Ultrasonic Velocities in Solid Argon*

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(Received 27 June 1966)

The pulse technique of echo ranging was used to measure the velocities of ultrasonic waves in cylindrical samples of solid argon for temperatures from 74°K to the triple point (83.80°K). The center portion of these cylinders of solid argon transported the acoustic waves in the manner of a single crystal. The direction of propagation of the ultrasonic waves was deduced to be [110]. Making use of the data of Jones and Sparkes for average continuous transverse waves taken at temperatures from 18 to 62°K, these pulsed ultrasonic-velocity data were extrapolated to the following values at 0°K: $v_l=1555$ m/sec; $v_{t1}=1000$ m/sec; $v_{t2}=835$ m/sec. The elastic constants at 0°K calculated from these values were $c_{11}=4.819\times10^{10}$ dyn/cm²; $c_{12}=1.277\times10^{10}$ dyn/cm²; $c_{44}=1.235\times10^{10}$ dyn/cm².

I. INTRODUCTION

In recent years, solid argon has become a topic of great interest and some very fine reviews[1–4] have been published about it and the other solidified inert gases. This interest has been further demonstrated by the symposium on rare-gas solids recently held at Durham, North Carolina.[5]

Some very important data which need to be obtained for solid argon are the elastic constants. A very accurate determination of single crystal velocities, in known directions of propagation, is necessary for the calculation of these quantities. Previous data have been reported only for the average velocities obtained from polycrystalline solid argon. Barker and Dobbs[6] measured the average velocities for temperatures between 65 and 80°K with an acoustic interferometer. Jones and Sparkes[7] measured the average velocity of transverse waves for temperatures from 18 to 62°K by determining the resonant frequency of forced, torsional oscillatious of a polycrystalline rod of solid argon. Lawrence and Neale[8] measured the average velocity of longitudinal waves for temperatures from 54 to 83°K by means of the diffraction-of-light technique.

The research reported below consisted of measurements on an essentially single crystal. Velocities were measured by the pulse technique of echo ranging for temperatures between 74°K and the triple point (83.80°K), and a subsequent calculation was made of the elastic constants. The calculation of the elastic constants depended upon a logical deduction for the direction of the propagation of the ultrasonic waves. Without unqualified proof of crystal direction from x-ray evidence, these reported elastic constants must remain suspect, but they are the first known attempt at obtaining values for these quantities. This was also the first time that the velocities of ultrasonic waves in solid argon have been successfully measured by means of a pulse technique.

Crystal-growth experiments[9] that were carried out in preparation for the ultrasonic measurements produced large, optically clear samples of solid argon. Etch patterns on a free surface of these samples indicated that grains having dimensions of 1 cm or greater were consistently produced. The ultrasonic studies on similar samples indicated that at least the center portion of the solid behaved as a single crystal, because the echoes were sharp and no back scattering from grain boundaries was observed. These remarks explain the careful use of the words, "measurements on an essentially single crystal."

II. APPARATUS AND PROCEDURE

The velocities of longitudinal and transverse ultrasonic waves in solid argon were measured by means of the pulse technique of echo ranging[10] for temperatures from 74°K to the triple point. Figure 1 shows the cell used for these measurements. A quartz transducer A with a diameter of 0.5 in. was used to send the ultrasonic waves through the solid argon. An x-cut transducer was used for longitudinal waves and a y-cut transducer for transverse waves. The transducer was mounted in a shallow well in a brass holder B and held in place by a thin brass cap C. Since the thin brass cap was actually only three small "fingers", most of the transducer could be in contact with the solid argon. Experience shows that this improved contact with the solid argon resulted in stronger, and thus more easily observed and measured, echoes. The fundamental frequency of the transducers was 10 MHz. They were gold-plated all over

* Work supported by the Robert A. Welch Foundation, Huston, Texas.
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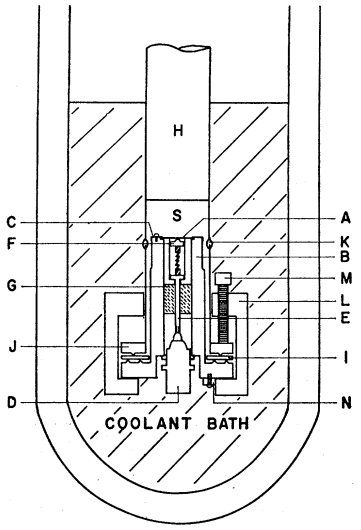

FIG. 1. Apparatus for ultrasonic experiments. The solid-argon specimen S has been grown directly on top of the quartz crystal transducer A.

except for a ring on one side, which allowed an electrical pulse to be applied to its center while its outside rim and opposite side were grounded. The pulses were transmitted from the electronics to a BNC connector D which was screwed into the brass holder so as to make a good electrical contact with a brass rod E. The rod was connected through a spring-loaded contact F to the transducer, and was held in place by means of epoxy G so that it was electrically insulated from the brass holder. Since the BNC connector was not vacuum-tight, the epoxy also served to seal off the hole through the brass holder to the growing chamber H. The brass holder had two concentric V rings which, with a soft aluminum gasket, sealed off the growing chamber. The brass flange was soft-soldered to a copper to Pyrex seal K. The V rings were compressed into the aluminum gasket by two half cylinders of brass, L, each containing three set screws M. The temperature was measured by means of a copper-constantan thermocouple attached to the brass holder at N.

Because earlier attempts to bond a transducer to the top of a cylinder of solid argon failed, it was decided that the best chance of obtaining a bond between the transducer and the solid argon was to actually grow the solid on the top of the transducer. The following detailed procedure gave successful results using the above apparatus. After the system was evacuated and flushed a few times, it was closed off with one atmosphere of gaseous argon in it at room temperature. Then the coolant was introduced into the Dewar and the bath level was raised until the metal crystal holder was cooled to about 77.5°K. The argon froze to the surface of the transducer, the holder, and the cap, and the space between the edge of the transducer and the brass holder was partially sealed. Argon gas was then slowly admitted to the growing chamber at a rate that would allow a little more solid to form while the vapor pressure was being increased slowly to slightly above the triple-point pressure. By the time any liquid argon was formed, there was a small amount of solid argon covering the transducer and firmly bonded to it, but very little argon had been allowed to get under the transducer. With a small pool of liquid on top, the solid was then grown to the desired thickness from the melt by the modified Bridgman method. Three leveling screws were attached to the bottom of the frame that supported the apparatus. The purpose of these screws was to orient the transducer parallel to the top of the liquid as the solid was growing. Then if the last bit of liquid was frozen very slowly, the top of the solid was flat and reasonably parallel to the transducer.

The method described above for growing solid argon for ultrasonic measurements was successful. Even so, care had to be taken to lower the temperature very slowly, because, if it was lowered too rapidly, the contracting solid argon broke its bond in some places near the outside edge of the transducer. Then, that section of the transducer was not loaded and consequently vibrated freely. This "ringing" was such that it masked any echoes that were present in the return signal.

Measurements were made for temperatures from 74°K to the triple point. Temperatures above 77.5°K were obtained by mixtures of liquid nitrogen and oxygen-enriched liquid air. Those below 77.5°K were obtained by pumping on a liquid-nitrogen bath. The pressure above the bath was regulated by means of a precision regulator (Cryonetics Corporation, Mark II), which was inserted into the pumping line.

TABLE I. Velocity of longitudinal waves v_l in solid argon.

Temperature (°K)	v_l (m/sec)
75.02	1353
75.93	1347
76.52	1343
77.00	1339
77.08	1339
77.50	1334±27[a]
78.10	1326
78.80	1332
79.40	1339
79.88	1321
80.20	1317
80.72	1313
80.83	1328
81.02	1319
81.38	1307
81.82	1292
81.92	1301
82.34	1297
82.40	1293
82.64	1295
82.80	1287
83.12	1290
83.20	1275
83.38	1276
83.50	1275
83.60	1270
83.61	1270
83.70	1259
83.80	1258

[a] All individual-specimen values were normalized to this absolute value. All other values have a possible relative error of 1%.

III. RESULTS

A. Velocity of Longitudinal Waves

The velocity of longitudinal waves obtained are listed in Table I. The direction of propagation will be assumed to be in the [110] direction for reasons to be discussed in a later section (Sec. IV A.).

The data for the velocity of longitudinal waves were obtained from three samples for temperatures from 74°K to the triple point. Because of some optical difficulty encountered in the measurement of the thickness of the samples, the velocities obtained were not identical for all the samples. The optical difficulty stemmed from the following sources: (1) the inaccuracy of the cathetometer used to measure the thickness when viewing through the three cylindrical glass surfaces (two belonging to the Dewar and one belonging to the growing chamber), and (2) a slight upward curvature at the very edge of the top of the solid-argon specimen next to the wall of the growing chamber. The possible error in the thickness measurements was estimated as ±0.4 mm. For solids from 5–7-mm thick, this meant a possible percentage error of from 6 to 8%. The average value of the velocity obtained from the three samples at 77.5°K is 1368 m/sec. Barker and Dobbs[6] reported values for the average velocity of longitudinal waves for temperatures from 67 to 79°K having a percentage error of 2% or less. Their value at 77.5°K was 1334 m/sec, which differed from the present value by about 2.5%. The observed data for the thickness of each specimen were adjusted so that the velocity at 77.5°K agreed with this value. This adjustment was well within the 6–8% estimated error for the measurement of the thickness for all three samples. The normalization at 77.5°K provided the opportunity to compare the present data with the previous extrapolated data above 80°K.

The possible error in the measurement of the traversal time was about 1% or less. Thus the temperature dependence (i.e., relative values) of the velocity of the longitudinal waves was probably correct within 1%. A correction for the contraction or expansion of the solid argon due to temperature changes was made.

B. Velocities of Transverse Waves

The velocities of transverse waves obtained are listed in Table II. The data were obtained from two samples and with both samples, two transverse waves, traveling simultaneously and independently through the solid (with different velocities), were observed. This is a well-known phenomenon that occurs for certain directions of propagation in single crystals and is predicted by the theory of the propagation of elastic waves in a crystal.[10] This phenomenon of simultaneous and independent propagation of two transverse waves was observed by Briscoe and Norwood[11] in single crystals of LiF and KI for propagation in the [110] direction. LiF and KI form face-centered-cubic (fcc) lattices as does argon. For reasons to be discussed in the next section, the direction of propagation in solid argon in the present work was chosen to be [110].

The possible errors discussed in the previous section also apply in this case, and a similar adjustment was made. The average values of the two velocities from the two samples at 77.5°K were $v_{t1}=728.3$ m/sec and $v_{t2}=663.8$ m/sec. Jones and Sparkes[7] measured the average velocity of transverse waves for temperatures from to 18 to 62°K, and a small extrapolation of their data to 77.5°K gave a value of 670 m/sec. The present data were adjusted so that this extrapolated value was halfway between the two values at 77.5°K. Thus $v_{t1}=700$ m/sec and $v_{t2}=642$ m/sec were the values to which the data from both samples were normalized (at 77.5°K). The values obtained were corrected for expansion or contraction of the sample. The present data are in agreement with the temperature dependence found by Jones and Sparkes, and further demonstrate that the slope of the extrapolation by Barker and Dobbs was incorrect.

IV. DISCUSSION

A. Direction of Propagation

The solid argon used for the ultrasonic measurements was grown directly on a quartz transducer that was highly polished and gold plated. Such a flat substrate could be expected to form a crystalline plane for the growth of solid argon deposited on it. The results ob-

TABLE II. Velocities of transverse waves v_{t1} and v_{t2} in solid argon.

Temperature (°K)	v_{t1} (m/sec)	v_{t2} (m/sec)
73.90	...	670
74.37	726	...
74.60	732	666
75.02	726	...
75.10	738	667
75.70	735	664
75.70	721	...
76.10	729	660
76.23	716	...
76.35	...	656
76.65	714	...
76.96	714	650
77.00	702	...
77.50	700±28[a]	642±26
78.00	673	...
78.38	675	...
78.80	662	...
79.15	666	...
79.45	659	611
79.87	660	...
80.24	657	...
80.84	648	...
81.50	651	...
82.10	630	577
82.88	596	571
83.25	592	579
83.70	575	571
83.73	571	560

[a] All separate specimen values were normalized to this value.

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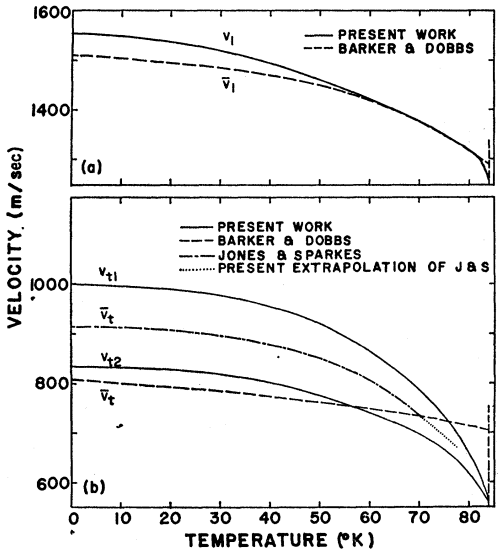

FIG. 2. Extrapolated curves for the velocities of (a) longitudinal and (b) transverse ultrasonic waves in solid argon. The data by Barker and Dobbs are from Ref. 6 and those by Jones and Sparkes are from Ref. 7.

tained from generating transverse waves in the solid argon indicated the presence of essentially a single crystal, i.e., the region through which the sound waves traveled behaved as a continuous medium and permitted clean, sharp echoes. The present apparatus was not designed for x-ray studies, so the actual crystal orientation could not be unequivocally determined. However, the simultaneous observation of the two transverse waves excluded at least two possible crystalline directions, the [100] and the [111] directions, because the two transverse waves in each of these directions have the same velocity[12] and would therefore give a single echo. The simplest direction to consider, which has two transverse waves with different velocities, is the [110] direction. This was also taken as the direction of propagation of the longitudinal waves since the growth conditions were identical. There are other crystal orientations in which two transverse waves with different velocities could be generated, but the spacing of the atoms in the planes related to these directions is larger. The question of crystal growth on the substrate is a complicated subject involving surface free energy and nucleation probability. The gold plated substrate has been thought to be amorphous so as not to influence the crystal growth of the argon solid above the transducer.

Meyer, Barrett, and Haasen[13] have reported small amounts of hexagonal-close-packed solid argon from x-ray evidence. However, Peterson, Batchelder, and Simmons[14] measured the x-ray lattice constant of single crystals of argon for temperatures from 60 to 83°K and found no evidence of the hcp phase. In the present work no evidence for the hcp phase was manifest in the ultrasonic signals nor in the vapor pressure of the solid as the temperature was cycled back and forth.

B. Elastic Constants

The following are the relations between the elastic constants and the velocities of elastic waves in the [110] direction for a cubic crystal:

$$\rho v_l^2=\tfrac{1}{2}(c_{11}+c_{12}+2c_{44}), \quad (1)$$

$$\rho v_{t_1}^2=\tfrac{1}{2}(c_{11}-c_{12})$$

for particle motion perpendicular to z axis, (2)

$$\rho v_{t_2}^2=c_{44} \text{ for particle motion parallel to } z \text{ axis.} \quad (3)$$

In the above equations v_l and v_t are, respectively, the longitudinal and the transverse wave velocities while c_{11}, c_{12}, and c_{44} are the three independent elastic constants for a cubic crystal. The intermolecular spacing in the direction of particle motion implies that v_{t_1} in Eq. (2) is the faster velocity.

Figure 2 shows a reasonable attempt at extrapolating the velocity data to 0°K and Fig. 3 shows the elastic constants that result from assuming propagation in the [110] direction. The elastic constants are an order of magnitude smaller for argon than for a salt like NaCl[15]

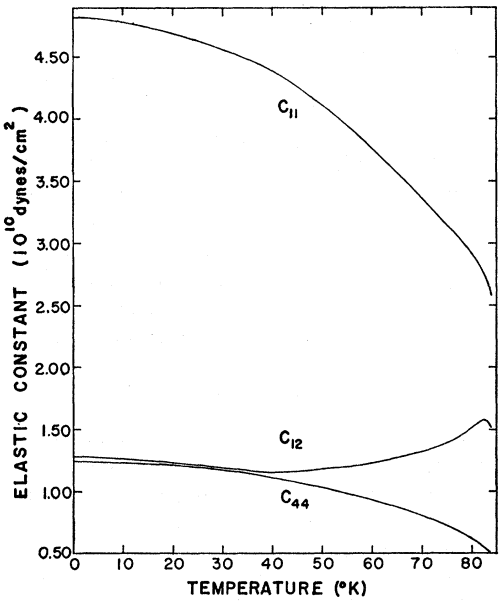

FIG. 3. Elastic constants calculated from the extrapolated values of the ultrasonic velocities. The direction of propagation of the ultrasonic waves was deduced to be the [110] direction.

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TABLE III. Smoothed values of elastic constants and related data for solid argon. Density ρ; longitudinal, v_l, and transverse, v_{t1} and v_{t2}, velocities; elastic constants, c_{11}, c_{12}, and c_{44}.

T(°K)	ρ(g/cc)[a]	v_l(m/sec)	v_{t1}(m/sec)	v_{t2}(m/sec)	$c_{11}(10^{10}$ dyn/cm^2)	$c_{12}(10^{10}$ dyn/cm^2)	$c_{44}(10^{10}$ dyn/cm^2)
0	1.7710	1555	1000	835	4.819	1.277	1.235
10	1.7705	1550	997	834	4.782	1.262	1.231
20	1.7641	1538	991	830	4.690	1.225	1.215
30	1.7518	1519	980	819	4.549	1.185	1.175
40	1.7349	1495	957	800	4.389	1.145	1.110
50	1.7148	1462	919	775	4.034	1.187	1.030
60	1.6919	1422	865	741	3.758	1.226	0.929
70	1.6657	1378	785	697	3.380	1.327	0.809
74	1.6539	1356	743	672.5	3.206	1.380	0.748
75	1.6509	1350	731.5	665.5	3.161	1.394	0.731
76	1.6478	1344	719	658	3.115	1.411	0.713
77	1.6446	1338	704.5	649	3.068	1.435	0.693
78	1.6414	1332	689.5	639	3.022	1.462	0.670
79	1.6382	1326	674	627.5	2.980	1.491	0.645
80	1.6349	1319.5	657	615	2.934	1.522	0.618
81	1.6316	1310.5	638	602	2.875	1.547	0.591
82	1.6282	1301	617.5	588.5	2.813	1.571	0.564
83	1.6247	1287	594	575	2.727	1.581	0.537
83.7	1.6224	1264.5	573	565	2.609	1.544	0.518

[a] The density data for temperatures from 0 to 70°K were those in Ref. 14 and those for temperatures from 74 to 83°K came from Ref. 15.

The temperature dependence of c_{12} that resulted from these calculations is difficult to explain if it is true. However, the maximum could be due to an incorrect fit of the high-temperature velocity data and the minimum could be due to an incorrect estimate of the extrapolated curves for the velocities.

Table III contains the values of the elastic constants obtained for temperatures from 0 to 83.7°K and the data used in calculating these values.

C. Debye Theta at 0°K

Blackman[16,17] proposed a formula to relate $\Theta_D(0)$ to the elastic constants in a cubic crystal.

$$\Theta_D^3=\frac{3}{4\pi}\left(\frac{h}{k}\right)^3\frac{s}{\rho^{3/2}v_a}(c_{11})^{1/2}c_{44}, \quad (4)$$

where s is the number of atoms in a unit cell of volume v_a and ρ is the density. This was derived for the case where the ratios c_{12}/c_{11} and c_{44}/c_{11} are small.

Use of the values of c_{11} and c_{44} that result from the extrapolated velocities (Table III) and the lattice constant (Ref. 14) in Eq. (4) gives a value of 93.6°K. This is slightly larger than the value of 93.3°K obtained from specific-heat data.[18] If a difference is to exist between the value of $\Theta_D(0)$ obtained from specific-heat data and that from elastic data, it may be due to anharmonicity which will make the value from elastic data larger. On the other hand, the experimental specific heat must be measured carefully to about 1°K before the true $\Theta_D(0)$ can be determined from the Debye specific-heat theory.

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D. Anharmonicity

A measure of anharmonicity is given by the deviation from the Cauchy relation ($c_{12}=c_{44}$) at 0°K. The quantity $(c_{12}-c_{44})/c_{12}$ expressed in percentage is about 3.3% for the present data. If the temperature dependence of c_{12} is correct relative to that of c_{44}, then the above quantity is even smaller (about 0.8%) between 20 and 30°K.

V. CONCLUSIONS

In summary, the experimental results indicated that the center portion of the cylinders of solid argon, grown directly on the transducer, behaved as a single crystal. Although the direction of propagation was not known, the ultrasonic evidence indicated that the waves were propagated in the [110] direction. With this assumption, elastic constants were calculated. The present work has demonstrated that a pulse technique of measuring ultrasonic velocities of solid argon is feasible and that measurements on single crystals of other rare-gas solids may be possible. An improvement of the technical skills involved will be required before scientists can make a very good determination of the elastic properties. That task will be difficult, and meanwhile the experimental results reported here may prove stimulating to solid-state theorists interested in solid argon.

ACKNOWLEDGMENTS

We wish to thank Dr. G. L. Pollack of Michigan State University and Dr. R. O. Simmons of the University of Illinois for their cooperation in supplying us with unpublished reports and reprints of their work and for their stimulating suggestions and criticisms.