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 $a_{36}(0\ \text{kbar}, T_0) = 3.52 \times 10^4\ \text{esu/cm}^2$ and $a_{36}\ (4.14\ \text{kbar}, T_0) = 3.24 \times 10^4\ \text{esu/cm}^2$, 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.

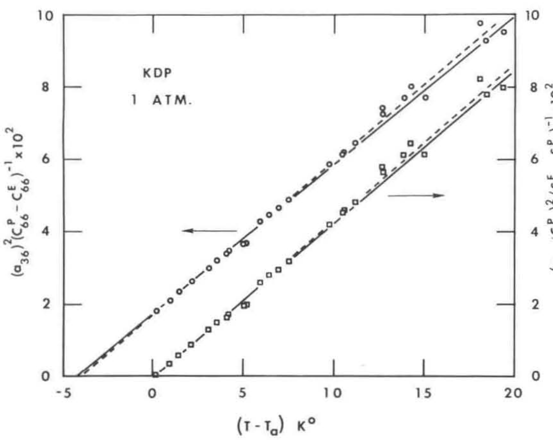

FIGURE 3 Elastic Curie-Weiss plots for 1 atm data (see text). Solid line is fit for $T - T_a < 4°$K, dashed line for $T - T_a < 20°$K.

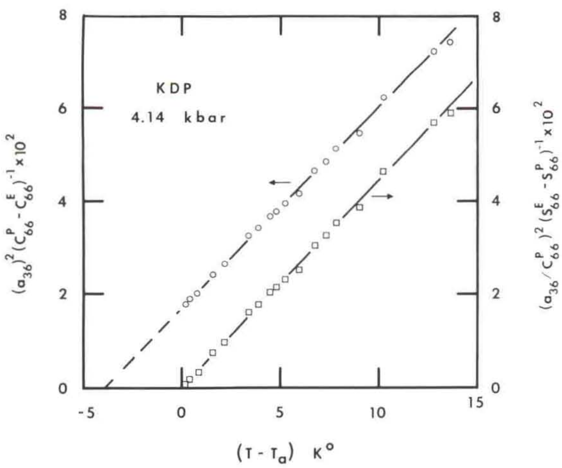

FIGURE 4 Elastic Curie-Weiss plots for 4.14 kbar data.

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

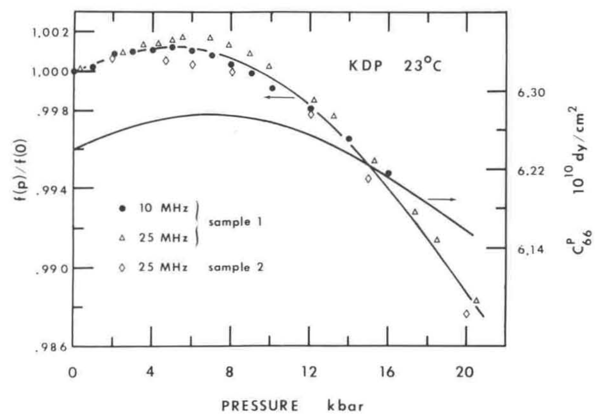

FIGURE 5 Pulse repetition rate ratio and elastic constant $C_{66}{}^P$ as a function of pressure at room temperature. The smooth curve drawn through the data points for $f/f(0)$ was used to deduce $C_{66}{}^P(p)$ (refer to text).

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 $\kappa = 3.6 \times 10^{-3}\ \mathrm{kbar}^{-1}$,

TABLE I

Pressure and temperature of some thermodynamic parameters of KH_2PO_4

Parameter α	α(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]	–	-7.8×10^{-3} (±15%)[a]
$C_{66}{}^P$ (normal elastic constant)	$7.00 \times 10^{10}\ dy/cm^2$ [b]	-6.5×10^{-4} [b]	1.2×10^{-3} (±10%)[c, d]
a_{36} (piezoelectric coupling)	3.52×10^{-4} (±2%)[c]	-4.0×10^{-3} [b]	-2.0×10^{-2} (±15%)[c]

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