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ANOMALOUS ACOUSTIC BEHAVIOR OF KH_2PO_4 AT HIGH PRESSURE*

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The pressure dependences of the elastic constants C_{11}, C_{33}, C_{44} and C_{66} of KH_2PO_4 have been measured to 20 kbar at room temperature. A monotonic increase with pressure is found for C_{11} and C_{33}, while C_{44} and C_{66} first increase then decrease with increasing pressure. This behavior of C_{44} and C_{66} may be associated with the high pressure (~ 40 kbar) phase transition suggested by the data of Rapoport.

THE ELASTIC constants of a solid normally increase with increasing hydrostatic pressure. There are, however, a few known examples of materials which have shear modes whose velocities decrease with increasing pressure, an effect which is apparently connected with pressure induced phase transitions in these materials.[1,2] We have observed anomalous acoustic behavior in tetragonal KH_2PO_4 (KDP) under pressure. Two of the elastic constants, C_{11} and C_{33}, behave normally, increasing nearly linearly with increasing pressure. The two shear constants C_{44} and C_{66}, however, first increase, then bend over and decrease with increasing pressure. This is the first observation of this type of behavior of which we are aware. The other two elastic constants, C_{12} and C_{13}, were not measured in this experiment.

The samples used had linear dimensions of about 0.8 cm and were carefully oriented and lapped. Quartz transducers 1/8 in. dia. were bonded to the sample with either Nonaq stopcock grease of phthalic anhydride–glycerin polymer. Measurements as a function of pressure were made at 10 MHz using the McSkimin pulse superposition technique,[3] and they were partially rechecked at 25 and also at 10 MHz on a second sample. Hydrostatic pressure was generated in a standard Bridgman type press with a 50–50 pentane–isopentane mixture for the pressure fluid. The 1 atm values of the elastic constants were measured at several frequencies to ensure that the correct cycles were being superpositioned.

In Table 1 are listed the room temperature, room pressure values of the four elastic constants measured, along with the results of the ultrasonic measurements of Haussühl[4] and the Brillouin scattering measurements of Brody.[5] In Fig. 1 are shown smooth curve values of the ratio of the elastic constants to their 1 atm value as a function of pressure. Both the C_{66} elastic constants measured at constant field, C_{66}^E, and at constant polarization, C_{66}^P, are shown, C_{66}^E being the constant measured experimentally and C_{66}^P being deduced from the known pressure dependence of the dielectric constant and piezoelectric coupling.[6]

Table 1. KDP elastic constants (10^{11} dyn/cm^2)

Elastic constant	This work (±1%)	Brody (±1%)	Haussühl
C_{11}	7.21	7.23	7.165
C_{33}	5.68	5.63	5.640
C_{44}	1.29	–	1.248
C_{66}^E	0.618	0.617	0.621

The ratios $C_{ij}/C_{ij}(0)$ were deduced from the ultrasonic data using the formula

$$\frac{C_{ij}}{C_{ij}(0)} = \frac{\rho}{\rho_0}\left(\frac{l}{l_0}\frac{f}{f_0}\right)^2$$

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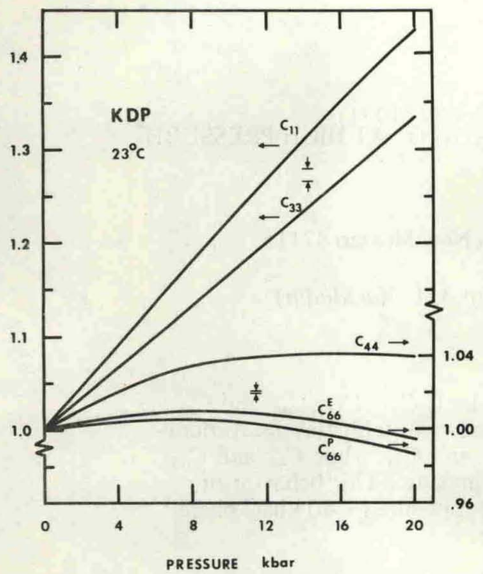

FIG. 1. Smooth curve values of the reduced elastic constants of KH_2PO_4 as a function of hydrostatic pressure at room temperature. The upper and lower error bars indicate the size of the data for the longitudinal and shear modes respectively. C_{66}^E and C_{66}^P are, respectively, the constant field and constant polarization values of C_{66}.

where $C_{ij}/C_{ij}(0)$, ρ/ρ_0, l/l_0 and f/f_0 are, respectively, the ratios of the elastic constant, mass density, ultrasonic path length and pulse repetition rate at pressure p to their 1 atm values. The changes in the unit cell dimensions as a function of pressure as measured by Morosin and Samara[7] were used to deduce ρ/ρ_0 and l/l_0. It should be noted that the fractional changes in these latter quantities under pressure are larger than the fractional changes in the shear elastic constants so that it is necessary to know ρ/ρ_0 and l/l_0 accurately to deduce accurate values of $C_{44}/C_{44}(0)$ and $C_{66}/C_{66}(0)$. The error bars on the figure indicate the scatter in the data. The upper error bar indicates the scatter in the data points of a typical run for the longitudinal modes. This scatter is relatively large because of bonding problems. The lower error bar pertains to the shear modes and represents more the degree of irreproducibility of the data from run to run than scatter within a single run, which was very small.

The magnitudes of the pressure derviatives of C_{11} and C_{33} are typical for materials with compressibilities comparable to KDP. We postulate that the anomalous behavior of C_{44} and C_{66} is in some way associated with a high pressure phase transition. High temperature, high pressure polymorphism has been observed in KDP by Rapoport[8] using differential thermal analysis techniques. At room temperature the transition of the phase labeled V by Rapoport should occur at ~ 40 kbar. (There was no evidence in our experiment of any transition occuring up to 20 kbar.) As nothing is known about the structure of the high pressure phases, it is not possible to predict what, if any, acoustic anomalies are to be expected.

The fact that C_{44} and C_{66} are small and decrease under high pressure indicates that the crystal structures becomes less stable with respect to the atomic displacements associated with these modes. It does not appear that either C_{44} or C_{66} is decreasing rapidly enough to become zero at 50 kbar, although the curves could, of course, bend over more steeply at higher pressures. However, there is no requirement that any elastic constant actually vanish at the transition pressure, as the transition could well be of first order. Shear mode behavior similar to what we have observed in KDP, namely an increase followed by a decrease of one or more elastic constants with increasing pressure, has been predicted (but not yet observed) for certain crystals of the sodium chloride and fluorite structures[1,2] which undergo high pressure transitions, and it is not reasonable that similar behavior could occur in crystals of the KDP type structure.

The phase diagram of $NH_4H_2PO_4$ (ADP) has been determined by Clark,[9] who found a transition which should occur at ~ 20 kbar at room temperature. If this transition is analogous to the KDP 40 kbar transition, similar and perhaps more pronounced acoustic anomalies may occur. Work is in progress to measure the pressure dependence of the elastic constants of this material.