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EFFECT OF PRESSURE ON THE SOFT ACOUSTIC MODE OF KH_2PO_4 (KDP)†

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The temperature dependence of the soft acoustic mode (elastic constant $C_{66}{}^E$) of paraelectric KH_2PO_4 in the vicinity of the ferroelectric transition temperature has been measured ultrasonically at atmospheric pressure at 4.14 kbar. The room temperature pressure dependence to 20 kbar has also been measured. The 1 atm data are in good agreement with the previous ultrasonic measurements of Garland and Novotny and the Brillouin measurements of Brody and Cummins. By combining the high pressure ultrasonic measurements with recent high pressure dielectric measurements, the pressure dependence of the "normal" elastic constant $C_{66}{}^P$ and the piezoelectric coupling constant a_{36} can be determined. It is found that a_{36} decreases by 2% kbar^{-1} and that $C_{66}{}^P$ first increases then decreases with increasing pressure. The latter effect may be associated with a possible pressure induced phase transition.

INTRODUCTION

For materials which undergo a ferroelectric phase transition of a displacive nature there generally exists a so-called soft optic or soft polarization mode which approaches zero frequency at the transition temperature.[1] Frequently this mode is strongly enough coupled to one or more acoustic modes of the system that anomalies in certain sound velocities and attenuations can be observed, and by studying these anomalies one can obtain useful information about the nature of the ferroelectric transition as well as about the optic-acoustic mode coupling. In the case of crystals of the KH_2PO_4 (KDP) type, the soft optic mode is believed to involve both vibrations of the K and P atoms along the polar axis and a tunneling motion of the protons in a double well potential.[2–4] This mode is coupled piezoelectrically to the xy shear acoustic mode, whose velocity is determined by the frequency dependent effective elastic constant C_{66}.[5,6] As the soft optic mode decreases in frequency a level-anticrossing effect forces the shear mode frequency to decrease until it reaches zero, triggering the ferroelectric transition. An equivalent way of viewing the transition is that the dielectric anomaly associated with the transition produces an anomaly in the static C_{66} elastic constant ($C_{66}{}^E$), causing this constant to become zero at the transition temperature.[7–9] The acoustic anomaly in KDP type crystals has been studied by Mason,[8] by Garland and co-workers,[9,10] and by Litov and Uehling[11] with ultrasonic techniques and by Cummins and co-workers[5,12,13] with Brillouin scattering.

Measurements of pressure effects in ferroelectric materials can provide information which is useful in elucidating the nature of the ferroelectric transition.[14] In KDP the c-axis dielectric constant has been measured as a function of temperature and pressure by Samara,[15] who found that the transition is suppressed at pressures greater than 17 kbar. The unit cell dimensions[16] and the Raman spectra of the soft optic mode[17] have been studied under pressure to about 3 kbar at room temperature. In this paper we report the results of some experimental work on the pressure-temperature dependence of the soft acoustic mode of KDP. We have measured the temperature dependence of the velocity of this mode in the paraelectric phase at atmospheric pressure (following Garland and Novotny[9]) and at 4.14 kbar. We have also measured the $C_{66}{}^E$ elastic constant as a function of pressure at room temperature. By combining these results with recent measurements of the χ_3 dielectric susceptibility as a function of temperature and pressure we can deduce the pressure dependence of the "normal" $C_{66}{}^P$ elastic constant and the a_{36} piezoelectric coefficient.

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THEORY

Because of the piezoelectric effect, xy shear displacements (strain component x_6) in KDP are coupled to the c-axis electrical polarization component P_3.[7] As a result of this, the normal modes of the system which involve xy shears are actually mixed polarization-strain modes, and therefore exhibit frequency dispersion in their velocities.

Several discussions of the propagation of mixed polarization-strain modes in piezoelectric materials, including KDP, exist in the literature[18, 19, 5] and only a brief summary of the results will be given here. The problem is generally treated phenomenologically: the free energy of the crystal is expanded as a power series in strain and polarization, this series having various phenomenological parameters as coefficients. Using response theory techniques, Dvorak[19] has derived a general expression within this phenomenological framework for the effective elastic constants for waves propagating with wave vector $\mathbf{k}$ and frequency ω. For the coupled soft modes of KDP this relation is

$$C_{66}^{*}(\omega) = C_{66}^{P} - a_{36}^{2}\chi_3^{x}(\omega). \tag{1}$$

Here C_{66}^{*} is the (complex) effective elastic constant; C_{66}^{P} is the "normal" elastic constant measured at constant polarization; a_{36} is the piezoelectric coefficient (assumed independent of ω) and $\chi_3^{x}(\omega)$ is the c-axis electric susceptibility of the clamped crystal. It is usual in the phenomenological theory to employ either a damped harmonic oscillator or a Debye relaxation model for the clamped dielectric susceptibility.[20, 21] However, since previous measurements of the xy shear velocity of KDP have shown that there is no frequency dispersion up to the GHz range,[5] it is legitimate to use the low frequency limit for the susceptibility. In this limit, the real part of $C_{66}^{*}(\omega)$, which determines the acoustic mode velocity, is given by

$$C_{66} = C_{66}^{P} - a_{36}^{2}\chi_3^{x}(0) = C_{66}^{E}. \tag{2}$$

Here C_{66}^{E} is the effective constant field elastic constant, and the right hand equality is a thermodynamic identity. Thus, for a typical pulsed ultrasonic measurement in the paraelectric phase, the constant electrical field value C_{66}^{E} is measured, because the frequencies used are much lower than the frequency of the polarization fluctuations (allowing the polarization to follow the strain), but high enough that free charge accumulation (which could cause a depolarizing field) does not occur.

From (2) we can see that as the transition is approached the large increase in $\chi_3^{x}(0)$, which is associated with the soft optic mode, produces a decrease in C_{66}^{E} (C_{66}^{P} is nearly temperature independent). In fact the ferroelectric transition is triggered when C_{66}^{E} becomes zero.[7] The goal of this work is to study the pressure dependence of the parameters in (2) for the paraelectric state. The temperature dependence of the free electric susceptibility $\chi_3^{\sigma}(0)$ at different pressures has recently been measured in this laboratory.[22] By combining the thermodynamic relationship between the free and clamped susceptibilities,[7]

$$\frac{1}{\chi_3^{x}(0)} - \frac{1}{\chi_3^{\sigma}(0)} = \frac{a_{36}^{2}}{C_{66}^{P}},$$

with (2), one obtains the following equation:

$$\frac{1}{C_{66}^{E}} = \frac{1}{C_{66}^{P}} + \left(\frac{a_{36}}{C_{66}^{P}}\right)^{2} \chi_3^{\sigma}(0). \tag{3}$$

Equation (3) will be used to compare the ultrasonic and dielectric data.

EXPERIMENT

The following three sets of measurements of C_{66}^{E} were made: (1) as a function of temperature at atmospheric pressure (following Garland and Novotny); (2) as a function of temperature at 4.14 kbar (60,000 psi); (3) as a function of pressure to 20 kbar at 23°C.

The samples used were obtained from Clevite and were from the same batch of material used for the dielectric measurements of Samara.[22] Orientation of the crystals to 1.5° was done by x-ray diffraction, and planeness and parallelism of the a faces was insured by careful lapping. The 1 atm measurements were made on two crystals, one with a path length of 0.76 cm and one of 0.18 cm. For the 4.14 kbar runs the thicker of these was used, while for the room temperature runs two other samples with path length of 0.83 and 0.40 cm were used. All these crystals had cross-sections of about (1 x 1) cm^2. For all the experiments shear wave with (010) polarization were propagated along the (100) path length.

For the low temperature runs the samples were mounted in a small brass holder, with two transducers held against the crystal faces by spring clips. Frozen n-propyl alcohol was used for the bonds and gave good echos, especially in the 4.14 kbar runs. The