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Phase transition in potassium dihydrogen phosphate induced by an applied static electric field

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Raman scattering experiments show that the potassium dihydrogen phosphate (KDP) crystal undergoes a phase transition at 20 K induced by a static electric field applied along the [001] direction relative to the orthorhombic structure. Qualitative changes occur in the Raman spectra of $X(ZX)Y$ and $X(YZ)Y$ scattering geometries for applied dc electric field intensities of the order of 4.7 kV/cm or higher. The phase transition exhibits an irreversible character similar to that presented by KDP under uniaxial pressure at 110 K. [S0163-1829(96)08434-2]

Potassium dihydrogen phosphate (KDP) is the prototype of a family of ferroelectric crystals with bridging hydrogen bonds. Its physical properties have been studied extensively in the last five decades.[1–17] Busch[18] was the first to show that KDP exhibits a ferroelectric phase transition at low temperature. Nowadays, it is known that KDP can undergo at least four crystalline modifications in the temperature range 10–525 K (KDP fusion point). The two most studied KDP phases, the tetragonal and orthorhombic phases, belong to $I\bar{4}2d$ (D_{2d}^{12}) and $Fdd2(C_{2v}^{19})$ space groups, respectively. The tetragonal phase is stable at room temperature and the orthorhombic phase exists below $T_c=122$ K. The monoclinic phase belonging to C_{2h} factor group is obtained when the crystal or a powder sample is heated to a temperature above 453 K.[19]

Recently, Raman spectra and polarization measurements have showed the occurrence of a phase transition in KDP taking place at temperatures near 60 K.[20] In this transition, the crystalline structure undergoes a change from C_{2v}^{19} space group (orthorhombic structure) to a C_s^i space group (monoclinic structure), where $i=1,2,3,4$.

Under uniaxial pressure, KDP undergoes two phase transitions when the force is applied along the [100] or [010] direction relative to the orthorhombic structure (ferroelectric phase) for temperatures near T_c.[21,22] One phase transition occurs at 125 K when the uniaxial pressure is of the order of 0.5 kbar. In this phase transition, the KDP crystal change from a tetragonal structure (D_{2d}^{12} space group) to an orthorhombic structure belonging to C_{2v}^r space group, with $r\neq 19$. The other phase transition occurs at 110 K when the uniaxial pressure is of the order of 0.3 kbar. This phase transition, maintains the KDP structure as orthorhombic, with the same factor group C_{2v}, but with a different class of the space group, different from the original 19.

By using Brillouin-Rayleigh scattering to study the KDP ferroelectric phase transition, Courtens and Gammon[23] have observed that the transition from the paraelectric to the ferroelectric phase is suppressed under hydrostatic pressure with removal of the static central peak. Western *et al.*[24] found a tricritical point when studying KDP under an electric field and a hydrostatic pressure.

In this work the effect of a static electric field on the normal modes of KDP is studied. The polarized Raman spectra of KDP at $T=20$ K shows that a diffuse phase transition takes place starting from fields intensities of the order of 4.7 kV/cm. We suppose that this transition is related with translations, librations and bending modes of the PO_4^{3-} ions.

KDP single crystals were grown from saturated solutions of KH_2PO_4 powder in tridistilled water by slow evaporation at controlled temperatures. The crystals obtained with this process were transparent and have good optical quality. The $6\times5\times1.5$ mm^3 crystals were prepared with silver electrode evaporated onto the large faces which are perpendicular to the ferroelectric c axis. The voltage applied in the sample were done by a source model 246 high voltage supply of the Keithley Instruments with a maximum output voltage of ±3 kV.

Raman measurements were done with a conventional equipment (argon ion laser and double monochromator), with an instrumental resolution of 1 cm^{-1} in all experiments. The crystallographic x and y axes of the orthorhombic structure are rotated 45° relative to the crystallographic x' and y' axes of the tetragonal structure. In the geometries of scattering X, Y and Z are relative to the crystallographic axes of the orthorhombic structure. Raman measurements at low temperature were obtained with samples placed in a close-cycle helium refrigerator. The temperature was controlled with a precision of ±0.1 K.

Raman spectra of the monoclinic phase of KDP at 20 K without applied dc electric field are shown in Fig. 1. The geometries chosen for the light scattering were $X(ZZ)Y$, $X(YX)Y$, $X(YZ)Y$ and $X(ZX)Y$, relative to the crystalline axes x, y, and z of the orthorhombic structure. These geometries yield Raman spectra for the $A'(ZZ,XY)$ and $A''(ZX,YZ)$ irreducible representations of the C_s factor group, respectively.[20] A typical KDP Raman spectrum (see Fig. 1) can be divided in two regions: (i) a high frequency region ($w>800$ cm^{-1}), with internal modes due to stretching of the PO_4^{3-} ions; (ii) a low frequency region ($w<800$ cm^{-1}), with modes due to librations and bending of the phosphate ions, as well as translations of all ions. The internal vibrations of PO_4^{3-} ions observed at 20 K are distributed among the irreducible representation of the C_s factor group

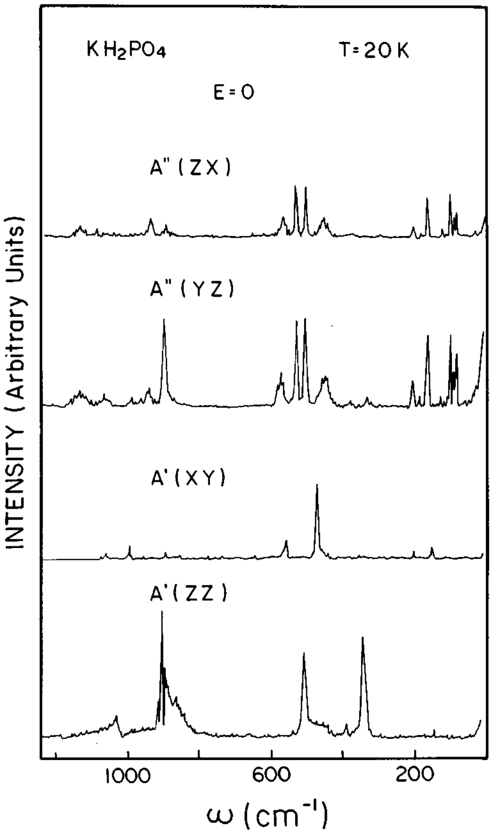


FIG. 1. KDP Raman spectra at 20 K in the monoclinic phase without a dc electric field. (a) and (b) $A'(ZZ,XY)$; (c) and (d) $A''(ZX,YZ)$.

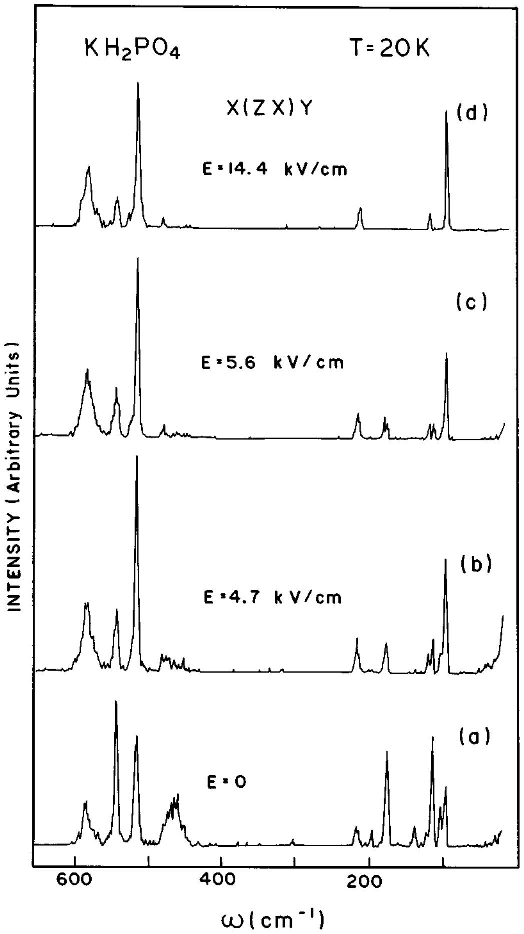


FIG. 2. KDP Raman spectra at 20 K of the $X(ZX)Y$ scattering geometry as a function of the dc electric field.

as $\Gamma_{\text{vib}}(\text{PO}_4^{3-})=A'(\nu_1,2\nu_2,3\nu_3,3\nu_4)+A''(\nu_1,2\nu_2,3\nu_3,3\nu_4)$. A detailed discussion on the distribution of the normal modes of KDP in the irreducible representations of the C_s factor group has been published elsewhere.[20]

A static electric field was applied along the [001] direction relative to orthorhombic structure of the KDP at 20 K. Qualitative modifications in the irreducible representations $A'(ZZ)$ and $A'(XY)$ were not observed, even with fields as high as 14.4 kV/cm. In contrast, qualitative modifications are observed in the Raman spectra of irreducible representations $A''(ZX)$ and $A''(YZ)$ for dc electric fields of the order of 4.7 kV/cm or higher.

Figure 2 shows the low frequency region of the Raman spectra as a function of applied dc electric field for the $A''(ZX)$ representation at 20 K. The spectrum labeled (a) corresponds to the monoclinic phase of KDP without an applied dc electric field. By increasing the dc electric field up to 14.4 kV/cm, we can observe slow and continuous qualitative modifications in the Raman spectra. The spectrum labeled (b) was obtained with the crystal under a dc electric field of 4.7 kV/cm when qualitative changes have started to appear. At this value of the field, the disappearance of the translations modes with frequencies of 140 and 200 cm^{-1} is observed, as well as a rapid decrease in the intensity of bending mode of phosphate ions at approximately 480 cm^{-1}. By increasing the dc electric field up to 5.6 kV/cm qualitative modifications occur that are shown in Fig. 2(c). These modifications are irreversible in the following way: all features seen in the Raman spectrum of Fig. 2(c) remain present when the dc electric field is turned of, and the crystal is maintained in this condition for an arbitrarily long time. To go back to Raman spectra of KDP in the monoclinic structure without an applied dc electric field, the temperature of the crystal has to be increased over the Curie temperature ($T_c=122$ K), and then cooled to temperatures below 60 K. Clearly, the phase transition from ferroelectric phase to this phase is not reversible. This irreversibility can be understood as a manifestation of a lowering in the cell potential due to an increase in the dipole interactions. A reduction of the dc electric field intensity is not sufficient to overcome the potential barrier created by dipole interactions. To overcome the potential barrier, thermal energy has to be transferred to the dipoles by increasing the temperature of the crystal above the Curie temperature (122 K). The paraelectric phase is observed in the Raman spectrum. Now, by cooling the crystal to temperatures below 60 K, the Raman spectrum of the monoclinic phase is reached. The irreversibility of this phase transition induced by a static electric field is similar to that already observed in KDP under uniaxial pressure.[21]

Figure 3 shows the Raman spectra of KDP as a function of the intensity of the dc electric field that was obtained with

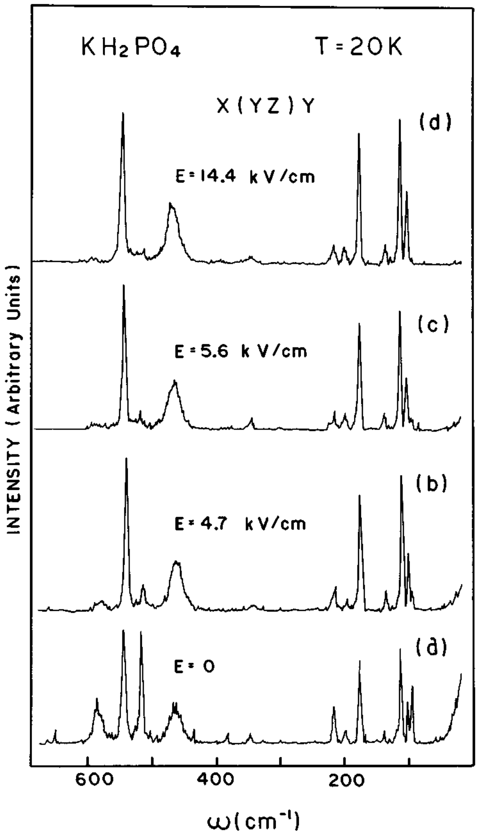


FIG. 3. KDP Raman spectra at 20 K of the $X(YZ)Y$ scattering geometry as a function of the dc electric field.

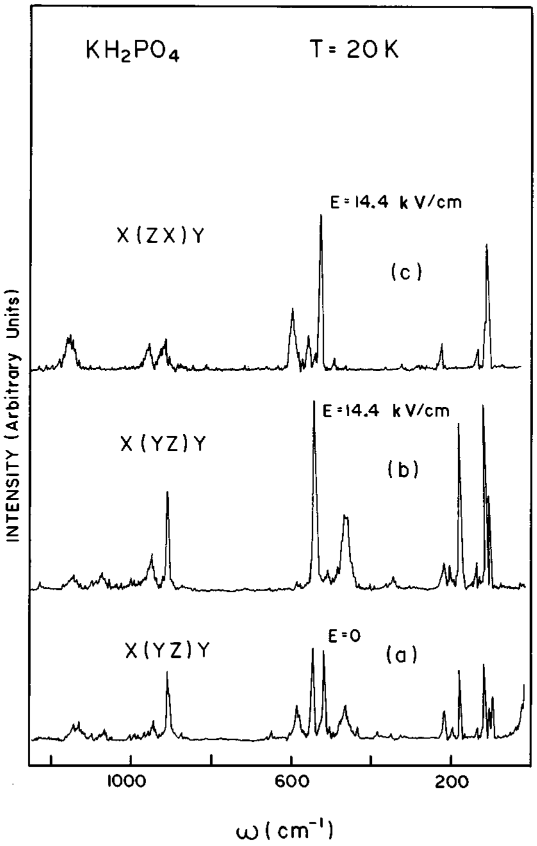


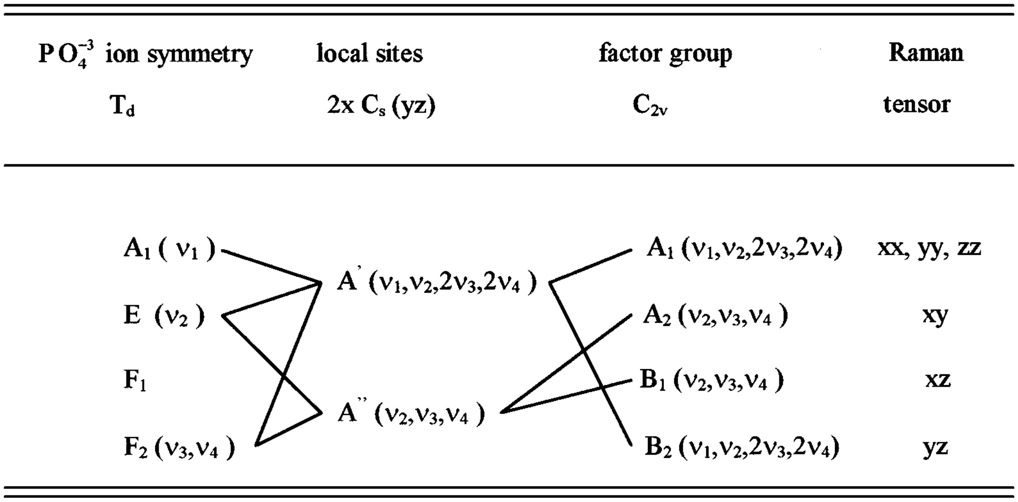
FIG. 4. KDP Raman spectra at 20 K of the $X(ZX)Y$ and $X(YZ)Y$ scattering geometries: (a) in the absence of a dc electric field; (b), (c) under dc electric field of the order of 14.4 kV/cm.

a $X(YZ)Y$ scattering geometry. While Fig. 3(a) is identical to Fig. 2(a), Fig. 3(b) shows an abrupt change in the intensities of the modes with frequencies of the order of 520 and 580 cm^{-1}. After the most visible modifications occurring for fields around 5.6 kV/cm, [see Figs. 2(c) and 3(c)], only qualitative changes are found with fields as high as 14.4 kV/cm in the $X(ZX)Y$ scattering geometry [see Fig. 2(d)]. This can be interpreted as a stabilization of the KDP lattice through a diffuse phase transition that takes place starting with fields of the order of $E_0 \cong 4.7$ kV/cm.

Figure 4(a) shows the Raman spectrum of the KDP crystal in the monoclinic phase at 20 K identical to Figs. 1(c) and Fig. 1(d). Figures 4(b) and 4(c) show the Raman spectra of the KDP crystal under dc electric field of the order of 14.4 kV/cm obtained with the $X(YZ)X$ and $X(ZX)Y$ scattering geometries. Clearly, the Raman spectra of Fig. 4 are qualitatively different. Figures 4(b) and 4(c) correspond to different irreducible representations that are diverse from the one without an applied dc electric field [Fig. 4(a)]. The Raman spectrum of the $X(ZX)Y$ scattering geometry shows shade of modes with frequencies around 580 and 915 cm^{-1} belonging to $X(YZ)Y$ scattering geometry. An explanation of these changes based on the motion of domain walls due to the applied static electric field can be ruled out since the dipoles are necessarily in C_1 local sites symmetries in the monoclinic structure, and the Raman spectrum shows the situation in each local site of the ions irrespective of the possible formation of domains. Changes occurring in the number of modes belonging to unidimensional representation can only be ascribed to a structural modification. A reasonable explanation for this observation, based in a group theoretical analysis, is as follows: the PO_4^{3-} ions change from C_1 local sites symmetries in a monoclinic structure with C_s factor group to C_s local sites symmetries in an orthorhombic structure with C_{2v} factor group, inducing a structural modification in the crystalline lattice of the KDP. An increase was found in the symmetry of the crystal with the applied dc electric field. To find it exactly it would be necessary to make an x-ray measurement at low temperature. Table I shows the correlation chart of the phosphate ions in the C_s local sites symmetries between the symmetry ion and the C_{2v} factor group. The changes of the PO_4^{3-} ions are suitable to increase the dipole interactions, producing a lowering of the cell potential that can explain the irreversible character of the phase transition that the KDP crystal exhibits under a dc electric field at 20 K. In the absence of a dc electric field, the stability of this phase is guaranteed by the increase of the dipole interactions.

A diffuse phase transition in KDP crystal induced by an applied static electric field was observed with Raman scattering measurements. It was found clearly distinctive, qualitatively different spectra as compared to that of the monoclinic phase. The spectra of this phase have sharp and well-defined structures. This phase is induced by changes in the local sites symmetries of the PO_4^{3-} ions in the KDP crystal

TABLE I. Correlation chart of the phosphate ions in the C_s local sites symmetries between the ion symmetry and the C_{2v} factor group.



under dc electric field intensities of the order of 4.7 kV/cm or higher. The electric field supplies the necessary stress to accommodate the phosphate ions in diverse C_1 local sites symmetries, as observed by the Raman measurements. This phase is irreversible in the sense that the Raman spectra of the monoclinic structure are only recovered when the crystal is heated over the Curie temperature and then cooled again to temperatures below 60 K, without an external electric field. In the absence of a dc electric field, the stability of this phase can be explained through the increase of the strength of the dipole interactions produced by a reduction of the cell potential.

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