

sure dependences of the individual elastic constants involved in this study. In order to do this we use Eq. (3).

In order to determine the elastic constants it is necessary to determine the dimensional changes of the sample as a function of pressure. If enough modes are measured to determine a complete set of elastic constants, it is possible by using standard methods to determine the dimensional changes and the elastic constant changes (as a function of pressure) simultaneously and self-consistently. If such a complete set of modes is not measured, then it is either necessary to have independent data for the dimensional changes (axial compressions as a function of pressure), or to devise some approximation for these changes. In the present work the changes in the elastic constants of the anomalous shear modes are small, and it is therefore desirable to have reasonably accurate knowledge of the dimensional changes. These changes were determined by different techniques for the different materials studied.

For KDP, data are available from the work of Morosin and Samara<sup>29</sup> for the axial compressions at high pressure. These authors determined volume vs pressure up to 20 kbar and the  $c/a$  ratio up to 3 kbar. To determine the  $a$ - and  $c$ -axis dimensions to 20 kbar we employed a linear extrapolation of the  $c/a$  ratio to this pressure. This extrapolation should be a reasonable approximation, as the  $c/a$  ratio does not change by a large amount.

For dKDP and RbDP compression data to 20 kbar are not available, and a complete set of acoustic modes was not measured at high pressure, so it is necessary to approximate the high-pressure axial compressions. This was done by assuming that the axial compressibilities are constant as a function of pressure. The values of the axial compressibilities actually used are given in Table I. It is estimated that the constant compressibility assumption may introduce errors in the axial compressions of around 1% at 20 kbar.

For ADP a complete set of six acoustic modes was measured, allowing the axial compressions and elastic constants to be determined self-consistently at high pressure. The procedure used for this calculation is a modification of the method of Cook<sup>30</sup> and is exactly the same procedure as was used previously in a study of the high-pressure elastic properties of rutile.<sup>16</sup>

A minor complication arises in the analysis of the data because of the fact that the KDP-type crystals are piezoelectric. Two kinds of effects may arise in this area. The first is that certain modes may exhibit "piezoelectric stiffening" if they are mixed acoustic-electromagnetic modes with a component of electric field parallel to the

propagation direction.<sup>31</sup> The second effect was briefly alluded to in the discussion of Eq. (1), namely, that if a strain component is piezoelectrically coupled to an electric-field component, then the stress-strain relations involving that particular strain component will depend on the electrical boundary conditions.<sup>28</sup> In particular, for the crystals under consideration, differences are expected for  $C_{66}^E$  and  $C_{66}^P$  and similarly for  $C_{44}^E$  and  $C_{44}^P$ . In our analysis we have considered only the piezoelectric effects described by Eq. (1); the other effects are generally small, and their evaluation is beyond the scope of the present investigation.

The effect described by Eq. (1) is important in the low-temperature ferroelectric phase transitions of the KDP-type materials, and has been extensively studied in recent years.<sup>32</sup> The ferroelectric transitions are accompanied by an anomaly in  $\chi_{33}^*$ , and this anomaly drives  $C_{66}^E$  to zero, triggering the transition. For the purposes of the present work it should be noted that  $\chi_{33}^*$  is fairly large at room temperature, especially for dKDP, because of the proximity of the ferroelectric transition. Applying pressure at room temperature moves the system away from the transition causing  $\chi_{33}^*$  to decrease significantly with increasing pressure. Although the difference  $C_{66}^P - C_{66}^E$  is quite small at room temperature (viz., Table II) it is possible that some of the nonlinearity in the data of Figs. 1-4 could be accounted for by this effect. It was therefore decided that an attempt should be made to determine the pressure dependence of the "normal" elastic constant  $C_{66}^P$ . In order to do this the pressure dependences of  $\chi_{33}^*$  and  $a_{36}$  must be determined. Dielectric measurements at high pressure on KDP-type materials have been made by Samara,<sup>33</sup> but very little is known about the pressure dependences of the piezoelectric coefficients. For KDP the pressure dependence of  $a_{36}$  up to 4 kbar has been determined by combining the results of high-pressure and low-temperature ultrasonic and dielectric measurements.<sup>34</sup> An extrapolation of these results to high pressure (20 kbar) is obviously crude, but it does allow a reasonably good estimate of  $C_{66}^P$  to be made at high pressure. An even cruder assumption was made for the case of dKDP, namely, that the logarithmic pressure derivative of  $a_{36}$  is the same for dKDP and for KDP. No attempt was made to determine  $C_{66}^P$  for RbDP or ADP.

#### IV. DISCUSSION

The results for the pressure dependences of the elastic constants of the four materials as obtained from the analysis discussed above are shown as solid lines in Figs. 1-3 and 5. The main feature of these figures is the pronounced nonlinear behavior of  $C_{44}$  and  $C_{66}$ . In Figs. 1 and 2 slight dif-

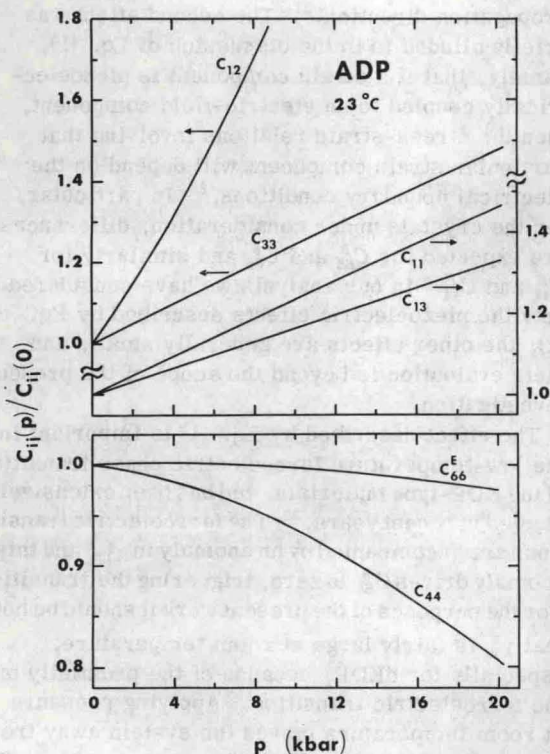


FIG. 5. Reduced elastic constants of ADP vs pressure.

ferences in the pressure dependences of  $C_{66}^E$  and  $C_{66}^P$  can be seen; however,  $C_{66}^P$  does exhibit a strongly nonlinear pressure dependence, illustrating that the curvature in the repetition rate data is not caused solely by the nonlinear dependence of the dielectric constant. The pressure derivatives of the various elastic constants evaluated at atmospheric pressure are listed in Table III.

One feature of the results which requires special comment is the pressure dependence of  $C_{12}$  in ADP. This constant increases by about 80% in 9 kbar, but this large fractional change is due to the atmospheric pressure value being small (refer to Table II) rather than to a large pressure derivative (refer to Table III).

The decrease of the  $C_{44}$  and  $C_{66}$  elastic constants with increasing pressure reported here shows that the crystal lattices become progressively less stable with respect to the corresponding static shear displacements as pressure increases. Similar behavior has been reported in the literature for the pressure dependences of shear modes of a variety of crystals, including a number of alkali halides (KF,<sup>3</sup> KCl,<sup>4</sup> KBr,<sup>5</sup> KI,<sup>3,6</sup> RbF,<sup>7</sup> RbCl,<sup>7-9</sup> RbBr,<sup>7,9</sup> and<sup>7,9</sup> RbI), SrO,<sup>10</sup> BaF<sub>2</sub>,<sup>11,12</sup> CdS,<sup>13</sup> and ZnS,<sup>14</sup> TiO<sub>2</sub>,<sup>15,16</sup> Cu<sub>2</sub>O,<sup>17</sup> CuCl,<sup>8</sup> and TeO<sub>2</sub>.<sup>19</sup> If a shear mode velocity could be driven to zero by increasing the pressure to a certain value, then this mode would be a so-called "soft mode," and

a structural phase transition would occur in which a static strain distortion (having the same symmetry as the soft mode) is the order parameter.

Unfortunately, the TeO<sub>2</sub> transition<sup>19</sup> is the only known example of a simple soft mode, pressure-induced structural transition. For the other materials mentioned above the situation is more complicated. In general the transitions are of first order, and the total elastic softening is quite small, generally only a few percent. In these instances the stability of the lattice must be considered as being determined by the general thermodynamic stability requirement (minimization of Gibbs free energy) rather than by such a simple criterion as, say, the Born criterion.<sup>14</sup> Even in the case of a transition where macroscopic strains are the only order parameters (i.e., a transition driven by a mechanical instability alone) it has been shown by Anderson and Blount<sup>35</sup> that cubic terms generally occur in a power-series expansion of the free energy, thereby producing a first-order transition. Although these considerations show that the detailed nature of the pressure-induced transitions we are considering is quite complicated, there is nevertheless strong evidence that incipient mechanical instabilities play an important role in these transitions. This point has been already emphasized in the literature.<sup>12,14</sup>

Attempts to correlate the anomalous acoustic-mode behavior in the KDP-type crystals with pressure-induced transitions are hampered on the one hand by the consideration just discussed above and on the other hand by a lack of detailed information about the transitions themselves. Nevertheless it appears from the information available that the anomalous acoustic modes are, in fact, in some way associated with the pressure-induced phase transitions. Unfortunately, the pressures at which the  $C_{44}$  and  $C_{66}$  modes extrapolate to zero are well outside our high-pressure capabilities. To determine these extrapolated pressures, parabolic fits to the high-pressure elastic-constant data (Figs. 1-3 and 5) of the form

$$C_{ij}(p)/C_{ij}(0) = 1 + Ap + Bp^2$$

TABLE III. Pressure derivatives of the elastic constants evaluated at  $p=1$  atm and  $T=23^\circ\text{C}$ .

	KDP $dC_{ij}/dp$	dKDP $dC_{ij}/dp$	RbDP $dC_{ij}/dp$	ADP $dC_{ij}/dp$
$C_{11}$	$16.4 \pm 0.5$	$15.1 \pm 0.5$	$15.4 \pm 0.5$	$16.4 \pm 0.5$
$C_{33}$	$9.6 \pm 0.2$	$8.8 \pm 0.2$	$8.9 \pm 0.2$	$8.2 \pm 0.2$
$C_{44}$	$0.74 \pm 0.04$	$0.67 \pm 0.04$	$0.22 \pm 0.04$	$-0.24 \pm 0.04$
$C_{66}^E$	$0.12 \pm 0.03$	$0.18 \pm 0.03$	$-0.09 \pm 0.03$	$0.07 \pm 0.03$
$C_{66}^P$	$0.07 \pm 0.04$	$0.02 \pm 0.08$	...	...
$C_{12}$	...	...	...	$2.7 \pm 0.7$
$C_{13}$	...	...	...	$3.3 \pm 0.5$