

Anomalous acoustic behavior of KH_2PO_4 -type crystals at high pressure*

I. J. Fritz

Sandia Laboratories, Albuquerque, New Mexico 87115

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The pressure dependences of the elastic constants of KH_2PO_4 , KD_2PO_4 , RbH_2PO_4 , and $\text{NH}_4\text{H}_2\text{PO}_4$ have been studied for pressures up to 20 kbar at 23°C. For $\text{NH}_4\text{H}_2\text{PO}_4$ a complete set of six constants was measured, while for the other three materials only C_{11} , C_{33} , C_{44} , and C_{66} were measured. For all four materials the C_{44} and C_{66} constants exhibit anomalous pressure dependences, while the other measured constants appear to have normal behavior. The anomalous constants all have striking nonlinear pressure dependences and all ultimately soften with increasing pressure. For KH_2PO_4 and KD_2PO_4 both the C_{66}^E and C_{66}^P constants were determined, and for these materials it is shown that the nonlinear pressure dependences are not due to piezoelectric coupling effects. The results of previous determinations of high-pressure phase transitions in the four crystals are reviewed, and the possible connection between the anomalous shear modes and pressure-induced phase transitions is discussed.

I. INTRODUCTION

The elastic properties of a material which undergoes a solid-state phase transition are often anomalous in the region of the transition, and the study of these anomalies has played an important role in furthering our understanding of a wide variety of transitions.¹ The elastic anomalies are generally manifested as an anomalous decrease in the velocity of one or more acoustic modes as the transition is approached; and in some instances the acoustic-mode velocities actually appear to go to zero at the transition. In these latter instances the anomalous acoustic modes may actually be considered as "soft modes" of the system.²

One area in which anomalous elastic behavior has been of interest for some time is the area of so-called "pressure-induced" solid-state phase transitions. These are transitions which occur when the pressure (usually hydrostatic pressure) of the material is raised above a certain value, but which generally cannot be made to occur by varying the temperature of the sample at atmospheric pressure. While the normal behavior of a solid subjected to hydrostatic pressure is for the elastic constants and acoustic velocities to increase with increasing pressure, anomalous elastic behavior has been observed for a fairly large number of crystals undergoing pressure-induced transitions, in the sense that the velocities of one or more shear acoustic modes decrease with increasing pressure as these transitions are approached from the low-pressure side.³⁻¹⁹ A decreasing acoustic velocity or elastic constant is an indication that the crystal is becoming less stable with respect to the strain pattern of the mode in question and may signal an impending structural phase transition.^{12,14}

Unfortunately, for most of the known examples of the kind of behavior just described, the transi-

tions have a strong first-order character and the total elastic softening of the anomalous modes are only a few percent. Therefore, it is difficult to ascertain the importance of the anomalous modes in the dynamics of the transition. Only one exception to this general picture has been found, and that is the pressure-induced pure-strain transition recently discovered in TeO_2 .¹⁹ In this case, the $C_{11} - C_{12}$ shear acoustic mode velocity decreases to zero at the transition pressure of 9 kbar. This mode is the soft mode for the transition and the transition is of second order.

In this paper anomalous high-pressure elastic behavior is reported for a series of isomorphous substances of the KH_2PO_4 (KDP) family. The four materials studied were KDP, KD_2PO_4 (dKDP), RbH_2PO_4 (RbDP), and $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP), all of which have tetragonal D_{2d} symmetry at room temperature. These materials exhibit striking anomalous behavior of the elastic constants C_{44} and C_{66} as a function of pressure at room temperature.²⁰ In all cases the anomalous elastic constants exhibit extremely nonlinear pressure dependences which appear essentially parabolic over the range of pressures measured. Although the anomalous modes extrapolate to zero velocity at pressures well beyond the limits of our apparatus, there is some evidence from other work²¹⁻²³ that these materials undergo pressure-induced transitions in the general vicinity of the pressures where the modes do extrapolate to zero velocity.

In Sec. II the experimental procedures used for collecting the data are described. In Sec. III the results of the experiments will be presented and the analysis of the data will be described. A final discussion of the results is presented in Sec. IV.

II. EXPERIMENTAL

The materials studied all have tetragonal D_{2d} symmetry²⁴ and their elastic behavior is deter-

TABLE I. Acoustic modes measured for KDP-type crystals. Modes 5 and 6 were measured for ADP only.

| Mode designation | Propagation direction | Mode type and polarization | Effective elastic constant |
|------------------|------------------------|----------------------------|--------------------------------|
| Mode 1 | [100] | L[100] | C_{11} |
| 2 | [001] | L[001] | C_{33} |
| 3 | [100] | S[001] | C_{44} |
| 4 | [100] | S[010] | C_{66} |
| 5 | [110] | S[110] | $\frac{1}{2}(C_{11} - C_{12})$ |
| 6 | 45° to [100] and [001] | QS 45° to [100] and [001] | See below ^a |

$$^a \frac{1}{4}[(C_{11} + C_{33} + C_{44}) - [(C_{11} - C_{33})^2 + 4(C_{13} + C_{44})^2]^{1/2}]$$

mined by six independent elastic constants: C_{11} , C_{12} , C_{13} , C_{33} , C_{44} , and C_{66} . The constants C_{12} and C_{13} were studied for ADP only, while the other four constants were measured for all four materials. In Table I a list of the various acoustic modes measured is given. In the first column are listed the mode designations used in subsequent discussion. In the second and third columns are the propagation and polarization directions of each mode as well as the mode type (L = longitudinal, S = shear). The effective elastic constant C' for each mode is listed in the last column. The mode velocities are given by the general formula $C' = \rho v^2$, where ρ is the mass density and v is the mode velocity.

The samples used in this work were obtained from various commercial sources (Clevite, Isomet, Quantum Technology, Ltd.). Samples with linear dimensions of between about 4 and 9 mm were oriented to within 2° of the appropriate orientations listed in Table I using standard x-ray techniques.

Acoustic-mode wave-velocity measurements were made by the McSkimin pulse-superposition technique,²⁵ with the general procedures being similar to those discussed in previous work.¹⁶

The transducers used had fundamental frequencies of either 5 or 10 MHz, and data were taken at frequencies of 5, 10, 15, 25, or 30 MHz. Coaxially plated quartz transducers of either $\frac{1}{4}$ in. or $\frac{1}{8}$ in. diameter were used. The transducers were bonded with either Nonaq stopcock grease or phthalic anhydride-glycerin polymer. Each of the data runs was repeated at least once under different measurement conditions (e.g. change of bonding material or rf frequency) to check for reproducibility of the data.

To obtain data at high pressure a standard Bridgman press with a 50-50 mixture of pentane and isopentane for the pressure fluid was used. All pressure runs were taken at room temperature. Pressure was measured by a calibrated manganin coil to an accuracy of 1%.

III. RESULTS AND DATA ANALYSIS

A. Room-temperature and atmospheric pressure results

The room-temperature and atmospheric pressure values of the elastic constants C_{ij} and the axial and volume compressibilities (κ_a , κ_c , and κ_V , respectively) are given in Table II, along with the values of these parameters as determined by Haussühl²⁶ for KDP, RbDP, and ADP and by Shuvalov and Mnatsakanyan²⁷ for dKDP. It should be noted that Table II has entries for C_{66} corresponding to both the value at constant electric field C_{66}^E and at constant electric polarization C_{66}^P for KDP and dKDP. These values are different because of the piezoelectricity of the KDP-type crystals, and in fact are related by the equation²⁸

$$C_{66}^E = C_{66}^P - a_{36}^2 \chi_{33}^x, \quad (1)$$

where a_{36} is a component of the piezoelectric stress tensor and χ_{33}^x is the c -axis clamped dielectric susceptibility. The experimentally measured

TABLE II. Room-temperature and atmospheric-pressure values of the elastic constants (units of 10^{11} dyn/cm²) and compressibilities (units of 10^{-12} cm²/dyn).

| | KDP | | dKDP | | RbDP | | ADP | |
|------------|---------|-----------|---------|-----------|---------|-----------|---------|-----------|
| | Ref. 26 | This work | Ref. 27 | This work | Ref. 26 | This work | Ref. 26 | This work |
| C_{11} | 7.165 | 7.21 | 6.93 | 6.88 | 6.697 | 6.78 | 6.877 | 6.83 |
| C_{33} | 5.640 | 5.68 | 5.45 | 5.57 | 5.296 | 5.28 | 3.402 | 3.39 |
| C_{44} | 1.248 | 1.29 | 1.265 | 1.25 | 1.020 | 1.03 | 0.862 | 0.864 |
| C_{66}^E | 0.621 | 0.618 | 0.594 | 0.590 | 0.358 | 0.358 | 0.601 | 0.602 |
| C_{66}^P | ... | 0.625 | ... | 0.620 | ... | ... | ... | ... |
| C_{12} | -0.627 | ... | -0.78 | ... | -0.549 | ... | 0.406 | 0.36 |
| C_{13} | 1.494 | ... | 1.22 | ... | 1.492 | ... | 2.038 | 2.00 |
| κ_a | 1.28 | ... | 1.39 | ... | 1.35 | ... | 0.83 | 0.85 |
| κ_c | 1.09 | ... | 1.21 | ... | 1.13 | ... | 1.95 | 1.95 |
| κ_V | 3.65 | ... | 3.99 | ... | 3.83 | ... | 3.61 | 3.65 |

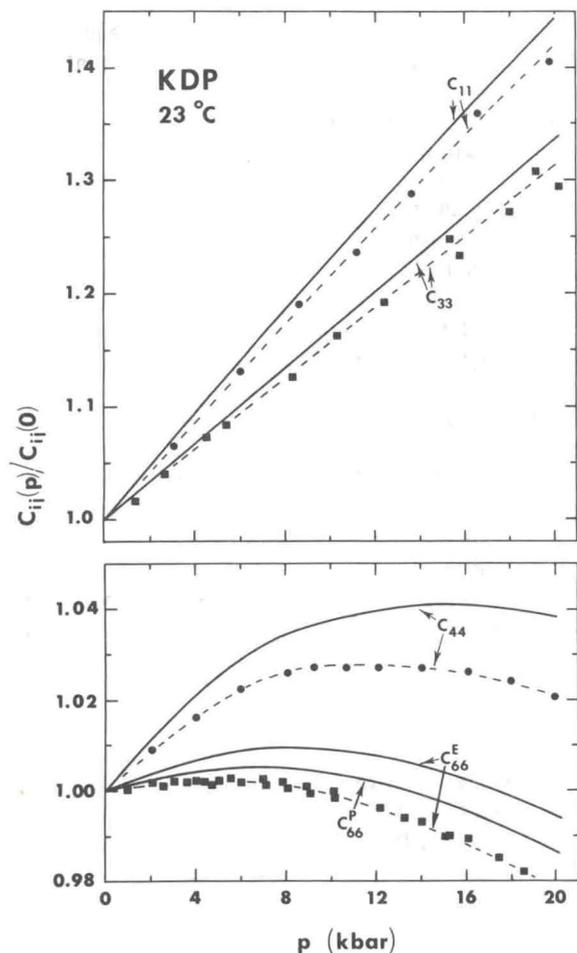


FIG. 1. Reduced plots of the pressure-dependent elastic constants of KH_2PO_4 (KDP). Data points and dashed lines represent $[f(p)/f_0]^2$, solid lines are the elastic constants (including the corrections for sample dimensional changes).

quantity is C_{66}^E , with C_{66}^P being calculated, when possible, from existing piezoelectric and dielectric data. We have only attempted to evaluate C_{66}^P for KDP and dKDP and the procedure for this calculation will be discussed below. The agreement of the elastic parameters determined in this work with the previous measurements listed in Table II is reasonably good (generally within 1 or 2%). The present data are not considered accurate to better than about 1% (in absolute value), because crystal orientation was not held to a close tolerance and because bonding effect corrections were not made.

B. High-pressure data

The data for the high pressure runs are shown in Figs. 1-4. For the pulse-superposition technique the experimentally measured quantity is the repetition rate oscillator frequency f as a function

of pressure p .

In Figs. 1-4 the measured values of $f(p)$ are indicated as discrete data points connected by smooth curves as visual guides. The following relations hold among f , the ultrasonic round trip transit time t , the ultrasonic path length l , the velocity v , the effective elastic constant C' , and the volume V :

$$\frac{f(p)}{f_0} = \frac{t_0}{t(p)} = \frac{l_0 v(p)}{l(p) v_0}, \quad (2)$$

$$\frac{C'(p)}{C'_0} = \frac{V_0}{V(p)} \left(\frac{l(p)f(p)}{l_0 f_0} \right)^2. \quad (3)$$

Here the zero subscripts indicate values at atmospheric pressure. In Figs. 1-3 the quantity $f^2(p)/f_0^2$ is plotted for comparison of this quantity (which represents the high-pressure elastic constants without correction for dimensional changes of the sample) with the actual (corrected) elastic constants (see below). In Fig. 4 the ADP data are plotted as $f(p)/f_0$.

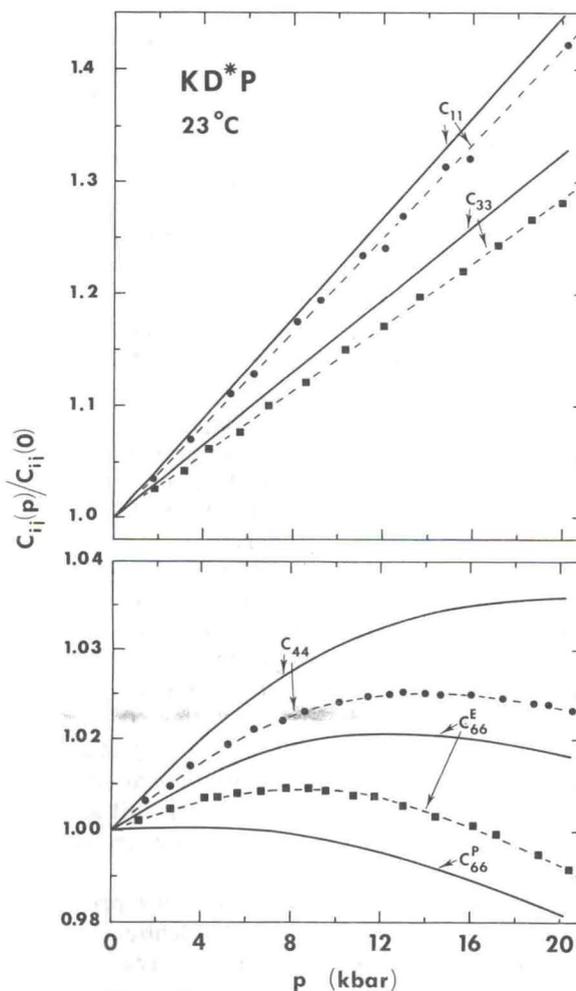


FIG. 2. Same as Fig. 1 for KD_2PO_4 (dKDP).

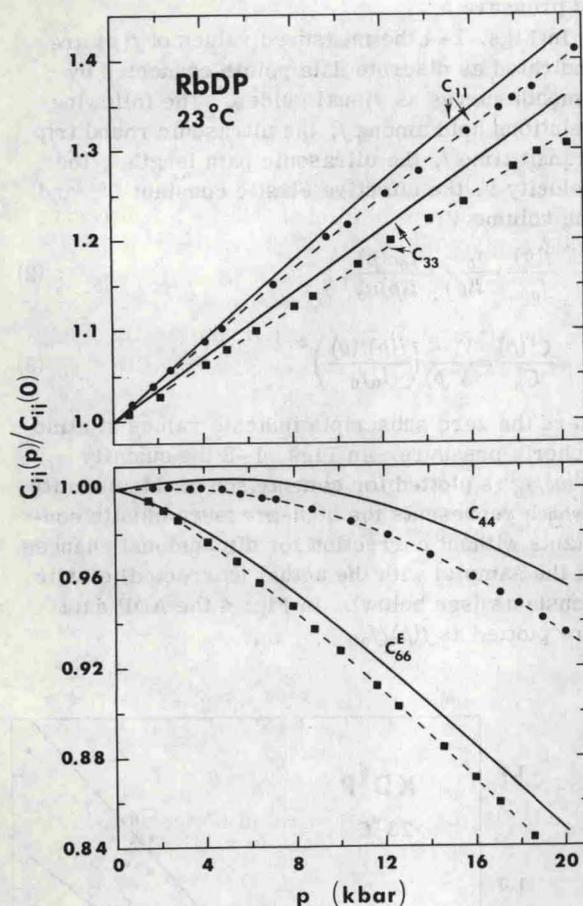


FIG. 3. Same as Fig. 1 for RbH_2PO_4 (RbDP).

The data in Figs. 1-4 show the important results of this series of experiments. Modes 1 (C_{11}) and 2 (C_{33}) show increases in velocity with increasing pressure which are typical of crystals with compressibilities of the same magnitude as those of the KDP-type crystals studied here, and therefore we conclude that the C_{11} and C_{33} elastic constants exhibit normal behavior. Modes 5 and 6 in ADP also exhibit normal pressure dependences, so that there is no reason to expect any anomalous behavior for the C_{12} or C_{13} elastic constants.

Modes 3 (C_{44}) and 4 (C_{66}), on the other hand, show strikingly unusual pressure dependences in all four materials studied. These two modes, which are the two pure shear modes propagating along an a -axis and polarized either along the c axis or along the other a axis, exhibit strongly nonlinear behavior over the pressure range of the measurements.

For KDP and dKDP the modes show pressure dependences that appear nearly identical, with the anomalous mode velocities first increasing with increasing pressure, then bending over and decreasing with further increase of pressure.

The maxima of the curves for the two materials occur at roughly the same pressures; for KDP the C_{66} mode maximum is at ~ 6 kbar compared to ~ 8 kbar for dKDP, while the C_{44} mode maximum is at ~ 11 kbar for KDP and ~ 13 kbar for dKDP. These results suggest immediately that deuteration has little, if any, effect on the anomalous elastic properties.

For RbDP (Fig. 3) the C_{44} mode repetition rate frequency is nearly independent of pressure up to ~ 6 kbar and subsequently begins to decrease with increasing pressure. The C_{66} mode for this material has a negative slope at all pressures and exhibits significant curvature as a function of pressure.

The results for ADP (Fig. 4) show a qualitative difference from the other three crystals in that the C_{44} mode decreases more rapidly with pressure than does the C_{66} mode, just the opposite of the behavior seen in Figs. 1-3. The C_{66} mode repetition frequency has a maximum at ~ 3 kbar. Again, both modes exhibit strongly nonlinear pressure dependences.

C. Analysis of data

Although the data points in Figs. 1-4 illustrate the salient qualitative features of the elastic anomalies for the KDP-type crystals we have studied, it is nevertheless instructive to proceed further and use the data to actually determine the pres-

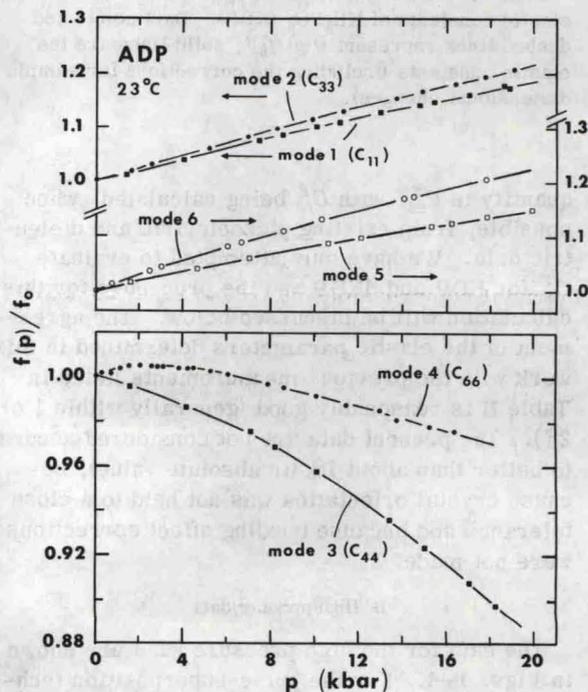


FIG. 4. Reduced repetition rate data $f(p)/f_0$ for $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP).

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 Samara²⁹ 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 Cook³⁰ and is exactly the same procedure as was used previously in a study of the high-pressure elastic properties of rutile.¹⁶

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.³¹ 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.²⁸ 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.³² The ferroelectric transitions are accompanied by an anomaly in χ_{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 χ_{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 χ_{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 χ_{33}^* and a_{36} must be determined. Dielectric measurements at high pressure on KDP-type materials have been made by Samara,³³ 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.³⁴ 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-

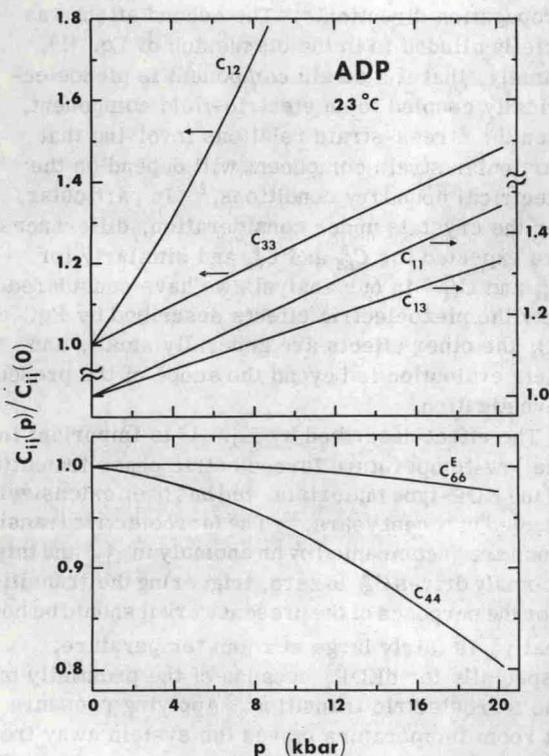


FIG. 5. Reduced elastic constants of ADP vs pressure.

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,³ KCl,⁴ KBr,⁵ KI,^{3,6} RbF,⁷ RbCl,⁷⁻⁹ RbBr,^{7,9} and^{7,9} RbI), SrO,¹⁰ BaF₂,^{11,12} CdS,¹³ and ZnS,¹⁴ TiO₂,^{15,16} Cu₂O,¹⁷ CuCl,⁸ and TeO₂.¹⁹ 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 TeO₂ transition¹⁹ 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.¹⁴ 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 Blount³⁵ 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.^{12,14}

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 ± 0.5 | 15.1 ± 0.5 | 15.4 ± 0.5 | 16.4 ± 0.5 |
| C_{33} | 9.6 ± 0.2 | 8.8 ± 0.2 | 8.9 ± 0.2 | 8.2 ± 0.2 |
| C_{44} | 0.74 ± 0.04 | 0.67 ± 0.04 | 0.22 ± 0.04 | -0.24 ± 0.04 |
| C_{66}^E | 0.12 ± 0.03 | 0.18 ± 0.03 | -0.09 ± 0.03 | 0.07 ± 0.03 |
| C_{66}^P | 0.07 ± 0.04 | 0.02 ± 0.08 | ... | ... |
| C_{12} | ... | ... | ... | 2.7 ± 0.7 |
| C_{13} | ... | ... | ... | 3.3 ± 0.5 |

TABLE IV. Parameters for quadratic fits of the form $C_{ij}(p)/C_{ij}(0) = 1 + Ap + Bp^2$ for C_{44} and C_{66} . p_0 is the (extrapolated) pressure for which $C_{ij} = 0$.

| | C_{44} | | | C_{66}^E | | | C_{66}^P | | |
|------|----------------------------|----------------------------|-----------------|----------------------------|----------------------------|-----------------|----------------------------|----------------------------|-----------------|
| | 10^3A (kbar $^{-1}$) | 10^4B (kbar $^{-2}$) | p_0 (kbar) | 10^3A (kbar $^{-1}$) | 10^4B (kbar $^{-2}$) | p_0 (kbar) | 10^3A (kbar $^{-1}$) | 10^4B (kbar $^{-2}$) | p_0 (kbar) |
| KDP | 5.60 | -1.84 | 91 | 2.07 | -1.17 | 102 | 1.43 | -1.05 | 105 |
| dKDP | 5.54 | -1.48 | 103 | 3.26 | -1.21 | 106 | 0.39 | -0.65 | 127 |
| RbDP | 1.78 | -1.98 | 76 | -4.94 | -1.36 | 70 | ... | ... | ... |
| ADP | 3.15 | -3.25 | 51 | 0.73 | -0.97 | 105 | ... | ... | ... |

have been made. The parameters A and B of these fits are given in Table IV along with the value p_0 of the pressure for which the elastic constant is zero. For KDP and dKDP both the C_{44} and C_{66} modes extrapolate to zero at a pressure near 100 kbar. (Because of the approximations used in determining C_{66}^P for dKDP, the value of p_0 for this mode is probably not as reliable as for the other modes.) For RbDP the extrapolated pressures are lower (76 kbar for C_{44} and 70 kbar for C_{66}), but, as in the case of KDP and dKDP, of nearly the same value. For ADP the C_{44} mode extrapolates to zero at about 50 kbar, whereas C_{66} extrapolates to zero at about twice this pressure (105 kbar). At first glance this result for ADP as well as the previously noted result that C_{44} decreases more rapidly with increasing pressure than does C_{66} may appear incongruous with the results for the other three materials. However, this result is really not particularly surprising as ADP has other properties that are different from the other crystals. For example, the c -axis compressibility is less than the a -axis compressibility, and the crystal undergoes an antiferroelectric transition at low temperatures rather than a ferroelectric one.

Several studies have been made of high-pressure polymorphism in KDP-type crystals, including DTA measurements to 40 kbar in KDP made by Rapoport,²¹ DTA measurements to 50 kbar in ADP made by Clark,²² and infrared absorption spectra to 60 kbar of KDP and RbDP of Blinc, Ferraro, and Postmus.²³

For KDP the DTA measurements²¹ indicate two possible transitions at room temperature. The first transition (II-IV) was not observed but merely inferred from a break in another phase boundary. This transition would be expected to occur below 10 kbar, but its existence is questionable. The second transition expected at room temperature (IV-V) should occur at about 30-40 kbar. The infrared work²³ did not indicate any well defined transitions up to a pressure of 60 kbar. Therefore for KDP there may be a pressure-induced transition, but further work is needed to define the transition pressure and investigate the nature of the

transition.

For RbDP the infrared data²³ indicate a transition at about 60 kbar. We saw above that the acoustic modes extrapolate to zero at around 70-76 kbar, so that the shear mode velocities are probably small in the vicinity of the transition and shear instabilities may play an important role in the transition.

For ADP the measurements of Clark²² (DTA and some PVT data) indicate two possible pressure-induced transitions at room temperature. The first should occur between 20 and 25 kbar. No evidence was obtained for this transition in our ultrasonic data or in dielectric data taken in this pressure range. The second transition extrapolates to room temperature at about 90 kbar. This pressure is near the extrapolated zero of C_{66} ; however, no phase boundary has been observed in the vicinity of 50 kbar, where C_{44} extrapolates to zero. Possibly there is a phase boundary that was not detected in the work of Ref. 22.

From the above discussion it is evident that there are pressure-induced transitions in the KDP isomorphs, but that these have not been well enough characterized to allow detailed comparison with the present ultrasonic data. One possible problem with the previous measurements (Refs. 21-23) may be that they were not made under conditions of hydrostatic pressure, and in fact some of them were made on powdered samples. Further investigation of these transitions is called for.

In summary, we have observed several striking examples of pressure-induced nonlinear elastic softening, and have attempted to show that these effects may be associated with pressure-induced phase transitions. Existing studies of high-pressure phase transitions in the KDP isomorphs appear incomplete and perhaps even contradictory. It is suggested that more work should be done in this area.

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- ¹Recent review articles emphasizing different areas in this general field include: C. W. Garland, in *Physical Acoustics*, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1970), Vol. VII, p. 51; B. Lüthi, T. J. Moran, and R. J. Polina, *J. Phys. Chem. Solids* **31**, 1741 (1970); L. R. Testardi, in *Physical Acoustics*, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1973), Vol. X, p. 194; and R. L. Melcher, *ibid.* (Academic, New York) (to be published), Vol. XII.
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