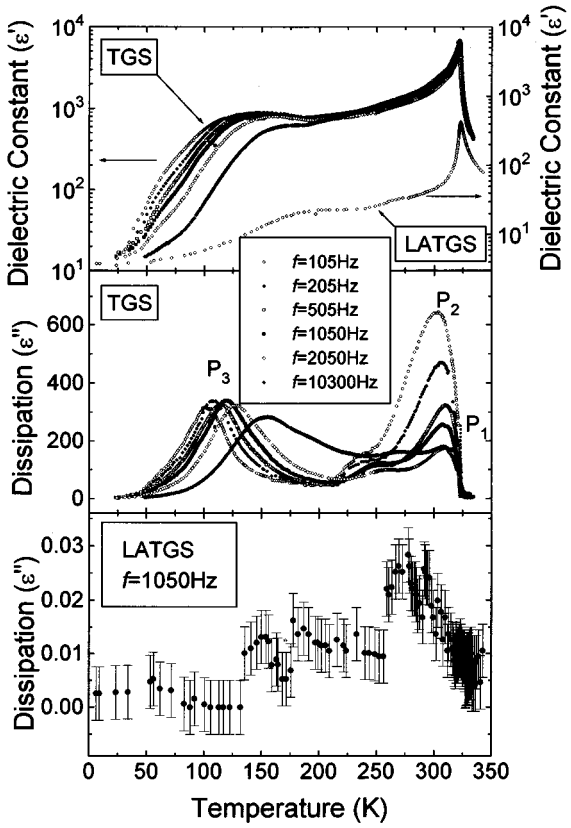

FIG. 5. Dielectric constant ϵ' and dissipation ϵ'' of TGS and LATGS versus temperature T and frequency f. The error bars of the dissipation data in LATGS indicate the measurement resolution.

The relaxation time τ of KDP and DKDP during domain freezing in the kHz range obtained by the present method seems different from those measured by the method of frequency scanning.[4,5,8,10–14] As aforementioned, this difference is due to the relaxation feature being smeared by the piezoelectric resonance around 10^5 Hz in the tetragonal KDP family,[4,5,10–14] when the method of frequency scanning is used. In fact, because the resonance does not exist in monoclinic CsH_2PO_4 (CDP), the relaxation time obviously obeys the Vogel-Fulcher relation.[12]

Shown in Fig. 5 is the temperature dependence of the dielectric constant ϵ' and dissipation ϵ'' in TGS and LATGS at different f. Identical to KDP and DKDP, there is also a λ-shaped peak of dielectric constant ϵ' just at T_C, and in a certain temperature range down from T_C, ϵ' exhibits an anomalously high value (a so-called ''plateau'' region) in TGS. Then at a temperature T_F, ϵ' sharply drops down to its phenomenological value. The ''kink'' position also moves to high temperature with increasing f.

The results of dissipation measurements of ϵ'' in TGS show that there are three peaks (P_1, P_2, and P_3) from 10 to 340 K, as shown in Fig. 5. The P_1 peak is always located at the critical point of the ferroparaelectric transition (T_C) as in Refs. 29 and 30, and the P_2 peak appears at ~10 K below T_C, whose high-temperature side tends to zero when temperature goes to T_C. These two peaks have been discussed by Wang and co-workers.[27–30] The asymmetric P_3 peak emerges around 100 K and the low-temperature side of P_3

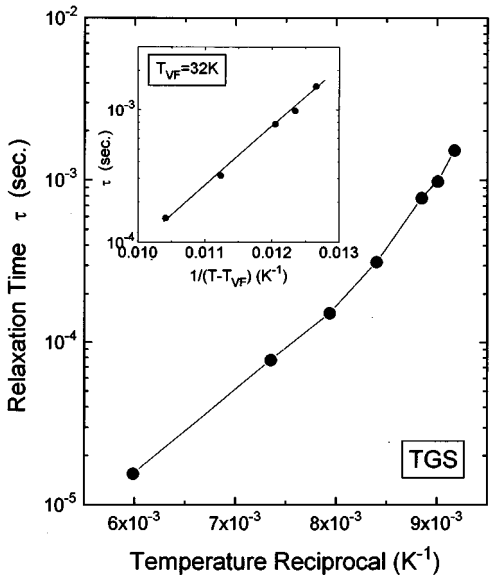

FIG. 6. Relaxation time τ of TGS versus temperature reciprocal in the kHz range. Inset: relaxation time τ versus reciprocal of T-T_{VF} with T_{VF} being 32 K.

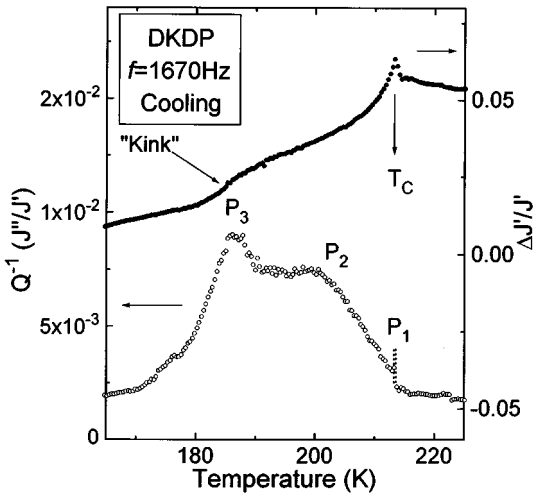

FIG. 7. Internal friction $Q^{-1}$and compliance J' of DKDP versus temperature T.

decreases more rapidly than its higher temperature side. These features of dissipation in TGS are also similar to that of the KDP family.[4–14]

In contrast, the dielectric constant of LATGS below T_C has the value predicted by the phenomenological Landau's theory, and the dissipation ϵ'' is $\sim 10^{-2}$ both below and above T_C (the error bars in the dissipation data in LATGS indicate the measurement resolution). This value is about 10^4 times smaller than that of TGS in its ferroelectric phase. As mentioned above, doping α-alanine into TGS induces an internal electric field that polarizes crystals to a monodomain state,[21–24] so it can be concluded that the ''kink'' in ϵ' and the P_3 peak of ϵ'' definitely originate from DW's through intercomparison of TGS and LATGS.

As shown in Fig. 5, the peak position T_P of P_3 shifts to high temperature with increasing frequencies f. In a same manner as that for KDP and DKDP, temperature dependence of the relaxation time τ can also be obtained from the frequency dependence of T_P (Ref. 20) and has been shown in Fig. 6. In TGS, τ is in accordance with an Arrhenius relation[20] at higher temperatures that is the same as that of Motegi, Ibaraki, and Nakamura,[16] but deviates from this relation at lower temperatures and also can be described by the Vogel-Fulcher formula [Eq. (1)] with T_{VF}=32 K (inset of Fig. 6). The reason why this low-temperature feature was not observed by Motegi, Ibaraki, and Nakamura[16] may be due to the paucity of data points (only three points) in Ref. 16. This feature is also slightly different from that of KDP and DKDP (Figs. 3 and 4), and it may originate because T_{VF} in TGS (32 K) is much lower than that in KDP (69 K) and DKDP (191 K). From Eq. (1), it is easily seen that $\tau = \tau_0 \exp(U/T)$ when $T_{\mathrm{VF}} \ll T$, i.e., an Arrhenius relation[20] at higher temperature.

Based on an analysis of relaxation time related to DW's and the similarity of dielectric constant ϵ' and dissipation ϵ'' in TGS and those in the KDP family, it can be concluded that there exists domain freezing in TGS with freezing temperature T_{VF} about 32 K.

As aforementioned, DKDP crystals undergo both ferroelectric and ferroelastic transitions at T_C,[6,25] and ferroelectric domain walls are also ferroelastic domain walls. So they can be driven by the external stress in internal friction measurements in a similar manner as that by an external electric field in dielectric measurements. Therefore, it is expected that internal friction Q^{-1} and compliance J' should have similar features as dielectric dissipation ϵ'' and dielectric constant ϵ' in DKDP.

The results of Q^{-1} and J' in DKDP versus temperature are shown in Fig. 7. Actually, they are quite similar to that of ϵ'' and ϵ', i.e., there is a λ-shaped peak of J' and a narrow Q^{-1} peak (P_1) just at T_C and another Q^{-1} peak (P_2) at $\sim$10 K below T_C. Between $\sim$190 to 210 K, there is a ''plateau'' region for J' and J'falls to a small value at $\sim$180 K. This feature also looks like a ''kink'' as for ϵ'. Within the temperature range of the ''kink,'' a Q^{-1} peak (P_3) emerges. Kuramoto,[4] Nakamura,[5] and Nakamura and Kuramoto[8] and Kubinec *et al.*[14] got the same temperature dependence of J' and Q^{-1}through a study of piezoelectric resonance effects in dielectric measurements. Therefore, internal friction measurements can be used to study domain freezing. One aspect we would like to stress is that the positions of the ''kink'' in J' and the P_3 peak of Q^{-1} is about 15 K lower than that in dielectric measurements, which means that apparent domain-freezing temperature is different between the two measurement methods. This difference may occur because the sample sizes used in the internal friction measurements are different to those in the dielectric measurements, for samples with different sizes have different freezing temperature as discovered by Bornarel,[6] and Bornarel and Torche.[7]

CuAlZnNi is ferroelastic and there are only ferroelastic domain walls,[19] so an electric field cannot cause them to move. Here, the internal friction method was used to study the dynamic properties of ferroelastic domain walls, and the results are shown in Fig. 8. Around 170 K there appears a ''kink'' in the compliance J' and an asymmetric Q^{-1} peak (P_3), and a P_2 peak is located at $\sim$20 K below M_S. This feature is quite similar to internal friction results in DKDP (Fig. 7). On the other hand, Wang *et al.*[9] discovered that the height of the P_3 peak of Q^{-1} is closely related to domain

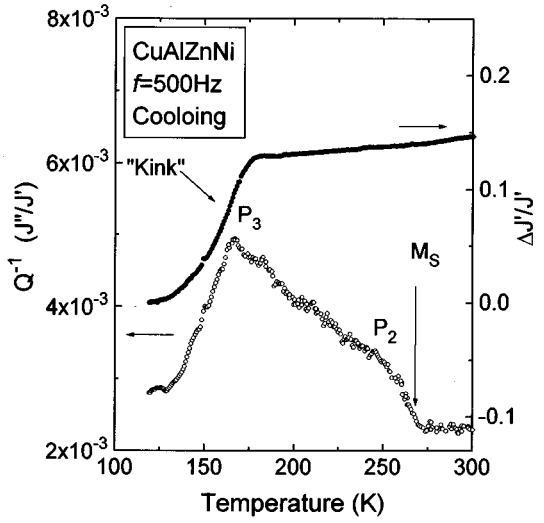

FIG. 8. Internal friction $Q^{-1}$and compliance J' of CuAlZnNi versus temperature T.

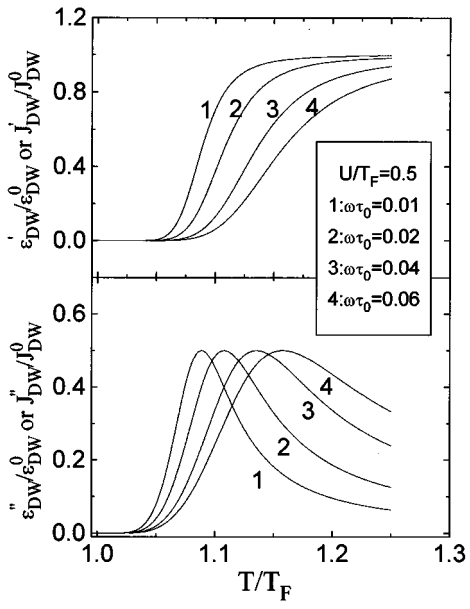

FIG. 9. Complex dielectric constant $\epsilon_{\mathrm{DW}}=\epsilon'_{\mathrm{DW}}-i\epsilon''_{\mathrm{DW}}$ and complex compliance $J_{\mathrm{DW}}=J'_{\mathrm{DW}}-iJ'_{\mathrm{DW}}$ ($Q^{-1}_{\mathrm{DW}}=J''_{\mathrm{DW}}/J'_{\mathrm{DW}}$) related to domain freezing versus temperature T calculated from Eqs. (7) and (9) with one set of U and τ_0 at different frequency $\omega(=2\pi f)$.

wall density. So it is inferred that the ''kink'' and the P_3 peak may be evidence of domain freezing in CuAlZnNi. Certainly further studies, such as varying frequencies, etc., are required to confirm this speculation.

IV. DISCUSSION

In the following, some striking features related to domain freezing are listed by summarizing Refs. 1–14 and our present results.

(1) Domain freezing exists not only in the KDP family[1–14] but also in TGS (Figs. 5 and 6), and there is preliminary evidence in CuAlZnNi (Fig. 8).

(2) During domain freezing, dielectric constant ϵ' and/or compliance J' decrease abruptly, and exhibit a ''kink.'' Within the temperature range of the ''kink,'' there appears a dissipation ϵ'' and/or internal friction Q^{-1} peak (P_3) which is asymmetric, i.e., its low-temperature side falls more rapidly than the high-temperature side[4,7,9,11,13,14] (Figs. 1, 2, 5, 7, and 8).

(3) There are two different relaxations that are all related to domain freezing. One appears in the kHz range, and the other around $\sim 10^8$ Hz. Their relaxation times can all be described by the Vogel-Fulcher relation [Eq. (1)][4,5,8,10,11–14] (Figs. 3, 4, and 6).

(4) Domain-freezing temperature T_F is dependent on defect density.[8,9]

(5) Domain freezing shows a size effect, i.e., domain-freezing temperature T_F decreases with increasing sample thickness d.[6,7]

(6) Domain-freezing temperature T_F shifts to low temperature when applied field increases,[7,9] and so on.

It is well known that defects can pin domain walls, and the fact that T_F is related to defects implies a model of domain freezing should take the pinning effect of defects to domain walls into account. In fact, Czarnecka, Stankowska, and Mielcarek[18] discovered that dielectric constant decreases with increasing concentration of L-threonine in TGS and they concluded that DW pinning plays an important role in the dielectric behavior.

As pointed out by Bornarel[6] and Bornarel and Torche,[7] one must consider the size effect of domain freezing, i.e., the dependence of T_F on sample thickness d, when a domain-freezing model is put forward. Experimental results show the relation between sample thickness $d$and the DW density N is that $N\sim 1/\sqrt{d}$ approximately,[33] and it is confirmed that the interaction between DW's becomes stronger with increasing N through both experimental observations[6,7,27,28] and theoretical calculations.[29,30] Therefore, the size effect of domain freezing implies that domain freezing is closely related to the interaction between domain walls.

The Vogel-Fulcher relation [Eq. (1)] indicates that relaxation time $\tau\rightarrow\infty$ at a nonzero temperature T_{VF} and it is usually used to describe the relaxation process related to phase transitions, such as the glass transition in polymers[34] and the melting transition in solids.[35] It is based on this that Kuramoto and co-workers[4,8,10] and Nakamura[5] proposed that domain freezing is a glass transition of dipoles in domain walls, but the DW pinning and the size effect of domain freezing were not taken into account by their model. Therefore, it is speculated that domain freezing may be a transition at T_{VF} with an order that appears on cooling or disappears on heating, and this order is closely related to the defect pinning to domain walls and the interaction between DW's. A supporting fact is that the collective-pinning effect of defects to flux[36–39] has these features. So in the same manner as that of flux pinning, the following is proposed.

(i) At low temperature, there exists collective pinning to DW's between randomly distributed defects, i.e., the pinning of different defects in a certain area in the DW plane is correlative; at the same time, the motion of DW's near the pinned walls is also restricted due to the interaction between

them. So, an effective pinning region ΔR like a bundle of vortices[3–39] forms, and the pinning in ΔR is correlative, i.e., a local order ΔR appears. According to Refs. 36–39, the collective-pinning energy $U_{\rm CP}$ is,

$$U_{\rm CP}=\sqrt{\langle U_{\rm IP}(\mathbf{r},\mathbf{u})U_{\rm IP}(\mathbf{r}',\mathbf{u}')\rangle}=U_{\rm CP}(\mathbf{r}-\mathbf{r}',\mathbf{u}-\mathbf{u}'), \quad (2)$$

where $\mathbf{r}$ is the position of a defect, $\mathbf{u}$ is the displacement vector of a DW, and $U_{\rm IP}(\mathbf{r},\mathbf{u})$is the individual pinning energy. One important effect of collective pinning is that $U_{\rm CP}\gg U_{\rm IP}$.[36–39]

(ii) With increasing temperature, collective pinning becomes weaker and local order ΔR decreases due to thermal fluctuations, and at a certain temperature T_F this correlation will be destroyed totally, i.e., $\Delta R=0$. At the same time, $U_{\rm CP}$ falls abruptly to $U_{\rm IP}$, i.e., the temperature dependence of pinning energy $U_{\rm PIN}$ near T_F is

$$U_{\rm PIN}=\begin{cases} U_{\rm CP} & \text{when } T<T_F \\ U_{\rm IP} & \text{when } T\geqslant T_F \end{cases} \xrightarrow{U_{\rm CP}\gg U_{\rm IP}} \begin{cases} \infty & \text{when } T<T_F \\ U_{\rm IP} & \text{when } T\geqslant T_F \end{cases} \quad (3)$$

or

$$\frac{1}{U_{\rm PIN}}=\begin{cases} 0 & \text{when } T<T_F \\ \dfrac{1}{U_{\rm IP}} & \text{when } T\geqslant T_F. \end{cases} \quad (4)$$

By taking into account the sharp but continuous change of pinning energy $U_{\rm PIN}$ near T_F, $1/U_{\rm PIN}$ can be expanded approximately as the following:

$$\frac{1}{U_{\rm PIN}}=\begin{cases} 0 & \text{when } T<T_F \\ \dfrac{T/T_F-1}{U} & \text{when } T\geqslant T_F \end{cases} \quad (5)$$

or

$$U_{\rm PIN}=\begin{cases} \infty & \text{when } T<T_F \\ \dfrac{U}{T/T_F-1} & \text{when } T\geqslant T_F. \end{cases} \quad (6)$$

Based upon Boltzmann statistics,[20] the relation between the relaxation time τ during domain freezing and the pinning energy $U_{\rm PIN}$ is

$$\tau=\tau_0\exp(U_{\rm PIN}/T) = \begin{cases} \tau_0\exp\left(\dfrac{U}{(T/T_F-1)T}\right) \xrightarrow{\text{near } T_F} \tau_0\exp\left(\dfrac{U}{T-T_F}\right) & \text{for } T>T_F \\ \to\infty & \text{for } T\leqslant T_F. \end{cases} \quad (7)$$

Equation (7) is just the Vogel-Fulcher relation [Eq. (1)] with $T_{\rm VF}$ equal to T_F. This means that the model proposed here can describe the relaxation related to domain freezing. Domain freezing is a process in which a local pinning order ΔR appears due to collective-pinning effect, and the effective pinning energy increases abruptly during this process, which leads to the relaxation time in accordance with the Vogel-Fulcher relation.[31,32] According to standard relaxation theory,[20] it is found that the complex dielectric constant $\epsilon_{\rm DW}=\epsilon'_{\rm DW}-i\epsilon''_{\rm DW}$ and complex compliance $J_{\rm DW}=J'_{\rm DW}-iJ'_{\rm DW}$ ($Q^{-1}_{\rm DW}=J''_{\rm DW}/J'_{\rm DW}$) due to the relaxation of DW's during domain freezing are

$$\epsilon_{\rm DW}=\epsilon'_{\rm DW}-i\epsilon''_{\rm DW}=\begin{cases} \displaystyle\int_0^\infty \epsilon^0_{\rm DW}\frac{g(\tau)}{1+i\omega\tau}\frac{d\tau}{\tau} & \text{for } T>T_F \\ \to 0 & \text{for } T\leqslant T_F \end{cases} \quad (8)$$

and

$$J_{\rm DW}=J'_{\rm DW}-iJ''_{\rm DW}=\begin{cases} \displaystyle\int_0^\infty J^0_{\rm DW}\frac{g(\tau)}{1+i\omega\tau}\frac{d\tau}{\tau} & \text{for } T>T_F \\ \to 0 & \text{for } T\leqslant T_F, \end{cases} \quad (9)$$

where $\epsilon^0_{\rm DW}$ and $J^0_{\rm DW}$ are the dielectric constant and compliance in the low-frequency limit, respectively, and $g(\tau)$ is the distribution function of τ.

According to Eqs. (7)–(9), Fig. 9 shows the calculated results for the complex constant $\epsilon_{\rm DW}=\epsilon'_{\rm DW}-i\epsilon''_{\rm DW}$ and the complex compliance $J_{\rm DW}=J'_{\rm DW}-iJ''_{\rm DW}$ ($Q^{-1}_{\rm DW}=J''_{\rm DW}/J'_{\rm DW}$) related to domain freezing versus temperature at different frequencies f. We do not fit Eqs. (7)–(9) with experimental data here because of the influence of the P_2 dissipation peak on the high-temperature side of P_3 (Figs. 1, 2, 5, 7, and 8). Nevertheless, the calculated results indicate that Eqs. (7)–(9) can describe the specific features of dielectric constant ϵ', dissipation ϵ'', compliance J',and internal friction Q^{-1} (''kink'' and P_3 peak) qualitatively. Certainly, further quantitative calculations are desirable.

What is discussed above is the pinning of defects to DW's and their influence on the relaxation of DW's. Conversely, the reaction of DW's to defects will also affect the relaxation of defects. If there is no interaction between DW's and defects, they will each relax according to a relaxation law. When the interaction is weak, these two relaxations will couple with each other, which is similar to the coupling of two resonators and the hybridizing of atomic or molecular-energy levels,[40] and two relaxations appear: one relaxation is similar to (but different from) the individual relaxation of DW's, which is called DW dominant relaxation for simplifi-

cation; the other is similar to the individual relaxation of defects, and is called defect-dominant relaxation. When the interaction is strong enough, the difference between DW dominant relaxation and defect-dominant relaxation will disappear. Obviously, the discussion based on the collective pinning of defects to DW's aforementioned expresses the DW dominant relaxation; we will discuss the defects-dominant relaxation next.

Below the domain-freezing point T_F, the interaction between DW's and defects is strong; as discussed above, defect-dominant relaxation should have the same relaxation features as DW dominant relaxation, and its relaxation time $\tau' \to \infty$. With increasing temperature, the interaction between DW's and defects becomes weaker because of thermal fluctuations, and the difference between defect-dominant relaxation and DW dominant relaxation becomes obvious. But temperature dependence of the relaxation time τ' of defect-dominant relaxation should also have the form of the Vogel-Fulcher relation near T_F:

$$\tau' = \begin{cases} \tau_0' \exp\left(\dfrac{U'}{T - T_{\rm VF}}\right) & \text{for} \quad T > T_F \\ \to \infty & \text{for} \quad T \leqslant T_F \end{cases}, \tag{10}$$

where τ_0' is the relaxation time in the high-temperature limit, and U' is nominal activation energy.

Also based upon standard-relaxation theory,[20] it is found that the complex-dielectric constant $\epsilon_{\rm DF} = \epsilon_{\rm DF}' - i\epsilon_{\rm DF}''$ and the complex compliance $J_{\rm DF} = J_{\rm DF}' - iJ_{\rm DF}''$ ($Q_{\rm DF}^{-1} = J_{\rm DF}''/J_{\rm DF}'$) are related to defect-dominant relaxation near T_F as

$$\epsilon_{\rm DF} = \epsilon_{\rm DF}' - i\epsilon_{\rm DF}'' = \begin{cases} \displaystyle\int_0^\infty \epsilon_{\rm DF}^0 \frac{g'(\tau')}{1 + i\omega\tau'} \frac{d\tau'}{\tau'} & \text{for} \quad T > T_F \\ \to 0 & \text{for} \quad T \leqslant T_F \end{cases} \tag{11}$$

and

$$J_{\rm DF} = J_{\rm DF}' - iJ_{\rm DF}'' = \begin{cases} \displaystyle\int_0^\infty J_{\rm DF}^0 \frac{g'(\tau')}{1 + i\omega\tau'} \frac{d\tau'}{\tau'} & \text{for} \quad T > T_F \\ \to 0 & \text{for} \quad T \leqslant T_F, \end{cases} \tag{12}$$

where $\epsilon_{\rm DF}^0$ and $J_{\rm DF}^0$ are the dielectric constant and compliance in the low-frequency limit, respectively, and $g'(\tau')$ is the distribution function of τ'.

A size of DW's that is much larger than that of point defects, so the relaxation time τ of DW's should be much longer than τ' for defects, and DW dominant relaxation will appear in the low-frequency range and defect-dominant relaxation at higher frequencies.[20] As mentioned above, some experiments show that there actually exist two relaxations in the kHz (Ref. 12, Figs. 1–6) and $\sim 10^8$ Hz[4,5,8,10–14] ranges, respectively, and both of them are related to domain freezing with their relaxation times being consistent with the Vogel-Fulcher relation [Eqs. (1), (7), and (10)]. Kuramoto[4] and Nakamura[5] confirmed that the relaxation in the kHz range is due to lateral movement of DW's, and relaxation in the 10^8 Hz region is also correlated with DW's, but does not originate from the motion of DW's. According to the model proposed presently, these two relaxations can be explained as DW dominant relaxation (low-frequency range) and defect-dominant relaxation (high-frequency interval). In fact, the equations used to fit experiments in the 10^8 Hz region in Refs. 4, 5, 8, and 10–14 are the same as Eqs. (11) and (12), and are obtained from the temperature dependence of relaxation time just as in Eq. (10).

In the present model, an effective-pinning region ΔR will form due to the collective pinning and interaction between DW's, and this leads to an increase of effective pinning energy $U_{\rm PIN}$. Obviously, the stronger the interaction is, the larger $U_{\rm PIN}$ is and the ability to resist thermal fluctuations increases: as a result, the domain-freezing temperature T_F shifts to higher temperature. On the other hand, DW density increases as the sample thickness decreases,[33] and the interaction between DW's becomes stronger.[6,7,26–30] So, it is concluded that T_F increases with decreasing sample thickness d. This conclusion is just the size effect of domain freezing that plays an important role in domain freezing as stressed by Bornarel[6] and Bornarel and Torche.[7] However, further quantitative studies are required.

The model proposed here has taken the collective pinning of defects to DW's into account. It is obvious that domain freezing is related to defects and the effective pinning energy $U_{\rm PIN}$ increases with increasing defect density: as a result T_F shifts to higher temperature. In samples irradiated by γ-rays, electrons, neutrons, and other particles, which lead to an increase of defect density, T_F moves to high temperatures.[9] But in ''lossy'' KDP (KDP doped with KOH), T_F decreases with increasing concentration of KOH.[8] Bornarel[6] pointed out that domain texture may be changed in ''lossy'' KDP due to doping of KOH, so further studies on this problem are required.

When an external field is applied to samples, a configuration force appears that is proportional to the external field,[29,30] and will cause DW's to move laterally. This force also leads to a tilt of DW pinning wells with a decrease of the effective-pinning energy of DW's and their ability to resist thermal fluctuations: as a result, T_F shifts to lower temperatures. In a strong field, some DW's in samples will disappear,[6,7] i.e., DW density becomes smaller, so the interaction between DW's will decrease.[6,7,26–30] Based on the present model, this will also lead to a decrease of effective pinning energy, and as a result, decrease of T_F.

In the case of vortices, the collective pinning will lead the flux lattice to form a pinned vortex glass.[36–39] The DW's arrange themselves as a superlattice[41–44] due to the interactions between them. There are questions regarding the collective pinning leading the superlattice to form pinned-domain-wall glass. There is not yet any direct evidence of such glass, and further studies are needed.

V. CONCLUSION

(1) By the method of temperature scanning, the temperature and frequency dependence of dielectric constant and dissipation in KDP and DKDP has been studied, and it is found that the relaxation time of domain freezing in the kHz range can be described by the Vogel-Fulcher relation, which is similar to that in the 10^8 Hz range.

(2) By the same method, the temperature and frequency

dependence of dielectric constant and dissipation in TGS and LATGS has also been studied. Evidence for domain freezing in TGS is presented through an analysis of relaxation time related to domain walls and intercomparison between TGS and LATGS.

(3) Studies of internal friction and compliance show preliminary evidence of domain freezing in CuAlZnNi alloy.

(4) A domain-freezing model is proposed based upon the collective pinning of randomly distributed pinning centers to domain walls, and some key experiments related to domain freezing, such as (1) the Vogel-Fulcher relation for relaxation time; (2) the size effect of domain freezing; (3) two kinds of relaxation in low- and high-frequency ranges, respectively; and (4) the dependence of T_F on applied field and defects, etc. are explained.

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