

Pressure-Induced Antiferroelectricity in Ferroelectric CsH_2PO_4

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(Received 27 June 1978)

A new phase in CsH_2PO_4 is induced by pressures above about 3.3 kbar; this phase is confirmed to be antiferroelectric by the observation of P - E double hysteresis loops. The qualitative change from the paraelectric-ferroelectric to the paraelectric-antiferroelectric transition caused by the pressure is interpreted to originate in the one-dimensional characteristics with the chainlike ordering of the hydrogen bond along the b axis in CsH_2PO_4 .

Cesium dihydrogen phosphate (CsH_2PO_4) belongs to the space group $P2_1/m$ in the monoclinic system¹ unlike the well-known tetragonal system in KH_2PO_4 in the paraelectric phase, and undergoes a phase transition from the paraelectric to the ferroelectric phase at -120°C at atmospheric pressure with cooling.¹⁻⁴ There is a large isotope effect on the transition temperature (T_c) by substitution of deuterium for hydrogen, and the T_c is -6°C for the deuterated analog³ CsD_2PO_4 which is isostructural with CsH_2PO_4 .⁵ Moreover, the transition temperatures for both compounds have recently been reported to decrease with increasing pressure (p) with slope $dT_c/dp = -5.6^\circ\text{C}/\text{kbar}$ for CsH_2PO_4 and $dT_c/dp = -8.5^\circ\text{C}/\text{kbar}$ for CsD_2PO_4 .⁶ Such behavior for CsH_2PO_4 suggests that the phase transition in CsH_2PO_4 as well as in KH_2PO_4 is microscopically explained by the tunneling model of the proton.^{6,7} Despite these similarities, CsH_2PO_4 has been found by neutron scattering study⁵ to have one-dimensional (1-D) nature characterized by the chainlike ordering of the hydrogen bond parallel to the ferroelectric b axis, which sets it apart from the KH_2PO_4 family. Furthermore, the electric field effect on the permittivity is more remarkable in the vicinity of the transition temperature in CsH_2PO_4 than in KH_2PO_4 .^{3,8}

In this Letter, we report that even as small a pressure as 3.3 kbar causes a drastic change, from the paraelectric-ferroelectric to the paraelectric-antiferroelectric transition. This fact ties nicely to the 1-D characteristics with the chainlike ordering of the hydrogen bond along the b axis in CsH_2PO_4 .⁵

CsH_2PO_4 single crystals were grown from an aqueous solution by the slow evaporation method⁴ at room temperature. A plate perpendicular to the b axis was cut out with a beryllium wire cut-

ter from a single crystal and gold was evaporated on its surfaces to act as electrodes. Each specimen was covered with a silicone varnish to protect it from moisture. The electrical capacitance of the specimen was measured at 1 kHz with a field smaller than 1 V/cm using a LCR (inductance, capacitance, resistance) meter and the spontaneous polarization was examined with an ordinary Sawyer-Tower circuit. A Cu-Be high-pressure vessel with 1:1 mixture of normal- and isopentane as a pressure transmitting fluid was used in order to apply the hydrostatic pressure to the specimen. The pressure was measured with Manganin gauges to an accuracy of $\pm 1.5\%$. All of the dielectric data were gathered for varying temperature (T) at a rate of $0.1^\circ\text{C}/\text{min}$ under various constant pressures up to 4.5 kbar. All of the observed values are reversible on lowering pressure with good reproducibility, and therefore the pressure applied to the specimen may be hydrostatic in spite of the increase in the viscosity of a pressure-transmitting fluid at low temperatures.

Figure 1 shows the temperature dependence of the relative permittivity along the ferroelectric b axis (ϵ_r) of CsH_2PO_4 under various constant pressures. It is found in Fig. 1 that the value of ϵ_r changes strikingly at the critical pressure (p_c) of about 3.3 kbar. At pressures lower than p_c , the ϵ_r in the paraelectric phase above the transition temperature (T_c) obeys the Curie-Weiss law. The value of T_c decreases with increasing pressure with a slope $dT_c/dp = -(8.5 \pm 0.3)^\circ\text{C}/\text{kbar}$. The peak value of ϵ_r decreases little by little with increasing pressure. At pressures near p_c , two peaks appear with cooling; one is at T_n and the other at T_t . This fact indicates the existence of two phase transitions; namely, the new phase is induced by the application of pressure. As we

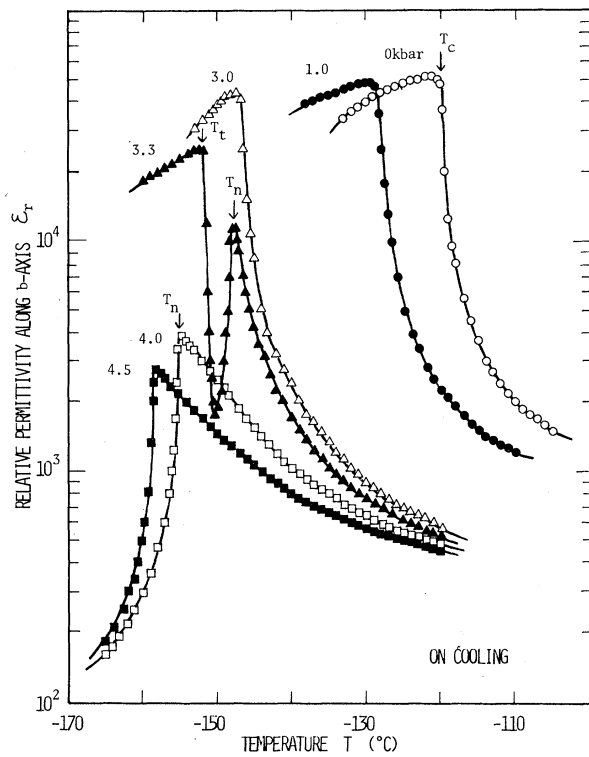


FIG. 1. The temperature dependence of the relative permittivity along the *b* axis of CsH₂PO₄ measured at 1 kHz with a field smaller than 1 V/cm under constant pressures.

compare the two peaks we find that (a) the peak value of ϵ_r at T_n is lower than that at T_t ; (b) the value of ϵ_r around T_n varies more steeply at temperatures below T_n than above T_n ; (c) the value of ϵ_r around T_t varies more steeply at $T > T_t$ than at $T < T_t$; and (d) the behavior of ϵ_r around T_t is similar to that around T_c at pressures below p_c . At pressures higher than p_c , only the peak of ϵ_r at T_n appears with cooling. The peak value of ϵ_r at T_n decreases with increasing pressure and is less than 10^{-1} of that at pressures below p_c , and the value of T_n also decreases with a slope $dT_n/dp = -(6.7 \pm 0.3)^\circ\text{C/kbar}$.

Such behavior for the peak of ϵ_r at T_n suggests that the phase transition at T_n is antiferroelectric.⁹ Consequently observation of the *P-E* double hysteresis loop which is characteristic of antiferroelectrics was tried at pressures above p_c . Figure 2(a) shows a clear *P-E* double hysteresis loop at $p = 3.7$ kbar at $T = -160^\circ\text{C}$ with an ac amplitude of 1.1 kV/cm and 60 Hz. In this case, the 60-Hz ac electric field was applied to the specimen as pulses for only 1 sec. It is noticed that the critical electric field estimated as the

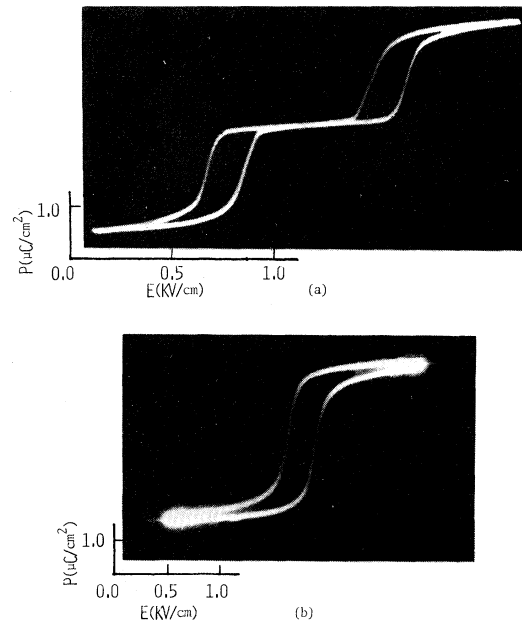


FIG. 2. (a) The *P-E* double hysteresis loop at $p = 3.7$ kbar and at $T = -160^\circ\text{C}$ with an ac amplitude of 1.1 kV/cm, and (b) the *P-E* hysteresis loop at $p = 3.0$ kbar and at $T = -155^\circ\text{C}$, along the *b* axis of CsH₂PO₄, where the 60-Hz ac electric field amplitude was applied to the specimen as pulses for 1 sec.

value of the field at the center of a loop has a very small value of 0.42 kV/cm. With heating, the area and the height of the double hysteresis loop get smaller, and then on passing through the transition temperature the loop disappears and finally the *P-E* relation becomes a straight line. It can be concluded by the observation of *P-E* double hysteresis loops that the new pressure-induced phase is antiferroelectric. On the contrary, Fig. 2(b) shows the *P-E* hysteresis loop at $p = 3.0$ kbar $< p_c$ and $T = -155^\circ\text{C} < T_c$ with an ac amplitude of 1.3 kV/cm and 60 Hz. By this loop, the phase at $p < p_c$ and $T < T_c$ is confirmed to be ferroelectric.

From the above experimental results, the pressure-temperature phase diagram of CsH₂PO₄ is determined as shown in Fig. 3. This phase diagram is similar to that of CsD₂PO₄ determined dielectrically.⁶ Phase III of CsD₂PO₄ seen in Ref. 6 may be antiferroelectric in view of the following points: (1) the similarity of phase diagram between CsD₂PO₄ and CsH₂PO₄; (2) CsD₂PO₄ is isostructural with CsH₂PO₄⁵; and (3) the pressure effect on the ϵ_r -*T* characteristic in CsD₂PO₄ is qualitatively similar to that in CsH₂PO₄.¹⁰ It is found in Fig. 3 that the paraelectric-ferro-

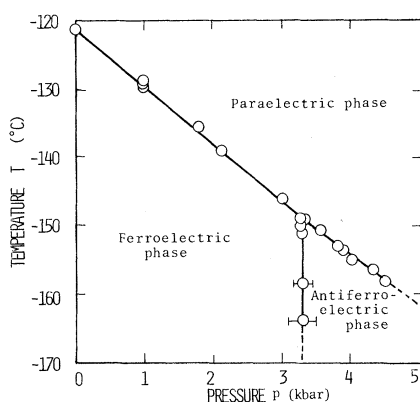


FIG. 3. The pressure-temperature phase diagram of CsH_2PO_4 .

electric-antiferroelectric phase triple point in CsH_2PO_4 exists at a pressure of 3.3 ± 0.2 kbar and a temperature of $-(148.5 \pm 0.2)^\circ\text{C}$.

By x-ray diffraction¹ and neutron scattering techniques,⁵ the ordering of hydrogen atoms in the bonds associated with the zigzag chains running along the ferroelectric b axis has been proposed to play an important role for the ferroelectric transition in CsH_2PO_4 and to exhibit one-dimensional characteristics, and the ferroelectric polarization has been suggested to be due to the atomic displacements of heavy atoms along the chain⁵ triggered by this ordering of hydrogen atoms.

It is found by the present work on CsH_2PO_4 that (A) the qualitative change from the paraelectric-ferroelectric to the paraelectric-antiferroelectric transition is caused by pressure as small as about 3.3 kbar, and (B) in the pressure-induced antiferroelectric the critical electric field¹¹ which induces the forced transition to the ferroelectric phase has a very small value of 0.42 kV/cm. The facts (A) and (B) indicate that the arrangement of polarizations along the b axis among the nearest-neighbor chains changes from parallel to antiparallel by the small pressure and vice versa from antiparallel to parallel by the small electric field, respectively. So we state that the paraelectric-ferroelectric phase transition for CsH_2PO_4 results from the weak three-dimensional ferroelectric correlation of polarizations among the chains along the b axis. The above facts will reflect the 1-D nature of the phase transition in CsH_2PO_4 .⁵

On the contrary, the paraelectric-ferroelectric phase transition for KH_2PO_4 results from the strong three-dimensional ferroelectric correla-

tion due to three-dimensional polarization fluctuations,^{5,12} and then the qualitative change of a paraelectric-ferroelectric phase transition by applying pressures has not been observed.^{7,13,14}

Judging from the situation mentioned above, the antiferroelectricity induced by the small pressure (about 3.3 kbar) in CsH_2PO_4 is interpreted to originate in the 1-D characteristics with the chainlike ordering of the hydrogen bond along the b axis.⁵ On the assumption that the polarizations along the chain are simply treated as an isolated dipole since the 3-D correlation of polarizations among the chains along the b axis is weak, the change of the dipolar arrangement along the chains from parallel to antiparallel by applying the pressure may be guessed to result from the following situation: With increasing pressure, the distance between two isolated dipoles gets shorter and the dipolar interaction becomes dominant, so that the antiparallel dipolar arrangement seems to appear because the dipolar interaction energy for the antiparallel arrangement of the two isolated dipoles becomes lower than that for the parallel arrangement.¹⁵

Further experiments on CsH_2PO_4 and CsD_2PO_4 under pressures with dielectric measurements are now in progress.

The authors would like to thank Professor K. Okada of Nagoya Institute of Technology for valuable discussions and thank T. Asano and N. Abe for their helpful assistance in this experiment.

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¹¹In KH_2PO_4 -type antipolar $\text{NH}_4\text{H}_2\text{PO}_4$, the ferroelectric phase has not been recognized to be induced by the application of electric field [see M. Marutaken, in *Landolt-Börnstein: Ferro- and Antiferroelectric Substances*, edited by T. Mitsui (Springer, Berlin, 1969), Vol. 3, p. 143]. Layered antiferroelectric cupric formate tetrahydrate characterized with the two-dimensional hydrogen-bonded network (which has two-dimensional ferroelectric planes stacked antiferroelectrically

along the c axis) has a large critical electric field of about 10 kV/cm at 3°C below the transition temperature [see K. Okada and H. Sugie, J. Phys. Soc. Jpn. 25, 1128 (1968)].

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Optical Excitation of the Surface Photoelectric Effect of Metals Using Synchrotron Radiation

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(Received 21 June 1978)

By fully exploiting the properties of synchrotron radiation, a surface photoyield spectrum of a metal, namely aluminum, was obtained for the first time. This type of spectrum has been theoretically discussed since 1928. The extreme surface sensitivity, which is implicit in the transition matrix element for the surface photoexcitation process, was experimentally confirmed. The applied photoemission technique, therefore, provides one of the most powerful tools for the investigation of charge distribution and dielectric response at metal surfaces.

The surface photoelectric effect in metals has been one of the most long-standing problems in metal physics. Theoretical treatments of the effect began in the early days of quantum mechanics within the Sommerfeld model of a metal (see Fig. 1) and still continue (see, e.g., Refs 1, 6-13). Since the surface photoelectric effect is of fundamental importance for the understanding of the quantum mechanical perturbation applied by an electromagnetic field to electronic states in a one-dimensional potential box because of the existence of potential steps, numerous attempts have been made in the last forty years to detect the effect experimentally (see, e.g., Refs. 14 and 15). The first experimental evidence for the mere existence of the effect was photoyield data from Al obtained in 1971¹⁶ which clearly showed contributions from the surface photoelectric effect excited by roughness-induced surface plasmons. Also, some evidence has been provided for the direct optical excitation of the effect.^{17,18}

In this Letter we report the first experimentally obtained surface photoyield spectrum of a

metal. A spectroscopic technique that fully exploits the properties of synchrotron radiation made it possible to separate unambiguously the photoyield caused by the surface photoelectric effect optically excited by p -polarized light from other contributions to the yield. The technique was applied to aluminum. Photoyield spectra were taken since it was shown by theory¹¹ that this type of photoemission spectra should most clearly exhibit features which are characteristic of the surface photoemission process in metals.

Figure 1(b) shows the geometry of the experiment. An aluminum surface, which is nature's best approximation to one side of a one-dimensional potential box, is rotated around two orthogonal axes with respect to a light beam with fixed orientation of the \vec{E} vector. Rotation around the θ axis varies the angle of incidence of the light. Rotation by 90° around the φ axis changes the polarization from perpendicular to parallel to the plane of incidence and vice versa at arbitrary angles of incidence θ . The experiments were performed using monochromatized and highly

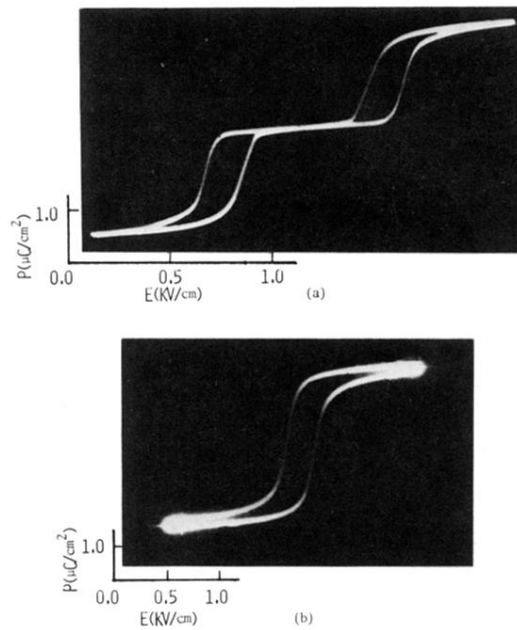


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