

Pressure Dependence of Permittivity and Antiferroelectric Polarization of Cupric Formate Tetrahydrate under Electric Field

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Abstract

The pressure dependence of relative permittivity for various electric fields at -20°C and -35.5°C of antiferroelectric cupric formate tetrahydrate was calculated and interpreted in terms of a phenomenological theory. The permittivity of the antiferroelectric phase decreased with increasing pressure, and the permittivity of the induced phase decreased with increasing electric field.

1. Introduction

Cupric formate tetrahydrate ($\text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$: abbreviated as CFT) belongs to space groups $P2_1/a$ in the monoclinic system, and undergoes a first-order phase transition from the paraelectric to the antiferroelectric phase at -39°C under atmospheric pressure with decreasing temperature.¹⁾

CFT consists of two alternately arranged layers along the c axis, a layer of crystalline water molecules and a layer of copper formates. The phase transition is characterized by the two-dimensional ordering of hydrogens in the layer of crystalline water molecules. The antiferroelectric axis is in the direction of the b axis.²⁾

Under atmospheric pressure, the double hysteresis loop between the polarization P and the electric field E has been observed in the antiferroelectric phase.¹⁾ Under hydrostatic pressure, (i) the transition temperature T_c increases linearly with increasing pressure p with a slope $dT_c/dp = 4.35^{\circ}\text{C}/\text{kbar}$ up to 10kbar.³⁾ (ii) data points of the real and imaginary parts of the complex permittivity are almost on a circular arc in the Cole-Cole diagram.⁴⁾ (iii) the P-E double hysteresis loop has been observed in the antiferroelectric phase at temperatures below the transition temperature and at pressures above the transition pressure, and some experimental results such as the frequency and pressure dependence of the permittivity have been reported.⁵⁾

In this paper, for CFT in the antiferroelectric phase at -20°C and -35.5°C under various electric fields, the relation between the reciprocal of permittivity and the pressure

was numerically elucidated in terms of a "Phenomenological Treatment of the Antiferroelectric Transition under Hydrostatic pressure." ⁶⁾

2. Specimen and Experiment

A specimen was a plate perpendicular to the *b* axis cut out with a beryllium-wire cutter from a single crystal which was grown at a constant temperature (20°C) by a slow evaporation method, and was typically about $5 \times 4 \times 0.3 \text{ mm}^3$. The spontaneous polarization was examined with an improved Sawyer-Tower circuit, ⁷⁾ and the electrical capacitance of the specimen was measured with an ac-bridge. The high-pressure apparatus which applied hydrostatic pressure to the specimen was a piston-in-cylinder type, 300 ton press with a liquid-solid system. ^{6), 8)}

3. Effect of Hydrostatic Pressure on Electric Field Dependence of Permittivity and Antiferroelectric Polarization

3. 1 Phenomenological Treatment

Since CFT exhibits the first-order antiferroelectric phase transition, when hydrostatic pressure *p* is applied to an antiferroelectric which is not piezoelectric, the free energy (the Gibbs function) for an antiferroelectric can be expanded as a function of ferroelectric polarization $Pm = Pa + Pb$ (observable) and antiferroelectric one $Pn = Pa - Pb$ (non-observable) where *Pa* and *Pb* are polarizations of sublattices, ⁹⁾ as follows :

$$F = cp^2/2 + W$$

$$W = \frac{1}{4} \{ (u + gp) (Pm^2 + Pn^2) + f(Pm^2 - Pn^2) \} + \frac{1}{8} \xi (Pm^4 + 6 Pm^2 Pn^2 + Pn^4) + \frac{1}{32} \zeta (Pm^6 + 15 Pm^4 Pn^2 + 15 Pm^2 Pn^4 + Pn^6) - EPm \quad (1)$$

where *c* is the elastic constant, *W* is the free energy with respect to polarizations, *g* is the electrostrictive constant, and *u*, *f*, ξ and ζ are phenomenological constants which are usually depend on temperature, and *E* is the electric field in an antiferroelectric. ^{6), 10)} From conditions for minimum free energy F ($\partial F / \partial Pm = 0$, $\partial F / \partial Pn = 0$ etc.) and equation (1),

$$E = \{ u + gp + f + \xi (Pm^2 + 3Pn^2) + 3\zeta (Pm^4 + 10Pm^2 Pn^2 + 5Pn^4) / 8 \} Pm / 2 \quad (2)$$

$$u + gp - f + \xi (3 Pm^2 + Pn^2) + 3 \zeta (5 Pm^4 + 10 Pm^2 Pn^2 + Pn^4) / 8 = 0 \quad (3)$$

The permittivity ϵ and the relative permittivity $\epsilon_r (= \epsilon / \epsilon_0)$ in the antiferroelectric phase under electric field (or bias field) *E* are obtained on putting the relation

$\partial Pm / \partial E = \epsilon - \epsilon_0 \approx \epsilon$ (for $\epsilon \gg \epsilon_0$ applying to ordinary antiferroelectrics) into equation (2) :

$$1/\epsilon = (u + gp + f)/2 + 3\xi(Pm^2 + Pn^2)/2 + 15\zeta(Pm^4 + 6Pm^2Pn^2 + Pn^4)/16 \quad (4)$$

where ϵ_0 is the vacuum permittivity. Solving equation (3) for Pn under the condition $\xi < 0$, we obtain

$$Pn^2 = \frac{1}{3\xi} \left[-(4\xi + 15\zeta Pm^2) + \sqrt{(4\xi + 15\zeta Pm^2)^2 - 3\zeta \{8(u + gp - f + 3\xi Pm^2) + 15\zeta Pm^4\}} \right] \quad (5)$$

When the electric field E exceeds the critical field E_c , the antiferroelectric phase changes from the antiferroelectric to the induced phase which is ferroelectric. In this phase, on putting the relation $Pn=0$ into equations (2) and (4), we obtain E and Pm as functions of p and Pm . By eliminating Pm in the above relations, we obtain the relation between E and ϵ :

$$E = \frac{1}{5} \left\{ 2(u + f + gp) + \frac{1}{\epsilon} + \xi P^2 \right\} P$$

where $P^2 = -\frac{4h}{5\xi} \left\{ 1 + \sqrt{1 - \frac{5}{6h} (u + f + gp - \frac{2}{\epsilon})} \right\}$ and $h = \frac{\xi^2}{\zeta}$ (6)

The antiferroelectric polarization and the permittivity under no bias ($E=0$) are obtained by putting the relation $Pm=0$ into equations (3), (4) and (5) under the condition $\xi < 0$:

$$Pn^2 = -\frac{4\xi}{3\zeta} \left\{ 1 + \sqrt{1 + \frac{3}{2h} (f - u - gp)} \right\} \quad (7)$$

$$\frac{1}{\epsilon} = \frac{1}{\epsilon_0 \epsilon_r} = 3f - 2(u + gp) + \frac{4h}{3} \left\{ 1 + \sqrt{1 + \frac{3}{2h} (f - u - gp)} \right\} \quad (8)$$

In the paraelectric phase, on putting the relation $Pa = Pb = 0$ or $Pm = Pn = 0$ into equation (4), we obtain

$$1/\epsilon = 1/\epsilon_0 \epsilon_r = (u + f + gp)/2 \quad (9)$$

3. 2 Pressure Dependence of Permittivity and Antiferroelectric Polarization under Electric Field

From the pressure dependence of the relative permittivity for CFT at 1 kHz, the following values for phenomenological constants have been obtained, using equations (1), (8) and (9) for $E=0$.^{11), 12)}

$$u = 2.49 \times 10^8 \text{ m/F}, \quad f = 3.95 \times 10^7 \text{ m/F}, \quad g = -3.82 \times 10^7 \text{ m/F} \cdot \text{kbar}, \quad h = 8.53 \times 10^7 \text{ m}^2/\text{F}^2, \\ \xi = -6.82 \times 10^{10} \text{ m}^5/\text{FC}^2, \quad \zeta = 5.46 \times 10^{13} \text{ m}^9/\text{FC}^4, \quad p_c = 4.4 \text{ kbar at } -20^\circ\text{C}, \text{ and} \\ u = 1.13 \times 10^8 \text{ m/F}, \quad f = 3.95 \times 10^7 \text{ m/F}, \quad g = -3.82 \times 10^7 \text{ m/F} \cdot \text{kbar}, \quad h = 8.53 \times 10^7$$

m/F , $\xi = -3.28 \times 10^{10} \text{m}^5/\text{FC}^2$, $\zeta = 1.26 \times 10^{13} \text{m}^9/\text{FC}^4$, $p_c = 0.91 \text{kbar}$, $Pnc = 5 \times 10^{-2} \text{C/m}^2$ at -35.5°C .

Let us put the above values into the appropriate equations, and phenomenologically explain the electric field dependence of permittivity and antiferroelectric polarization under hydrostatic pressure of antiferroelectric CFT belonging to the first-order transition.

Fig. 1 shows the pressure dependence of the reciprocal of relative permittivity $1/\epsilon_r$ at -20°C (i) under no bias field ($E=0$), as calculated from equation (9) for the paraelectric phase and from equation (8) for the antiferroelectric phase, and (ii) under bias field ($E=E$), by eliminating Pm from the relations between $1/\epsilon_r$, p and Pm , and between E , p and Pm which are obtained by putting Pn^2 as given by equation (5) into equations (4) and (2), respectively, for the antiferroelectric phase, and by calculating from equation (6) for the induced phase. Fig. 1 also shows the pressure dependence of the antiferroelectric polarization (spontaneous polarization of the sublattice) calculated from equation (7) under no bias field for the antiferroelectric phase.

Fig. 2 shows the same characteristic at -35.5°C .

It follows from Fig. 1 and Fig. 2 that (i) ϵ_r of the antiferroelectric phase decreases with increasing pressure and the rate of decrease is greater with decreasing electric field E , (ii) ϵ_r of the induced phase decreases with increasing electric field E , while ϵ_r of the antiferroelectric phase increases with increasing electric field, (iii) application of electric field to the sample causes narrowing of the antiferroelectric range, and (iv) the spontaneous polarization Pn changes discontinuously at the transition pressure.

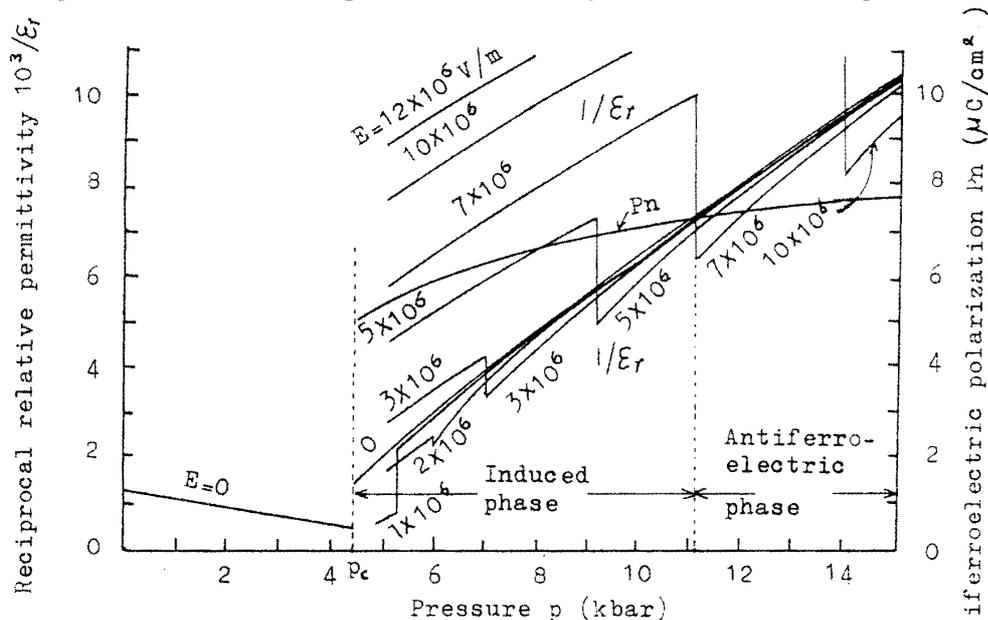


Fig. 1 Pressure dependence of reciprocal relative permittivity for various electric fields at -20°C .

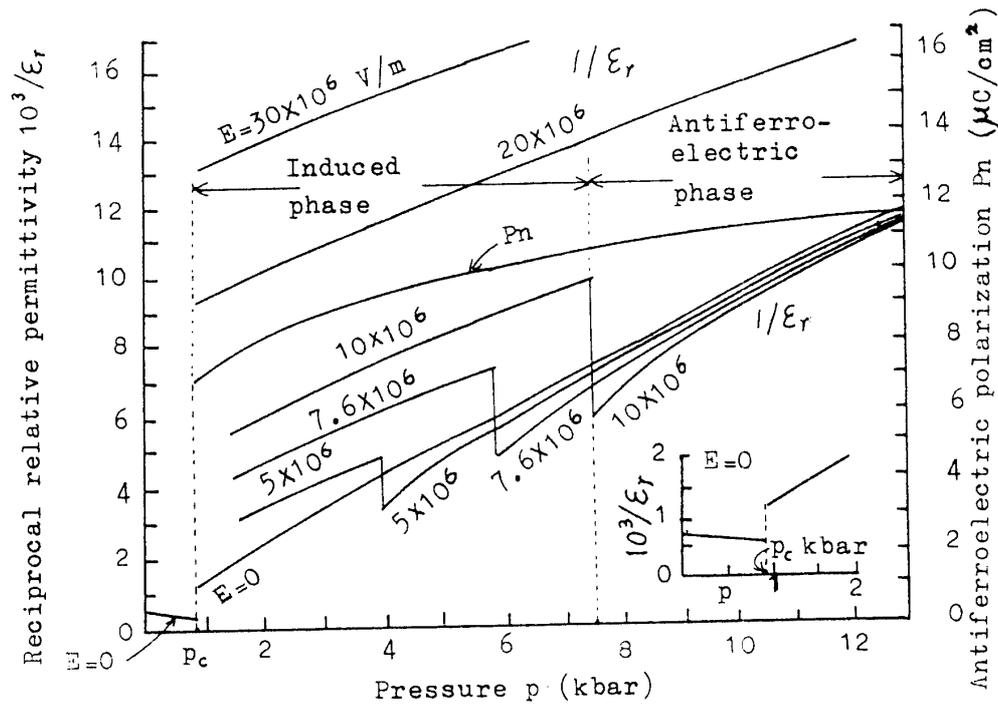


Fig. 2 Pressure dependence of reciprocal relative permittivity for various electric fields at -35.5°C .

3. 3 Electric Field Dependence of Permittivity under Hydrostatic Pressure

Fig. 3 and Fig. 4 show the electric field dependence of the reciprocal of relative permittivity $1/\epsilon_r$, for various pressures at -20°C and -35.5°C , respectively. The value of $1/\epsilon_r$ decreases with the electric field E in the antiferroelectric phase, drops at the critical field E_c , and increases with E in the induced phase.

It is found from Fig. 3 and Fig. 4 that the antiferroelectric range becomes narrower as the hydrostatic pressure decreases.

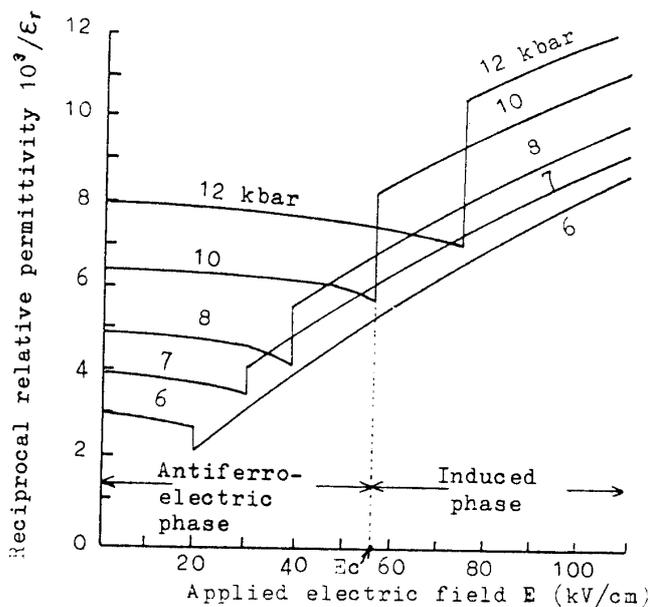


Fig. 3 Electric field dependence of reciprocal relative permittivity for various hydrostatic pressures at -20°C .

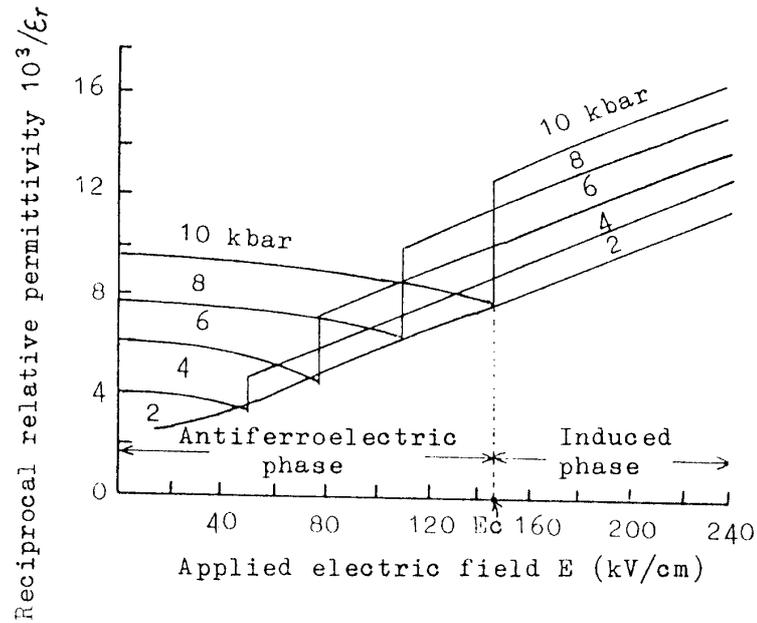


Fig. 4 Electric field dependence of reciprocal relative permittivity for various hydrostatic pressures at -35.5°C .

4. Electric Field Dependence of Transition Pressure

CFT also changes from the antiferroelectric to the induced phase at the transition pressures p_c as the pressure decreases, and the transition pressure varies with the applied electric field E . Fig. 5 shows the electric field dependence of transition pressure. It is found from Fig. 5 that the transition pressure increases almost linearly with increasing electric field with a slope $dp_c/dE=0.108\text{kbar} \cdot \text{cm}\cdot\text{kV}^{-1}$ for -20°C , and $0.066\text{kbar} \cdot \text{cm}\cdot\text{kV}^{-1}$ for -35.5°C in a range 2 to 12kbar. The values of transition pressure are 9.2kbar for -20°C and 4.0kbar for -35.5°C at $E=50\text{kV} \cdot \text{cm}^{-1}$, for example.

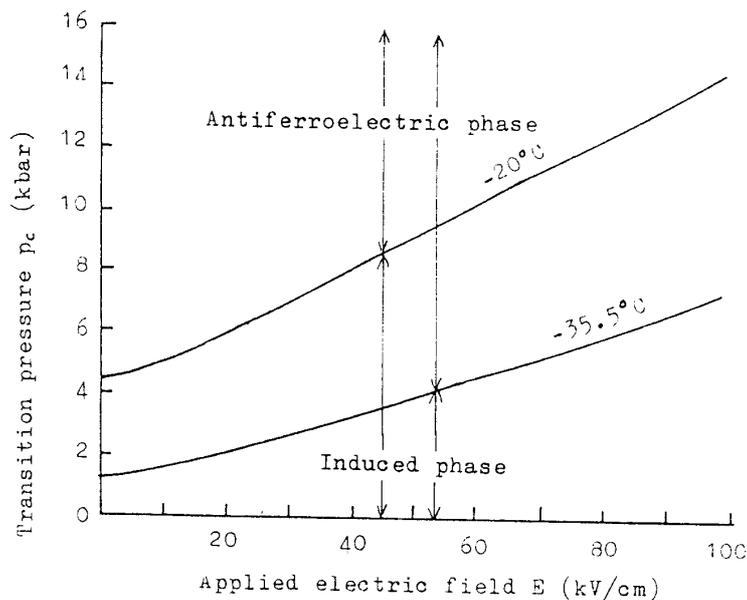


Fig. 5 Transition pressure p_c as a function of applied electric field E .

5. Conclusion

The reciprocal of relative permittivity $1/\epsilon_r$ under no bias field ($E=0$) decreases linearly with increasing pressure in the paraelectric phase below the transition pressure p_c , and increases linearly in the antiferroelectric phase above p_c . The value of $1/\epsilon_r$ under the bias field E decreases with decreasing pressure p in the antiferroelectric phase, and jumps at p_c , and also decreases with decreasing p in the induced phase.

It is found that application of electric field to the CFT causes narrowing of the antiferroelectric range, and application of pressure to the CFT causes an expansion of the antiferroelectric range. The antiferroelectric polarization P_n increases with increasing pressure in the antiferroelectric field.

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