Instability of the dielectric constant of $Cd_2Nb_2O_7$

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An anomalous instability (over time) and an anomalous thermal hysteresis of the dielectric constant have been discovered in $Cd_2Nb_2O_7$ in the temperature interval 40–80 K. The $Cd_2Nb_2O_7$ may contain an incommensurate phase in the temperature interval 80 K $= T_5 > T > T_6 =$ 44 K.

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Five phase transitions occur[1] in $Cd_2Nb_2O_7$, at $T_1 = 200$, $T_2 = 196$, $T_3 = 188$, $T_4 = 83$, and $T_5 = 80$ K. At room temperature the crystal has the space group $Fd3m\text{-}O_h^7$; the symmetry of the low-temperature phases has not been established. Below $T_{Curie} = T_3$, $Cd_2Nb_2O_7$ is a ferroelectric.[2] The ferroelectric properties of $Cd_2Nb_2O_7$ single crystals have not been studied adequately.

It has been suggested[3] that yet another phase transition may occur in $Cd_2Nb_2O_7$, at a temperature T_6 roughly in the interval 50–70 K. In the present experiments we studied the dielectric function $\epsilon(T)$ and the loss tangent $\tan\delta$ in $Cd_2Nb_2O_7$ at low temperatures. The samples were single crystals; the measurements were carried out at a frequency of 1 kHz in an alternating electric field of 6 V/cm, applied along the [111] direction. The sample temperature was regulated within ± 0.01 K.

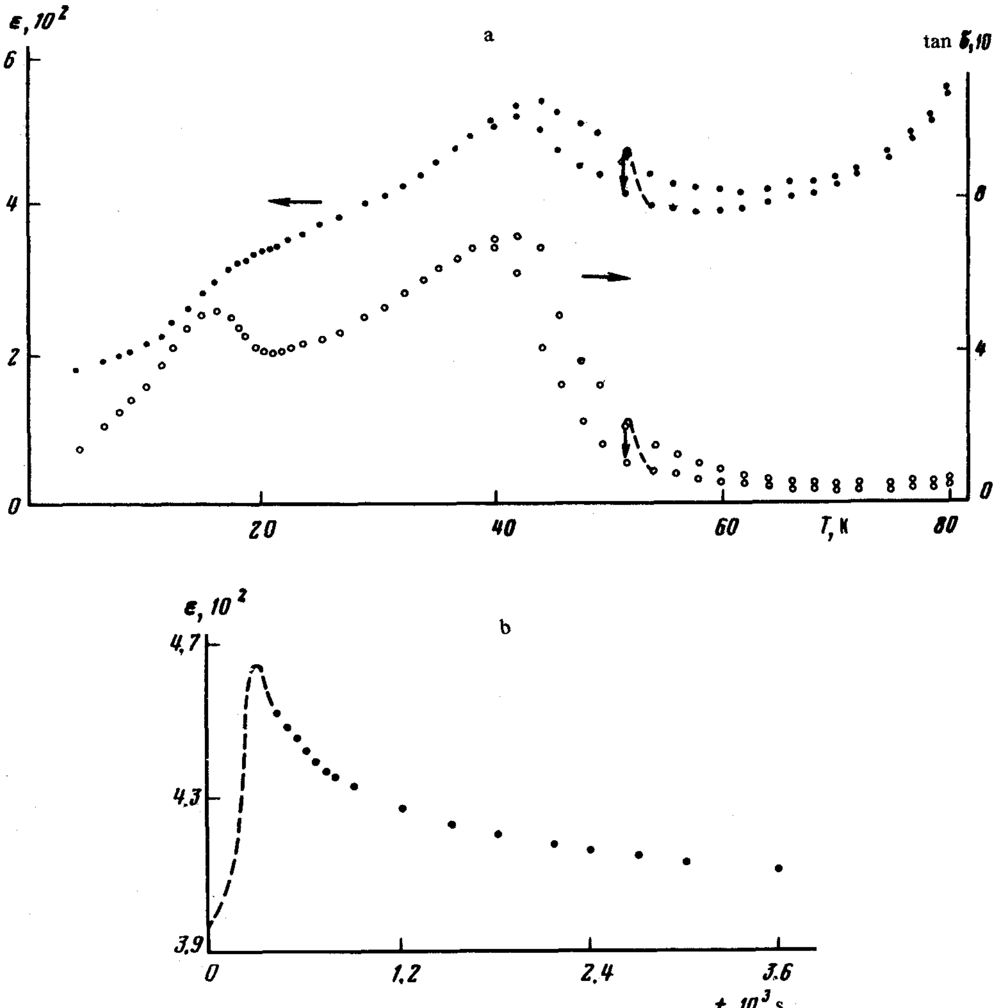

FIG. 1. a—Temperature dependence of ϵ and $\tan\delta$ in $Cd_2Nb_2O_7$, obtained as the sample was cooled. At a given temperature, the higher value is observed when the sample reaches the given temperature, and the lower value is observed 40 min later; b—time dependence of ϵ in $Cd_2Nb_2O_7$ at $T' = 51.7$ K. The dashed curve shows the behavior of ϵ and $\tan\delta$ as the temperature is lowered from $T'' = 53.9$ to $T' = 51.7$ K.

The anomalous features on the $\epsilon(T)$ and $\tan\delta$ curves (Fig. 1a) confirm that a phase transition[3] occurs at $T_6 = 44$ K, and they also indicate a phase transition in $Cd_2Nb_2O_7$ at $T_7 = 19$ K. The anomalous feature at T_6 is accompanied by a thermal hysteresis typical of a first-order phase transition: When the sample is heated, the maximum on the $\epsilon(T)$ curve is observed at 46 K, but when the sample is cooled the maximum occurs at 44 K. Over the temperature interval 60–75 K, $\tan\delta$ is small, on the same order of magnitude as in the paraelectric phase, i.e., $\sim 2\times 10^{-3}$. Over the temperature interval 40–80 K, there are an anomalous instability over time and an anomalous thermal hysteresis of the dielectric function, which indicate that the phase transition at T_6 is not an ordinary structural phase transition.

The instability of the dielectric function and of the loss tangent in $Cd_2Nb_2O_7$ is observed in the vicinity of T_5 and T_6 but not in the vicinity of other phase transitions. This instability consists of a decrease in $\epsilon(T)$ and $\tan\delta$ over time at a fixed temperature; the instability becomes significant at temperatures below ~ 75 K (as indicated schematically by the solid arrow in Fig. 1a). This instability is observed above the phase transition temperature. As T_6 is approached from above, the instability intensifies: There is a progressively greater decrease in ϵ and $\tan\delta$ over time, and the time required for relaxation to an equilibrium value increases. Figure 1b shows a representative time dependence of ϵ. This is the first observation of this type of anomalous instability of the dielectric constant over time at ferroelectric phase transitions[4] or at incommensurate-commensurate phase transitions.[5,6]

Furthermore, in the temperature interval in which the dielectric function is unstable it exhibits an anomalous thermal hysteresis. This hysteresis is of the same nature as that observed at incommensurate-commensurate structural phase transitions in Rb_2ZnCl_4, Rb_2ZnBr_4 (Ref. 5), and $(NH_4)_2BeF_4$ crystals.[6] In $Cd_2Nb_2O_7$ the hysteresis is observed near T_5 and T_6 even when the heating and cooling are alternated without passage through T_6 (Fig. 2). In $Cd_2Nb_2O_7$, in contrast with Refs. 5 and 6, the dielectric

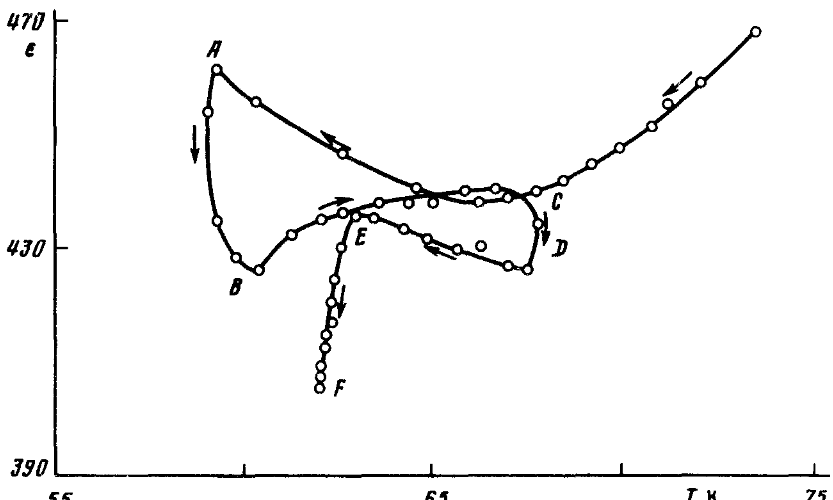

FIG. 2. The thermal hysteresis of $\epsilon(T)$ above T_6.

constant changes as we go from the cooling curve to the heating curve (or vice versa); instead it changes in a more complicated way (curves ABC and CDE in Fig. 2). The decrease in ϵ in regions AB, CD, and EF illustrates the temporal instability of the dielectric function.

These aspects of the behavior of the dielectric constant in $Cd_2Nb_2O_7$ seem to be linked to a metastable domain structure near T_5 and T_6. One possible manifestation of this sort of quasidomain structure (solitons) is seen in the incommensurate phase. According to Refs. 7–9, an unstable quasidomain structure is observed in the incommensurate phase as the temperature of the incommensurate-commensurate phase transition is approached ($T_c = T_6$ in this particular crystal). Since the sinusoidal shape of the incommensurate wave is distorted here, and the modulation period increases, the thickness of the quasidomain walls decreases, and the distance between them increases. Such changes should cause an increase in the dielectric constant, an instability of this constant over time, and a thermal hysteresis.

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