

Temperature-uniaxial pressure phase diagram of KH_2PO_4

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In this work we present the uniaxial pressure-temperature phase diagram of KH_2PO_4 (KDP), for temperatures near the ferroelectric phase transition at 122 K. Using Raman measurements we show that under uniaxial pressure the KDP undergoes two metastable transitions: (i) from tetragonal D_{2d}^{12} phase to orthorhombic $C_{2v}^{j \neq 19}$ phase at 126 K and $\sigma_6 = 1.12$ kbar, and (ii) from orthorhombic C_{2v}^{19} phase to the same orthorhombic $C_{2v}^{j \neq 19}$ phase as before, at 110 K and $\sigma_6 = 0.3$ kbar. We discuss the reversibility paths of these metastable phases, and provide an explanation to the appearance of the $C_{2v}^{j \neq 19}$ phase, based on the Gibbs free energy density of the system. [S0163-1829(99)10005-5]

KH_2PO_4 (KDP) was one of the earliest ferroelectric crystals to be discovered¹ and probably is the most extensively investigated.² At room temperature, the KDP is in the paraelectric phase and belongs to the $I42d$ (D_{2d}^{12}) space group. At 122 K the free crystal (mechanically unstressed and electrically unbiased) undergoes an almost second-order transition to the ferroelectric phase with $Fdd2$ (C_{2v}^{19}) space group symmetry. Two other phase transitions for KDP have also been observed. At 453 K the crystal goes to a monoclinic nonpolar phase belonging to the C_{2h} factor group.³ Around 60 K it presents a diffuse phase transition⁴ to another polar monoclinic structure belonging to a space group C_s^i , where $i = 1, 2, 3, 4$.

The behavior of the ferroelectric transition $D_{2d}^{12} \rightarrow C_{2v}^{19}$ under hydrostatic pressure and/or DC electric field was widely investigated.⁵⁻¹¹ As the factor group D_{2d} is piezoelectric, the crystal is also a secondary ferroelastic system in the phase C_{2v}^{19} : a spontaneous strain S_6 appears in addition to the spontaneous polarization P_3 ; the piezoelectric coefficient d_{36} exhibits the same Curie-Weiss behavior of the dielectric susceptibility χ_{33} . Surprisingly, no study seems to exist in the literature before 1994 on the effect of uniaxial pressure on the phase transition. Moreover, we know of no work investigating the transitions under DC electric field above a few kV/cm. Recently our group discovered¹² that moderated uniaxial pressure σ_6 , induces transition from the D_{2d}^{12} and C_{2v}^{19} phases to a metastable orthorhombic phase belonging to a space group C_{2v}^j , $j \neq 19$. The reversibility criteria of these phase transitions, when temperature and uniaxial pressure are cycled both in the clockwise and counter-clockwise direction, are discussed in Ref. 13. Further, if the crystal is in the ferroelectric phase of symmetry C_s^i , intense electric field E_3 can induce first-order phase transition to the phase of symmetry C_{2v}^j .¹⁴

In this paper, we present the phase diagram for the KDP transitions on the plane (σ_6, T) for temperatures in the range from 110 to 130 K, using previous results reported in Refs. 12 and 13. The reversible and irreversible paths for the $D_{2d}^{12} \rightarrow C_{2v}^{j \neq 19}$ and $C_{2v}^{19} \rightarrow C_{2v}^{j \neq 19}$ metastable transitions are discussed. Moreover, from the properties of the Gibbs free energy density function of the system, we provide an explanation of the origin of the thermodynamically metastable $C_{2v}^{j \neq 19}$ phase.

The experiments were performed on crystals grown by slow evaporation, at controlled temperature, from solutions of commercial powder (Vetec) in tridistilled water. Monocrystals of good optical quality were cut and polished into parallelepipeds of dimensions $4 \times 3 \times 3$ mm³ for experiments under pressure. Care was taken to obtain good parallelism of the faces on which the uniaxial stress was to be applied. The parallelepipeds faces were orthogonal to the [110], [110], [001] directions of the tetragonal D_{2d}^{12} structure. It should be remarked that the crystallographic x, y axes of orthorhombic structure are rotated 45° relative to the X, Y axes of the tetragonal one. The stress apparatus uses a lever and a spring with $k = 2.59$ N/m. The force is measured through the use of two linear voltage differential transformers (LVDT) previously calibrated. The sample in its pressure holder can be placed in a dewar where the temperature can be controlled in the range from 80 to 300 K, with a resolution of ± 0.1 K. The crystal symmetry changes were investigated by Raman spectra. The 488 nm line of an argon laser, with light power around 1 W, was focused with a spherical lens on spots with diameter about 200 μm inside the crystal. The Raman spectra were analyzed in a double monochromator (Spex 1402) set for resolution of about 1 cm^{-1} . The experiments were performed in several crystal samples with reproducible results.

It is well known that if an external uniaxial pressure is applied, the symmetry of the deformed crystal is determined by the symmetry elements that are common to both the unstrained crystal and the strain ellipsoid. According to Ref. 12, a compressive force applied along the [001] direction leaves the crystal symmetry unaltered whereas a force applied along [100], [010] or [110] directions reduces the crystal symmetry for both tetragonal and orthorhombic structures of KDP. In Figs. 1(a) and 1(b) we show part of the stress dependent Raman spectra for the low frequency, taken at 126 and 110 K, respectively. The force was applied in the [110] direction of the D_{2d}^{12} symmetry of the tetragonal structure. The geometry chosen for the scattering was $(X-Y)(Z, X \pm Y)Z$, since it is the geometry that most clearly shows the quantitative changes in the Raman spectrum when the phase transition takes place, and then allows relatively easy identification of the transition points. In order to comply with the symmetry analysis presented in Ref. 12, the modifications

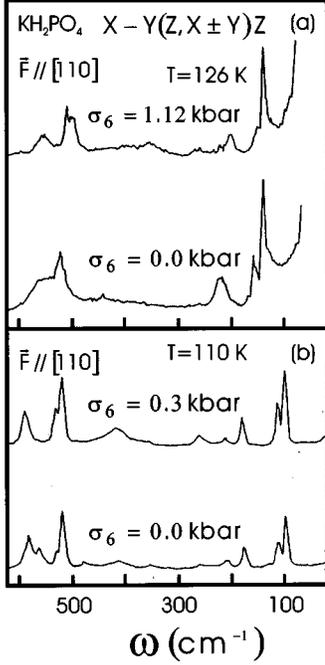


FIG. 1. Raman spectra of KDP, with E symmetry, as a function of temperature and uniaxial pressure. (a) $T=126$ K and $\sigma_6 = 1.12$ kbar, and (b) $T=110$ K and $\sigma_6 = 0.3$ kbar. The force is along the $[100]$ direction of the tetragonal phase.

observed are an evidence that the KDP crystal under uniaxial stress, undergoes a phase transition from D_{2d}^{12} symmetry to $C_{2v}^{j \neq 19}$ symmetry at 126 K and from C_{2v}^{19} symmetry to the same $C_{2v}^{j \neq 19}$ symmetry as before at 110 K. Similar Raman spectra can also be obtained in the whole temperature range from 110 to 130 K and for pressures as high as 1.12 kbar.

Following the procedure described in Ref. 13 to investigate the reversibility criteria of these phases, we can draw the phase diagram of KDP on the plane (σ_6, T) as shown in Fig. 2. The dashed lines indicate phase borders which can be crossed both ways and the solid line indicates a phase border which can be crossed only in the direction to the phase with $C_{2v}^{j \neq 19}$ symmetry. Therefore, if the system is in the phase $C_{2v}^{j \neq 19}$, it can be transformed to the phase C_{2v}^{19} only through a cycle of heating up to above the transition to the phase D_{2d}^{12} (with bias or without bias) and cooling down without bias or under small bias. We have checked that the crystal stays in the phase $C_{2v}^{j \neq 19}$ for several hours without mechanical bias if the temperature is low enough to prevent the transition to the paraelectric phase. Squares, triangles and open circles stand for the experimental observation of the phases D_{2d}^{12} , C_{2v}^{19} , and $C_{2v}^{j \neq 19}$, respectively. It should be observed that there is a coexistence point of three phases at $T=121$ K and $\sigma_6 = 0.16$ kbar.

The experiments suggest that the phase of symmetry $C_{2v}^{j \neq 19}$ is thermodynamically stable under moderated uniaxial mechanical pressure and metastable without this restriction, if the temperature is below the transition point to the paraelectric phase. We propose an explanation of this based on the properties of the Gibbs free energy density of the system. For a system in thermodynamic equilibrium, i.e., in a truly stable state, the Gibbs free energy is a function only of the intensive parameters and the temperature. Following

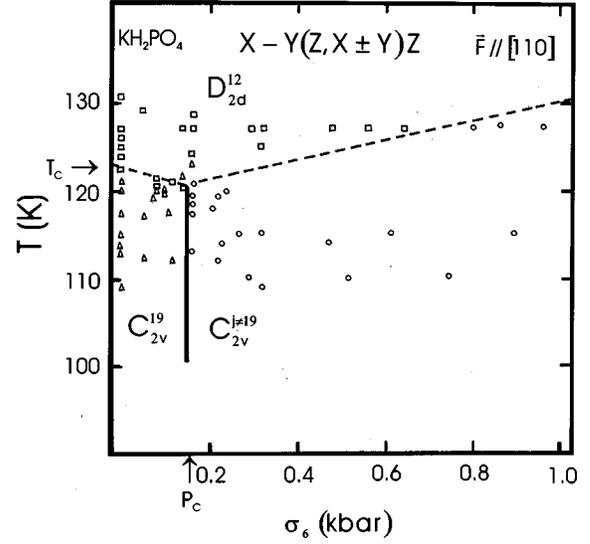


FIG. 2. Phase diagram of KDP on the plane (σ_6, T) for temperatures near the Curie point at 122 K. The dashed lines indicate phase borders which can be crossed both ways and the solid line indicates a phase border which can be crossed in the direction to the $C_{2v}^{j \neq 19}$ phase. Squares, triangles, and open circles stand for the experimental observation of the phases D_{2d}^{12} , C_{2v}^{19} , and $C_{2v}^{j \neq 19}$, respectively. The arrow indicates the critical pressure point where there is a coexistence of three phases at $T=121$ K.

Landau and Devonshire¹⁵ the general Gibbs potential \tilde{G} can be expanded in a Taylor series of the spontaneous polarization P_3 and the stress σ_6

$$\begin{aligned} \tilde{G}(T, P_3, \sigma_6) = & \tilde{G}_0(T) + \frac{1}{2} a_0 (T - T_0^s) P_3^2 + \frac{1}{4} b P_3^4 + \frac{1}{6} c P_3^6 \\ & + \frac{1}{8} d P_3^8 + \frac{1}{10} e P_3^{10} - \sigma_6 S_6 - h_{36} P_3 S_6 \\ & + \frac{1}{2} C_{66}^P S_6^2 + \dots, \end{aligned} \quad (1)$$

where $\tilde{G}_0(T)$ is the background lattice free energy density, T_0^s is the clamped Curie temperature which is the instability point in the absence of coupling to the elastic degrees of freedom, S_6 is the strain, h_{36} is the piezoelectric coefficient, C_{66}^P is the elastic stiffness coefficient, and the other coefficients are temperature independent. The stable or metastable states can be obtained from the equilibrium conditions

$$\frac{\partial \tilde{G}}{\partial P_3} = 0, \quad (2a)$$

$$\frac{\partial \tilde{G}}{\partial \sigma_6} = 0. \quad (2b)$$

For $\sigma_6 = 0$, Eq. (2b) gives $S_6 = h_{36} P_3 / C_{66}^P$ and Eq. (1) can be written as

$$\begin{aligned} \tilde{G}(T, P_3, 0) = & \tilde{G}_0(T) + \frac{1}{2} a_0 (T - T_0) P_3^2 + \frac{1}{4} b P_3^4 + \frac{1}{6} c P_3^6 \\ & + \frac{1}{8} d P_3^8 + \frac{1}{10} e P_3^{10} + \dots, \end{aligned} \quad (3)$$

where $T_0 = T_0^S + h_{36}^2 / a_0 C_{66}^P$.

The expansion in Eq. (3) with $e = 0$, has been considered by many authors.^{16–20} The values of the coefficients a_0 and b obtained from measurements of $P_3(t)$ for $E_3 = 0$ and $E_3 \neq 0$ or of other nonlinear electrical properties of the crystal. The bulk of the data also suggest that the coefficient d is very small. Many authors could fit their data by assuming $d = 0$.^{17–19} On the other hand, Sidnenko and Gladkii¹⁸ proposed rather large values of d , but that was based on the assumption that $c = 0$ and this seems to contradict the conclusion of their own results. Vallade²⁰ considered both coefficients c and d as fitting parameters for his data on nonlinear electric susceptibility. He concluded that the best fitting is obtained with a small value for d and a large value for c . His values for the coefficients, in esu units, are $a_0 = 3.9 \times 10^{-3}/\text{K}$, $b = (-1.85 \pm 0.25) \times 10^{-11}$, $c = (3.3 \pm 0.5) \times 10^{-19}$, and $d = (0.87 \pm 0.5) \times 10^{-27}$. In this paper, we provide an explanation of the existence of the $C_{2\nu}^{j \neq 19}$ phase below 122 K, by assuming that $d = 0$, and that the e coefficient is negative. Figure 3 shows plots of $\tilde{G}(110, P_3, 0) - \tilde{G}_0(110)$ as a function of the spontaneous polarization P_3 for some values of e . It can be seen that even small values of e ($e < 0$) can create a second minimum for $\tilde{G} - \tilde{G}_0$ relatively close to the point $P_3 = P_{3s}$, where P_{3s} is the spontaneous polarization in the space $C_{2\nu}^{19}$. Of course, to stabilize the system we have in this case to add to Eq. (3) a term $(1/12) f P_3^{12}$, with $f > 0$. Hence, we conclude that for any value of e smaller than -0.03×10^{-35} esu, the minimum at P_{3s} is unstable under the application of a uniaxial pressure. When the dipoles are in the second minimum, they do not have energy enough to overcome the potential barrier and go back to the minimum at P_{3s} , even releasing the pressure back to $\sigma_6 = 0$ kbar. Only when the temperature is increased above 122 K (stable D_{2d}^{12} phase) and decreased below it, the stable $C_{2\nu}^{19}$ phase can be reached. This irreversibility can be understood as an evidence of a lowering of the cell potential due to an increase in the dipole interactions. Similar procedure can be adopted to describe the existence of the $C_{2\nu}^{j \neq 19}$ phase above 122 K.

In conclusion we have shown from Raman measurements that under moderated uniaxial pressure parallel to the [110] direction, KDP undergoes two phase transitions, namely: (i) from the tetragonal D_{2d}^{12} structure to the orthorhombic $C_{2\nu}^{j \neq 19}$ structure at 126 K and $\sigma_6 = 1.12$ kbar, and (ii) from the

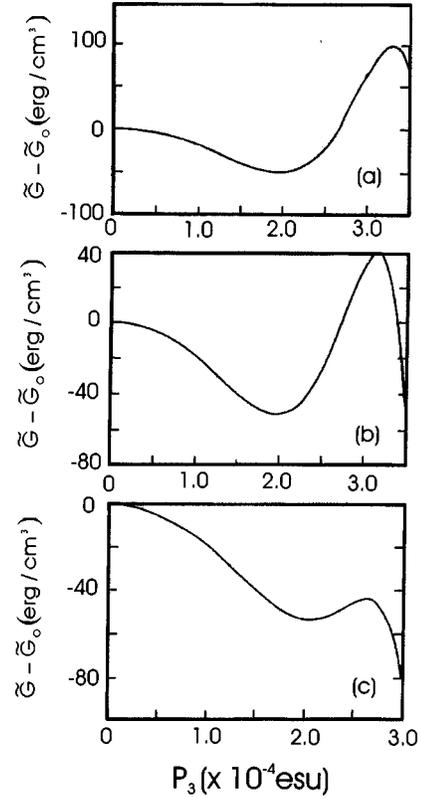


FIG. 3. Plot of the general Gibbs free energy $\tilde{G}(110, P_3, 0) - \tilde{G}_0(110)$ as a function of the spontaneous polarization P_3 for some values of e . (a) $e = -0.025 \times 10^{-35}$, (b) $e = -0.03 \times 10^{-35}$, and (c) $e = -0.05 \times 10^{-35}$. In this simulation we have used the values obtained by Vallade in Ref. 20 for the constants a_0 , b , and c .

orthorhombic $C_{2\nu}^{19}$ to the same orthorhombic $C_{2\nu}^{j \neq 19}$ as before, at 110 K and $\sigma_6 = 0.3$ kbar. The reversibility of these metastable transitions when temperature and pressure are cycled around the phase borders was studied. We observed that the $D_{2d}^{12} \rightarrow C_{2\nu}^{j \neq 19}$ transition is reversible whereas the $C_{2\nu}^{19} \rightarrow C_{2\nu}^{j \neq 19}$ transition is irreversible when the stress is released back to $\sigma_6 = 0$ kbar. Summing up all the results, we were able to draw for the first time the phase diagram of KDP on the plane (σ_6, T) . In order to explain the existence of the thermodynamically unstable $C_{2\nu}^{j \neq 19}$ phase, we have expanded the phenomenological Gibbs free energy density of the system up to P_3^{10} [see Eq. (1)]. It is observed that even small values of e produces a second minimum for the crystal energy, which is related to the metastable $C_{2\nu}^{j \neq 19}$ phase.

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