*Ferroelectrics*
1973, Vol. 5, pp. 17–23



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

I. J. FRITZ

*Sandia Laboratories, Albuqerque, New Mexico 87115, U.S.A.*

*(Received 11 November 1972)*



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 $\chi_3$ 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.

† This work was supported by the U.S. Atomic Energy Commission.

## 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 $\omega$. 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 $\omega$) 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

sample holder fitted inside a heavy beryllium copper pressure cell, which provided good temperature uniformity over the sample. Temperatures were measured to a precision of 0.02°K with a copper-constantan thermocouple mounted inside the pressure cell. The pressure cell was suspended inside a liquid nitrogen cryostat whose temperature was controlled to ±0.01°K to a Cryogenic Research TC-101 controller. The beryllium copper cell could be pressurized to 60,000 psi of helium gas, and the pressure, which was measured on a calibrated Bourdon gauge, was maintained at ±100 psi of the nominal value.

A two transducer, shock excited, pulse echo technique was used for the low temperature work. This technique has been described in detail by Beattie and Samara.[23] Briefly, a short rectangular voltage pulse is applied to the transmitting transducer which rings for a few cycles at its resonant frequency, producing a sound pulse of around 0.5–1.0 $\mu$sec duration in the crystal. The echos are picked up by the second transducer and displayed on an oscilloscope trace. Round trip delay times are determined by measuring the echo separation against a signal from a time mark generator. This method is sufficiently accurate for the present experiment, as the delay times ranged from about 9–50 $\mu$sec. For the 1 atm, low temperature runs 10 MHz transducers were used with the thicker crystal and 5 MHz transducers with the thinner one. The 5 MHz measurement allowed more accurate measurements to be made near the transition where the attenuation is large. The 4.14 kbar runs were done at 10 MHz. All the low temperature measurements were confined to the temperature range 20°K above the transition temperature.

The only problem encountered in the transit time measurement was that the leading part of the echo train was strongly attenuated as the transition was approached. An attempt was made to keep track of the number of cycles that were "lost" as the attenuation increased in order to determine the correct transit time, which was less than the time between the strongest cycles of successive echos. This correction was as large as 10 cycles at 10 MHz, representing around 1–2% of the total transit time.

The mesaurements of $C_{66}{}^E$ at room temperature as a function of pressure were performed in a standard Bridgman type press utilizing a 50–50 pentane-isopentane mixture as the pressure transmitting medium. The measurements were made at 10 and 25 MHz using the McSkimin pulse superposition method[24] and were checked at 25 MHz on another sample.

## RESULTS AND DATA ANALYSIS

The results of the measurements were analyzed along the following lines. First, the measured transit times were used to deduce $C_{66}{}^E$ for the three sets of data described above. The data from the low temperature measurements were then combined with the dielectric data of Samara[22] to deduce the $a_{36}$ piezoelectric constant at 1 atm and at 4.14 kbar, with the assumption that the normal elastic constant $C_{66}{}^P$ is pressure independent to 4.14 kbar. This last assumption was checked by deducing $C_{66}{}^P$ as a function of pressure from room temperature measurements of $C_{66}{}^E$ and $\chi_3(0)$ as a function of pressure. A more detailed discussion of these procedures will now be given.

### *Determination of $C_{66}{}^E$*

The relation between the round trip transit time $t$, the crystal mass density $\rho$, and the path length $l$ of the sound propagation is $C_{66}{}^E = \rho(2l/t)^2$. In order for one to deduce the temperature and pressure dependence of $C_{66}{}^E$ from the transit time measurements, it is thus necessary to know the temperature and pressure variations of the lattice parameters. Since these variations are small, $l$ and $\rho$ were taken to be constant over the 20°K temperature range investigated in each of the low temperature experiments. The actual values used were those for $T = 123$°K, $p = 1$ atm and for $T = 105$°K, $p = 4.14$ kbar. These values were deduced from the thermal expansion data of Mason[8] and the compressibility data of Morosin and Samara.[16] For the room temperature experiment, the variation of $\rho$ with pressure is known to 20 kbar from Ref. 16, and the variation of $l$ with pressure was deduced by extrapolating to 20 kbar the (linear) variation of $c/a$ with pressure found up to 3 kbar in this reference.

Figures 1 and 2 show $C_{66}{}^E$ for the low temperature runs plotted against $T - T_a$, where $T_a$ is the Curie temperature of the soft acoustic mode. $T_a$ was determined from linear fits to an elastic Curie-Weiss law, which will be discussed in more detail below. The value of $T_a$ at 1 atm and its decrease under pressure are in good agreement with other measurements.[15] Figure 1 shows the 1 atm data along with some of the Brillouin scattering data of Brody and Cummins,[12,25] which are in excellent agreement with our results. Although not shown here, the ultrasonic data of Ref. 9 are also in good agreement with our data.

The insert to Figure 1 shows the behavior near the transition on an expanded scale with a solid line

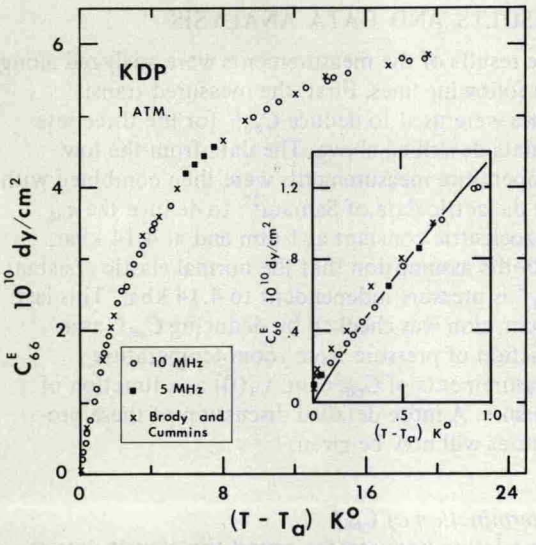


FIGURE 1 Elastic constant $C_{66}{}^E$ as a function of temperature at 1 atm pressure. $T_a$ is the ferroelectric transition temperature. The data points of Brody and Cummins (Ref. 5) were obtained by Brillouin scattering. The solid line in the insert represents elastic Curie-Weiss fit to the data.

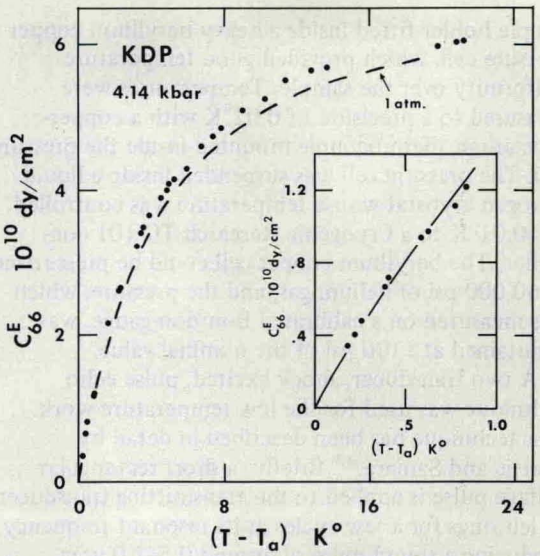


FIGURE 2 Same as Figure 1 except pressure is 4.14 kbar. Dashed line represents the 1 atm data of Figure 1.

representing the Curie-Weiss fit included. Within about 0.2°K of $T_a$ both the Brillouin and ultrasonic data deviate slightly to the high side of the fit, which was made over a 4°K temperature interval. This effect could be due to a slight misalignment of the samples faces, which would cause the measured velocity to depend on a combination of elastic constants, and therefore not be exactly zero at the transition.

Figure 2 shows the 4.14 kbar data. Included in this figure is a dashed line showing the 1 atm behavior and, again, in the insert a solid line representing the Curie-Weiss fit. The main feature of this plot is that, as a function of $T - T_a$, the 4.14 kbar data fall higher than the 1 atm data, an effect which will be shown below to result mainly from a decrease in the piezoelectric coupling under pressure. One further feature of the low temperature $C_{66}{}^E$ data which should be noted is that if these data are plotted as a function of $(T - T_a)/T_a$, then the 1 atm and 4.14 kbar points fall on a single curve within the scatter of the experimental data. This unexpected result will be discussed further below.

*Comparison to Dielectric Data*

As mentioned above, the two sets of low temperature data were compared to the dielectric measurements to deduce the pressure dependence of the piezoelectric coupling. The "free" susceptibility can be described by the following expression[7]

$$\chi_3{}^{\sigma}(0) = \frac{1}{4\pi}\frac{C}{T - T_a},$$

where the Curie constant $C$ has values of 2925°K and 2830°K at 1 atm and 4.14 kbar, respectively.[22] Equation (3) can therefore be rewritten as an elastic Curie-Weiss law:

$$\frac{1}{\chi_3{}^{\sigma}(0)} = \frac{4\pi}{C}(T - T_a) = \left(\frac{a_{36}}{C_{66}{}^P}\right)^2 (S_{66}{}^E - S_{66}{}^P)^{-1}, \quad (4)$$

where $S_{66} = C_{66}{}^{-1}$. To compare the dielectric and acoustic measurements, the following procedure was used. The temperature dependences of the parameters $a_{36}$ and $C_{66}{}^P$ are known from the measurements of de Quervain[26] and of Mason,[8] so that we can write $a_{36}(p,T) = a_{36}(p,T_0)f(T - T_0)$ and $C_{66}{}^P(p,T) = C_{66}{}^P(p,T_0)g(T - T_0)$, where $T_0$ is some convenient reference temperature taken here as 122°K, and where $f$ and $g$ were taken to be

$$f(T) = 1 - 0.0040\,(T - T_0),$$

and

$$g(T) = 1 - 0.00065\,(T - T_0).$$

We make the assumption that $C_{66}{}^P(p, T_0)$ is constant to 4 kbar. As will be discussed below, the changes of $C_{66}{}^P$ with pressure are small enough to be neglected for the present purposes. With this

assumption, all the quantities on the RHS of (4) are known except $a_{36}(p,T_0)$ and a plot of the RHS of (4) modulo $a_{36}^2(p,T_0)$ as a function of temperature at each of the two pressures yields a straight line with slope $4\pi/(Ca_{36}^2(p,T_0))$. Knowing $C$ from the dielectric measurements allows $a_{36}$ to be determined. We find $a_{36}(0\text{ kbar}, T_0) = 3.52 \times 10^4$ esu/cm$^2$ and $a_{36}$ (4.14 kbar, $T_0$) $= 3.24 \times 10^4$ esu/cm$^2$, so that the logarithmic pressure derivative of $a_{36}$ is

$$\frac{1}{a_{36}}\frac{da_{36}}{dp} = -(2.0 \pm 0.3)\%\text{ kbar}^{-1}.$$

A liberal uncertainty has been ascribed to this quantity due to the indirect method in which it was determined.

Figures 3 and 4 show the elastic Curie-Weiss plots of the ultrasonic data at 1 atm and 4.14 kbar respectively. Two lines are shown on each figure, one representing (4) and the other representing (2), the elastic Curie-Weiss law corresponding to the clamped dielectric susceptibility. In Figure 3, fits taken over two temperature ranges ($T - T_a < 4°$K and $T - T_a < 20°$K) are shown; the fit over the smaller range was used in the data analysis.

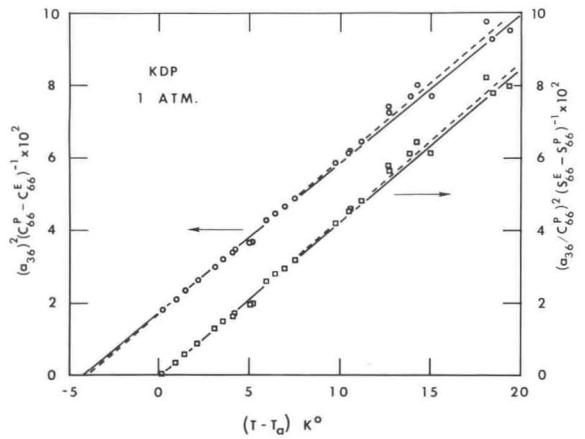


FIGURE 3 Elastic Curie-Weiss plots for 1 atm data (see text). Solid line is fit for $T - T_a < 4°$K, dashed line for $T - T_a < 20°$K.

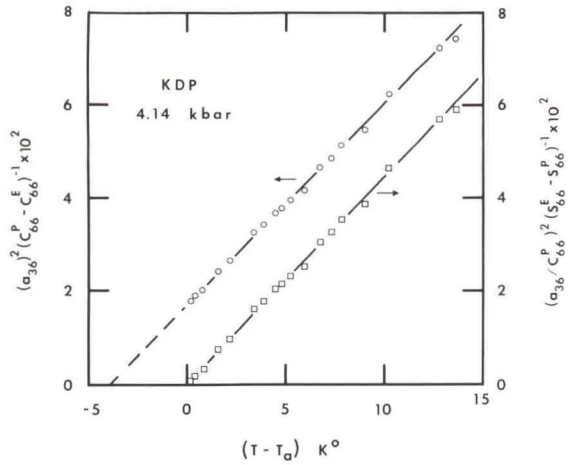


FIGURE 4 Elastic Curie-Weiss plots for 4.14 kbar data.

*Room Temperature Measurements*

In order to test the assumption that $C_{66}^P$ is pressure independent to 4 kbar, room temperature measurements of $C_{66}^E$ and $\chi_{33}^\sigma(0)$ were made, from which $C_{66}^P$ could be deduced by utilizing (3). In Figure 5 the ultrasonic data, represented as a plot of

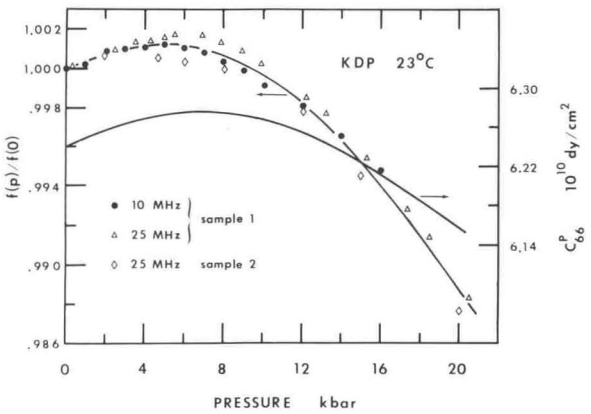


FIGURE 5 Pulse repetition rate ratio and elastic constant $C_{66}^P$ as a function of pressure at room temperature. The smooth curve drawn through the data points for $f/f(0)$ was used to deduce $C_{66}^P(p)$ (refer to text).

the pulse repetition ratio $f(p)/f(p = 0)$ as a function of pressure, is shown. This quantity is related to the elastic constant by the relation[24]

$$\frac{C_{66}^E(p)}{C_{66}^E(0)} = \frac{\rho}{\rho_0}\left(\frac{lf}{l_0 f_0}\right)^2.$$

The length and density changes were determined from Ref. 16 as described above, and $C_{66}^P$ was determined from (3) assuming that $a_{36}$ decreased by 2% kbar$^{-1}$, as calculated above. The extrapolation of this decrease to 20 kbar is, of course, somewhat uncertain. The pressure dependence of $C_{66}^P$ is shown in Figure 5. Two features are to be noted. First, $C_{66}^P$ increases by only about 0.1% kbar$^{-1}$ between 0 and 4 kbar, justifying the above assumption that the important changes in the elastic Curie-Weiss plots are due to changes in $a_{36}$ and $C$ with pressure. A correction for the small increase in $C_{66}^P$ was actually included in

the above determination of $a_{36}$ from the 4.14 kbar data. The second feature is that $C_{66}{}^P$ is a decreasing function of pressure above around 9 kbar. This effect is believed to be connected with the possible existence of a pressure induced phase transition (at ~ 40 kbar) which is suggested by the DTA data of Rapoport.[27] This has recently been discussed by the author[28] in a study of the room temperature pressure dependence of four of the KDP elastic constants.

The results obtained from the analysis of our three sets of data have completed the determination of the temperature and pressure dependences of the phenomenological parameters governing the soft acoustic mode behaviour of KDP. These results are summarized in Table I. It should be noted that all of the parameters were determined under adiabatic conditions

*Discussion and Conclusion*

Our results for $C_{66}{}^E$ at atmospheric pressure are in excellent agreement with the work of Refs. 5 and 9. The only disagreement we have with this previous work is that we do not find that plots of $(C_{66}{}^P - C_{66}{}^E)^{-1}$ and $(S_{66}{}^E - S_{66}{}^P)^{-1}$ vs. temperature fall on a straight line as did Garland and Novotny;[9] it is necessary to include the temperature dependences of $a_{36}$ and $C_{66}{}^P$ in (4) and (5) to obtain linear plots.

The value of $a_{36}$ obtained by comparing the 1 atm ultrasonic and dielectric data agrees to 1% with the literature value.[26] Thus we are confident that our data analysis yields correct values for $a_{36}$ both at 1 atm and at 4.14 kbar, and we believe the value of the $a_{36}$ pressure derivative to be accurate to ± 15%. The logarithmic isobaric temperature derivative of $a_{36}$ is [8,26]

$$a_{36}{}^{-1}\,(da_{36}/dT)_p = -4.0 \times 10^{-3}\,(^\circ\mathrm{K})^{-1}$$

Changes in $a_{36}$ as a function of temperature can be considered as arising from two sources: a volume dependent contribution which arises from the thermal expansion of the crystal and a pure temperature contribution due to anharmonic lattice effects. The exact thermodynamic expression that relates the pressure and temperature derivatives of $a_{36}$ to the various axial compressibilities and thermal expansivities is somewhat complicated for tetragonal symmetry. In fact, the separation of the "pure" volume and temperature effects requires a determination of one of the uniaxial strain derivatives. This separation can be effected approximately, however, by using the thermodynamic relation that holds for cubic symmetry. This relation is

$$\frac{1}{a}\left(\frac{\partial a}{\partial T}\right)_p = -\frac{\beta}{\kappa}\left(\frac{\partial a}{\partial p}\right)_T + \frac{1}{a}\left(\frac{\partial a}{\partial T}\right)_V, \tag{6}$$

where

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

is the thermal expansion and

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

is the compressibility. (The subscripts on $a_{36}$ have been dropped.) This relation is exact for tetragonal symmetry provided that the $c/a$ ratio is exactly independent of temperature and pressure. Although this condition is not exactly satisfied for KDP, we can still use (6) to gain some insight to the relative magnitudes of the temperature and volume effects. Using Mason's value[8] of $\beta = 1.0 \times 10^{-4}\ (^\circ\mathrm{K})^{-1}$ and Morosin and Samara's value[16] of $\kappa = 3.6 \times 10^{-3}$ kbar$^{-1}$,

TABLE I

Pressure and temperature of some thermodynamic parameters of $KH_2PO_4$

| Parameter $\alpha$ | $\alpha$(122° K, 1 atm.) | $\frac{1}{\alpha}\left(\frac{d\alpha}{dT}\right)_p$ (K°)$^{-1}$ | $\frac{1}{\alpha}\left(\frac{d\alpha}{dp}\right)_T$ (kbar)$^{-1}$ |
|---|---|---|---|
| $C$ (free Curie constant) | 2925° K (±1%)[a] | – | $-7.8 \times 10^{-3}$ (±15%)[a] |
| $C_{66}{}^P$ (normal elastic constant) | $7.00 \times 10^{10}$ dy/cm$^2$ [b] | $-6.5 \times 10^{-4}$ [b] | $1.2 \times 10^{-3}$ (±10%)[c,d] |
| $a_{36}$ (piezoelectric coupling) | $3.52 \times 10^{-4}$ (±2%)[c] | $-4.0 \times 10^{-3}$ [b] | $-2.0 \times 10^{-2}$ (±15%)[c] |

[a] Ref. 22.
[b] Ref. 8.
[c] This work.
[d] Initial slope, becomes negative above ~ 9 kbar.

we find the value of $a_{36}{}^{-1}(\partial a_{36}/\partial T)_V = -4.6 \times 10^{-3}$ $(°K)^{-1}$ for the "pure" temperature changes in $a_{36}$. Thus the "pure" temperature contribution to $(da_{36}/dT)_p$ is nearly an order of magnitude larger than (and of opposite sign from) the "pure" volume contribution.

It was noted above that if the $C_{66}{}^E$ data is plotted as a function of the reduced temperature $\eta = (T - T_a)/T_a$, then the low temperature data taken at 1 atm and at 4.14 kbar fall on a single curve. The question naturally arises as to whether this "universal" behavior has any physical significance. It is widely accepted[7] that the fundamental anomaly in KDP is the dielectric anomaly, and that the acoustic anomaly is a consequence of the dielectric behavior as described by (3). We have examined the dielectric data and find that neither $\chi_3{}^\sigma$ nor $\chi_3{}^x$ are universal functions of $\eta$. In fact the "universal" behavior of $C_{66}{}^E$ appears to arise as a coincidence of the pressure and temperature dependence of the quantities $C_{66}{}^P$, $a_{36}$, and $\chi_3{}^x(0)$, and we believe that this behavior has no deeper physical meaning.

In summary, by combining our ultrasonic measurements of $C_{66}{}^E$ at 1 atm and at 4.14 kbar with recent dielectric measurements as a function of temperature and pressure, we have completed the determination of the pressure and temperature dependence of the parameters which govern the soft acoustic behavior of KDP in the paraelectric phase.

ACKNOWLEDGEMENTS

The author would like to thank Dr. G. A. Samara for permission to use his dielectric measurement data prior to publication and for useful discussions concerning this work. The technical assistance of S. Peerman and S. Hatcher is gratefully acknowledged.

REFERENCES

1. W. Cochran, *Advanc. Phys.* **9**, 387 (1960); *Advan. Phys.* **10**, 401 (1961).
2. R. Blinc, *J. Phys. Chem. Solids* **13**, 204 (1960).
3. P. G. deGennes, *Solid State Comm.* **1**, 132 (1963).
4. K. K. Kobayashi, *J. Phys. Soc. Jap.* **24**, 497 (1968).
5. E. M. Brody and H. Z. Cummins, *Phys. Rev. Lett.* **21**, 1263 (1968).
6. V. Dvořák, *Czech. J. Phys.* **B20**, 1 (1970).
7. F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon Press, New York, 1962), Chap. III.
8. W. P. Mason, *Phys. Rev.* **69**, 173 (1946).
9. C. W. Garland and D. B. Novotny, *Phys. Rev.* **177**, 971 (1969).
10. E. Litov and C. W. Garland, *Phys. Rev.* **B2**, 4597 (1970).
11. E. Litov and E. A. Uehling, *Phys. Rev.* **B1**, 3713 (1970).
12. E. M. Brody and H. Z. Cummins, *Phys. Rev. Lett.* **23**, 1039 (1969).
13. I. J. Fritz *et al.* in *Proceedings of the Second International Conference on Light Scattering in Solids*, edited by M. Balkanski (Flammarion, Paris, 1971), p. 415.
14. G. A. Samara, in *Advances in High Pressure Research*, edited by R. S. Bradley (Academic, New York, 1969), Vol. 3, Chap. 3.
15. G. A. Samara, *Phys. Rev. Lett.* **27**, 103 (1971).
16. B. Morosin and G. A. Samara, *Ferroelectrics* **3**, 49 (1971).
17. P. S. Peercy and G. A. Samara, to be published.
18. D. G. Sannikov, *Sov. Phys. Solid State* **4**, 1187 (1962).
19. V. Dvořák, *Can. J. Phys.* **45**, 3903 (1967).
20. I. P. Kaminow and T. C. Damen, *Phys. Rev. Lett.* **20**, 1105 (1968).
21. R. L. Reese *et al.*, *Solid State Comm.* **9**, 327 (1971), and to be published..
22. G. A. Samara, unpublished data.
23. A. G. Beattie and G. A. Samara, *JAP* **42**, 2376 (1971).
24. H. J. McSkimin, *JASA* **33**, 12 (1962); H. J. McSkimin and P. Andreatch, *JASA* **34**, 609 (1962).
25. E. M. Brody, Thesis, The Johns Hopkins University (1969) unpublished.
26. M. deQuervain, *Helv. Phys. Acta* **17**, 509 (1944).
27. E. Rapopart, *J. Chem. Phys.* **53**, 311 (1970).
28. I. J. Fritz, *Solid State Comm.* **12**, 79 (1973).