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Equation of state for the pressure- and temperature-induced transition in ferroelectric telluric acid ammonium phosphate

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A careful experimental investigation of the ferroelectric-paraelectric transition in uniaxial ferroelectric telluric acid ammonium phosphate induced by pressure and by temperature in the vicinity of the phase transition has been carried out. Dielectric-constant and hysteresis-loop data allow the determination of the combined equation of state as a function of both temperature and pressure, relating accurately polarization, field, pressure, and temperature in the neighborhood of the transition.

Solid-state pressure-induced phase transitions are similar to temperature-induced phase transitions in many respects. The analogy between the role played by hydrostatic pressure in the former case, with the role played by thermal energy, in the latter, can be exploited to obtain a compact equation of state describing simultaneously the pressure and the temperature dependence of the relevant pair of conjugated variables (polarization and electric field in a ferroelectric). To make a proper quantitative investigation of the equation of state in the vicinity of the transition, accurate data, in terms of the hydrostatic pressure as well as in terms of temperature, are needed. Uniaxial ferroelectric telluric acid ammonium phosphate[1–8] (TAAP) chemical formula $|Te(OH)_6|\cdot|2NH_4H_2PO_4|\cdot|(NH_4)_2PO_4|$, is a good candidate for investigation, because it has (for ambient pressure, 1 bar) a second-order phase transition[2] to the paraelectric state at $T_c(0)\approx 320$ K, conveniently above room temperature, and also because it possesses a negative pressure coefficient,[4,5] $dT_c(p)/dp\approx -3.58$ °C/kbar, which allows investigation of pressure-induced transitions at constant temperatures between room temperature and 320 K. This crystal is monoclinic at room temperature ($Pn, Z=2$). At the ferroelectric transition the change in space group is $P2/n \leftrightarrow Pn$. The main feature of the atomic arrangement is the presence of two distinct anionic groups: TeO_6 and PO_4. Two types of planes perpendicular to the [101] direction can be distinguished. In the first type one can find PO_4 groups and NH_4O_n polyhedra, while in the second one, one has TeO_6 groups in addition to PO_4 groups and NH_4O_n polyhedra.[6] Four types of hydrogen bonds N-H-O linking PO_4 tetrahedra are present. All of them are asymmetric and the protons are *ordered* in the ferroelectric phase.[7] This ordering was confirmed also by the increase of T_c upon deuteration and Raman studies,[8] which showed that the groups of TeO_6, PO_4, and NH_4 do not undergo changes that could trigger the phase transition.

In this work we present and analyze high-resolution data ($\Delta p \approx 1.5$ bar steps, in an interval of about 3 kbar; $\Delta T \approx 0.01$ °C steps, in intervals of about 5 °C) on the dielectric constant and hysteresis loops for TAAP single crystals, undertaken with the aim of determining a combined pressure and temperature equation of state.

The samples were small platelets, $3\times 2\times 1.2$ mm^3 in size, cut from a larger single crystal grown from water solution, coated with silver paste electrodes deposited on the main surfaces. The sample holder, in which pressure and temperature could be accurately controlled, as mentioned before, was an adapted LC10 Unipress cell. Measurements of dielectric constant and loss factor were performed with a HP Precission LCR Meter 4384A ($E_{\mathrm{meas}}=1$ V/cm, $f=1$ kHz). Automatic data, together with temperature and pressure readings were collected by means of a top desk computer. A Diamant-Drenck-Pepinsky bridge and a NICOLET 310 digital oscilloscope were used to do the digitalized hysteresis loops measurements ($E_{\mathrm{meas}}=1.8$ kV/cm, $f=50$ Hz). A computer program was used to correct for internal bias in the hysteresis loops.

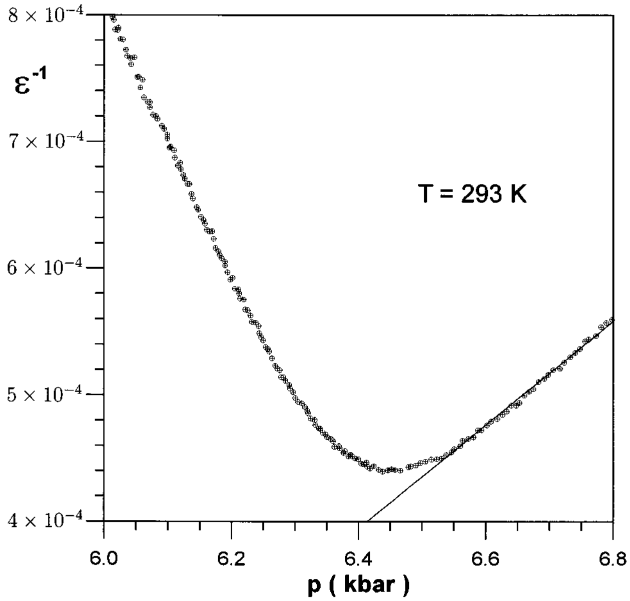

FIG. 1. Inverse dielectric constant ε^{-1} as a function of hydrostatic pressure at $T=293$ K for TAAP. Straight line indicates the Curie-Weiss behavior at $p>p_c=5.13$ kbar (note that vertical scale starts at $\varepsilon^{-1}=4\times10^{-4}$).

Figure 1 shows dielectric-constant data as a function of pressure through the transition at room temperature. The data can be fitted well with a Curie-Weiss-type law with pressure.

Figure 2 gives similar dielectric-constant data as a function of temperature through the transition at several pressures, which also follow well a Curie-Weiss law. It may be noted that $\varepsilon_{\max}$ becomes smaller for lower transition temperatures.

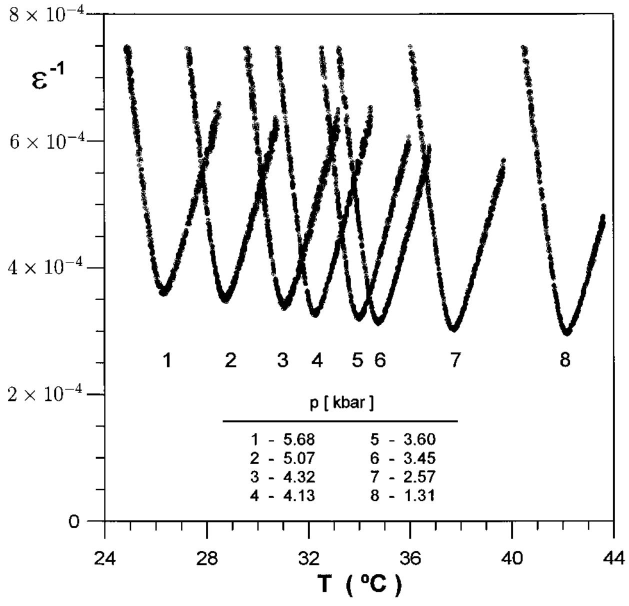

FIG. 2. Isobars of the temperature dependence of the inverse dielectric constant ε^{-1} for TAAP.

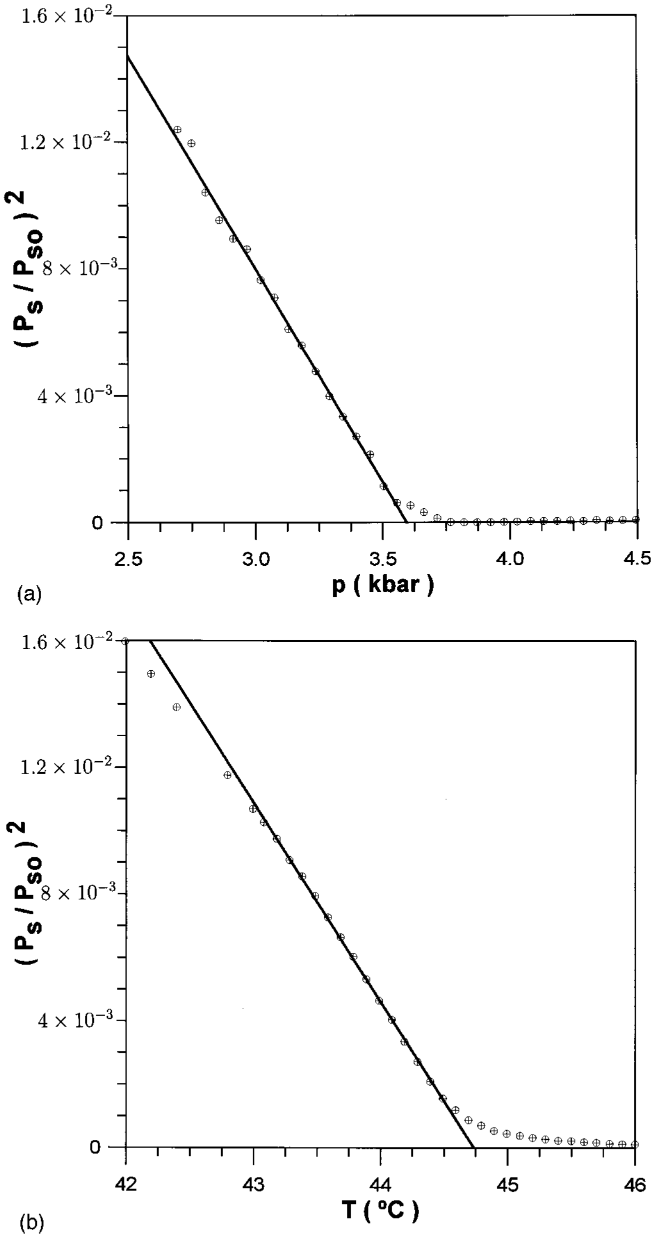

FIG. 3. Normalized spontaneous polarization square $(P_s/P_{so})^2$ vs pressure at $T=306.65$ K (a), and vs temperature at ambient pressure (1 bar) (b). $P_{so}=2.12$ μC/cm^2 is the saturation spontaneous polarization.

Figures 3(a) and 3(b) display normalized square spontaneous polarization as a function of temperature (a) at ambient pressure (1 bar), and pressure (b) at constant temperature $T=306.65$ K. It may be noted that, because of the lack of perfect compensation in the hysteresis loops, T_c and p_c are slightly overestimated.

Two sets of hysteresis-loop data, one at constant pressure (ambient pressure, i.e., 1 bar), and another at constant temperature ($T=306.65$ K, i.e., near and below the ambient pressure Curie temperature) are represented in Fig. 4 in scaled form. They fit well a combined equation of state, discussed below, which is easily deduced from basic considerations. It must be noted that we are not aware of previous descriptions of observed pressure and temperature behavior near a ferroelectric transition by means of a single equation of state.

In an order-disorder ferroelectric phase the existence of microscopic dipole moments reversible under the action of an external electric field can be associated with the presence of a double potential minimum along the polar axis of the

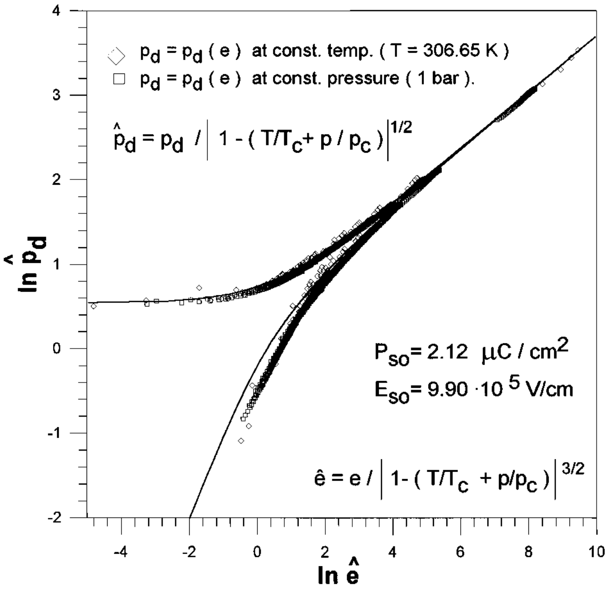

FIG. 4. Simultaneous scaling equation of state for the pressure-induced and the temperature-induced ferroelectric transition in TAAP. The continuous line is the theoretical scaling equation of state $\hat{e} \cong \pm \hat{p}_d + \frac{1}{3}\hat{p}_d^3$, with a − sign for $T < T_c$ and for $p < p_c$, and a + sign for $T > T_c$ and for $p > p_c$. $T_c(p=1\text{ bar})=317.25$ K, $p_c(T=0\text{ K})=76.87$ kbar; $P_{so}=2.12$ μC/cm^2 the saturation spontaneous polarization, and $E_{so}=9.90\times10^5$ V/cm, the saturation spontaneous field, give the best fit to the theoretical equation of state.

unit cell for specific constituent ions. In the paraelectric, i.e., fully disordered, phase the jump probability per unit cell and unit time of those specific ions between the two symmetric minima is usually given by $\pi(\phi)=\nu e^{-\phi/k_BT}$, where $\nu \approx k_B\Theta_D/h$ is the attempt frequency, and ϕ the potential barrier height between the two minima. If the barrier height is increased by a small amount $d\phi$, the jump probability should decrease in such a way that

$$d\pi_0(\phi) = -(1/\phi^*)\pi_0 d\phi, \tag{1}$$

and then

$$\pi_0(\phi) = \pi_0(0)e^{-\phi/\phi^*}. \tag{2}$$

Here ϕ^* can be given in terms of the critical barrier height at which the ferroelectric-paraelectric transition, induced either by rising temperature or rising hydrostatic pressure, takes place. In a transition induced by temperature only (i.e., under ambient pressure) we have[9]

$$\phi_{\text{eff}}(T_c,0) = \beta N\mu^2 = k_B T_c, \tag{3}$$

where T_c is the transition temperature and $E_{so}\mu = \beta N\mu^2$ is the electrostatic energy of the spontaneous field acting on the unit dipole μ. In a transition induced by pressure only (at 0 K) also

$$\phi_{\text{eff}}(0,p_c) = \beta N\mu^2 = \Delta v_c p_c, \tag{4}$$

where p_c is the critical hydrostatic pressure and Δv_c the associated change in unit cell volume v_c needed to bring about the pressure-induced transition.

Consequently, in the general case of $T < T_c$, $p < p_c$ we may take

$$\phi^* = \phi_{\text{eff}}(T,p) = \beta N\mu^2\left(\frac{T}{T_c} + \frac{p}{p_c}\right). \tag{5}$$

This expression is used in the following to get in a straightforward manner a combined pressure/temperature equation of state for the ferroelectric transition.

In equilibrium under zero external field at the paraelectric phase, where the double potential minimum is symmetric, the number of dipoles per unit-volume pointing in the + direction (N_2) and in the − direction (N_1) are related by $N_2\pi_{21} = N_1\pi_{12}$, and since $\pi_{12} = \pi_{21} = \pi_0$, one has $N_1 = N_2 = N/2$. In general, however, i.e., under an effective field

$$E_{\text{eff}} = E + \beta P_d + \gamma P_d^3 + \delta P_d^5 + \cdots \tag{6}$$

one has

$$\pi_{21} = \pi_0(0)e^{-(E+\beta P_d+\cdots)\mu/\phi^*},$$

$$\pi_{12} = \pi_0(0)e^{(E+\beta P_d+\cdots)\mu/\phi^*}, \tag{7}$$

which, in equilibrium ($N_2\pi_{21} = N_1\pi_{12}$) leads to

$$\frac{P_d}{N\mu} = \frac{(N_2-N_1)\mu}{(N_2+N_1)\mu} = \tanh\left(\frac{(E+\beta P_d+\cdots)\mu}{\phi^*}\right) \tag{8}$$

and, using Eq. (5), to the combined equation of state

TABLE I. H=heating; C=cooling; D=decreasing of pressure. $T_c = T_c(p=0) = 317.25$ K and $p_c = p_c(T=0) = 76.87$ kbar were used for all data. $T_c(p\neq0)$ is the actual transition temperature for a specific pressure $p\neq0$; $p_c(T\neq0)$ is likewise the actual transition pressure for a specific temperature $T\neq0$.

	$T_c(p)$ (K)	p (kbar)	$T_c(p)/T_c$	(p/p_c)	$\{[T_c(p)/T_c]+(p/p_c)\}$
H	299.56	5.688	0.944	0.074	1.018
C	299.56	5.688	0.944	0.074	1.018
H	302.00	5.071	0.951	0.066	1.017
C	301.90	5.071	0.951	0.066	1.017
H	304.36	4.452	0.959	0.058	1.017
C	304.22	4.327	0.958	0.056	1.015
H	304.61	4.452	0.960	0.058	1.018
C	304.30	4.452	0.959	0.058	1.017
H	305.58	4.074	0.963	0.053	1.016
C	305.42	4.137	0.962	0.054	1.016
H	307.28	3.601	0.968	0.047	1.015
C	307.14	3.601	0.968	0.047	1.015
H	308.12	3.394	0.971	0.044	1.015
C	307.94	3.452	0.970	0.045	1.015
H	310.98	2.556	0.980	0.033	1.013
C	310.83	2.578	0.979	0.033	1.013
H	315.35	1.310	0.994	0.017	1.011
C	315.30	1.315	0.993	0.017	1.010
	T (K)	$p_c(T)$ (kbar)	(T/T_c)	$p_c(T)/p_c$	$\{(T/T_c)+[p(T)/p_c]\}$
D	293.15	5.13	0.924	0.067	0.991

$$\frac{P_d}{N\mu}=\tanh\left\{\left(\frac{T}{T_c}+\frac{p}{p_c}\right)^{-1}\left(\frac{E+\beta P_d+\cdots}{\beta N\mu}\right)\right\}, \tag{9}$$

or

$$\frac{E}{\beta N\mu}=\left(\frac{T}{T_c}+\frac{p}{p_c}\right)\tanh^{-1}\left(\frac{P_d}{N\mu}\right)-\beta P_d\left[1+\left(\frac{\gamma}{\beta}\right)P_d^2+\left(\frac{\delta}{\beta}\right)P_d^4+\cdots\right], \tag{10}$$

which can be written in dimensionless form as

$$e=\left(\frac{T}{T_c}+\frac{p}{p_c}\right)\tanh^{-1}p_d-p_d(1+gp_d^2+hp_d^4+\cdots), \tag{11}$$

where p=pressure and p_d=reduced dipolar polarization must not be confused. $T_c=T_c(p=0)$ is the transition temperature at $p=0$, and $p_c=p_c(T=0)$ is the transition pressure at $T=0$ K.

For a continuous second-order transition,[10] close to the ordinary critical point ($p_d \ll 1$), Eq. (11) can be put in scaled form as

$$\hat{e}\cong\pm\hat{p}_d+\frac{1}{3}\,\hat{p}_d^3, \tag{12}$$

where

$$\hat{e}\equiv e\Big/\left|1-\left(\frac{T}{T_c}+\frac{p}{p_c}\right)\right|^{3/2},$$

$$\hat{p}_d\equiv p_d\Big/\left|1-\left(\frac{T}{T_c}+\frac{p}{p_c}\right)\right|^{1/2}. \tag{13}$$

As shown in Fig. 4, Eqs. (12)–(13) describe simultaneously the pressure-induced and the temperature-induced ferroelectric transition of TAAP simply and fairly accurately. From p_c and T_c we estimated the unit cell volume change associated with the phase transition as $\Delta v_c=k_B T_c/p_c=0.565$ Å^3 (the actual unit cell volume is $v_c=922.73$ Å^3).

Table I illustrates the good fit of data for $T_c(p)$ and $p_c(T)$ from Figs. 1 and 2 to Eq. (9), in which $(T/T_c+p/p_c)$ playsthe same role as T/T_c in a transition at zero pressure and as p/p_c in a transition at zero temperature.

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