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 μsec 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 μsec. 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 ρ, 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 ρ 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 ρ 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

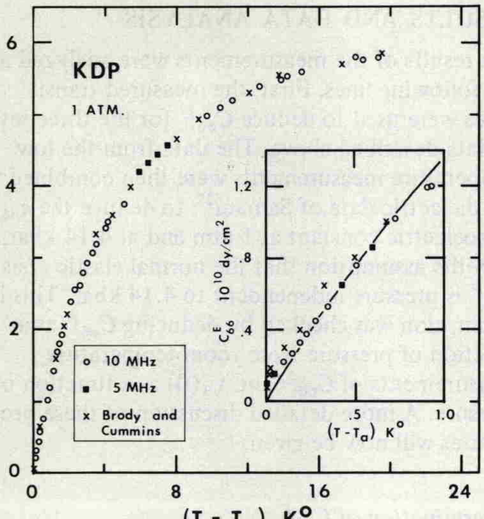

FIGURE 1 Elastic constant $C_{66}{}^{E}$ as a function of temperature at 1 atm pressure. T_a is the ferroelectric transition temperature. The data points of Brody and Cummins (Ref. 5) were obtained by Brillouin scattering. The solid line in the insert represents elastic Curie-Weiss fit to the data.

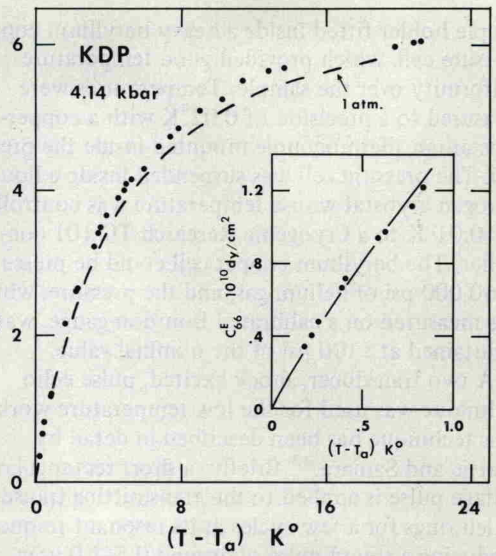

FIGURE 2 Same as Figure 1 except pressure is 4.14 kbar. Dashed line represents the 1 atm data of Figure 1.

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:

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

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