

New Phase Transition in KDP

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Received January 22, 1992

Raman and pyroelectric measurements in KDP below the transition from the paraelectric phase to the ferroelectric phase **indicate** the occurrence of another phase transition. This **transition** is explained as due to a lowering of the local symmetry of the phosphate ions in the unit cell.

I. Introduction

It was first shown by Busch¹ that Potassium Dihydrogen Phosphate, KH_2PO_4 (KDP), exhibits a phase transition at low temperature. KDP is a prototype of a family of crystals with bridging hydrogen bonds and its physical properties have been extensively studied²⁻¹³. Above the Curie temperature T_c , KDP has tetragonal structure belonging to space group $I4_2d$ (D_{2d}^{12}). The orthorhombic phase belongs to space group $Fdd2$ (C_{2v}^{19}) and exists at temperatures lower than $T_c=122$ K.

A partial identification of the Raman-active modes of the ferroelectric phase at $T = 20$ K was done by Agrawal and Perry¹⁴. Detailed measurements of the frequencies and linewidths of KDP Raman-active modes in a temperature interval from 10 K to 471 K have been published elsewhere¹⁵⁻¹⁶. It was shown that a strong anharmonicity is present and acts on Raman modes in the transition from the ferroelectric to the paraelectric phases.

In this work we present a study of the polarized Raman spectra at temperatures below T_c . Results from pyroelectric measurements in the same temperature interval are also presented. It is shown that a diffuse phase transition takes place at temperatures around 60 K. This transition is related to a freezing of librational modes of the PO_4^{-3} ions, with a lowering of their local symmetry.

II. Experimental

KDP single crystals were grown by slow evaporation, at controlled temperatures, of supersaturated solutions of KH_2PO_4 powder in tridistilled water. Samples obtained from these crystals were transparent, with good optical quality and measuring approximately $6 \times 8 \times 20 \text{ mm}^3$. Raman measurements were done with a conventional equipment (argon ion laser and double monochromator) yielding an instrumental resolution of

1 cm^{-1} in all experiments. The pyroelectric coefficient was determined at constant stress using the dynamic technique of Lang and Steckel¹⁷. In this method the sample is shunted by a high value calibrated resistor, usually $10^9 - 10^{10}$ ohms. The voltage produced by the sample, while its temperature is slowly and uniformly varied, is measured by a high impedance electrometer. Under these conditions, it can be shown that the voltage is related to the pyroelectric coefficient by

$$V = pAR_s(dT/dt) \quad (1)$$

where V is the voltage, p is the pyroelectric coefficient, A is the sample area, R_s is the resistance of the shunt resistor and dT/dt is the rate of change of the absolute temperature. Raman and pyroelectric measurements at low temperature were obtained with samples placed in a closed-cycle helium refrigerator where the temperature could be controlled within ± 0.1 K.

III. Group Theory analysis

The primitive cell of KDP contains two molecules in both phases. A group theoretical analysis of the normal modes of KDP at the center of the Brillouin zone has been done by Schur¹⁸⁻¹⁹. A distribution of the 48 normal modes among the irreducible representations of the factor group C_{2v} is:

$$\Gamma = 11A_1 + 11A_2 + 13B_1 + 13B_2 \quad (2)$$

These modes are separated as acoustic modes, translations, librations and internal vibrations of the H^+ , K^+ and PO_4^{-3} ions. All these ions occupy $C_2(z)$ symmetry sites in the orthorhombic structure. A_2 symmetry modes are Raman active and infrared inactive and A_1 , B_1 and B_2 modes are Raman and infrared active. Internal vibrations of the PO_4^{-3} ions are distributed among the irreducible representations of the C_{2v} factor group as:

$$\begin{aligned} \Gamma_{\text{vib}}(\text{PO}_4^{-3}) = & A_1(\nu_1, 2\nu_2, \nu_3, \nu_4) \\ & + A_2(\nu_1, 2\nu_2, \nu_3, \nu_4) + B_1(2\nu_3, 2\nu_4) \\ & + B_2(2\nu_3, 2\nu_4) \end{aligned} \quad (3)$$

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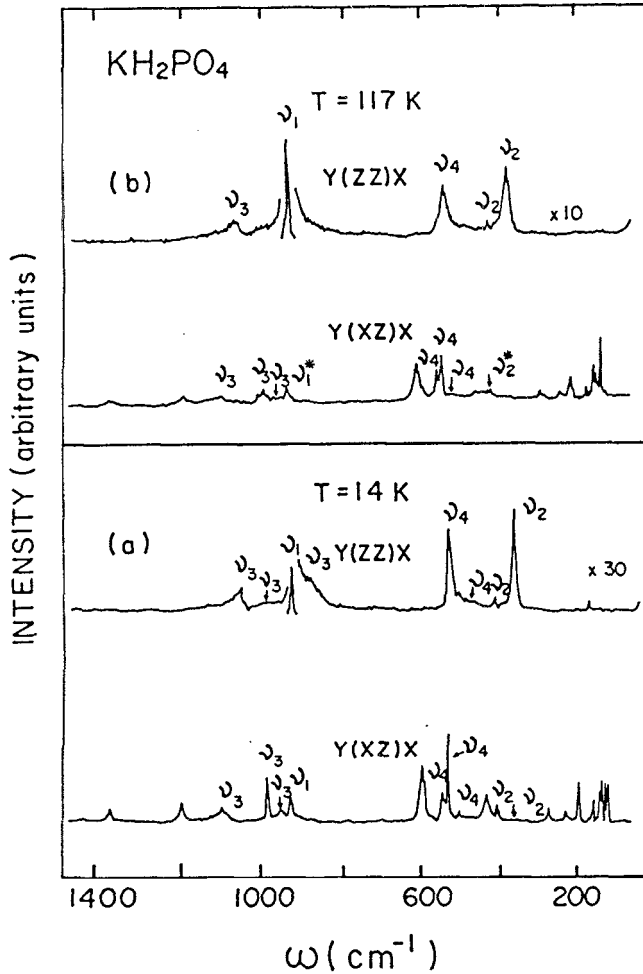


Figure 1: Raman spectra of KDP. (a) $T = 14$ K, $A_1 - Y(ZZ)X$, $(B_1 + B_2) - Y(XZ)X$. (b) $T = 117$ K, same geometries as in (a).

The effective correlation is acting only on two KDP molecules in the primitive cell.

IV. Results and Discussion

A. Raman measurements

The number of internal Raman modes due to vibrations of the PO_4^{-3} ions at 117 K is consistent with these ions residing in sites with $C_2(z)$ local symmetry, as discussed in Sect. III. However, this is not the case at $T = 14$ K. An analysis of the distribution of these modes by group theory methods has shown that the PO_4^{-3} ions should be in sites with C_1 local symmetry, for temperatures below 50 K. Figure 1 shows Raman spectra of KDP taken at 14 K and 117 K. A detailed analysis of the Raman spectra of KDP for a large range of temperatures and under applied uniaxial stresses is given elsewhere²⁰. In Figure 1, scattering geometries were $Y(ZZ)X$ and $Y(XZ)X$, relative to the tetragonal structure. These geometries yield Raman spectra for the A_1 and $B_1 + B_2$ irreducible representations, respec-

tively, of the C_{2v} factor group. Modes of $A_1(z)$ symmetry are purely TO modes, while $B_1(x)$ and $B_2(y)$ modes are of mixed nature. Internal vibrations of the PO_4^{-3} ions, such as ν_1 and ν_3 (stretching) and ν_2 and ν_4 (bending), are seen in the spectra of Figure 1. In the low frequency region ($\omega < 300$ cm^{-1}), the spectra display the external modes (librations and translations) of the PO_4^{-3} , K^+ and H^+ ions. Modes with frequencies higher than 1200 cm^{-1} are due to vibrations of the OH groups. We did not observe any indication of cell doubling effects.

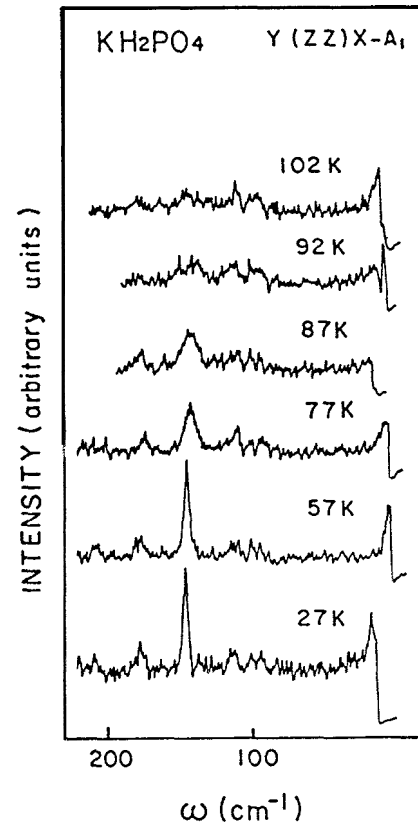


Figure 2: Low frequency A_1 symmetry Raman spectra of KDP, taken at various temperatures.

The internal vibrations of PO_4^{-3} ions, observed at 14 K, are distributed among the irreducible representations of the C_{2v} factor group as:

$$\Gamma_{\text{vib}}(PO_4^{-3}) = 9A_1 + 9(B_1 + B_2) \quad (4)$$

This distribution is clearly in disagreement with the one shown in Eq. 3. It is seen that the PO_4^{-3} ions do not occupy sites with $C_2(z)$ symmetry at 14 K. A plausible explanation for this discrepancy is given by assuming that KDP undergoes a structural phase transition of the order-disorder type, between 14 and 117 K. Other evidences for such transition, from pyroelectric results, are given in Sect. IV.B.

A detailed study was done on the lattice mode with frequency 150 cm^{-1} belonging to A_1 symmetry. This

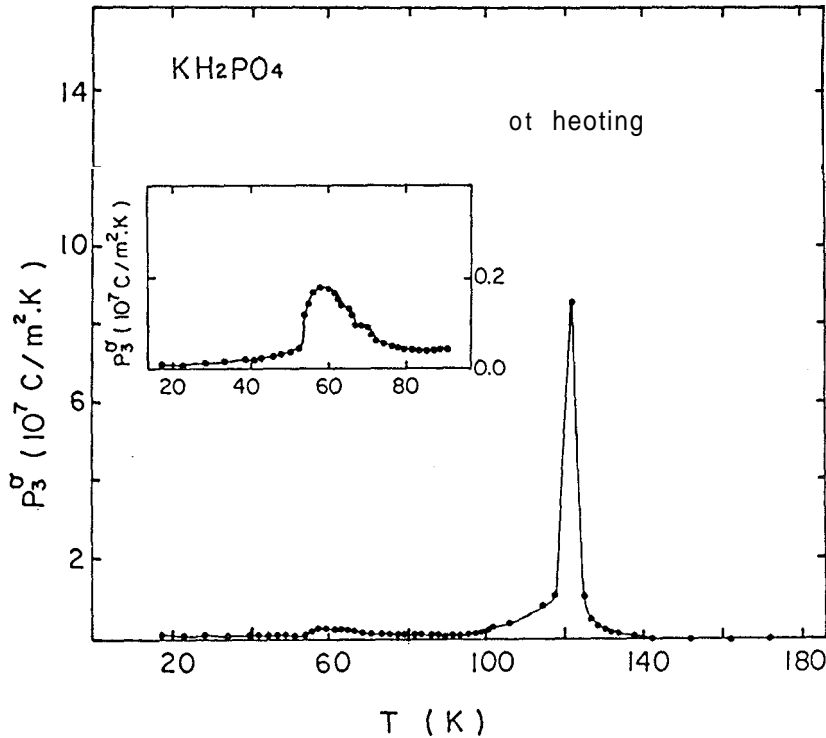


Figure 3: Temperature dependence of the pyroelectric coefficient P_3^σ in a heating cycle. Inset: blown-up vision of the anomaly around 60 K.

Raman band is shown in Figure 2, for the temperature range from 14 K to 102 K. It is seen that the intensity of the band decreases while its linewidth increases in the temperature range from 57 to 102 K. This is the same interval where some bands due to internal vibrations of the phosphate ions disappear, as discussed above. We did not observe any soft mode or any indication of cell doubling in this temperature range. The distribution of internal modes of the phosphate ions at temperatures below 50 K is consistent with these ions occupying sites with C_1 local symmetry. From a group theoretical analysis, it was seen that a C_{2v} factor group cannot accommodate PO_4^{-3} ions in sites with C_1 local symmetry without a Brillouin zone folding. However a monoclinic structure with a C_s factor group can accommodate PO_4^{-3} ions in sites with C_1 local symmetry. Table 1 shows the correlation chart for phosphate ion vibrations between C_{2v} and C_s factor groups. Any of the two possible correlations between C_{2v} and C_s factor groups will give the same distribution of the internal modes of the phosphate ions, with a monoclinic structure of C_s factor group. Comparing our results with the analysis of Table 1, we conclude that KDP changes, at a temperature around 117 K, from the orthorhombic structure with C_{2v} factor group to a monoclinic structure with C_s factor group.

B. Pyroelectric measurements

Pyroelectric measurements were done both upon

cooling and heating KDP crystal between 20 K and 300 K. Plates were cut from KDP crystal with planes both parallel or perpendicular to the polar crystallographic c axis, relative to the tetragonal structure. The ferroelectric phase transition is detected in the pyroelectric curves for samples in any of the two orientations and both in cooling and heating cycles. An anomaly in the pyroelectric coefficient at temperatures below the Curie point was observed only in the heating cycle. Figure 3 shows the pyroelectric coefficient P_3^σ in a heating cycle, from 20 to 180 K, for crystal plates perpendicular to the c axis. The inset in Figure 3 shows a detailed graph of the anomaly in the pyroelectric coefficient P_3^σ , around 60 K, with a solid line drawn over the experimental points. The same anomaly, somewhat weaker, is observed in the pyroelectric coefficients P_1^σ or P_2^σ (according to the correlation shown in Table 1), relative to the a or b crystallographic axes of the orthorhombic structure, respectively. The nonlinear temperature variations of P_3^σ allow the evaluation of the changes in the spontaneous polarization AP_s , through the equation

$$\Delta P_s(T) = \int_{T_1}^{T_2} P_3^\sigma(T) dt \quad (5)$$

Dots in Figure 4 represent AP_s for KDP as computed from Eq. 5. For comparison, a curve is drawn in Figure 4, from results published by von Arx and Boutle²¹. The measurements from these authors were done in the temperature interval from 100 to 125 K.

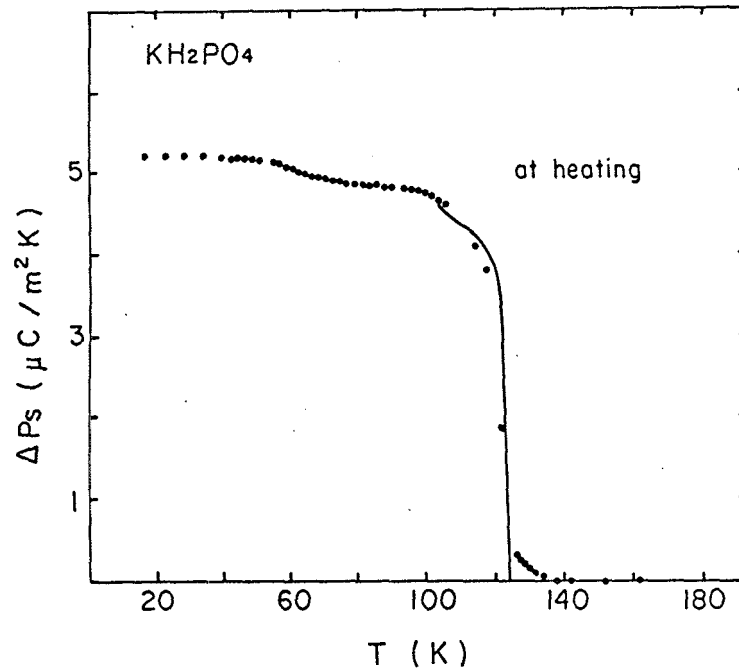


Figure 4: Temperature dependence of the spontaneous polarization of KDP. Points are experimental data. Solid line drawn from results of Ref. 21.

Monoclinic $\sigma(ZX)$	Orthorhombic C_{2v}	Monoclinic (YZ)
A'	$A_1(\nu_1, 2\nu_2, \nu_3, \nu_4)$	A'
A''	$A_2(\nu_1, 2\nu_2, \nu_3, \nu_4)$	A''
	$B_1(2\nu_3, 2\nu_4)$	
	$B(2\nu_3, 2\nu_4)$	

Table 1: Correlation chart between the orthorhombic phase and two possible monoclinic phase.

Our results in the same range of temperatures are in excellent agreement with their results. A small spontaneous polarization, at temperatures slightly above the Curie point, is probably due to an instability of the lattice when approaching T_c . The hump in the polarization curve at temperatures near 60 K suggests that the KDP crystal undergoes a phase transition, in agreement with Raman results, discussed in Sect. IV.A. The slight increase of the polarization for temperatures below 60 K is surprising since the electric dipole component in the c-direction should decrease when its site symmetry is lowered from $C_2(z)$ to C_1 . This decrease in the dipole component in the c-direction has to be compensated by a decrease in the primitive cell volume resulting in a net increase of the polarization along the z-axis, as

observed in Figure 4.

V. Conclusion

Raman spectra and polarization measurements indicate the occurrence of a phase transition in KDP taking place at temperatures near 60 K. A disorder created by the rapid rotation of the PO_4^{-3} ions inside the unit cell disappears with a freezing of this motion. After the phase transition the ions occupy sites with C_1 site symmetry. There is no doubling of the unit cell during this process but the crystalline structure undergoes a change from a C_{2v}^{19} space group (orthorhombic structure) to a C_1^i space group (monoclinic structure), where $i = 1, 2, 3$ or 4. This is necessary to accommodate the phosphate ions in sites with C_1 local symmetry, as required by the Raman observations. The phase transition is also seen in the pyroelectric curves in the same temperature region.

Acknowledgements

Financial support from Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Financiadora de Estudos e Projetos (FINEP) and Coordenadoria de Apoio ao Pessoal de Ensino Superior (CAPES) is gratefully acknowledged.

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