

Effect of deuteration on the coupled modes in KH_2PO_4 †

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The effect of deuteration on the frequencies and pressure dependences of the coupled proton-lattice modes in the ferroelectric phase of KH_2PO_4 is reported. Both modes increase in frequency and their pressure derivatives change sign with deuteration.

I. INTRODUCTION

Measurements of the pressure dependence of the Raman spectra in potassium dihydrogen phosphate (KH_2PO_4 or KDP) and its isomorphs have provided useful information concerning the nature of the soft-mode response¹ and transition mechanism² in this crystal class. Studies of the temperature dependence of the Raman spectra showed that the proton motion is coupled to an optic mode of the lattice in the paraelectric phase of these materials³; measurement of the pressure dependence of the Raman spectra of KDP demonstrated that the modes remain coupled in the ferroelectric phase.^{2,4} We have extended these measurements to investigate the effects of deuteration on the coupled modes. The purpose of this comment is to present results of pressure and temperature measurements of the Raman spectra of $\text{K}(\text{H}_{1-x}\text{D}_x)_2\text{PO}_4$, which can be used to further examine the applicability of various models for the phase transition in these hydrogen-bonded ferroelectrics.

Substitution of deuterium for hydrogen in crystals of the KDP class is known to have a large effect on the ferroelectric properties of these materials. For example, deuteration increases the transition temperature from 122 to 230 °K,⁵ the Curie constant C from 2925 to 4100 °K, and the saturated spontaneous polarization P_s from 5.1 to 6.2 $\mu\text{C}/\text{cm}^2$.⁶ Furthermore, the pressure derivatives of the above-mentioned parameters decrease appreciably with deuteration.

The Raman spectrum of the coupled-mode system also changes with deuteration. Although the soft mode is overdamped at atmospheric pressure in the paraelectric phase of KDP, it can be made underdamped with modest pressure.¹ However, attempts to fit the soft-mode spectra of deuterated KDP with a damped harmonic oscillator response yield such large ratios of damping Γ_a to frequency ω_a that this mode has been described as a relaxational excitation.⁷ In the present measurements it was also found that the response in deuterated KDP (we denote "fully" deuterated KDP as dKDP) could

not be made underdamped with available pressures (≤ 10 kbar).

II. EXPERIMENTAL RESULTS

It has previously been noted that the soft-mode spectra of KDP and dKDP are qualitatively different in the ferroelectric phase.⁸ The spectrum of KDP consists of two well-resolved modes (labeled ω_+) for $T \ll T_c$, while the mode labeled ω_- is absent in dKDP. The absence of ω_- in dKDP identifies this mode with the proton motion. The manner in which the spectra change with deuteration is shown in Fig. 1 for $T \ll T_c$.

Although both ω_{\pm} remain well resolved as the deuterium concentration increases, the intensity of the proton branch ω_- decreases monotonically with decreasing proton concentration. The frequencies of both ω_{\pm} increase slightly with increasing deuterium concentration; these frequencies are summarized in Table I for various (nominal) deuterium concentrations.

The pressure dependences of ω_{\pm} are illustrated in Fig. 2 and summarized in Table I for $T \ll T_c$. For pure KDP, both ω_+ and ω_- decrease with increasing pressure for $T < T_c$, whereas the other modes display normal frequency increases with pressure. The anomalous pressure dependences of ω_+ and ω_- indicate that the proton and lattice motion are coupled in the ferroelectric phase and are used to identify ω_- as the soft mode of the transition.⁴ These conclusions are based on the observation that the transition temperature decreases with pressure ($dT_c/dP = -4.6$ °K/kbar for KDP⁹), so that the system approaches the transition with increasing pressure for $T < T_c$. The transition temperature also decreases with increasing pressure for dKDP ($dT_c/dP = -2.4$ °K/kbar¹⁰) and similar arguments should apply. However, it is evident from the data shown in Fig. 2 that the frequencies of the modes ω_+ and ω_- no longer decrease with pressure for heavily ($\geq 50\%$) deuterated KDP. In fact, not only are the signs of $d\ln\omega_{\pm}/dP$ normal (i.e., positive) for this case, but their magnitudes (Table I) are comparable to those of the normal lattice modes in KDP which had

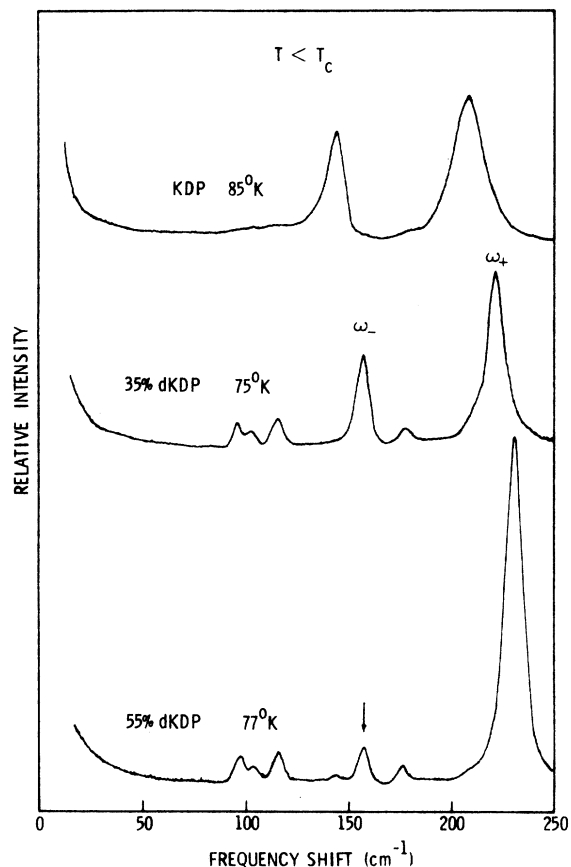


FIG. 1. Atmospheric pressure Raman spectra for $K(H_{1-x}D_x)_2PO_4$ for different (nominal) x values at $T \ll T_c$.

pressure derivatives ranging from $d \ln \omega_i / dP \cong +0.1\%/kbar$ to $d \ln \omega_i / dP \cong 0.8\%/kbar$. These results thus seem to suggest that the proton mode (ω_-) is no longer the soft mode of the system in heavily deuterated KDP.

III. DISCUSSION

A successful model for the transition mechanism in KDP-type crystals must not only explain the static and dynamic properties of pure KDP, but

TABLE I. Frequencies and logarithmic pressure derivatives of ω_{\pm} at $T \ll T_c$ for $K(H_{1-x}D_x)_2PO_4$, for various values of x . The quoted values of x are nominal values.

x	0	0.35	0.55	0.80	0.93
ω_- (cm^{-1})	149	157	158	160	161
ω_{\pm} (cm^{-1})	213	221	225	228	230
$\partial \ln \omega_- / \partial P$ ($\%/kbar$)	-1.0	0.0	+0.55	+0.6	+0.6
$\partial \ln \omega_{\pm} / \partial P$ ($\%/kbar$)	-0.6	-0.3	+0.15	+0.25	+0.3

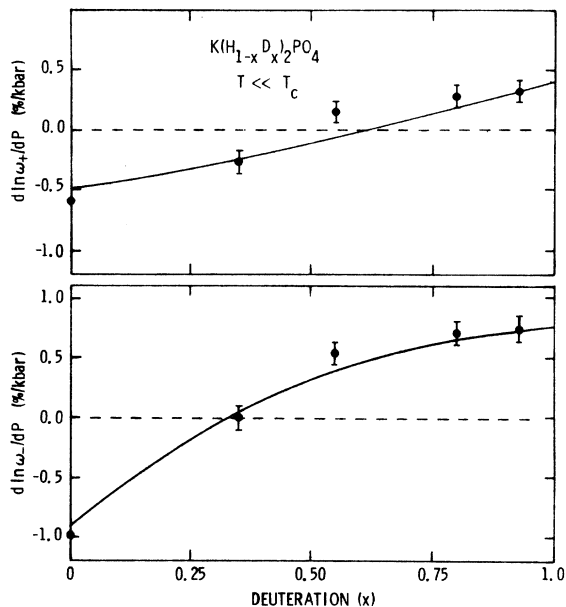


FIG. 2. Logarithmic pressure derivatives of ω_{\pm} and ω_- versus deuteron concentration x . The solid curve is the calculated pressure dependences from Ref. 17.

also the effect of deuteration on these properties. The tunneling model was introduced by Blinc¹¹ to explain the dramatic increase in T_c upon deuteration. This model was subsequently modified¹²⁻¹⁴ to take into account proton-lattice interactions. The coupled proton-lattice (modified tunneling) model has been successful in describing the dynamic and static properties of nondeuterated KDP.^{2,15}

This modified tunneling model predicts a transition temperature $\beta_c = 1/kT_c$ given by¹³

$$4\Omega/\bar{J} = \tanh \beta_c \Omega, \quad (1)$$

where Ω is the tunneling frequency ($2\hbar\Omega = \Delta E$, where ΔE is the tunneling splitting) and \bar{J} is the sum of the proton-proton and lattice interactions. For nondeuterated KDP, $\Omega_p = 85 \text{ cm}^{-1}$ and $\bar{J}_p = 440 \text{ cm}^{-1}$ at atmospheric pressure.² The tunneling frequency is expected to decrease with deuteration so that for dKDP one has $\beta_c \Omega_d \ll 1$. Under this condition, Eq. (1) reduces to

$$\bar{J}_d = 4kT_{c,d}, \quad (2)$$

which yields $\bar{J}_d = 640 \text{ cm}^{-1}$. If it is assumed that \bar{J} is dominated by long-range forces, then $\bar{J} \propto \mu^2$, where μ is the dipole moment per K- PO_4 group.¹⁴ The spontaneous polarization is given by

$$P_s = 2N\mu \langle S^z \rangle, \quad (3)$$

where N is the number of dipoles per unit volume, and $\langle S^z \rangle$ is the expectation value of the z component of the pseudospins ($\langle S^z \rangle = \frac{1}{2}$ if the system is completely aligned). If the system is completely

aligned, these considerations predict that the ratio of the saturated spontaneous polarizations for dKDP and KDP will be

$$P_{s,d}/P_{s,p} = (\bar{J}_d/\bar{J}_p)^{1/2}. \quad (4)$$

The ratio calculated from the \bar{J}_i is 1.21, which agrees with the measured ratio of $6.2/5.1 = 1.22$. The changes in T_c and P_s with deuteration are thus consistent with this model; however, this treatment indicates that not only does the tunneling frequency decrease with deuteration, but also the interaction \bar{J} increases with deuteration.

More detailed calculations are required to examine the dynamics of the mixed crystals. Specifically, in partially deuterated materials, one must consider the proton-deuteron interaction \bar{J}_{pd} in addition to the proton-proton interaction \bar{J}_p , and deuteron-deuteron interaction \bar{J}_d . Very recently, such an extension of the tunneling model was given by Stinchcombe and de Seabra Lage¹⁶ for the para-

electric phase. The coupled-mode model was also recently extended by Blinc, Pirc, and Žekš¹⁷ to discuss the dynamics of the mixed crystals in the ferroelectric phase. The pressure derivatives of ω_{\pm} evaluated from their treatment are in excellent agreement with the measured pressure derivatives, as can be seen from the comparison in Fig. 2. The coupled-mode model thus appears to account for the changes in the dynamics with deuteration; however, further examination of the model is required to see if it also self-consistently predicts the changes in the transition temperature and static dielectric properties with deuteration.

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