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Dielectric dispersion at the zero-field lock-in transition in thiourea crystal

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Splitting of the dielectric-constant peak at $T \simeq 177.1$ K was observed in the high-frequency measurements at zero bias field in the very narrow range of temperature across the $\frac{1}{8}$ lock-in transition in thiourea. This frequency-dependent splitting of the dielectric-constant peak associated with the $\frac{1}{8}$ lock-in transition could be explained in terms of temperature-dependent relaxation time.

Thiourea crystal [$SC(NH_2)_2$], a classic system of the type-II incommensurate phase transition, has a wide range of temperature from $T_I = 202$ K to $T_C = 169$ K showing the incommensurate state at zero external field.[1] External application of pressure[2] or electric field,[3-7] however, reveals lock-in phases of commensurate modulation wave vectors at $\delta = \frac{1}{3}, \frac{1}{7}, \frac{1}{8}$, and $\frac{1}{9}$ inside the incommensurate region. The $\frac{1}{9}$ lock-in phase was revealed also at zero external fields,[1,3,4,8,9] but the $\frac{1}{8}$ lock-in phase was marginal in the experimental findings at zero bias fields. The $\frac{1}{8}$ lock-in phase has drawn special attention for apparently contradictory results of some experimental observations: no zero-field anomalies in neutron diffraction,[4] birefringence,[6] and heat capacity,[8] but a large anomaly in the zero-field dielectric susceptibility.[3,8] The stability range of the $\frac{1}{8}$ lock-in phase was found to be as narrow as 0.5 K at zero field, but increase nonlinearly with applied bias field E.[5] The stable region of the $\frac{1}{8}$ lock-in phase widens and shifts with increasing bias fields so that at higher bias fields the dielectric anomalies observed at the separated boundaries of the lock-in phase may appear as a splitting of the single peak of dielectric anomaly at zero bias field.[5] This field dependence of the $\frac{1}{8}$ lock-in phase stability was confirmed in the neutron-diffraction experiment where the lock-in plateau for the commensurate modulation wave vector at $\delta = \frac{1}{8}$ was observed in the different ranges of temperature depending on the bias field strength.[7] The $\frac{1}{8}$ lock-in phase is also ferroelectric with a very small spontaneous polarization of the order of 10^{-3} times the value of the low-temperature ferroelectric phase below $T_C = 169$ K.[1,8] Since the $\frac{1}{8}$ lock-in phase is a polar phase with a finite spontaneous polarization we may expect domain-wall structures in this intermediate ferroelectric phase associated with the discommensuration.[3] We can thus expect to observe a dielectric dispersion in this lock-in phase as for the normal ferroelectrics of a finite domain-wall mobility. In the previous works the bias field effect has been a focus of concern, and the frequency dependence has not been considered in the study of the $\frac{1}{8}$ lock-in phase. However, a distinct difference can be noticed between dielectric data of different authors corresponding to low frequency[1] and very high- frequency[9,10] measurements.

Single crystal of thiourea was grown by a slow evaporation from the saturated solution of thiourea in methanol. Samples of size $7 \times 5 \times 0.5$ mm^3 were vacuum coated with aluminium for capacitor electrodes. An impedance analyzer (HP4192A) was employed to measure capacitance and dielectric loss of the sample in the cryostat in the frequency range between 10 kHz to 13 MHz. Two different procedures, that is, varying frequencies at each of fixed temperatures and varying temperatures at each of fixed frequencies were found to give the same results within the range of experimental errors.

In Fig. 1 we show the dielectric-constant dependence on temperature at various frequencies as measured for thiourea crystal in both the cooling [Fig. 1(a)] and the warming cycles [Fig. 1(b)]. At frequencies of 10 and 100 kHz no splitting was observed but splitting was observed at frequencies higher than 630 kHz. With increasing frequency of the probe field the separation of the split peaks was observed to increase. The observed maximum peak temperatures are plotted as a function of the probe frequency in Fig. 2, where we find a splitting of ~ 1 K at 10 MHz and a small thermal hysteresis between cooling and warming cycles. This small thermal hysteresis may be understood if we recall the so-called global hysteresis existing in the whole range of incommensurate phase[11] so that modulation wave vector measurements (δ) and lock-in anomaly peak temperature ($T_{1/8}$) are observed to be different between cooling and warming cycles. Memory effects do appear usually in the case of fixing at definite temperatures for over several hours. We may also expect that the competing interactions in the narrow region of the $\frac{1}{8}$ lock-in transition would put the system very unstable as in the metastable states of the first-order transition. We have also confirmed the same results of observation between the two cases: varying frequencies at each of fixed temperatures and varying temperatures at each of fixed frequencies, which also suggests no significant memory effect in the present results of ours. However, our thermal cycling was limited to the narrow range of temperature in the neighborhood of the $\frac{1}{8}$ lock-in transition. The experimental results of ours at zero bias field resemble very much the bias field-induced splitting of the same dielectric anomaly.[5]

The lock-in transition is derived from the competition between the umklapp terms of the periodic lattice potential and the long-range elastic interactions.[12] In the

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specific case of the $\frac{1}{8}$ lock-in phase the umklapp interaction P_q^n is given as coupled with the macroscopic polarization P_0 so that dc bias field should enhance the lattice potential contribution to widen the stability range of the $\frac{1}{8}$ lock-in phase.[3,13] This theory may well explain the dc bias field-induced splitting of the dielectric-constant peak associated with the $\frac{1}{8}$ lock-in transition, but does not explain well our observation of the frequency-dependent splitting of the same dielectric-constant peak. We may first question if there may be a dispersion effect in the frequency range of our measurements in this $\frac{1}{8}$ lock-in phase. In Fig. 3 we present Cole-Cole plots[14] of our dielectric data at several temperatures within the lock-in phase. From the Cole-Cole plots we can confirm some dipolar relaxations in the narrow temperature range from 176.87 to 177.35 K but no signs of relaxation at temperatures either above 177.45 or below 176.75 K. Although the Cole-Cole plot is not exactly the semicircle corresponding to one single Debye relaxation time we may as-

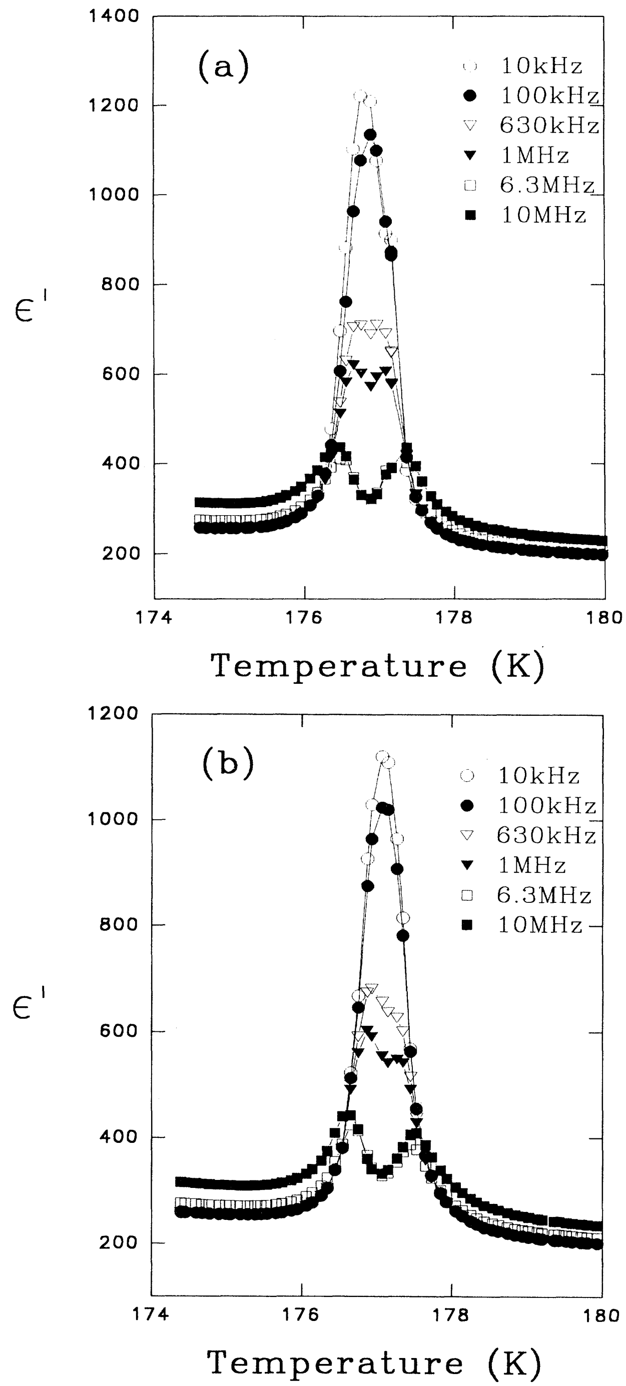

FIG. 1. Temperature dependence of dielectric constant ϵ' as observed in (a) the cooling cycle and also in (b) the warming cycle at several frequencies of 10 kHz (○), 100 kHz (●), 630 kHz (▽), 1 MHz (▼), 6.3 MHz (□), and 10 MHz (■).

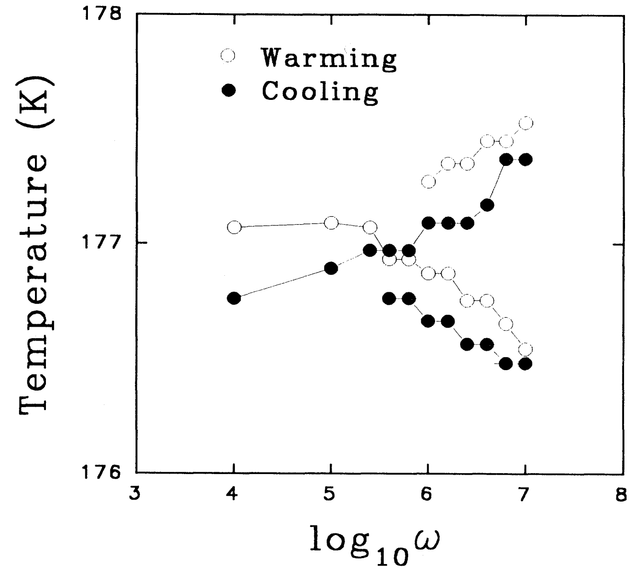

FIG. 2. Splitting (ΔT) dependence on frequency of the $\frac{1}{8}$ lock-in transition anomaly peak of dielectric constant for warming (○) and cooling (●) cycles.

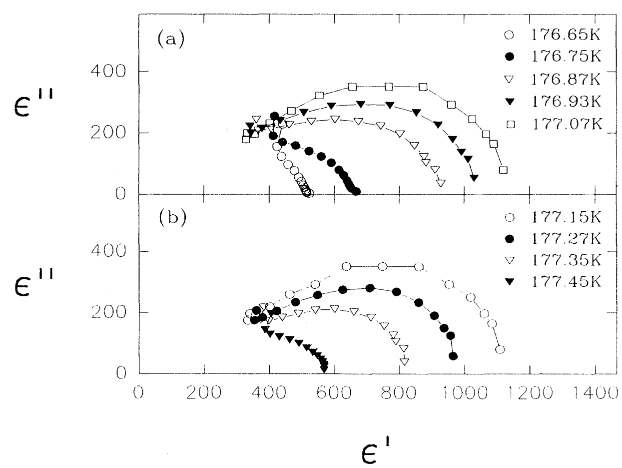

FIG. 3. Cole-Cole plots between real (ϵ') and imaginary (ϵ'') parts of dielectric constants measured as a function of frequency at several temperatures in the $\frac{1}{8}$ lock-in phase for a $T < 177.10$ K (a) and (b) for $T > 177.10$ K.

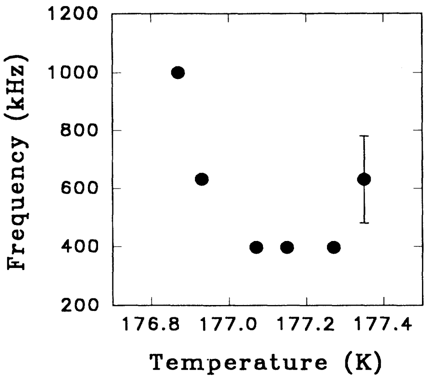

FIG. 4. Effective relaxation frequency $[\Omega(T)=1/\tau(T)]$ dependence on temperature as obtained from the Cole-Cole plots of Fig. 3. Error bar is indicated at the data point for $T=177.35$ K.

sign an effective relaxation frequency as corresponding to the midpoint extremal of the semicircular arc. In Fig. 4 we show the effective relaxational frequency dependence on temperature as obtained from the Cole-Cole plots, where the relaxational frequency is seen to decrease rapidly as the temperature reaches 177.1 K corresponding to the midpoint of the narrow range $\frac{1}{8}$ lock-in phase. If we assume the semicircular Cole-Cole plot corresponding to the effective Debye relaxation, we may well use

$$\epsilon'(T,\omega)=\frac{\epsilon'(T,\omega=0)}{1+\omega^2\tau^2(T)} \tag{1}$$

to fit our experimental data $\epsilon'(T,\omega)$ of Fig. 1, where $\tau(T)$ represents the effective relaxation time. Since no significant difference is found between 10 Hz and 10 kHz,[3] we have used our data of $\epsilon'(T,\omega=10\text{ kHz})$ to obtain $\epsilon'(T,\omega=0)$. The best fit to our 10 kHz data then gives

$$\epsilon'(T,\omega=0)=\frac{C_M}{B_M+(T-T_M)^2} . \tag{2}$$

Similarly for $\tau(T)$ the relaxation frequency data $\Omega(T)$ of Fig. 4 was used to obtain the best fit function as given by

$$\Omega(T)=\frac{1}{\tau(T)}=C_m(T-T_m)^2+\Omega_m . \tag{3}$$

Using Eq. (1) and the best fit functions for $\epsilon(T,\omega=0)$ and $\tau(T)$ we have obtained $\epsilon'(T,\omega)$ curves of Fig. 5 showing a splitting at $\omega>630$ kHz in the same temperature region as Fig. 1.

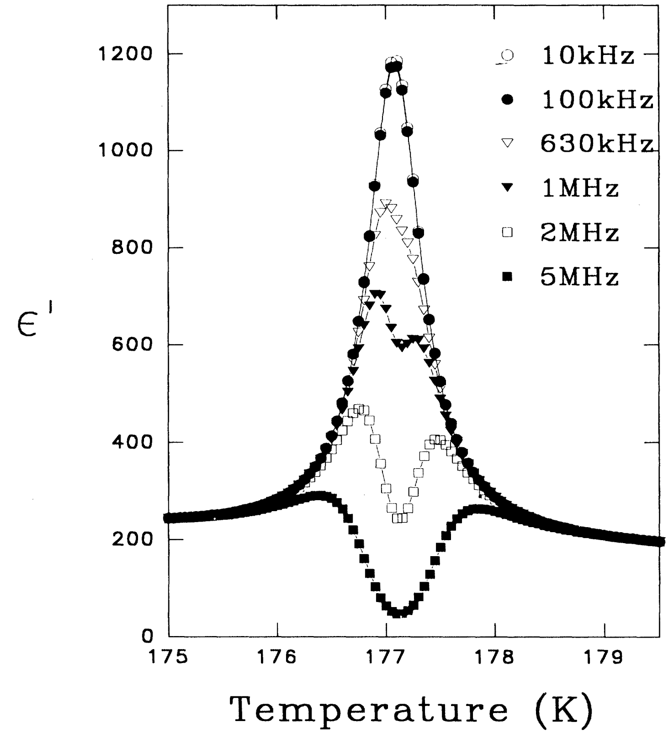

FIG. 5. Calculated temperature dependence of dielectric constant ϵ' at several frequencies from 10 kHz to 5 MHz on the basis of the effective Debye relaxation of Eq. (1) in the text.

Although the rigorous analysis may require a full set of dielectric data extending beyond the frequency range of our measurements, and correspondingly a modified Cole-Cole plot we may still conclude that there is certainly a very narrow range ($\sim$0.5 K) of dielectric relaxation (possibly discommensurations) at relatively low frequencies associated with the $\frac{1}{8}$ lock-in transition at zero bias field.

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