

FIG. 3. Variation of c_{44} with pressure. The dashed curve near the top represents data taken in phase O_I at 180°K, where the lattice parameter is not well known. The vertical dashed lines at 190° and 200°K represent first-order phase changes from the ordered tetragonal phase to the O_{II} phase. $T_1=190^\circ\text{K}$, $T_2=200^\circ\text{K}$, $T_3=210^\circ\text{K}$, $T_4=220^\circ\text{K}$, $T_5=240^\circ\text{K}$.

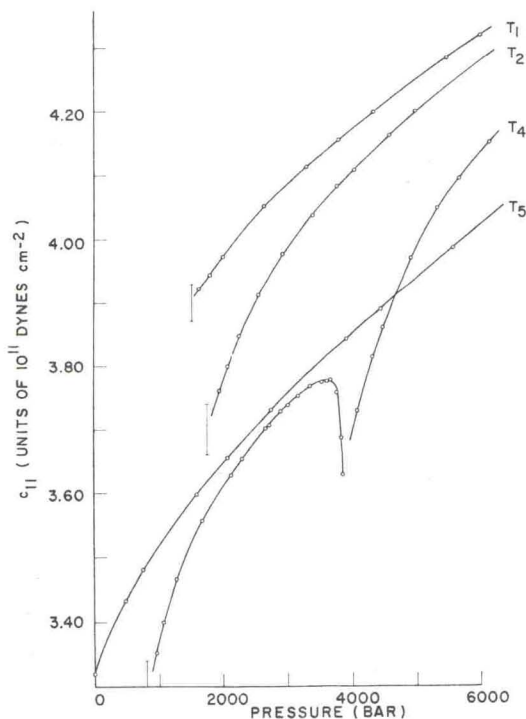


FIG. 4. Variation of c_{11} with pressure. No data could be obtained in the ordered tetragonal phase. The transition pressures for the first-order O_I-O_{II} phase change at T_1 and T_2 and for the O_T-D lambda transition at T_4 were obtained from c_{44} data; these pressures are indicated by vertical bars. $T_1=190^\circ\text{K}$, $T_2=200^\circ\text{K}$, $T_4=220^\circ\text{K}$, $T_5=240^\circ\text{K}$.

displacement method which was subject to considerable hysteresis. It is a curious accident that both Bridgman and Stevenson failed to make any observations in the region of the $O_{II}-D$ lambda line.

The parts of the phase diagram which are shown with dashed lines are not at all well known, and these dashed lines should be viewed as rough approximations to the actual phase lines. However, the O_I-O_T transition temperatures at atmospheric pressure are well established to be 78°K on cooling and 108°K on warming.¹⁴ The initial slope at 108°K can be estimated from the thermodynamic data of Cole¹⁵ and the Clapeyron equation. The value of $\Delta S=0.29$ cal deg⁻¹ mole⁻¹ combined with a value of $\Delta V=0.78$ cm³ mole⁻¹ taken from recent x-ray work⁹ gives a slope of 15 bar deg⁻¹. This initial slope is shown as a short solid line in Fig. 1.

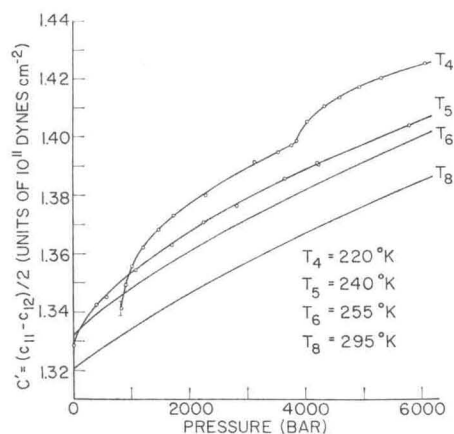


FIG. 5. Variation of $C'=(c_{11}-c_{12})/2$ with pressure. The curves at 255° and 295°K are taken from Paper I. No data could be obtained in the ordered tetragonal phase. The O_T-D lambda transition pressure at T_4 is indicated by a vertical bar.

The transition from O_I to the ordered tetragonal phase was not studied in the present work because single crystals frequently cracked on going through this first-order phase change. This region may be difficult to study with any method if the extreme hysteresis and sluggishness observed in the O_I-O_T phase transition at one atmosphere persist up to the triple point with the O_{II} phase.

Constant-Temperature Data

The experimental values of c_{44} , c_{11} , and C' are shown as functions of pressure at various constant temperatures in Figs. 3-5. In most runs, pressure measurements were made for both increasing and decreasing pressures. The time necessary for equilibrium upon changing the pressure could easily be monitored by observing the in-phase frequency change with time. Generally, 20 min

¹⁴ C. C. Stephenson and H. E. Adams, J. Chem. Phys. **20**, 1658 (1952).

¹⁵ A. G. Cole, Ph.D. thesis, M.I.T., 1952.

was ample time for equilibrium except for points very close to the transition lines. In these cases 30 min was usually long enough. In no case was hysteresis observed. In Fig. 3 the lower portions of the curves at 190°, 200°, 210° and 220°K represent data in the tetragonal phase and should be considered as "average" shear constants \bar{c}_{44} ; see Paper I for further details. As seen from Figs. 4 and 5, it was not possible to get any data in the tetragonal phase for c_{11} and C' due to the very large attenuation in that phase for the acoustic waves yielding these constants.¹⁶ In Fig. 5 the solid curves shown at 255° and 295°K are taken from Paper I and are included for comparison. These curves have been shifted up by 0.18% to make them internally consistent with the present data. Smooth-curve values of the effective elastic constants as a function of pressure are given in Table I.

Let us now make an estimate of the errors associated with the measurements of the various quantities needed to calculate the elastic constants. The uncertainty in the path length is about 0.02% at 1 atm, and the error due to changes in length with pressure or temperature is probably less than 0.05% even in the regions close to the transitions. The frequency of pulse generation can be measured to within 0.01% consistently. Before this frequency can be used to obtain the round-trip transit time, a correction must be made for the phase shift γ . Since this seal correction never exceeded 0.02% of the measured frequency, even a large error in estimating γ should not cause more than a 0.01% error in the transit time. Variations in temperature during a pressure run could produce an error in c_{ij} of 0.02%, but uncertainties in the pressure determination would not cause a noticeable error. The random error in c_{ij} from the above causes is less than 0.2%. All data collected from several different crystals agree to within this limit of error.

A known source of systematic error is the increase in the velocity due to diffraction effects.¹⁷ The velocities were corrected for this effect, and the magnitude of the correction was 0.035% for c_{11} , 0.016% for c_{44} , and 0.01% for C' . An unknown systematic error may occur in calculating the phase shifts since the seal corrections were based on the properties of the bonding material

¹⁶ This is presumably due to scattering from small tetragonal domains. An attempt was made to obtain a single-domain crystal by exerting a lateral (biaxial) compression perpendicular to one of the original cubic axes. Spring-loaded or screw-tightened plates on the crystal faces did not work; and in order to apply larger and more uniform pressures, the crystal was "potted" in a disk of methylmethacrylate and ethylene glycol dimethacrylate polymer. This polymer has a larger thermal expansion coefficient than ammonium bromide and upon cooling applied a considerable lateral pressure to the sample. This method did not align the tetragonal domains along the unstressed direction but did apply enough pressure to the sample to cause a slight increase in the value of the average shear constant. Thus, it does not appear feasible to align the domains with a modest biaxial pressure on the sides of the crystal.

¹⁷ H. J. McSkimin, J. Acoust. Soc. Am. **32**, 1401 (1960); **33**, 539 (1961).

TABLE I. Smooth-curve values of the effective adiabatic elastic constants as functions of pressure at various temperatures. All entries are given in units of 10^{11} dyn cm^{-2} . Values of the adiabatic bulk modulus $1/\beta^S = (c_{11} - 4C'/3)$ are also given at two temperatures. At 190° and 200°K, the transition pressure p_t is indicated for the first-order phase change from the ordered tetragonal phase to the O_{II} phase. At 210° and 220°K, the critical pressure p_λ is indicated for the O_T - D lambda transition (lower p_λ value) and the D - O_{II} lambda transition (higher p_λ value). At 240°K, no transitions are observed below 6 kbar. The values reported for c_{44} in the ordered tetragonal phase should be interpreted as average shear constants for that phase.

p (kbar)	c_{11}	c_{44}	p (kbar)	c_{11}	c_{44}
$T_1 = 190^\circ\text{K}$					
0	...	0.7315	1.8	3.946	0.993
0.5	...	0.754	2.0	3.974	1.001
1.0	...	0.777	3.0	4.087	1.037
1.5	...	0.7995	4.0	4.173	1.070
1.53 = $p_t(O_T - O_{II})$			5.0	4.253	1.1025
1.6	3.917	0.986	6.0	4.323	1.134
$T_2 = 200^\circ\text{K}$					
0	...	0.727	1.8	~3.71	0.9655
0.5	...	0.752	2.0	3.778	0.976
1.0	...	0.780	3.0	3.987	1.018
1.6	...	0.819	4.0	4.107	1.054
1.65 = $p_t(O_T - O_{II})$			5.0	4.202	1.087
1.7	...	0.9595	6.0	4.280	1.1195
p (kbar)	c_{44}	p (kbar)	c_{44}	p (kbar)	c_{44}
$T_3 = 210^\circ\text{K}$					
0	0.729	1.5	0.887	3.0	0.982
0.7	0.788	2.0	0.911	3.5	1.0075
1.0	0.813	2.4	0.929	4.0	1.028
1.2	0.832	2.523 = p_λ	0.935	5.0	1.065
1.3	0.849	2.6	0.947	6.0	1.100
1.339 = p_λ	0.876	2.8	0.9675		
p (kbar)	c_{11}	c_{44}	C'	$1/\beta^S$	
$T_4 = 220^\circ\text{K}$					
0	...	0.735	
0.4	...	0.7675	
0.6	...	0.7875	
0.7	...	0.801	
0.8	...	0.829	
0.817 = p_λ	...	0.845	~1.34	...	
0.9	3.326	0.851	1.351	1.525	
1.0	3.368	0.856	1.357	1.559	
1.4	3.496	0.874	1.369	1.671	
2.0	3.609	0.899	1.379	1.770	
2.5	3.680	0.919	1.386	1.832	
3.0	3.736	0.939	1.392	1.880	
3.4	3.770	0.955	1.396	1.909	
3.6	3.778	0.963	1.398	1.914	
3.7	3.774	0.967	1.399	1.909	
3.8	3.735	0.971	1.400	1.869	
3.870 = p_λ	>3.6	0.9735	1.401	...	
3.9	...	0.977	1.402	...	
4.0	~3.68	0.987	1.406	...	
4.1	3.732	0.995	1.408	1.854	
4.5	3.864	1.019	1.414	1.978	
5.0	3.986	1.042	1.419	2.093	
5.5	4.072	1.062	1.423	2.174	
6.0	4.137	1.081	1.427	2.235	
$T_5 = 240^\circ\text{K}$					
0	3.321	0.793	1.328	1.550	
0.5	3.434	0.815	1.344	1.642	
1.0	3.515	0.836	1.353	1.710	
2.0	3.646	0.875	1.367	1.823	
3.0	3.755	0.913	1.379	1.917	
4.0	3.850	0.950	1.388	1.999	
5.0	3.938	0.987	1.397	2.075	
6.0	4.024	1.022	1.405	2.151	