PHYSICAL REVIEW B VOLUME 13, NUMBER 2 15 JANUARY 1976

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

I. J. Fritz
Sandia Laboratories, Albuquerque, New Mexico 87115
(Received 21 August 1975)

The pressure dependences of the elastic constants of KH_2PO_4, KD_2PO_4, RbH_2PO_4, and $NH_4H_2PO_4$ have been studied for pressures up to 20 kbar at 23 °C. For $NH_4H_2PO_4$ 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 transitions 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 $NH_4H_2PO_4$ (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 appartus, there is some evidence from other work[21-23] 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} symmetry[24] 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]	$S[1\bar{1}0]$	$\frac{1}{2}(C_{11}-C_{12})$
3	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 Haussühl[26] for KDP, RbDP, and ADP and by Shuvalov and Mnatsakanyan[27] 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 equation[28]

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

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/cm^2) and compressibilities (units of 10^{-12} cm^2/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