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 measurements[21] 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 work[23] 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 data[23] 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 Clark[22] (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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