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‡Supported in part by the Purdue Research Foundation.

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Vanishing of the Ferroelectric and Antiferroelectric States in KH_2PO_2 -Type Crystals at High Pressure*

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(Received 3 May 1971)

The ferroelectric phase of KH_2PO_4 and the antiferroelectric phase of $\text{NH}_4\text{H}_2\text{PO}_4$ vanish at hydrostatic pressures >17 and 33 kbar, respectively. The results are qualitatively discussed in terms of the coupled proton-lattice model developed by Kobayashi and others, and they reemphasize the important role of the hydrogen bond in these crystals. We discuss possible important changes with increasing pressure in the character of the ferroelectric mode in KH_2PO_4 .

The purpose of this Letter is to report and discuss the observation of the vanishing of the ordered ferroelectric (FE) state in KH_2PO_4 (KDP) and antiferroelectric (AFE) state in $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP) at high pressures and low temperatures. The work is the first of its kind, and the results reveal important information concerning the nature of the phase transitions in these important hydrogen-bonded crystals. Before presenting the results and discussing their implication, a brief account of the background which motivated the work is useful.

At high temperatures KDP and ADP are isomorphous—tetragonal $\bar{I}42d$ —and are paraelectric (PE). The crystal structure consists of tetrahedral PO_4 groups connected by a network of O-H...O hydrogen bonds which lie very nearly in the basal planes. On cooling, KDP transforms to an orthorhombic (Fdd_2) FE phase at 123°K with spontaneous polarization along the c axis, whereas ADP transforms to an orthorhombic ($P2_12_12_1$) AFE phase at 148°K. One of the most intriguing features of the behavior of these crystals is the crucial role played by the protons in the transition. This is most evidenced by the ~80% (for KDP) and ~60% (for ADP) increases in transition temperatures observed on complete deuteration.

Very extensive experimental and theoretical work has been reported, particularly on KDP, and several models for the FE behavior of this

crystal have been proposed.¹ Although many questions remain unsettled,¹ the picture that has emerged and the point of view taken here is that the onset of ferroelectricity in KDP is triggered by an order-disorder transition of the protons in the H bonds, and that the motion of the protons is strongly coupled to the displacements of the other ions (particularly along the c axis). In the PE phase each proton can occupy either of two equilibrium positions along the H bond (i.e., there is a double-minimum potential), but it is ordered on one of them in the FE phase. The ordering is such that in a single domain all protons order near "upper" or "lower" oxygens of the PO_4 groups, depending on the polarity. In the AFE phase of ADP the ordering is such that the protons occupy one "upper" and one "lower" corner of each PO_4 tetrahedron, and the resulting coupling to the lattice is modified so as to cause antiparallel ionic displacements and an AFE phase. It has been recognized that the shape of the potential along the H bond is strongly dependent on the length of the bond. Since the H bond is mechanically the weakest link in the crystal structure, the properties of these crystals can be expected to be strongly pressure dependent. This was largely the motivation of the earlier low-pressure work.²⁻⁶

The details of the proton-lattice coupling and transition in KDP are very complicated, and quantitative models are lacking. However, a

convenient description which appears to incorporate the essential features and is adequate for our purposes is afforded by the Hamiltonian introduced by Kobayashi and others,⁷⁻⁹ namely $H = H_P + H_L + H_{PL}$. Here H_P describes the tunneling motion of the protons as well as their mutual interaction; H_L describes the lattice vibrations, specifically the TO mode of the K-PO₄ group along the c axis; and H_{PL} describes the proton-lattice coupling which is taken as bilinear in the proton and phonon coordinates. The Hamiltonian is solved for the coupled modes of the system. It is found that,^{7,8} in the limit of long wavelengths ($\vec{q}=0$), the frequency ω_- of one of the coupled modes, which is given by

$$\hbar^2 \omega_-^2 = \Omega [4\Omega - (J + 4F_j^2/\omega_j^2) \tanh(\Omega/kT)], \quad (1)$$

vanishes at a critical temperature T_c (which is the Curie temperature of the crystal) given by

$$\tanh(\Omega/kT_c) = 4\Omega(J + 4F_j^2/\omega_j^2)^{-1}. \quad (2)$$

In Eqs. (1) and (2), Ω is the proton tunneling frequency (2Ω being the splitting of the ground-state energy), J is the proton-proton interaction energy (identical to the exchange interaction of the Ising model), ω_j is the phonon frequency of the j th branch, and F_j is the proton-lattice coupling parameter.

According to Kobayashi,⁷ F_j is given by

$$F_j^2 \simeq [4\pi e^*^2/V]^{1/2} \frac{1}{4} \hbar^2 \delta^2 / \mu, \quad (3)$$

where e^* is an effective ionic charge and μ the reduced mass of the K-PO₄ group, V is the unit cell volume, and δ is the separation of the two potential minima along the H bond. It can also be shown that $J \propto \delta^2/V$.¹⁰ Furthermore, Ω is of course also a strong function of δ . Thus, all of the important parameters of the theory—namely, Ω , J , and F_j —are functions of δ .

As mentioned earlier, the shape of the potential encountered by the proton along the H bond is strongly dependent on the length of the bond, R . Consideration of various forms of a double-minimum potential³ (e.g., the double harmonic oscillator and some semiempirical potentials) leads to two pertinent results. With decreasing R , both δ and the height of the energy barrier between the two potential minima decrease. More importantly, if R becomes sufficiently short, then the potential reduces to a steep single-minimum potential; thereby the proton moves to the center of the bond and $\delta \rightarrow 0$. For the above model, it is then seen that under such a circumstance the proton tunneling, proton-proton interaction,

and proton-lattice coupling (described by F_j) vanish, and no transition takes place. The present investigation was undertaken to investigate this expected vanishing of the ordered state at high pressure as well as to study the behavior of the transition at low temperatures.

We have investigated the effects of temperature and hydrostatic pressure on the dielectric properties and phase transitions of KDP and ADP. Oriented single-crystal samples were used. The pressure measurements were made in two different apparatuses. Measurements up to 4.5 kbar were performed in a cell using helium gas as the pressure fluid. Measurements to higher pressure were made in a piston-cylinder apparatus using silver chloride as the pressure medium. In this apparatus the pressure was varied only at $T \geq 290^\circ\text{K}$, where the silver chloride is soft and capable of transmitting the pressure uniformly to the sample. Excellent agreement was obtained between data taken in the two apparatuses over their range of overlap. Details of the experimental techniques will be presented elsewhere.

Figure 1 shows the temperature dependence of the static dielectric constant ϵ_c of KDP mea-

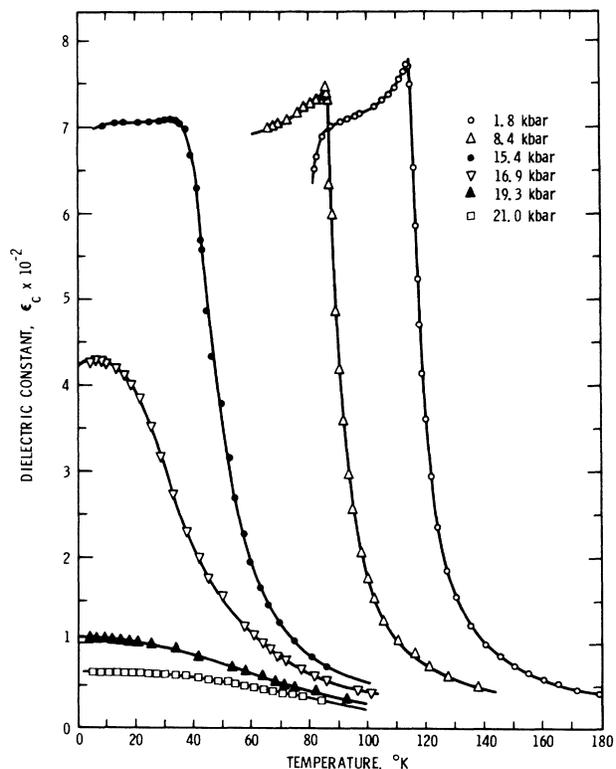


FIG. 1. Isobars of the static dielectric constant measured along the c axis versus temperature for KH_2PO_4 . The PE-to-FE transition vanishes at pressures >17 kbar.

sured along the c axis at different pressures. Up to ~ 15 kbar, the main effect of pressure is a large decrease of the transition temperature T_c . At higher pressures and the corresponding lower temperatures, the transition becomes rounded and less well defined. This is to be expected since the transition involves ionic displacements, and these displacements become sluggish at low temperatures. For the 16.9-kbar isobar there is still evidence for a transition at $\sim 8^\circ\text{K}$, but for pressures >17 kbar the transition vanishes. This is evidenced by the data for the 19.3- and 21-kbar isobars in Fig. 1, where there is no transition.

At high temperatures, ϵ_c in the PE phase obeys the Curie-Weiss law, $\epsilon_c = C/(T - T_0)$, over a wide temperature range. The extrapolated Curie temperature T_0 decreases with pressure at the same rate as does T_c . The Curie constant C decreases at a rate of 7×10^{-3} kbar $^{-1}$. At the higher pressures, deviations from the Curie-Weiss law occur for $T < 55^\circ\text{K}$, and these deviations become larger as we go to higher and higher pressures and, therefore, lower temperatures. Such deviations, which are associated with quantum lattice effects, are to be expected since the Curie-Weiss law is only a high-temperature approximation. At low temperatures, the data can be treated by an anharmonic-oscillator model in a manner similar to that employed by Barrett¹¹ for KTAO_3 and SrTiO_3 .

The 19.3- and 21.0-kbar data in Fig. 1 suggest the presence of a soft, $\tilde{q} = 0$, TO mode in KDP at these conditions. If this is the case, then the relatively large decrease in ϵ_c between the two pressures can be interpreted as resulting from a large increase in the frequency of this mode, in a manner similar to that observed in the perovskites.¹² This mode should be akin to, but probably differs in essential details from, the "FE mode" (a coupled proton-lattice mode) first observed by Kaminow and Damen¹³ in the PE phase at 1 bar. The difference is in the degree of proton-lattice coupling and the influence of this coupling on the character of the mode. The coupling is strong at 1 bar, but is expected to be very weak or nonexistent at ~ 20 kbar. The H-bond length R decreases by 0.13% per kbar (see later discussion); and at 20 kbar, R is reduced to $\sim 2.44 \text{ \AA}$. For such a short bond the potential is a steep, essentially harmonic well,³ so that there should be very little if any proton-lattice coupling (in the sense of the above model). Clearly, light and/or neutron scattering studies at high pres-

sure will be extremely useful in elucidating these features. The change in the character of the "FE mode" as the proton-lattice coupling weakens at high pressure should provide a better insight into the nature of this coupling.

Figure 2 shows the shift of T_c with pressure for KDP. The data were obtained on three crystals and in the two pressure apparatuses. The initial shift is linear with slope equal to $-4.6 \pm 0.1^\circ\text{K/kbar}$, in good agreement with some of the earlier work.^{2,5} The slope increases at high pressure with indication that $T_c \rightarrow 0^\circ\text{K}$ with infinite slope. Above 10 kbar the results obey the empirical expression $T_c^2 = k(p^* - p)$, with $p^* = 17.1$ kbar and $k = 710 \pm 10^\circ\text{K}^2/\text{kbar}$. We note in passing that the T_c vs p data can be fit by an expression such as Eq. (2), but the fit is not unique, and difficulty occurs at the high-pressure end. This is largely because the details of the H-bond potential and its variation with pressure are not known. We shall not dwell on this here.

The behavior of ADP is qualitatively similar to that of KDP. In ADP, the large dielectric constant anomaly is along the tetragonal a axis, and the PE-AFE transition is strongly first order.

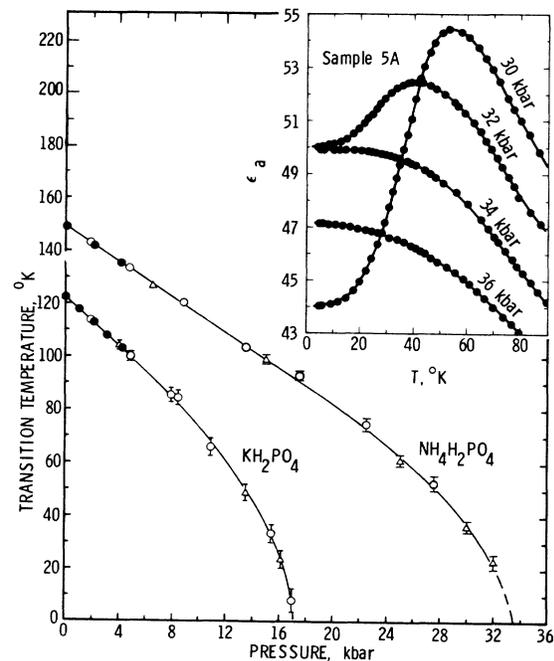


FIG. 2. Shifts of the transition temperatures of KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ with pressure. For each crystal, data on three samples and obtained in two different pressure apparatuses are shown. The closed circles represent data taken in the helium-gas apparatus. The inset shows the vanishing of the PE-to-AFE transition temperature in $\text{NH}_4\text{H}_2\text{PO}_4$ at pressures ≥ 34 kbar.

The transition temperature decreases with increasing pressure and ultimately vanishes at $p > 33$ kbar. The vanishing of the AFE phase is shown in the inset in Fig. 2. The 30- and 32-kbar isobars clearly show the transition, whereas no transition occurs at 34 and 36 kbar. Further evidence for the vanishing of the AFE phase is provided by the fact that in the AFE state ϵ_a increases with pressure from a value of ~ 8 at 1 bar to 50 at 32 kbar and then reverses direction and decreases at higher pressures as is shown in Fig. 2. The decrease in ϵ_a with pressure is the expected behavior for the PE phase. Figure 2 shows the pressure dependence of the transition temperature of ADP. Data on three crystals are shown. The initial shift is linear with a slope of $-3.40 \pm 0.05^\circ\text{K}/\text{kbar}$, which is in excellent agreement with an earlier value.⁵ We note (see inset, Fig. 2) that at low temperatures the transition becomes spread over a relatively large temperature range. For the data in Fig. 2 we arbitrarily defined the transition temperature as that at which the transition is half complete.

Finally, a comparison between the values of the initial shift of the transition temperature T_c of KDP and ADP with pressure is revealing. The initial logarithmic derivatives ($d \ln T_c / dp$) are -3.75×10^{-2} per kbar and -2.30×10^{-2} per kbar, respectively. This difference turns out to be almost completely due to a difference in the compressibility of the H bond in the two crystals. The a -axis compressibilities ($\partial \ln a / \partial p$) are $(-1.27$ and $-0.82) \times 10^{-3}$ per kbar for KDP and ADP, respectively. If it is assumed that the bond length R scales with the a axis, which is a good assumption for these crystals, then we can calculate the change in T_c with R . The results are $d \ln T_c / dR = 11.8 \text{ \AA}^{-1}$ for KDP and 11.2 \AA^{-1} for ADP. (At 1 bar, $R \approx 2.50 \text{ \AA}$ for both crystals.) Within all of the experimental uncertainties, the two values are essentially the same. Thus, even though the low-temperature phase is FE in KDP and AFE in ADP, which implies differences in the proton-lattice coupling, the above result provides strong evidence that it is the H bond which plays the key role in determining the transitions in these crystals. At sufficiently high pressure the ordering

of the protons and the resulting FE and AFE transitions vanish.

It is of interest to note here that the similarities in the pressure response between KDP and ADP are in marked contrast with the behavior of the FE and AFE perovskites. For these latter crystals the FE and AFE modes exhibit opposite pressure dependences.¹² Thus, the pressure results point to important differences in the basic mechanisms in the two classes of crystals and indirectly re-emphasize the role of the H bond in KDP and ADP.

A more complete account of this work along with results on the deuterated crystals and the spontaneous polarization will be published elsewhere.

It is a pleasure to acknowledge the excellent technical assistance of P. E. Hammons, and the advice of D. B. McWhan and A. L. Stevens in the design and construction of the high-pressure, low-temperature apparatus.

*Work supported by the U. S. Atomic Energy Commission.

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