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THE VELOCITY OF SOUND IN SOLID KRYPTON

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October 1970

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Ultrasonic pulse-echo measurements have been carried out on specimens of solid krypton prepared in a rigid-tail helium cryostat. Values were obtained from polycrystalline specimens for longitudinal sound waves from 52 to 115 K and transverse sound waves from 95 to 115 K, and from a single crystal for longitudinal sound waves travelling in a nearly $\langle 110 \rangle$ direction from 94-114 K. Extrapolations to 0 K of polycrystalline velocities are consistent with previous deductions made from measurements of bulk modulus and heat capacity. The present velocity results are compared with model calculations based on m-6 Mie-Lennard-Jones pair potentials but there is only fair agreement. The adiabatic bulk modulus was obtained from the longitudinal and transverse polycrystalline velocities. The agreement between the model calculations and experimental values of the bulk modulus is again only fair.

From the present bulk modulus values, the Grüneisen parameter of solid krypton was evaluated. From the longitudinal velocity in the nearly $\langle 110 \rangle$ direction and the polycrystalline velocities the second-order elastic constants were determined at 114 K. The difference $c_{12} - c_{44}$ was also estimated at temperatures 0 K and near the triple point.

From the difference between the present "lattice" compressibility results and other measurements of the "bulk" isothermal compressibility, the thermal vacancy concentration in solid krypton has been determined. The agreement with previous measurements of vacancies by direct means is good.

An examination of all the data now available for solid krypton indicates that no single existing model describes successfully both the high and low temperature thermoelastic properties of this substance.

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I. INTRODUCTION

Noble gas crystals have long held the interest of experimenters and theoreticians alike. The short-range, weak interatomic forces which characterize the atoms of the noble gases and the simple fcc structure of the solids lend themselves to theoretical models, from which properties of these solids might be calculated from the first principles and compared directly to experimental results. Many reviews have been written on the subject of the noble gas crystals.¹⁻⁶

The experimental difficulties involved in working with these crystals are formidable, however. The solids have low melting points, high vapor pressure and very large coefficients of thermal expansion. Many experiments have been performed on the noble gas crystals and many thermodynamic properties have been measured, particularly on solid argon, yet there is still a lack of sufficient data on the velocity of sound and elastic constants of these crystals. The necessity for having large single crystals, the inability to grow crystals oriented along major axes, large attenuation of excited waves in these crystals, and the very difficult problem of maintaining transducer bonding have severely hampered experimenters.

Almost all of the elastic constant data that are available on noble gas crystals is on solid argon. Recently, Keeler and Batchelder⁷ measured the velocity of sound for transverse and longitudinal waves in single crystals of solid argon from 77 to 3 K and by extrapolation of these data, the elastic constants at 0 K were estimated. Their results indicate that models using only central two-body forces are not sufficiently accurate for describing the elastic properties of solid argon.

On the other hand, Born-von Kármán fitting of phonon dispersion data on argon at 4 K by Batchelder et al.⁸ was found to be less satisfactory when these elastic constants were used as constraints than when constants from two-body model calculations were used.

Earlier, elastic constant measurements were made on solid argon from 74 to 84 K by Moeller and Squire⁹ and velocity of sound measurements along $\langle 100 \rangle$ and $\langle 110 \rangle$ directions, from 4 to 77 K were made by Gsanger et al.¹⁰ Temperature-dependent measurements of the longitudinal velocity in polycrystalline argon have been made by Barker and Dobbs,¹¹ and by Lawrence and Neale.¹² Jones and Sparkes¹³ made transverse wave velocity measurements on polycrystalline argon. Only two results have been reported on solid krypton. Measurements of the velocity of sound of longitudinal waves traveling along the $\langle 110 \rangle$ direction were taken at 4, 77, and 90 K by Peter et al.,¹⁴ and the longitudinal wave velocity in the $\langle 110 \rangle$ direction at 79 K and about 300 bar can be inferred from the phonon dispersion curves of Daniels et al.¹⁵ Recently Gornall and Stoicheff¹⁶ report elastic constant measurements of solid xenon at 156 K by the method of Brillouin spectroscopy.

The most difficult problem to overcome in measuring the velocity of ultra-sound in noble gas crystals is the preparation of high quality specimens bonded to a transducer. Of the two basic methods tried by other investigators, that of growing the crystal on the transducer and imbedding the transducer in the crystal after it has been grown, the latter has been the most successful.

Barker and Dobbs¹¹ grew fine-grained polycrystalline argon specimens from the vapor, on top of a transducer. Using an ultrasonic interferometer they were able to measure velocities for temperatures from 65 to 80 K. The bonding problem was partially solved by a mechanism which mechanically pressed

the solid against the transducer. A plane surface opposite the transducer was prepared by a rotating cutting tool.

Lawrence and Neale¹² deposited the solid on the transducer at the temperature that the velocity was measured. They measured sound velocities in polycrystalline argon from 54 to 83 K by an optical diffraction method.

Gsanger et al.¹⁰ measured the velocity of sound in single grains of argon from 4 to 77 K using pulse-echo techniques by melting a warm yoke containing parallel transmitting and receiving transducers into the solid after the specimen had been grown. Their results show considerable scatter and are uncertain, however.

Moeller and Squire,⁹ after unsuccessful attempts to bond a transducer to the top of their argon specimens were able to measure sound velocities by the pulse-echo technique, between 74 K and the triple point of argon, by growing the specimens on top of their transducers. Separate specimens had to be prepared for work above and below 78 K, respectively, so the measurements show some discontinuity in the middle of their temperature range.

The most successful attempt, however, has been by Keeler and Batchelder⁷ on argon single crystals using the pulse-echo technique. After their specimens had grown to a height of 5 to 8 mm the 10 Mhz quartz transducer was imbedded into the solid, parallel to the lower substrate forming the bottom of the specimen tube. Good bonding occurred only if the transducer was warm enough to slightly melt the argon specimen. The melt was then further solidified until more solid was on top of the transducer than below it. This method allowed the echo from the crystal-substrate interface to be observed without interference from the echo off the top surface of the specimen. Velocity measurements were made from 3 to 77 K, although the temperature dependence

of the velocity is uncertain below 15 K. Possibly, strains appeared in the crystal caused by differential thermal contraction at the transducer-solid interface and substrate-solid interface.

The purpose of the present work was to investigate the various techniques for measuring the velocity of sound and elastic constants of solids¹⁷⁻¹⁸ and to apply these techniques toward acquiring new data on solid krypton.

II. EXPERIMENTAL METHOD

Because of the known difficulty of any measurements which require bonding of an ultrasonic transducer to a noble gas solid, a variety of experimental techniques were examined and developed. First, the cryostat suitable for specimen preparation, x-ray orientation, and temperature control of large specimens was constructed. The cryostat and methods of preparing specimens are described here. Second, both optical diffraction and ultrasonic pulse-echo methods for determining elastic wave properties were adapted to cryogenic conditions. The optical method was refined to a point of permitting measurements at very low power input to the specimen. Its accuracy was proven on a calcium fluoride crystal (Appendix I). Some difficulties appeared in applying the method to solid krypton, however (Appendix II). Therefore, the pulse-echo method was used to obtain data on the noble gas solids reported in the present work.

A. Cryostat

Fig. (1) shows the general configuration of the cryostat constructed and assembled for the present work. It is similar to the type described by Windecker.¹⁹ It provides for crystal preparation, visual observation, x-ray orientation, temperature control, and measurement of ultrasonic wave velocities.

A 5.0 liter liquid helium dewar, purchased from the Supairco Company, was modified by the addition of a rigid tail assembly. An additional liquid nitrogen jacket surrounds the liquid helium tail section and supports a liquid nitrogen temperature radiation shield. Another shield, inside the liquid nitrogen temperature shield and surrounding the sample chamber, is in thermal

contact with the liquid helium reservoir. The innermost (liquid helium) reservoir was filled with liquid nitrogen for temperature control above 77 K.

The vacuum jacket was fitted with a 5 cm diameter, 0.12 mm thick Mylar window for taking Laue photographs, and two 12.5 mm diam. optical windows and a 1 mm thick, 5 cm x 1 cm window for full viewing of the transparent specimen. Other small windows were used for additional illumination and more flexibility in viewing the upper and lower portions of the specimen tube. The liquid nitrogen temperature shield was similar except that heat-absorbing glass (Corning Type I-69) was used for minimizing radiant heat transfer to the specimen chamber. A beryllium x-ray window was placed on the liquid nitrogen temperature shield to provide heat shielding at the x-ray port.

The liquid helium shield had cut-out optical ports instead of glass windows and its x-ray port was covered with 0.012 mm aluminized Mylar.

The radiation shields were gold plated to decrease cryostat pump-out time and minimize coolant loss rates. The vacuum jacket was nickel plated as was the sample chamber.

A stainless steel, spiral tube, 3.2 mm diam. with 0.1 mm wall thickness, permitted fluid helium (or nitrogen) to be drawn from the helium reservoir and circulated around the sample chamber for cooling purposes.

Heating wires, thermometer wires, and one rf lead from the transducer (the other lead was grounded by direct contact with the transducer mount) were brought to the sample chamber through ports in the manifold of the vacuum jacket through 3.2 mm diam., 0.1 mm wall thickness stainless steel tubing. The sample chamber and tubes which enter the sample chamber can be isolated from the main vacuum and filled with helium exchange gas via a system of valves and a manostat.

Figure 1. Cross-section of cryostat assembly. a: Five liter liquid helium reservoir. b: Twelve liter liquid nitrogen reservoir. c: Support plate, 2.5 cm. thick. d: Perforated stainless steel cylinder supporting the lower nitrogen reservoir. e: Eight liter liquid nitrogen reservoir. f: Epoxy fiberglass double cylinder connected to the lower nitrogen reservoir and to the liquid helium tail. g: Stainless steel bellows. h: Stainless steel tube supporting the liquid helium shield and sample chamber. i: Inconel support posts. j: Heat exchange coil. k: Glass window for viewing upper portion of the specimen tube. l: Optical window. m: Liquid helium radiation shield. n: Liquid nitrogen radiation shield. o: Glass window for full viewing of specimen tube. p: Heat-absorbing glass window. r: Room temperature glass window. s: Beryllium x-ray window. t: Mylar x-ray and vacuum window.

1. Specimen Chamber

Fig. (2) shows a cut-away view of the thick-walled copper sample chamber. An indium gasket seals the upper and lower sections. Three Inconel posts, 4.5 cm long, 0.48 cm diam and 0.07 mm wall thickness, support the sample chamber and provide insulation from the helium reservoir tail.

There are seven glass windows cemented to the sample chamber. One 5 x 1 x 0.1 cm window is epoxied directly to the copper wall at the rear of the sample chamber. A small frame of 0.05 mm thick "Kapton" (polypyromelitimide film) is epoxied around the glass to insure a good vacuum seal.²⁰ This window is used for the length measurements and observations of the specimen. Six other glass windows were epoxied²¹ to two molybdenum frames which were then epoxied²¹ directly to the copper wall of the sample chamber. The two 14.5 mm diam by 3.2 mm thick circular glass windows were of high quality glass, with surfaces flat to 1/4 wavelength, which could be used for optical experiments. These windows also allowed specimen-to-film distance of the Laue x-ray camera to be precisely set by observations through a microscope of the front surface of the specimen. The remaining four windows were used for illumination and observations of the specimen.

After many cooling cycles the epoxy sealing the glass windows tended to leak. A mixture of 300 to 400 mesh aluminum powder and silicone vacuum grease was used for sealing the small leaks.

A 90 ohm heater ("gradient heater") is wrapped around the copper block at the top of the specimen tube allowing precise control over the crystal growth rate.

Figure 2. Cutaway view of the specimen chamber. a: Capillary tube for specimen gas. b: Standoff for capillary tube. c: Support rod for idle gear. d: Indium "O"-ring. e: Position of primary platinum resistance thermometer. f: Molybdenum frame for glass windows. g: Idle gear. h: Conduit for bead chain. i: Conduit for heating and thermometer wires. j: Heat exchange coil. k: Thermometer well. l: Kapton specimen tube. m: Beryllium x-ray window. n: 10 Mhz. quartz transducer.

Gold plated 10 Mhz quartz transducers, 0.6 cm on each side, used for exciting longitudinal and transverse waves were fixed to copper mounts shown in Fig. (2). The transducers were soldered in place with Woods metal and the edges were covered with a thin coat of epoxy²¹ to insure a tight vacuum seal. The transducers sit on a ledge 0.25 mm deep and 0.25 mm wide, cut out from the center of the mounts. Good thermal contact between transducer mount and sample chamber is insured by a copper braid between the transducer mount and bottom of the sample chamber. Without the braid, the bearings of the specimen rotation mount tend to isolate the specimen.

A stainless steel capillary tube 0.8 mm outside diam. carries the specimen gas to the sample tube.

A mechanism devised by Windecker,¹⁹ included in the design of the sample chamber, allows rotation of the specimen about a vertical axis. A bead chain fed into the sample chamber through 3.2 mm outside diam stainless steel tubes turns the worm gear. The flexible capillary tube is spiraled around the upper portion of the sample chamber to allow rotation of the specimen tube. An idle-gear system placed next to the specimen tube insures that the bottom and top of the specimen tube rotate together, since the Kapton specimen tube itself is not rigid enough to insure this.

2. Specimen Tube

Specimen tubes were constructed with DuPont's Kapton polyimide film, 0.05 mm thickness. A square cross-section tube 1 cm on a side and 4.9 cm long was formed by overlapping the Kapton on one side of the tube and sealing it with epoxy.²⁰ Epoxy was also used to seal the tube to the copper transducer base and gas inlet block.

For optical experiments, rectangular holes 6 mm high and 4 mm wide were cut in the Kapton and square glass windows 12.5 mm on a side, 0.75 mm thick, were epoxied²⁰ to the specimen tube. Unfortunately, however, when the tube was filled with liquid or when the solid was near the triple point, the vapor pressure caused the window to bulge, resulting in rather uncontrolled distortion of the optics of the diffraction system, described in Appendix II. Although thicker windows would minimize the problem of bulging windows, the larger heat conduction of the glass would compound the problem of trying to grow large single crystals.

3. Temperature Control

Initial cooling of the sample chamber was accomplished by pumping cool gas through the heat exchange tube which was wrapped around the top of the sample chamber. The flow was regulated by the manostat and needle valve arrangement of Peterson.²² The sample chamber could be warmed by passing current through two 165 ohm heater wires epoxied²⁰ uniformly around the lower section of the sample chamber.

During crystal growth and at temperatures about 110 K, temperature control was accomplished by using heaters only. Below 110 K a balance of cool gas flow and heater current was needed for temperature stability. Temperatures between 77 K and 65 K were reached by pumping on liquid nitrogen. Temperatures below 65 K were obtained by using liquid helium. Temperatures were measured by germanium and platinum resistance thermometers. A Minneapolis-Honeywell germanium resistance thermometer was included for measurements below 20 K. Above 20 K a Leeds and Northrup type 8165 platinum resistance thermometer, calibrated

with a similar NBS calibrated thermometer was used for temperature measurements. This thermometer was placed near the specimen tube and is in thermal contact with the sample chamber via a bakelite mount and exchange gas. Another thermometer, a glass-encased two-terminal platinum resistor by Engelhard Industries, was imbedded in the upper portion of the sample chamber and in thermal contact via Apiezon N-grease and exchange gas (as was the germanium thermometer). The Engelhard thermometer was used primarily for temperature control sensing. The thermometers were provided with constant current supplies.

Thermometer emf's were balanced against the emf from a Leeds and Northrup Type K3 potentiometer having a constant current supply. Changes in thermometer emf's were detected by a Leeds and Northrup Model 9834 null detector. Changes in temperature were then detected, as emf shifts, by the null detector. The null detector output fed to the temperature controller (see Fig. (3)) varied the grid voltage of the vacuum tube and thereby adjusted the plate current. The variations in the plate current adjusted the heater output to maintain temperature stability to about ± 0.03 K. The use of a variable bias voltage permitted the equilibrium heater current to be set anywhere from 0 to 40 ma.

4. X-ray Apparatus

Crystal quality and orientation of single crystals was determined from back-reflection Laue photographs. A camera similar to that of Peterson, Batchelder and Simmons²³ was used. Before x-ray photographs were made, specimens were separated from the specimen tube wall by pumping and then cooled

Figure 3. Schematic diagram of the heating control system. The input signal is the output of the null detector. Heating current can be varied from 0 to 40 ma by varying the bias voltage.

to 4 K. Usable pictures from krypton specimens could be taken, however, for temperatures up to 45 K.

A telescope and x-ray flat-plate camera were aligned perpendicular to each other on the optical table used for diffraction of light experiments (see Appendix I). The crosshair of the telescope was positioned to be 5 cm from the plane of the x-ray film. The table, placed under the cryostat and adjusted with the front surface of the specimen allowed the specimen orientation to be determined with an uncertainty less than two degrees.

5. Length Measurements

The vertical length of specimens grown was determined from observations of the specimen through a Gaertner Scientific Corp. cathetometer. Observations were made through the glass windows at the rear of the cryostat. The top surfaces of the specimen were generally smooth and well defined, except for the extreme edges of the specimens which were always slightly higher than the center of the crystal. The edges were approximately 0.5 mm higher than the rest of the crystal surface and extended less than 0.5 mm in from the edges of the crystal. This end effect was the same for all polycrystalline specimens regardless of length and had no measurable effect on the velocity of sound measurements.

The length measurements made from the transducer to the top surface of the specimens are estimated to be accurate to ± 0.004 cm for polycrystalline specimens used for longitudinal velocity measurements, to ± 0.003 cm for specimen 5 (single crystal with vertical direction near $\langle 110 \rangle$), and to ± 0.003 cm for specimens used for transverse velocity measurements in polycrystals. The larger uncertainty in the length measurements of polycrystalline specimens

grown on the longitudinal mode transducer was due to some difficulty in accurately locating the top surface of that transducer.

Longitudinal velocity measurements were made on crystals approximately 1.5 cm in height whereas transverse wave measurements were generally made on specimens only 0.5 to 1.3 cm long. The estimated uncertainty in velocity measurements due to uncertainties in length measurements is approximately 0.3% for polycrystals used in measuring longitudinal waves, 0.4% in polycrystals used in measuring transverse waves and 0.2% in specimen 5.

B. Specimen Preparation and Macrostructure

"Research grade" krypton and argon gases were used for growing all specimens. The argon gas was supplied by Matheson Co. Krypton gas for specimen 5 was supplied by Linde Co. Krypton gas for other specimens was supplied by Matheson Co. Lot analysis of the krypton gases used states the following impurity content (in ppm by volume)

Specimen 5: $\text{Ar} < 10$, $\text{Xe} < 10$, $\text{O}_2 < 5$, $\text{N}_2 < 50$, $\text{H}_2 < 3$, NO and $\text{CO}_2 < 25$, $\text{CH}_4 < 25$.

Specimens 9-16: $\text{Xe} < 24$, $\text{N}_2 < 10$, $\text{O}_2 < 1$.

Specimens 17-27: $\text{CO}_2 < 4$, $\text{O}_2 < 4$, $\text{H}_2 < 4$, $\text{Ar} < 4$, $\text{He} < 4$.

The gases were handled by a portion of the system of Windecker¹⁹ (see Fig. (4)). Contamination of the gases was minimized by helium leak testing the stainless steel tubes, valves, and storage vessels, by long evacuation times and by purging of the system.

1. Polycrystals

Polycrystalline krypton specimens, grown on longitudinal mode quartz transducers were prepared as described below.

Figure 4. Schematic diagram of gas handling system. The volume of the large storage vessel is 15 liters, the small storage vessel approximately 2 liters.

The sample chamber was evacuated and cooled to approximately 116 K. Krypton gas was then admitted to the specimen tube at a pressure between 650 torr and 750 torr and liquid would soon start collecting. When sufficient liquid had collected the temperature of the sample chamber was lowered rapidly to between 100 K and 110 K. The lower temperatures resulted in slightly smaller grain sizes. Growth rates varied from 6 mm/hr. to 12 mm/hr depending on the temperature of the sample chamber. The result of this cooling was unidirectional solidification of solid krypton. The solid-liquid interface, although flat near the center of the crystal, had edges which grew ahead of the center portion. If the completed solid did not have a top surface smooth enough for accurate pulse-echo measurements the solid was warmed to near the triple point and either a small amount of warm krypton gas was introduced to the specimen tube or the gradient heater above the specimen tube was turned on, causing a slight amount of melting at the top. The top was then quickly solidified.

Warming the crystal to within a degree or two of the triple point often resulted in a better transducer bond if the crystal was allowed to sit at that high temperature for about twenty-four hours.

A few tenths of a torr of helium exchange gas was admitted to the sample chamber before cooling the crystal to minimize any thermal inhomogeneities and increase the speed at which the specimen came to its equilibrium temperature. The sample chamber was then cooled in approximately 5 K intervals and the velocity measurements made. The transducer bond was usually broken near 95 K because of differential thermal contraction, except for one polycrystal for which velocity measurements were taken down to 51.5 K.

After the velocity measurements were made the crystal was warmed up and pumped on to separate the crystal from the Kapton tube. This "thermal etching" revealed clearly the intersections of grain boundaries with the specimen surface and allowed determination of grain sizes in the polycrystalline specimens. Photographs of most specimens were taken through a cathetometer telescope with a Polaroid camera. These photographs, which showed the grain structure fairly well, allowed accurate determinations of the grain size in many specimens and permitted comparisons of the quality and grain structure to be made between many of these crystals.

Two specimens of polycrystalline argon were grown on the same X-cut transducer and in the manner described above. Growth rates were about 1 cm/hr and grain sizes somewhat larger than in the krypton crystals.

Polycrystalline krypton samples were about 1.5 cubic centimeters in volume and approximately 12 mm in length. Argon samples were 0.7 cc and 1.0 cc with 6 mm and 8 mm lengths. The average grain size observed in krypton polycrystals was approximately 0.1 mm^2 for crystals grown over X-cut transducers and up to 1.0 mm^2 for crystals grown over AC-cut transducers. Argon polycrystals had grain sizes approximately 0.10 cm^2 .

Polycrystalline krypton specimens were grown on 10 Mhz transverse wave quartz transducers in a way similar to the procedure used for growing polycrystals on longitudinal mode transducers. The specimens used for measuring transverse wave velocities were between 5 mm and 13 mm long and generally had larger grain sizes than the specimens used for measuring longitudinal velocities. The transducer base was cooled to about 110 K. At this temperature there was usually only one echo available for transit time measurements.

The oscilloscope, however, was calibrated when two echoes were present and rechecked during the time the transverse velocity measurements were made on specimens 16 through 27. Measurements near the triple point were made by melting a small amount of the crystal near the base and solidifying the liquid slowly. This would generally result in a good transducer bond, and two or three echoes would be visible. Approximately 1 mm of solid was melted in this process of rebonding the crystal.

Polycrystalline argon crystals were grown on the 10 Mhz AC-cut transducer as were the krypton polycrystals. The argon specimens were approximately 5 mm in length with grain sizes from less than 0.1 cm^2 to almost 0.2 cm^2 . Transverse velocity measurements were made on specimen Ar-6 by warming the crystal to near the triple point (where two echoes then became visible) and then cooling to 77.5 K.

2. Single Crystal

Attempts to grow one large single crystal of solid krypton were not entirely successful. In several cases only two or three large vertical grains were present but quantitative measurements of the transit time could not be made. The grain boundaries lay across the transducer, which resulted in very irregular echo patterns. Specimen Kr-5, however, did have a large single crystal core with the $\langle 110 \rangle$ direction nearly vertical, and velocity measurements were taken for that specimen.

All specimens grown were examined by a 4X telescope. There were no indications of any microscopic holes, vapor tubes, cracks or other inhomogeneities which would indicate that the specimens were not clear and dense. An

examination on one typical specimen under a higher power (about 20X) telescope again showed no internal inhomogeneities.

3. Some Details

Some specimens of particular interest are now described more fully.

Specimen Kr-5, 1.6 cm in length, was grown over a longitudinal mode, 10 Mhz transducer which had a 0.5 mm thick frame of germanium surrounding the transducer. The germanium frame (used in an attempt to encourage epitaxy) was a single crystal with the $\langle 110 \rangle$ direction perpendicular to the top surface of the specimen base. The crystal was grown at a rate never exceeding 0.75 mm/hr and averaging 0.5 mm/hr. When the crystal was completed the top was very smooth and five very well-defined echoes were visible. Velocity measurements could be made at temperatures down to 94.5 K. Thermal etching of the crystal indicated that there was a single crystal core, about 7 mm in diameter, surrounded by a fine-grained polycrystalline crust approximately 1.5 mm thick. The absence of grain boundaries in the core after evaporation of the crust, combined with x-ray Laue photographs of the core, showed that velocity measurements had been made on a single crystal of krypton. The direction of the vertical was determined from the Laue photographs and found to be nearly $\langle 110 \rangle$. Precisely, the orientation was $\theta = 86^\circ$, $\phi = 47^\circ$, where θ is the polar angle and ϕ is the azimuthal angle.

Specimen Kr-9 was grown over a 10 Mhz longitudinal mode transducer by cooling the base of the liquid column rapidly to 107 K. The growth rate varied from 6.6 mm/hr to 9.6 mm/hr. The length of the crystal was 13.4 mm.

Only one echo was present after the crystal was completed, but by warming the specimen to approximately 111 K and waiting about 16 hours the top of the crystal became smoother and two echoes could be clearly seen. Measurements of velocity were made to 96 K. Velocity measurements were made between 78.7 and 83 K by rebonding the transducer to the krypton specimen with solid argon.

Attempts to rebond the solid krypton to the transducer with solid argon were made at temperatures near 78 K by evaporating some solid krypton away from the Kapton wall and base and filling the space near the bottom of the crystal with liquid argon. The liquid was cooled until it solidified. In one case one echo was visible and velocity measurements were made between 79 K and 83 K. The uncertainty in these measurements is relatively large, however (see Fig. 6).

It is interesting to note that when the argon was pumped away the krypton had a frosty appearance where it was in contact with the solid or liquid argon. The vapor pressure of solid krypton at temperatures near the triple point of solid argon is approximately 10 torr. Therefore a negligible amount of krypton was removed during the time the argon was removed from the specimen tube.

Specimen Kr-15 was grown to a length of 11.4 mm by cooling the specimen tube base to 100 K. The top was not smooth and the specimen was warmed to approximately 115 K where warm krypton gas was admitted to the specimen tube. The top melted slightly and after resolidification four echoes were visible. Velocity measurements were made to 51.5 K. The average grain size of Kr-15 was less than 0.10 mm^2 , the lowest of all specimens.

Specimen Kr-21 was grown over a 10 Mhz transverse mode transducer. The base was cooled to about 108 K but the top was not smooth and only one echo was

visible. Nevertheless one measurement at 110 K was made after the crystal had stopped growing and had warmed up slightly. The specimen was then warmed to 115.5 K and remained at that temperature for almost 20 hours. When no echo appeared, the base of the specimen was then melted (approximately 1 mm of solid was melted). After solidifying, two very clear echoes were visible. Velocity measurements were made from 115.7 to 107.5 K. Average grain size of this specimen was 0.2 mm^2 . The length of this crystal was 0.87 cm.

Specimen Kr-24 was grown to a length of 0.7 cm by cooling the base to 110.5 K. After the crystal stopped growing a good echo pattern was visible and velocity measurements were made to 90 K. The average grain size of this specimen was about 1 mm^2 .

Specimen Ar-6 was grown over the transverse mode transducer to a length of 0.5 cm by cooling the base of the column of liquid argon to 78 K. The top of the crystal was not smooth enough to measure the velocity of sound. The crystal was then warmed to 83.8 K with the gradient heater on to smooth the top; two echoes then became visible without melting any of the solid. Velocity measurements were made from 83.5 to 77.5 K. The average grain size of this specimen was less than 0.1 cm^2 . Table I summarizes the measured characteristics all usable crystals.

Table I.

Krypton Specimen	Temperature of base during growth	Initial specimen length in mm	Average grain size in cm ²	Bonding method	Acoustic mode	Temperature range of velocity measurements	Remarks
5	115	16.40	single grain	a	L	94-114	5 echoes visible
9	107	13.35	<.005	b	L	96-111 79-83	Rebonded at 79 K with solid argon
10	107	13.10	<.005	a	L	109	weak echo pattern
11	107	11.20	<.005	a	L	98-109	4 echoes visible
12	107	11.40	<.005	b	L	114	echo pattern weak
15	100	12.58	<.001	c	L	52-115	4 strong echoes
16	107	10.90	<.005	a	T	107	• • •
17	110	9.75	<.01	c	T	115	• • •
18	103	13.10	<.005	c	T	112-115	top surface very smooth
19	102	8.65	<.005	c	T	108-115	• • •
20	107	7.95	<.01	a	T	110	4 echoes visible
21	108	8.67	~.002	c	T	108-115	• • •
22	114	6.35	~.01	a	T	98-115	• • •
24	111	6.95	~.01	a	T	98-111	good echo pattern with 2 echoes
25	110	6.20	~.01	a	T	110	• • •
26	111	7.55	<.01	a	T	111	• • •
27	110	6.70	<.01	b	T	104-110	top surface very smooth
Argon specimen							
1	78	7.60	~0.1	a	L	78	top smoothed by melting slightly
2	78	5.50	~0.1	a	L	78	• • •
3	78	5.30	~0.1	a	T	77	• • •
4	78	5.45	~0.1	a	T	78	• • •
6	78	5.50	~0.1	b	T	78-84	top smoothed by melting slightly

- a. Transducer bonding maintained after crystal had been grown.
- b. Transducer bonded to the crystal by raising the temperature of the specimen, after growing, and waiting 10-20 hours for the echo pattern to appear.
- c. Transducer bonded to the crystal by slightly melting the base of the specimen and then resolidifying the liquid.
- L. 10 Mhz longitudinal acoustic waves.
- T. 10 Mhz transverse acoustic waves.

III. RESULTS

As a check on the accuracy of the present apparatus for measuring sound velocities by the pulse-echo method, measurements were made on a single crystal of calcium fluoride by the pulse-echo technique and by the diffraction of light from acoustic waves. Appendix (I) describes the pulse-echo technique in more detail and compares the present results for calcium fluoride with the results of other investigators.

As a check for possible systematic errors at cryogenic temperatures, velocity measurements were made on several argon polycrystals grown in the same two specimen tubes that were used for the krypton measurements. The results of the sound velocities measured on five specimens are shown in Fig. (5) and may be compared there to the results of Keeler and Batchelder,⁷ Barker and Dobbs,¹¹ Jones and Sparkes¹³ and Lawrence and Neale.¹²

The results of longitudinal velocities measured in five specimens of polycrystalline krypton all grown in the same specimen tube are shown in Fig. (6). The transducer bond was maintained in specimen 15 down to 51.5 K. Specimen 15 also had the smallest average grain size of all specimens grown. These measurements extrapolated to 0 K are consistent with the value stated by Urvas, Losee and Simmons.²⁴ The estimated error in the smoothed value of the longitudinal velocities, from 52 to 115 K, is 0.8%.

Fig. (7) shows the results of transverse velocity measurements made on 11 specimens of polycrystalline krypton, all grown in the same specimen tube. These results are extrapolated to the 0 K value of Urvas et al.²⁴ The estimated error in the transverse velocities from 95 to 115 K is 2%.

Figure 5. Present results for the longitudinal and transverse sound velocities in polycrystalline argon with comparisons to the results of previous investigators. Longitudinal velocities were measured on two specimens, and confirm a value derived from work by Keeler and Batchelder.⁷ Transverse velocities were measured on three specimens, and confirm both the value and temperature coefficient of the same workers.

Figure 6. Velocity of longitudinal sound measured for five polycrystalline krypton specimens. The extrapolation is made to the 0 K value reported by Urvas, Losee and Simmons.²⁴ Specimen 9 was rebonded near 80 K with solid argon and these measurements are relatively uncertain.

Figure 7. Velocity of transverse sound measured in eleven polycrystalline krypton specimens. Use of many specimens should yield an appropriate polycrystalline average. The measurements are extrapolated to the 0 K value of Urvas, Losee and Simmons.²⁴

The velocity of longitudinal sound was measured in a single crystal of krypton. The direction of propagation was determined by Laue photographs of the crystal and found to be nearly $\langle 110 \rangle$. Velocity measurements were made over the temperature range 94.5 to 114 K and are shown in Fig. (8) adjusted to the $\langle 110 \rangle$ direction, as described in Section IV below.

Table II gives smoothed values of the velocity of sound and adiabatic bulk modulus of solid krypton from the present work.

Figure 8. Longitudinal sound velocity in solid krypton, corrected to the $\langle 110 \rangle$ direction. Comparisons are made with the pulse-echo measurements of Peter, Korpiun, and Lüscher¹⁴ and the phonon dispersion results of Daniels et al.¹⁵ The methods of these workers are described in the text Section IV F. Also shown are the theoretical calculations of C. Feldman and M. L. Klein²⁵ based on a quasi-harmonic model using 6-12 and 6-13 Mie-Lennard-Jones potentials and nearest neighbors only.

Table II

Table of Smoothed Values for Solid Krypton. Velocities in units of m/sec,
 B_S in units of 10^9 N m^{-2}

T	$\bar{v}_\ell$	$\bar{v}_t$	$\bar{v}_\ell \langle 110 \rangle$	B_S
0	1382	770	...	3.46
10	1381	770	...	3.45
20	1378	770	...	3.42
30	1371	769	...	3.34
40	1360	768	...	3.23
50	1344	766	...	3.09
60	1323	761	...	2.94
70	1296	749	...	2.77
80	1263	728	...	2.60
90	1223	699	1138	2.43
100	1178	667	1199	2.26
110	1129	634	1159	2.09
114	1108 ± 10	621 ± 12	1144 ± 11	2.01 ± 0.11

IV. DISCUSSION AND COMPARISONS

A. Polycrystalline Properties at 0 K.

The 0 K longitudinal and transverse polycrystalline velocities of Urvas et al. to which the present velocity measurements are extrapolated are determined from calorimetric and static elastic measurements.²⁴ At 0 K the caloric characteristic temperature is given by

$$\theta^c(0) = \frac{h}{k} \left[\frac{4\pi V}{9N} \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \right]^{-1/3} \quad (1)$$

and the adiabatic bulk modulus by

$$B_s(0) = \rho \left(v_l^2 - \frac{4}{3} v_t^2 \right), \quad (2)$$

where h is the Planck constant, k the Boltzmann constant, V the bulk molar volume, ρ the bulk density and v_l and v_t the longitudinal and transverse wave velocities, respectively. Both v_l and v_t at 0 K can be determined from the two expressions given above. Table (III) summarizes experimental information on the polycrystalline elastic properties of krypton at 0 K.

Initially it might seem that comparison of experimental values at 0 K with theory would be the most straightforward test of both. At present this is not the case. Experiments of high accuracy have been shown to be especially difficult at the lowest temperatures. There, transducer bonding is the worst problem and direct x-ray experiments have some uncertainty due to possible interaction of the noble gas solid specimens with the necessary helium pressure fluid. On the other hand, the theoretical models have often had enough free

parameters available to produce a fit to a given experimental property. And the fit, or lack of it, to other relevant experimental properties may not have been written out for explicit display, even though the theories are simplest at $T = 0$.

That the first expectations need to be refined can be illustrated by considering the Cauchy relation $c_{12} = c_{44}$, well-known to be the criterion for central interatomic forces in static cubic crystals. Salter showed explicitly, in a central force model, that zero-point effects in noble gas crystals were already sufficiently large to produce, in a central force model for krypton, a value $\delta = (c_{44} - c_{12})/c_{12}$ of 7%. Subsequently, Hüller, Götze and Schmidt²⁸ showed that inclusion of three-body forces of the Axilrod-Teller type had the opposite tendency, that is, to make δ negative. Questions of the appropriate interatomic potential and of the appropriate dynamical model thus become entangled.

Many theoretical predictions have been made which yield $B(0)$, $v_l(0)$ and $v_t(0)$. Representative values from these are shown in Table IV. Unfortunately it will be apparent in later sections that a good fit near $T = 0$ does not insure a satisfactory fit with experiment at finite temperatures. The most recent and elaborate calculation at low temperatures, by Barker and coworkers²⁹ for argon, in fact specifically disagrees with current experimental results of elastic properties of that substance.

TABLE IV. Calculated and experimental values of the static bulk modulus $B(0)$, the longitudinal sound velocity $v_l(0)$, and the transverse sound velocity $v_t(0)$ for noble gas crystals at $T = 0$.

Table III. Polycrystalline elastic properties of Krypton at $T = 0$ K.

θ^c , caloric characteristic temperature (K); B, bulk modulus (kbar); v_ℓ and v_t (m/sec).

θ^c	B	v_ℓ	v_t
$71.8 \pm .7$	34.6 ± 0.4	1382 ± 10^a	770 ± 8^a
$71.7 \pm .7^b$	34.4 ± 0.4^c	1379 ± 10	769 ± 8
$71.9 \pm .3^d$	34.4 ± 0.4^c	1380 ± 8	772 ± 4

a) Present velocity of sound measurements extrapolated to 0 K.

b) Beaumont, Chihara and Morrison, reference 26.

c) Urvas, Losee and Simmons, reference 24.

d) Feingold and Phillips, reference 27.

Selected theoretical estimates of polycrystalline elastic properties of noble gas solids at $T = 0$ K. B , bulk modulus (k bar), v_ℓ and v_t (m/sec).

	Ar				Kr			Xe		
B	26.0 ^a	24.3 ^b	26.1 ^c	29.2 ^d	32.3 ^a	30.0 ^b	32.1 ^c	36.4 ^a	32.6 ^b	36.4 ^c
v_ℓ	1617 ^a	1525 ^b	1619 ^c	1646 ^d	1359 ^a	1276 ^b	1352 ^c	1304 ^a	1201 ^b	1304 ^c
v_t	927 ^a	845 ^b	930 ^c	892 ^d	776 ^a	703 ^b	773 ^c	743 ^a	659 ^b	744 ^c

a) C. Feldman et al. (L-J 6-12), reference 31

b) Hüller et al. (L-J 6-12) with three body forces), reference 28

c) Barron and Klein (6-12 NN), reference 30

d) Barker et al. (anharmonic with three-body forces), reference 29

B. Polycrystalline Properties at Finite Temperature

1. Experiment

The present measurements of ultrasonic velocities in polycrystalline krypton are the first to be reported. They are useful for comparisons with theory which are made below and they are immediately useful to other work on x-ray scattering in this laboratory, which requires values for elastic wave velocities in corrections for thermal diffuse scattering.

The results of the present velocity measurements on argon are in agreement with Keeler and Batchelder⁷ and with Barker and Dobbs.¹¹ The

temperature dependence of v_t agrees with Keeler and Batchelder but not with the early results reported by Jones and Sparkes.¹³

Keeler and Batchelder used the pulse-echo method, with the transducer imbedded into the top of their specimens, to measure the sound velocity of single crystals of argon from 3 to 77 K. At temperatures below 20 K, however, an unexpected maximum was observed and velocities near 0 K were therefore obtained by an extrapolation from higher temperature. These maxima were attributed to thermal strains in the crystal. Their stated errors are about 0.4% for longitudinal velocities, and 1% for transverse velocities. Elastic constants were determined and have stated errors of 2% for c_{11} and c_{44} and 7% for c_{12} . The largest source of error was in the length measurements of the specimens which were 5 to 8 mm long, with an uncertainty of $\pm .02$ mm. This short specimen length also introduces an uncertainty of about 0.05% in transit times due probably to difficulty in identifying corresponding cycles in the initial and reflected pulses.

Barker and Dobbs, using an acoustical interferometer, were able to measure velocities in polycrystalline argon specimens from 65 to 80 K. The uncertainty in the longitudinal velocities varied from 1/2% at 67 K to 2% at 79 K. The transverse velocities had estimated errors of 3 to 4%. The specimens were prepared by depositing solid from the vapor on to a cooled surface. It is possible that specimens prepared in this manner would not be as clear and dense as specimens grown from the melt. Preliminary investigations, however, indicated the specimens would be compact and transparent³² with grain size dimensions of approximately 0.1 mm for growth rates of 0.1 mm/min.

Jones and Sparkes measured transverse velocities in polycrystalline argon from 18 to 62 K by measuring the resonant frequency of torsional oscillations of a rod of solid argon. Although this method avoids bonding problems encountered in pulse-echo work there were difficulties in determining the precise dimensions of the rod and also problems with end corrections. Measurements were more accurate at lower temperatures and could not be made above 65 K due to grain growth and vaporization. The results were estimated to be accurate to 4%.

2. Comparisons to Theoretical Calculations

The polycrystal velocities can be expressed in terms of single crystal elastic constants. The relationship between the elastic constants and polycrystalline sound velocities is given by Hill.³³ There is an uncertainty in the results of about 1% due to the difference between the Voigt and Reuss expressions. The Voigt and Reuss expressions are given below. They are

$$\rho v_l^2 = B_s + 4/3 G \quad (3)$$

and

$$\rho v_t^2 = G, \quad (4)$$

where ρ is the density, B the bulk modulus

$$B = \frac{1}{3} (c_{11} + 2c_{12}), \quad (5)$$

and

$$G(\text{Voigt}) = 1/5 (c_{11} - c_{12} + 3c_{44}) \quad (6)$$

$$G(\text{Voigt}) - G(\text{Reuss}) = \frac{3[2c_{44} - (c_{11} - c_{12})]^2}{5[4c_{44} + 3(c_{11} - c_{12})]} \quad (7)$$

The Voigt expressions reduce to

$$\rho v_{\ell}^2 = \frac{1}{5} (3c_{11} + 2c_{12} + 4c_{44}) \quad (8)$$

$$\rho v_t^2 = \frac{1}{5} (c_{11} - c_{12} + 3c_{44}) \quad (9)$$

The derivation by Voigt makes the assumption that the strain is uniform throughout an aggregate of crystals whereas Reuss assumes the stress is uniform. In either case the derivations are only approximate although the measured values for many solids have been shown to lie almost midway between the two expressions. Hill gives several numerical examples to illustrate the difference.

Transverse and longitudinal sound velocities have been calculated by Barron and Klein at 0 K, using the Mie-Lennard-Jones 6-12 potential

$$\phi = [6m\epsilon / (m-6)] \left[\frac{1}{m} \left(\frac{R}{R_0} \right)^m - \frac{1}{6} \left(\frac{R}{R_0} \right)^6 \right], \quad (10)$$

where ϕ is the pair potential, R the internuclear distance, and ϵ , R_0 , and m are parameters. They calculated the strain dependence of the first few even moments of the phonon frequency spectrum for nearest-neighbor and all-neighbor

models.³⁰ Elastic constants were determined at 0 K and polycrystalline wave velocities calculated from the Voigt and Reuss expressions given previously.

The elastic constants are expressed as follows:

$$c_{11} = \frac{1}{V} \frac{\partial^2 E(L)}{\partial e_1^2} + \frac{E(Z)}{V} \beta_{11}(1) \quad (11)$$

$$c_{12} = \frac{1}{V} \frac{\partial^2 E(L)}{\partial e_1 \partial e_2} + \frac{E(Z)}{V} \beta_{12}(1) + p \quad (12)$$

$$c_{44} = \frac{1}{4V} \frac{\partial^2 E(L)}{\partial e_4^2} + \frac{E(Z)}{V} \beta_{44}(1) - \frac{1}{2} p \quad (13)$$

where $E(L)$ is the static lattice energy, $E(Z)$ is the zero-point vibrational energy, p the pressure, and e_1, e_2, e_4 the usual strain parameters. $E(Z)$ is proportional to the first moment of the phonon frequency spectrum,

$$E(Z) = \frac{3}{2} \hbar \langle \omega \rangle = \frac{9}{8} \hbar \omega_D(1) , \quad (14)$$

where $\langle \omega^n \rangle$ is the n^{th} moment and $\omega_D(n)$ is the maximum frequency of a Debye distribution of the n^{th} moment. The strain dependence of $\omega_D(n)$ can be written

$$\begin{aligned} \omega_D(n) = & \omega_D(n) \{ 1 - \gamma(n)(e_1 + e_2 + e_3) \\ & + \frac{1}{2} \beta_{11}(n)(e_1^2 + e_2^2 + e_3^2) + \beta_{12}(n)(e_2 e_3 + e_3 e_1 + e_1 e_2) \\ & + 2\beta_{44}(n)(e_4^2 + e_5^2 + e_6^2) \} \end{aligned} \quad (15)$$

where $\gamma(n)$ and $\beta_{ij}(n)$ are dimensionless coefficients, calculated by Barron and Klein for the first few even n .

Their results are shown in Fig. (9) and Fig. (10). The measured sound velocities are higher than either the 6-12 or 6-13 potentials predict at high temperatures although the Voigt value of the longitudinal velocity, calculated from the 6-13 potential, does fall within the limits of experimental error. At lower temperatures the results based on the 6-12 potential are lower than the present experimental results for longitudinal waves but the transverse velocity measurements agree with the 6-12 potential calculations at low temperature. The longitudinal velocities measured at the lower temperatures lie between the 6-12 and 6-13 potential calculations.

C. Feldman, M. Klein and G. Horton³¹ have also calculated quasi-harmonic single crystal elastic constants at various temperatures for solid krypton based on the m-6 Lennard-Jones interatomic potential, equation (10), using a nearest neighbor model and fit to the lattice constant and the sublimation energy at 0 K. A more realistic repulsive force would be one with an exponential dependence, however calculations then become more difficult. For convenience the exponential dependence is replaced by a high power dependence on distance. Values for m are generally chosen between 10 and 14.

In calculating the elastic constant (from the second order term in the Taylor expansion of the Helmholtz free energy), this model includes the third order and fourth order terms in the expansion of the potential in a conventional perturbation theory. Other higher order terms are not considered. The contributions from the third and fourth order force constants are about the same although sometimes the third order term is larger. Multibody forces are not considered as a matter of convenience. However, we note that Barker, Klein and Bobetic²⁹ indicate that for argon at 0 K c_{11} and c_{12} are substantially

affected by three-body forces whereas the shear constants $1/2 (c_{11} - c_{12})$ and c_{44} are unaffected. The difference between nearest neighbor and all neighbor models is not great because of the short range nature of the van der Waals forces. Considering only nearest neighbor interactions simplifies the calculations and makes comparisons to previous theoretical work possible.

From the values of Feldman et al.,³¹ the polycrystalline values of the transverse and longitudinal velocities have been calculated and compared to the present experimental results. See Figs. (9) and (10). The limits of uncertainty on the theoretical calculations represent the difference between the Voigt and Reuss values of sound velocities.

As previously mentioned, the paper by Barker, Klein and Bobetic²⁹ indicates that the calculations for the shear waves are unaffected by the inclusion of three-body forces whereas c_{11} and c_{12} are affected. These authors use a pair potential, the Barker-Pompe form, very different from equation (10). Including three-body forces in the models discussed would result in a larger calculated value of v_l but essentially no change in v_t . If the contributions in krypton are of the same magnitude as in argon, and if the form of the pair potential used does not change the contribution by three-body forces, then both v_l and v_t would be in agreement with the 6-12 model calculation at 0 K.

We note that the elastic constants calculated from the 6-13 potential are larger than the elastic constants calculated from the 6-12 potential. This is due to the increase in steepness of the $m = 13$ repulsive force. The parameters R_0 and ϵ in equation (10) are substantially the same for both 6-12 and 6-13 potentials so that an increase in the energy density results in a smaller increase in strain for the $m = 13$ model, or in other words, the elastic constants are larger.

Figure 9. Smoothed values of the velocity of longitudinal sound in polycrystalline krypton compared with the polycrystalline velocity calculated from the single crystal elastic constants from the quasi-harmonic model of Feldman, Klein and Horton³¹ for the m-6 Lennard-Jones potential using a nearest neighbor (NN) model. The error bars represent the difference between the Voigt and Reuss limits of the calculated velocity. The 0 K values of Barron and Klein³⁰ using the Lennard-Jones 6-12 potential for nearest-neighbor and all neighbor (AN) models are also shown.

Figure 10. Smoothed values of the velocity of transverse sound in polycrystalline krypton are compared with the polycrystalline velocity calculated from the single crystal elastic constants from the quasi-harmonic model of Feldman, Klein and Horton³¹ for the m-6 Lennard-Jones potential using a nearest neighbor (NN) model. The error bars represent the difference between the Voigt and Reuss limits of the calculated velocity. The 0 K values of Barron and Klein³⁰ using the Lennard-Jones 6-12 potential for nearest neighbor and all-neighbor (AN) models are also shown.

C. Adiabatic Bulk Modulus

The adiabatic bulk modulus can be expressed in terms of the density and the longitudinal and transverse polycrystalline velocities at all temperatures by a relation like equation (2),

$$B_s = \rho(v_l^2 - \frac{4}{3} v_t^2) . \quad (16)$$

On Fig. (11) the present results for B_s are compared to the x-ray results of Urvas, Losee and Simmons²⁴ and to the measurements by Coufal et al.³⁵ They are within the specified errors in the x-ray work.

The bulk modulus, B_s , is also related to the second-order elastic constants by equation (5) and to the isothermal bulk modulus, B_T , by

$$B_s = \left(\frac{1}{B_T} - \frac{\beta^2 VT}{C_p} \right)^{-1} \quad (17)$$

where C_p is the specific heat at constant pressure, T the temperature and β the volume thermal expansivity.

The adiabatic bulk modulus has been calculated from the single crystal elastic constants given by the quasi-harmonic model of Feldman, Klein and Horton.³¹ It is compared to the present experimental results in Fig. (12). The temperature dependence at high temperatures differs from the experimental values but the results of the 6-13 nearest neighbor (NN) model are in essential agreement with the measured values near $T = 0$.

The isothermal bulk modulus has been calculated by M. Klein, V. Goldman, and G. Horton³⁴ in an "improved" self-consistent phonon scheme (ISC)

Figure 11. Smoothed values of the adiabatic bulk modulus calculated from the polycrystalline velocity measurements. Comparisons are made to the x-ray results of Urvas, Losee and Simmons,²⁴ and the measurements of Coufal, Veith, Korpiun and Lüscher.³⁵

using a similar two-body potential of the Mie-Lennard-Jones type. From C_p values of Beaumont,²⁶ and V and β values of Losee and Simmons,³⁶ the adiabatic bulk modulus has been calculated according to equation (17). The values thus determined from Klein et al. are also compared to the present experimental values on Fig. (12). The results of the ISC model agree with the experimental values to within the limits of adjustment possible in the model by putting $m = 13$ in the potential, equation 10. At higher temperatures the temperature dependence is not, however, in close agreement with the present results. In general the ISC model fits the experimental values better at low temperature primarily because of the difficulty in describing the thermal expansion at high temperature.

The results for the adiabatic bulk modulus of solid argon from the work of Moeller and Squire⁹ disagree with the x-ray results of Urvas, Losee, and Simmons.²⁴ In order to seek agreement with these two works, the assumptions made by Moeller and Squire regarding specimen orientation and length were varied. A computer search was carried out in the irreducible portion of the Brillouin zone for different assumed propagation directions (See Appendix III for details of the computer program) which would result in B values agreeing with the results of Urvas et al. The conclusion of the analysis was that the ultrasonic measurements did not necessarily disagree with the results of Urvas et al. The bulk modulus values of Keeler and Batchelder agree with Urvas et al. to within the limits of experimental error. The present results confirm the work of Keeler and Batchelder and do not change the conclusions in the paper by Urvas, Losee and Simmons.

Figure 12. Comparisons of the present results for the adiabatic bulk modulus with the theoretical bulk modulus calculations based on the single crystal elastic constants given by the quasi-harmonic, 6-12 and 6-13 nearest neighbor model of Feldman, Klein and Horton³¹ and with the calculation of Klein, Goldman and Horton³⁴ in an improved self-consistent phonon scheme using a two-body potential of the Mie-Lennard-Jones type.

D. Grüneisen Parameter

The thermal Grüneisen parameter is defined by the expression

$$\gamma = -\frac{1}{3N} \sum_i \frac{d \ln \omega_i}{d \ln V}, \quad (18)$$

where ω_i is a phonon eigenfrequency of the solid. In general, the ω_i depend upon volume at a given temperature, and in addition they depend upon temperature at a given volume. In terms of the scalar thermodynamic properties V , β , C_p , and B_s , the Grüneisen parameter can be written

$$\gamma = \beta B_s V C_p^{-1}. \quad (19)$$

From the specific heat values of Beaumont and coworkers,²⁶ thermal expansivity and molar volume measurements of Losee and Simmons,³⁶ and the present results for the adiabatic bulk modulus, the temperature dependence of the Grüneisen parameter for solid krypton has been calculated. The smoothed values are shown in Fig. 13.

Barron, in a model-independent calculation,³⁸ showed that $\gamma_\infty \equiv \gamma(0)$ and $\gamma_0 \equiv \gamma(-3)$, the high- and low-temperature limiting values, respectively, can be found from the 0 and -3 moments of the quasi-harmonic phonon spectrum and that the largest variation in γ should occur near the temperature $\theta/5$. This prediction is in qualitative agreement with the present results. Knowledge of the temperature variation of γ also yields $\gamma(-2)$ and $\gamma(-1)$. These are useful in correcting to constant volume the results of x-ray scattering experiments such as those of Windecker¹⁹ and of Kabat in this laboratory.

The results of a conventional perturbation expansion of the partition function used with nearest neighbor, central two-body forces (PT) is also shown.³⁷ An interatomic potential of the form, equation (10), was used. These calculations are based on the Born-von Kármán theory of lattice dynamics which assumes the rms deviation of the nucleus about the lattice site is small compared to the lattice spacing. The calculations apparently break down for $T > 1/3 T_M$, where T_M is the melting temperature. At $T_M/3$ the rms amplitudes of vibration are greater than 6% of the nearest-neighbor distance and result in very large anharmonic effects. Calculations³⁴ based on a quasi-harmonic model using the same potential are also shown in Fig. (13) for comparison. One sees that although a quasiharmonic model can apparently fit the temperature dependence of B_s fairly well (Fig. 12), the Grüneisen parameter itself is poorly represented.

Also shown in Fig. (13) are the more recent results of the improved self-consistent phonon scheme (ISC) of Klein, Goldman and Horton³⁴ in which the same central two-body potential of the Mie-Lennard-Jones type is used. The scheme in effect sums all even-order anharmonic terms in the free energy and also includes an approximation for the leading odd-order terms F_3 , etc. The present experimental results agree with ISC calculation, particularly at higher temperatures. At temperatures near $\theta/5$, however, the measured γ is lower than predicted by any of the above models. One suspects that the assumed potential may be responsible for this discrepancy.

Fig. (14) compares the measured Grüneisen parameters of solid argon, krypton and xenon using the present work for krypton, values from Keeler and Batchelder⁷ for argon at high temperature (confirmed by the present work Fig. 5), Tilford and Swenson³⁹ for argon at low temperatures, and the data from

Figure 13. Smoothed values of the measured Grüneisen parameter for krypton are compared with the theoretical calculation of Klein, Goldman and Horton³⁴ in an improved self-consistent phonon scheme based on a 6-12 potential (ISC), with the calculation of Klein, Horton and Feldman³⁷ based on the conventional perturbation expansion used with a nearest neighbor 6-12 potential (PT), and with a similar calculation of the quasi-harmonic model (QH). Note that here the QH model appears much less satisfactory than it does for the bulk modulus alone, Fig. 12.

Figure 14. Grüneisen parameters of solid argon, krypton, and xenon. The present results are used for krypton. For argon at high temperatures, bulk moduli obtained from the work of Keeler and Batchelder⁷ are used. At low temperatures, the argon curve is that of Tilford and Swenson,³⁹ who used the compressibility data of Peterson and coworkers.⁵⁴ For xenon, the Grüneisen parameter shown was calculated from tabulated values of C_v and χ_t by Trefny and Serin,⁵⁵ from measurements of thermal expansion up to 105 K by Tilford,⁴⁰ from a classical law of corresponding states for the expansion above 105 K, and from a value for the molar volume near $T = 0$ K by Sears and Klug.⁵⁶

Tilford,⁴⁰ Sears and Klug⁵⁶ and Trefny and Serin⁵⁵ for the xenon curve. No existing theoretical models are able to show the family relationship of argon, krypton and xenon over the whole temperature range. In particular, the high temperature results for argon are anomalous. For all of the noble gases the results derived from all two-body model calculations are higher than the experimental results at low and moderately low temperatures.

E. Thermal Vacancy Content from Elastic Measurements

In principle, thermal vacancy concentration in a solid can be estimated from the measured difference between the bulk and lattice isothermal compressibilities.³⁶ This is now possible in krypton, for the first time for any solid.

If χ_T is the bulk compressibility and χ_{TX} the lattice compressibility then

$$\chi_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = \chi_{TX} + \frac{nv}{kT}, \quad (20)$$

where n is the vacancy concentration and v is the free volume of formation for a vacancy. The volume of formation may be taken to be v_a , the volume per atom.⁴¹

The smoothed values of the adiabatic bulk modulus of the present work are converted to isothermal compressibility by the relation like equation (17)

$$\chi_{TX} = \frac{1}{B_s} + \frac{\beta^2 VT}{C_p}, \quad (21)$$

where the x-ray values of β , V , C_p were used. Present measured values represent the lattice compressibility because at 10 MHz the time intervals between stress reversals are very short compared to the times required for vacancy generation and diffusion throughout the solid. The vacancy concentration can then be expressed in the following form:

$$n = (x_T - x_{TX}) \frac{kT}{v} . \quad (22)$$

Using the smoothed values of the macroscopic isothermal compressibility results of Coufal et al.³⁵ and the present values for x_{TX} one may then determine the vacancy concentrations from 80 to 115 K. See Fig. (15).

F. Longitudinal $\langle 110 \rangle$ Velocity

In specimen Kr-5, a single crystal with vertical direction nearly $\langle 110 \rangle$, five echoes were observed at 114 K. The leading edges of the first and second echoes are shown in Fig. (16). The fact that the echo pattern was very well defined indicates the absence of any grain boundaries in the path of the acoustic wave. Also, thermal etching of the specimen (as described in Sect. II.B.3) failed to reveal the presence of any grain boundaries in the acoustic path.

According to Waterman,⁴² if the elastic constants of a crystal are known, the dependence of the wave velocities on orientation (about the high symmetry axes) can be determined easily for small misorientation angles. In particular, for longitudinal waves travelling in the $\langle 110 \rangle$ direction, the fractional change in velocity is given by

Figure 15. Thermal vacancy content in solid krypton. Values are calculated from equation (22) of text from the difference between the smoothed bulk values of the isothermal compressibility of Coufal et al.³⁵ and the smoothed values of the lattice isothermal compressibility of the present work. The uncertainty at 115 K is about 1.0×10^{-3} . Data points shown are the direct measurements of Losee and Simmons.⁴¹

Figure 16. Photograph of the leading edges of the first and second ultrasonic echoes observed in specimen Kr-5 at 114 K. The time scale is $0.1 \mu\text{sec/div.}$ Specimen Kr-5 was a single crystal with the vertical direction nearly $\langle 110 \rangle$.

Krypton
Specimen 5

First Echo

Second Echo

$$\frac{\Delta v_\ell}{v_\ell} = \frac{K_1 \theta^2 [(2K_3+1)\cos^2 \phi + (2K_4-5)\sin^2 \phi]}{2(c_{11}+c_{12}+2c_{44})} \quad (23)$$

where θ is the polar misorientation angle, ϕ the azimuthal angle and

$$K_1 = c_{11} - c_{12} - c_{44}, \quad (24)$$

$$K_3 = K_1/(c_{44} - c_{11}) + 2, \quad (25)$$

$$K_4 = K_1/2(c_{11} + c_{12}) + 3/2. \quad (26)$$

From the transverse and longitudinal wave velocities in polycrystalline krypton and the longitudinal wave velocity in the direction nearly $\langle 110 \rangle$, one can estimate the elastic constants and the velocity of sound corrected to the $\langle 110 \rangle$ direction. For a misorientation from the $\langle 110 \rangle$ direction given by $\theta = 4^\circ$, $\phi = 2^\circ$, the correction in velocity is less than 0.4%. The method devised here for estimating the elastic constants is given next.

A computer search was made with various values of c_{ij} to find the values of c_{11} , c_{12} and c_{44} which give the polycrystal experimental values of v_t and v_ℓ and the longitudinal velocity in the $\langle 110 \rangle$ direction equal to the experimental values in the nearly $\langle 110 \rangle$ direction. These elastic constants were then used to determine the change in velocity between the $\langle 110 \rangle$ direction and the true direction in specimen Kr-5. A new search was then made to find values of c_{11} , c_{12} and c_{44} which gave the experimental values of v_t and v_ℓ for the polycrystal and the longitudinal velocity in the $\langle 110 \rangle$ direction equal to the corrected velocity value of specimen Kr-5.

The estimated absolute error in the velocity measurements of Kr-5 is 0.3%. The length measurement has an uncertainty of 0.2% and the transit time 0.1%. The estimated uncertainty in the velocities corrected to the $\langle 110 \rangle$ direction is 1% with a contribution to the uncertainty of about 0.7% due to errors in x-ray orientation of the crystal and in correcting the velocity to the $\langle 110 \rangle$ direction.

The experimental results are compared in Fig. 8 to the measurements of Peter et al.¹⁴ and to the velocity at 79 K and about 300 bar inferred from the phonon dispersion data of Daniels et al.¹⁵ The results of Peter et al.¹⁴ are of low precision and appear to be high for measurements made at 77 and at 90 K.

Peter et al.¹⁴ measured sound velocities of solid krypton at 4.2, 77 and 90 K by the pulse-echo method. Their krypton specimen macrostructure was analyzed by Bragg scattering of thermal neutrons. The sample was made up of grains with dimensions of about 5 mm and velocities were reported to be propagating only in the (111) plane. With the variation of longitudinal velocities in the (111) plane estimated to be only about 1%, the measured velocity was compared to longitudinal velocities in the $\langle 110 \rangle$ direction. Peter et al.¹⁴ reported an uncertainty in their velocity in the $\langle 110 \rangle$ direction of about 6%, but their values still do not fall within the experimental limits of the present work. Results of similar experiments by the same group on argon show a large amount of scatter and, in addition, the very unexpected result that the longitudinal velocity in the $\langle 100 \rangle$ direction is larger than the velocity in the $\langle 110 \rangle$ direction.

The sound velocity inferred from the results of Daniels et al. was obtained from the initial slope of a least squares fit of a second-neighbor interplanar force model to the phonon dispersion data obtained from coherent inelastic neutron scattering. The method is described more fully below.

The Born-von Kármán theory of lattice dynamics describes the atomic motions in a crystal by lattice waves considered as uncoupled harmonic oscillators. The frequency ω of the oscillator is related to the wave vector q by a dispersion relation. In this theory, where the forces are a linear function of the displacements of atoms from their equilibrium sites, the solution to the equation of motion can be written (for symmetry directions)

$$M\omega^2 = \sum_{n=1}^N \Phi_n (1 - \cos(\pi n q / q_{\max})) \quad (27)$$

where $q_{\max}$ is the q value where the neutron dispersion curve begins to repeat and Φ_n is effectively an interplanar force constant. The neutron data of Daniels et al.¹⁵ were fit to this expression for $N = 2$. The elastic constants are expressed in terms of the force constants by⁴³

$$B_a c_i = \sum_{n=1}^N \frac{1}{2} n^2 \Phi_n \quad (28)$$

where B and c_i , the effective elastic constant, depends on the branch considered. For example, for the longitudinal mode in the $\langle 110 \rangle$ direction one has

$$B = 2$$

and

$$c_i = (c_{11} + c_{12} + 2c_{44})/2 . \quad (29)$$

Values obtained from this analysis (in units of 10^9 N m^{-2}) are,⁴⁴ for $T = 79 \text{ K}$, $p = 300 \text{ bar}$:

$$c_{11} = 3.46$$

$$c_{12} = 2.53$$

$$c_{44} = 2.53$$

$$B_s = 2.84$$

$$v(\text{long. } \langle 110 \rangle) = 1373 \text{ m/s.}$$

A correction of about 3% was made to determine the velocity at zero pressure. This estimate was based on the estimated changes in the bulk modulus between 0 and 300 bar.²⁴ For $T = 79 \text{ K}$, $p = 0$, one then finds

$$v(\text{long. } \langle 110 \rangle) = 1331 \text{ m/s.}$$

These values appear to be slightly high but probably do not lie outside the uncertainty of the fitting procedure. The precision of original neutron data did not justify fits for N greater than 2. The experimental value of B_s from the present work at 79 K is $2.61 \times 10^9 \text{ N m}^{-2}$.

Comparisons may also be made with the theoretical calculations of Feldman and Klein.²⁵ Calculated velocities are shown in Fig. 8 for the 6-12 and 6-13 Mie-Lennard-Jones potentials acting between nearest neighbors only. The experimental results are in agreement with the values calculated from the 6-13 potential.

G. Second-Order Elastic Constants

The longitudinal velocity in the $\langle 110 \rangle$ direction is related to the elastic constants by the following expression:

$$\rho v_{110}^2 = \frac{1}{2} (c_{11} + c_{12} + 2c_{44}) . \quad (30)$$

The velocities in polycrystalline material, according to Hill,³³ can be expressed in terms of the single crystal elastic constants as described by equations (3) and (4). By varying the values of c_{11} , c_{12} and c_{44} until the values of v_t , v_l , $v_{\langle 110 \rangle}$ were in agreement with the experimental results, the elastic constants were determined. The limits of uncertainty resulting from this method are rather large, however. The elastic constants have been calculated at $T = 114$ K, at which

$$v \text{ (long. } \langle 110 \rangle) = 1144 \pm 11 \text{ m/sec}$$

$$v_t = 621 \pm 12 \text{ m/sec,}$$

$$v_l = 1108 \pm 10 \text{ m/sec,}$$

and are, expressed in units of 10^9 N m^{-2} ,

$$c_{11} = 2.95 \pm .7$$

$$c_{12} = 1.55 \pm .3$$

$$c_{44} = 1.45 \pm .3 .$$

A small error in the slope of the smoothed velocity data at the higher temperatures results in a much larger uncertainty in the temperature

dependence of the elastic constants. For this reason, no attempt has been made to extract a temperature dependence of the elastic constants from the present velocity data.

The anisotropy is given by:

$$A = 2 c_{44} / (c_{11} - c_{12}) . \quad (31)$$

For $T = 114$ K one finds $A = 2.1$ for krypton. For an isotropic crystal A would be 1.0.

The deviation δ from the Cauchy relation is given by

$$\delta = \frac{c_{44} - c_{12}}{c_{12}} . \quad (32)$$

For $T = 114$ K one has $\delta = -.07$.

For crystals which obey the Cauchy relation $c_{12} = c_{44}$, that is, $\delta = 0$.

Feldman, Klein and Horton³¹ have calculated quasi-harmonic single crystal elastic constants in solid krypton using the m-6 Lennard-Jones potential acting between nearest neighbors. If their values are extrapolated linearly to 114 K from approximately 80 K, they appear consistent with the experimentally determined values within the limits of error for the 6-12 and 6-13 potentials with the exception of c_{12} , calculated from the 6-13 potential which is slightly higher than the experimental value. However, as mentioned previously, next to conventional perturbation theory, the quasi-harmonic model is the least reliable at the higher temperatures.

Gornall and Stoicheff¹⁶ measured the elastic constants of solid xenon at 156 K by the method of Brillouin spectroscopy. The stated error for their

measurements is about 3%. The advantage of their technique is that only small crystals are necessary and they are not disturbed during the course of taking measurements. The xenon crystals were grown from the melt in a quartz tube with an inside diameter of 1 mm. Single crystals were identified and oriented by Laue diffraction techniques.

Gornall and Stoicheff compare their results to calculations of M. L. Klein (private communication) based on the L-J 6-12 nearest-neighbor self-consistent phonon theory. Only c_{11} is appreciably different from the theoretical values. The experimental result for c_{11} is about 22% lower than the calculated value.

Table (V) compares the elastic constants, anisotropy and δ for argon, krypton, and xenon at high temperatures. The anisotropy and c_{44} value of argon appears low in view of the experimental results for krypton and xenon and the theoretical estimates for argon. Also the c_{11} value of xenon seems too low and the anisotropy slightly higher than expected. In fact, a larger value of c_{11} for xenon would result in a lower value of the anisotropy and similarly a larger value of c_{44} for argon would result in a larger value of the anisotropy.

Table V

Table V. Measured elastic properties of heavy noble gas crystals at high temperatures. Elastic constants are in units of 10^9 N.m^{-2} .

	c_{11}	c_{12}	c_{44}	A	δ	T, K	$T_{\text{melt}}, \text{ K}$
Ar ^(a)	2.70	1.39	.887	1.35	-.36	80	84
Kr ^(b)	2.95	1.55	1.45	2.1	-.07	114	116
Xe ^(c)	2.98	1.90	1.48	2.74	-.21	156	161

- a) Keeler and Batchelder, reference 7
- b) Present work
- c) Gornall and Stoicheff, reference 16

H. An Attempt to Estimate $(c_{12} - c_{44})$

It is possible to estimate the difference between the single crystal adiabatic elastic constants c_{12} and c_{44} from the measurements of polycrystalline sound velocities. We proceed in the following manner. From theoretical calculations of elastic constants of C. Feldman, Klein and Horton,³¹ the difference between the Voigt and Reuss values of the polycrystalline sound velocities can be estimated. For transverse wave velocities for their model of krypton, the difference between the Voigt value and the average of Voigt and Reuss values varies from 2.6% near 0 K to approximately 1.8% at the triple point. For longitudinal velocities the difference is only about 1%. If v_t and v_ℓ are the measured velocities, then

$$v_t (\text{Voigt}) = v_t (1 + \Delta_t) \quad (33)$$

$$v_\ell (\text{Voigt}) = v_\ell (1 + \Delta_\ell) \quad (34)$$

where $\Delta_t = .022 \pm .004$ and $\Delta_\ell = .01 \pm .002$.

Using the simple Voigt expression alone, therefore, for v_t and v_ℓ one has

$$\rho v_t (\text{Voigt})^2 = G_v \quad (35)$$

and

$$\rho v_\ell (\text{Voigt})^2 = B_s + \left(\frac{4}{3}\right)(G_v), \quad (36)$$

$$\text{where } G_v = \frac{1}{5} (c_{11} - c_{12} + 3c_{44}), \quad (37)$$

and

$$B = \frac{1}{3} (c_{11} + 2c_{12}) , \quad (38)$$

From the above expression one finds:

$$c_{12} - c_{44} = \rho (v_l(\text{Voigt})^2 - 3 v_t(\text{Voigt})^2) \quad (39)$$

therefore $c_{12} - c_{44} = (2.8 \pm 1.7) \times 10^8 \text{ N m}^{-2}$,

and at 115.75 K

$$c_{12} - c_{44} = (1.4 \pm 1.4) \times 10^8 \text{ N m}^{-2}.$$

The large uncertainty in the difference of $c_{12} - c_{44}$ makes it difficult to establish the temperature dependence from 0 K to the triple point. However, it appears that the value of $c_{12} - c_{44}$ for temperatures near the t.p. is about constant.

Nevertheless at 0 K, one has $c_{12} > c_{44}$ and the Cauchy relationship $c_{12} = c_{44}$ is not obeyed. That is, if $\delta = \frac{c_{44} - c_{12}}{c_{12}}$ is the deviation from the Cauchy relation, then one has $\delta < 0$. Barrón and Klein³⁰ have calculated the anharmonic elastic constants at 0 K using a quasiharmonic model and the two-body Lennard-Jones 6-12 potential for both nearest-neighbor and all-neighbor interactions. Their method is outlined above in Sect. IV. A. One sees there that the effect of including zero-point motion is to make δ positive. However, Hüller, Götze and Schmidt²⁸ have found that the effect of three-body forces of the Axilrod-Teller type is to cause the sign of δ to change, so that near 0 K it becomes negative.

Barker, Klein and Bobetic²⁹ have also made calculations on argon where three-body forces are considered. Table (VI) summarizes the experimental inferences and theoretical calculations of $c_{44} - c_{12}$ at 0 K.

The calculations of Hüller et al. describes the experimental inferences in this form fairly well. We recall, however, that their model gave very low values for the longitudinal and transverse wave velocities in polycrystals (Sect. IV. A., above). The best model of Barker et al. is, as expected, the anharmonic with three body forces.

Table VI

Table VI. Values estimated for the quantity.

$(c_{44} - c_{12})$ at 0 K, in units of 10^9 N/m^2 .

Element	Measured	Calculated						
Ar	$-0.19 \pm .16^a$	$+.09^c$	$-.08^d$	$+.08^e$	$-.02^f$	$+.06^g$	$+.28^h$	$+.36^i$
Kr	$-0.28 \pm .17^b$	$+.06^c$	$-.18^d$	$+.05^e$	...	...	...	...
Xe	...	$+.04^c$	$-.23^d$	$+.03^e$	...	...	...	...

- a. Keeler & Batchelder, reference 7.
- b. Present work.
- c. Barron and Klein (nearest neighbor), reference 30.
- d. Hüller, Götze & Schmidt (L-J potential including three-body forces), reference 28.
- e. C. Feldman, M. L. Klein and G. K. Horton (L-J potential), reference 31.
- f. Barker, M. L. Klein & M. V. Bobetic, reference 29. Anharmonic with three-body forces.
- g. " " " harmonic with three-body forces.
- h. " " " anharmonic, no three-body forces.
- i. " " " harmonic, no three-body forces.

V. SUMMARY

In a rigid-tail helium cryostat the velocities of longitudinal and transverse sound have been measured by the standard pulse-echo technique on a large number of polycrystalline krypton specimens of varying lengths. The velocity of longitudinal sound has also been measured in a single crystal krypton specimen with the acoustic wave traveling in a nearly $\langle 110 \rangle$ direction. All crystals were grown from the melt over a 10 Mhz X-cut or AC-cut quartz transducer. Differential thermal expansion prevented measurements from being made to low temperatures, but extrapolations of the present results to 0 K agree with the values at 0 K determined from bulk modulus and heat capacity measurements.

Measurements on polycrystalline specimens of argon were also made and discriminate between the results of previous investigators.

The adiabatic bulk modulus has been calculated from the velocity of sound and is in reasonable agreement with the results of other investigators.

Agreement between the present velocity measurements (and resulting bulk modulus) and theoretical calculations based on various existing models is only fair, however.

The thermal vacancy concentration in krypton has been determined from the difference between the lattice and bulk compressibility and is found to be in agreement with the vacancy content obtained by direct measurements. Also calculated were the Grüneisen parameter, second-order elastic constants near the triple point and the difference between c_{12} and c_{44} at 0 K and near the triple point.

In general, there is no existing model which is able to describe accurately both the high and low temperature thermoelastic properties of solid krypton.

APPENDIX I. METHODS OF MEASURING THE VELOCITY OF SOUND AND SECOND-ORDER ELASTIC CONSTANTS IN SIMPLE SOLIDS

Three methods of measuring the velocity of sound and second-order elastic constants in simple solids were applied to a single crystal of calcium fluoride. These methods were a) standard ultrasonic pulse-echo techniques, b) diffraction of light from continuous ultrasonic waves, and c) diffraction of light from pulsed ultrasonic waves.

A. Specimen

A single crystal of calcium fluoride was purchased from the Harshaw Chemical Co. It was strain-free, optical quality, and exhibited x-ray Laue spots without structure. The sample was cubical in shape with two faces (100) planes and the remaining four faces oriented so as not to be low-index planes. An X-cut transducer placed on one of the high-index faces enabled excitation of transverse and longitudinal acoustic waves simultaneously in all crystal directions. Transducers placed on a (100) face produced acoustic waves traveling in the $\langle 100 \rangle$ direction.

The (100) faces were oriented to within 0.3° of (100), as determined by back-reflection Laue photographs, and were separated by 3.095 ± 0.001 cm. The two high-index faces used were determined to be nearly (520) planes (the normal to these faces was 22.2° from the $\langle 100 \rangle$ direction in a $\langle 010 \rangle$ zone; $\theta = 22.2^\circ$, $\phi = 0^\circ$) and separated by 3.102 ± 0.001 cm.

B. Pulse Echo Technique

The velocity of sound can be determined from the transit time measured between successive echoes of a pulse generated in the solid and the path length traveled by the pulse. If t is the transit time between two successive echoes, L the length of the crystal, then v , the velocity is given simply as

$$v = 2L/t . \quad (AI-1)$$

X-cut and AC-cut quartz transducers, 1.2 cm in diameter, were used as generators of longitudinal and transverse wave pulses and also as detectors of the echoes. The transducers bonded to the crystal with Fisher Scientific Co. Nonaq stopcock grease. Pulses 2 μ sec long and 10 Mhz frequency were generated by an Arenberg High Power Pulsed Oscillator Model PG-650-C. This signal was fed to an Arenberg Model UB-100-S.N. balancing network then amplified by an Arenberg low frequency amplifier Model PA-620-L and Wide Band Amplifier Model WA-600E. The amplified signal was observed on a Tektronix Type 545B oscilloscope with a Type 1A1 dual-trace plug-in unit. Transit times were measured by means of the delay time multiplier of the Tektronix oscilloscope. A Tektronix Model 184 time mark generator was used for calibration of the oscilloscope.

Transit times were measured between many different cycles of a series of successive echoes and an average value was obtained. Care must be taken to insure that transit times are being measured between corresponding parts of each of the echoes examined. In the longitudinal mode for example, there is some attenuation of the leading edge which is used as a reference point and there is some elongation of the echo at the trailing edge. The severity of the problem is

related to the difference between the acoustic impedance of transducer and specimen.⁴⁵ For large mismatching of impedances (product of density and appropriate wave velocity) such as in the case of calcium fluoride there is no serious attenuation or distortion and the leading edge of many echoes can be easily identified. For solid krypton, argon, and neon the difference in impedance of specimen and transducer is even greater and the problem becomes negligible.

See Fig. (17) for a schematic diagram of the electronics.

The elastic constants of calcium fluoride, at room temperature, were determined by measuring the velocity of sound of 10 Mhz longitudinal waves traveling in the $\langle 100 \rangle$ direction, 10 Mhz transverse waves traveling in the $\langle 100 \rangle$ direction and 10 Mhz longitudinal waves traveling in the (100) plane but at an angle 22.2° from the $\langle 100 \rangle$ direction (near the $\langle 520 \rangle$ direction). Then if ρ is the density of the solid, the relationship between the elastic constants and velocities for a cubic crystal are given by:

$$\langle 100 \rangle \quad c_{11} = \rho v_l^2 \quad (\text{AI-2})$$

$$\langle 100 \rangle \quad c_{44} = \rho v_t^2 \quad (\text{AI-3})$$

$$c_{12} = [(c_{11}^2 + s^2 c_{44}^2 - \rho v^2)].$$

$$(c_{44}^2 + s^2 c_{11}^2 - \rho v^2) \cdot (1/c_s^2)^{1/2} \quad (\text{AI-4})$$

where $c^2 = \cos^2 \theta$ and $s^2 = \sin^2 \theta$ and v is the velocity of a longitudinal wave traveling in the (100) plane at an angle $\theta = 22.2^\circ$ from the $\langle 100 \rangle$ direction.¹⁷

Figure 17. Schematic diagram of the electronics for measuring the velocity of sound by ultrasonic pulse-echo technique. The crystal must be prepared with a plane face parallel to the face on which the acoustic transducer is fixed. Pulse transit times are measured by means of the oscilloscope; they can be converted to velocities once the specimen dimensions are known.

The results of the measurements were:

$$v_l \langle 100 \rangle = 7202 \pm 3 \text{ m/sec}$$

$$v_t \langle 100 \rangle = 3261 \pm 2 \text{ m/sec}$$

$$v_l (\theta = 22.2^\circ) = 6955 \pm 3 \text{ m/sec.}$$

Then from equations (AI-2 to 4) one obtains the values

$$c_{11} = 16.49 \times 10^{10} \text{ N/m}^2$$

$$c_{12} = 4.52 \times 10^{10} \text{ N/m}^2$$

$$c_{44} = 3.38 \times 10^{10} \text{ N/m}^2 .$$

The estimated possible error in each of c_{11} and c_{44} is 0.07% mainly due to uncertainties in the length measurements. The uncertainty in c_{12} is estimated to be about 1% due to an uncertainty in θ of nearly 0.1 degree and the dependence of c_{12} on θ , c_{11} and c_{44} .

Transit times were checked by remeasuring the transit times for the same crystal specimen on a Matec Inc. Model PR-20 Attenuation Comparator. The results of these measurements were essentially identical to those made with the Arenberg oscillator and calibrated Tektronix oscilloscope. The attenuation characteristics of the calcium fluoride specimen were very good, with twenty to thirty echoes clearly visible when the crystal was excited by 10 Mhz acoustic waves.

C. Diffraction of Light from Continuous Waves

1. Theory

It is possible to measure optically the wavelength of acoustic waves in transparent solids because these acoustic waves cause periodic changes in the index of refraction of the solid. When a beam of light is passed through a solid excited by acoustic waves, the light is diffracted much the same as if it were passing through a diffraction grating.

If the wavelength and frequency of an ultrasonic wave in a crystal are known then, for frequencies in the megahertz region (no dispersion), the velocity of that wave is given simply by $v = \lambda f$ where λ is the wavelength and f the frequency. The wavelength of acoustic waves traveling in various directions in the calcium fluoride sample were measured by observations of the diffraction pattern of the light of a He-Ne gas laser beam directed perpendicular to the ultrasonic beam.

The simplified Raman-Nath theory⁴⁶ successfully predicts the separation and intensities of the diffracted orders of light scattered from progressive and standing waves. The result of this theory, based on the evaluation of the diffraction integral for a phase grating, is that the light is observed at scattering angles α given by

$$\sin \alpha = n \frac{\lambda_L}{\lambda_s} \quad (\text{AI-5})$$

where λ_L is the wavelength of light, λ_s is the wavelength of the acoustic wave and n an integer. The intensity for the n^{th} order spot is given by

$$I_n = J_n^2(u) \quad (\text{AI-6})$$

where

$$u = 2\pi\mu\ell/\lambda_L, \quad (\text{AI-7})$$

in which μ is the peak change in the refractive index caused by the sound wave and ℓ is the distance the light travels in the sound beam. The theory is based on the assumption that the light beam passing through the acoustic beam has the same waveform as the ultrasonic waveform. For sinusoidal waves this condition is satisfied provided that one has

$$2\pi^2 n^2 \mu / \lambda_s \ll 1. \quad (\text{AI-8})$$

Extermann and Wannier⁴⁷ have shown that the Bessel function expression, Eq. AI-6, overestimates the intensities of higher orders.

For first order and small α :

$$\lambda_s = \frac{\lambda_L}{\alpha} = \frac{\lambda_L F}{D} \quad (\text{AI-9})$$

where F is the focal length of the detection system and D the linear displacement, in the focal plane, of the diffraction peak from the central beam.

2. Apparatus

Fig. (18) shows a schematic top view of the optical table designed and constructed for measuring the velocity of sound by diffraction of light techniques. This table supports a folded optical system consisting of a) Perkin-Elmer Corp. Model 5200 helium-neon gas laser and beam expander which has

Figure 18. Schematic diagram of the optical table. a: Mirror, mounted on a moveable stage, with additional rotational motion about a vertical axis and translational motion along two parallel tracks. b: Lens, mounted on a moveable stage with focal length approximately 181 cm and translational motion along the two parallel tracks. c: Specimen. d: Fixed double slit. e: Drill rod tracks, 1.9 cm diam. f: Photodiode with 100 μ diam pinhole mask. g: Mount for detector allowing translational motion along the tracks. h: Moveable stage allowing for vertical motion and translational motion perpendicular to track "e". i: Laue film holder. j: X-ray beam collimator, 0.63 mm diam. k: X-ray tube. l: He-Ne gas laser.

a 2 mw output at 6328 Å and expanded beam 1 cm in diameter, b) lens, 3.8 cm aperture with 1/4% anti-reflection coating and a focal length approximately 181 cm mounted on a Gaertner Scientific Corp. x-y coordinate positioning stage, c) photodetector, d) fixed double slit and e) Mo target x-ray tube and camera for taking Laue orientation photographs.

The laser is supported in a rigid mount. The lens and mirror mounts are free to move along two parallel tracks (1.9 cm diam drill rods). The mirror mount has an additional motion of rotation about a vertical line passing through the front face of the mirror. The photodetector is also mounted on two similar tracks at an angle of 12° to the mirror-lens tracks. The x-ray apparatus, laser mount, and tracks are rigidly attached to a 1.9 cm thick aluminum plate stiffened by additional channeling. This table is mounted on a 86 cm by 86 cm wide by 80 cm high aluminum box which is provided with translational adjustments in both horizontal and vertical directions normal to the laser beam axis, with rotational adjustment about a vertical axis, and with limited rotational adjustment about a horizontal axis passing through the x-ray beam collimator.

The x-ray beam and laser beam axes are lined up perpendicular to each other by deflecting the laser beam precisely 90° with a pentaprism and aligning the x-ray beam collimator coaxial with the deflected light beam. This system lends itself to precise measurements of the velocity of sound by the diffraction of light by oriented crystals and can be used easily in conjunction with the cryostat described in this work, Sect. IIA of text.

The center of the diffracted beam was determined by scanning the diffracted spot with an EG&G Inc. Type SGD-100 silicon-diffused photodiode covered with a 100 µm diam pinhole. This device, mounted on a Gaertner Scientific Corp. coordinate positioning stage (No. M326), allowed x and z positions in

the focal plane of the optical system to be measured with an accuracy of $\pm 2.5 \mu\text{m}$. The output signal of the photodiode was fed to a Keithley Electrometer Model 600A. The center of the diffracted beam was then determined by scanning the spot until the maximum signal output of the photodiode was observed.

The effective focal length of the system as a whole, F , was determined accurately as follows: A fixed double slit was placed between the laser and the calcium fluoride crystal. The interference pattern was observed and the separation between maxima of orders up to ten was measured and an average separation was determined. Although such Young's interference maxima are broad, a precise average separation could be obtained (no precise multiple slit of appropriate dimensions was obtainable when required). We note that this method works even when the specimen does not have plane-parallel faces (see Appendix II). Direct scanning along the optical axis y is useless, of course; for such a system working at $f/50$, the structure of the focus is extremely elongated.⁴⁸

If F is the system focal length, d the separation between centers of the slits, and a the distance between successive maxima then for small angles α

$$F = ad/\lambda_L. \quad (\text{AI-10})$$

Using equation AI-9 one has simply

$$\lambda_s = ad/D. \quad (\text{AI-11})$$

The separation of slits of the fixed double slit was measured with a Gaertner Corp. traveling microscope to an uncertainty of less than 0.1%. If f is the

frequency of the acoustic wave then the velocity v is given by

$$v = \lambda df/D . \quad (\text{AI-12})$$

Because the transducer is loaded one must exercise some care in measuring the frequency of the acoustic wave. It can of course, be determined approximately by direct observation of the signal on the screen of the oscilloscope. A conventional frequency counter is not much better, when short pulses are used, as described below in Sect. D. However, a more precise method of measuring the CW frequency used here was to superimpose the signal from the loaded oscillator (approximately 10 Mhz) with a 10 Mhz signal from a time mark generator (TMG) and to measure the beat frequency. The frequency at which the loaded transducer vibrates is then given by $f = 10 \text{ Mhz} \pm f'$ where f' is the measured beat frequency (usually about 0.5 Mhz). The frequency f was measured to an accuracy of 0.05%.

See Figs. (18) and (19) for schematic diagrams of the optical table and electronics.

The strain amplitude in calcium fluoride was measured by the method described by Parker, Kelly and Bolef.⁴⁹ For a longitudinal wave traveling in the $\langle 100 \rangle$ direction the strain amplitude of the fundamental wave, E is given by

$$(E)^2 = \left(\frac{2\lambda_L}{\pi T n^3} \right)^2 \frac{P+N}{2A} \left(1 - \frac{P+N}{2A} \right) \quad (\text{AI-13})$$

where T is the width of the ultrasonic beam which the light beam passes, p is a photoelastic constant, n is the index of refraction, and P , N , and A are the

Figure 19. Schematic diagram of electronics and optical table used for sound velocity measurements by the diffraction of light from ultrasonic waves in a transparent crystal. In this method, unlike that of Fig. 17, the physical dimensions of the crystal need not be known. In Fig. 21 an entire diffraction pattern is shown, obtained by placing a photographic plate in the plane of the detector.

intensities of the first positive, first negative and central orders of the diffraction pattern, respectively. These relations are valid in the regime $\lambda_s \gg \lambda_L$, a condition which was fulfilled. The strain amplitude was determined for a 10 Mhz X-cut, 12 mm diam quartz transducer. The oscillator was operated at $1/2$ the maximum power level, where E is proportional to the square root of the power level. An RCA No. 929 vacuum phototube with a 1 mm diam mask and having a linear response for the range of light intensities measured was used to detect the diffracted light from the beam of the Perkin-Elmer 2 mW He-Ne gas laser. A Keithley Model 600A Electrometer was used to measure the output signal from the phototube.

For calcium fluoride one has $n = 1.43$ at $6328 \text{ \AA}^0$,
 $p = p_{12} = 0.228$, ($p = p_{12}$ when the incident beam is polarized perpendicular to the acoustic wave, as was the case for the present measurement)

$T = 10 \text{ mm}$, and

$\lambda_L = 6328 \text{ \AA}^0$.

When the measured intensities $P \cong N$ and A were put in eq. (AI-13) one obtained the result

$$E = (2.6 \pm .5) \times 10^{-6}.$$

D. Diffraction of Light from Pulsed Ultrasonic Waves

In the diffraction of light experiments using CW oscillations a large amount of power, on the order of 1 watt, is generated at the transducer. Although for the calcium fluoride crystal at room temperature the effect is

negligible, for solid krypton the amount of heat input to the crystal would be so large that it would be impossible to maintain proper temperature control with the present system. For this reason a method of diffracting light from pulsed ultrasonic waves was developed.

The velocity of pulsed longitudinal acoustic waves traveling in the $\langle 100 \rangle$ direction was measured by detecting the diffracted beam from the pulsed acoustic wave. Pulses of 4 μ sec to 20 μ sec duration at a repetition rate of 500/sec were generated in the calcium fluoride crystal and a Princeton Applied Research Co. Model HR-8 lock-in amplifier was used to detect the diffracted beam (see Fig. (20)). The power input then for the pulsed method is only 0.2 to 1.0% of the power level used for the CW operation.

The lock-in amplifier was used to trigger the Tektronix oscilloscope and the signal from the gate "A" of the oscilloscope was used to trigger the oscillator. The signal from the fast photodetector was sensed by the lock-in amplifier with a Type A preamp and again the center of the diffracted beam was determined by looking for the maximum signal while scanning the diffracted beam with the movable stage.

The dominant frequency of the pulse was determined by the method of measuring the beat frequency of the superimposed pulse and 10 Mhz signal of the time-mark generator.

E. Results

With the transducer placed on the high-index face of the calcium fluoride crystal and the laser beam directed along the $\langle 100 \rangle$ direction, the complete diffraction pattern was observed (see Fig. 21). Due to limited latitude

Figure 20. Schematic diagram of the electronics and optical table for velocity of sound measurements by diffraction of light from pulsed ultrasonic waves in a transparent crystal. Pulsed operation reduces the power input to the specimen to less than 1% of that employed in the method of Fig. 19.

- a: Output reference signal for triggering oscilloscope,
- b: Oscilloscope trigger (Ext.),
- c: Gate "A" of oscilloscope,
- d: Input trigger for oscillator.

LOCK-IN
AMPLIFIER

OSCILLATOR

LASER

CRYSTAL

LENS

CHANNEL 1-2

OSCILLOSCOPE

TMG

MIRROR

DETECTOR

Figure 21. Photograph of the diffraction pattern from 6328 Å laser light directed normal to 10.4 Mhz acoustic waves in calcium fluoride. Focal length of the system was 181.2 cm. The transducer surface is perpendicular to the z direction and the direction of the laser beam is normal to the plane of the page. The outer ring originates from transverse acoustic waves, the inner ring from longitudinal acoustic waves. The pattern shows four-fold symmetry because the light was incident along a $\langle 100 \rangle$ crystal direction.

of the plate, the real sharpness of the pattern is not adequately represented in the reproduction.

With an X-cut or AC-cut transducer placed on the (100) face and the incident laser beam in the $\langle 010 \rangle$ direction, only one pair of diffracted spots is observed, resulting from longitudinal or from transverse waves, respectively, traveling in the $\langle 100 \rangle$ direction.

The elastic constants c_{11} and c_{44} were determined from measurements of spot separation observed when X-cut and AC-cut transducers were placed on the (100) face and the laser beam was directed perpendicular to the $\langle 100 \rangle$ direction. The elastic constant c_{12} was determined by measuring the spot separation of the transverse wave (fast shear) traveling along the $\langle 110 \rangle$ direction where, as shown in Fig. 22,

$$\rho v_{t_2}^2 = 1/2(c_{11} - c_{12}) \quad (\text{AI-14})$$

The accuracies of the velocity measurements are estimated to be 0.3% for the transverse and longitudinal waves traveling in the $\langle 100 \rangle$ direction and 0.6% for the shear wave traveling in the $\langle 110 \rangle$ direction. Contributions to the total uncertainty are: f the frequency, 0.05%; d the separation between the center of the slits 0.1%; a the distance from the central beam to the first maximum in the interference pattern of the fixed double slit, 0.1%; and finally, D the displacement of the diffracted peak from the central beam, 0.05% for waves traveling in the $\langle 100 \rangle$ direction and 0.35% for the transverse wave traveling in the $\langle 110 \rangle$ direction.

Figure 22. Schematic diagram of the diffraction pattern observed when longitudinal and transverse waves are simultaneously excited in a crystal and the incident light beam is normal to the (100) plane. The relationships between the spot separation along the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions and the elastic constants are given.

$$100 \quad \rho v_L^2 = C_{11}$$

$$\rho v_T^2 = C_{44}$$

$$110 \quad \rho v_{T_2}^2 = \frac{1}{2} (C_{11} - C_{12})$$

$$C_{11} = \frac{K}{(dd)^2}$$

$$C_{44} = \frac{K}{(aa)^2}$$

$$C_{12} = K \left[\frac{1}{(dd)^2} - \frac{2}{(bb)^2} \right]$$

$$K = 4\rho(\lambda_L F f)^2$$

ρ = density

f = CW frequency

F = system focal length

λ_L = wavelength of light

The results of the measurements are:

$$F = 181.2 \text{ cm}$$

$$d = 0.2763 \text{ cm}$$

$$a = 0.04150 \text{ cm}$$

$$D (\text{long. } \langle 100 \rangle) = 0.1664 \text{ cm}$$

$$D (\text{trans. } \langle 100 \rangle) = 0.3628 \text{ cm}$$

$$D (\text{trans. } \langle 110 \rangle) = 0.2799 \text{ cm}$$

Then one obtains

$$v_l \langle 100 \rangle = 7217 \text{ m/sec}$$

$$v_t \langle 100 \rangle = 3268 \text{ m/sec}$$

$$v_{t_2} \langle 110 \rangle = 4331 \text{ m/sec} .$$

And these correspond to values of the elastic constants

$$c_{11} = 16.56 \times 10^{10} \text{ N/m}^2$$

$$c_{12} = 4.63 \times 10^{10} \text{ N/m}^2$$

$$c_{44} = 3.396 \times 10^{10} \text{ N/m}^2$$

These results are in agreement with those values obtained by the pulse-echo technique.

For the pulse length used here in the diffraction of light from pulsed ultrasonic waves, the pulse train was longer than the width of the laser beam

and so the diffracted beam can be interpreted as a CW train being turned on and off periodically.

The result of the measurement of light diffracted from pulsed ultrasonic waves is:

$$v_l \langle 100 \rangle = 7215 \text{ m/sec}$$

which corresponds to a value

$$c_{11} = 16.55 \times 10^{10} \text{ N/m}^2.$$

This is in agreement with the other measurements.

Table (VII) lists the results of this work and those of other investigators who have measured the adiabatic elastic constants of calcium fluoride. The values of c_{11} measured here are slightly higher than all the other measurements reported, whereas the values of c_{12} and c_{44} are slightly lower than the average value of the earlier measurements.

The results of previous investigators have differed rather markedly, especially for the constant c_{12} . The agreement achieved in the present work for values obtained by independent methods is therefore gratifying. Different factors enter into the estimate of error in each of the two methods used here. Whereas the pulse echo work is of course independent of any properties of the optical system, the optical work is quite independent of the specimen dimensions and of the transit time calibration.

Table VII
Adiabatic Elastic Constants of Calcium Fluoride

Investigator	Method	T, K	ρ gm/cc	c_{11} 10^{10} N/m ²	c_{12} 10^{12} N/m ²	c_{44} 10^{10} N/m ²	c_{11}/c_{44}
Voigt (1910) ^a	Mechanical	300	3.180	16.38 ^(c)	4.48	3.38	4.84
Bh'g'vtn (1955) ^b	Not specified	293	3.180	16.44 ^(c)	5.02	3.47	4.74
Bergman (1949) ^d	Optical, CW	293	3.18	16.44 ^(c)	4.63	3.61	4.56
(1957)	Optical, CW	293	3.8	16.28 $\pm$.16	4.33 $\pm$.04	3.34 $\pm$.03	4.88
Huffman & Norwood (1960) ^e	Pulse echo	300	3.1795	16.4 $\pm$.13	5.3 $\pm$.2	3.37 $\pm$.007	4.87
Haussuhl (1963) ^f	Optical, CW	293	3.1804	16.357 $\pm$.034	4.401 $\pm$.02	3.392 $\pm$.015	4.88
Wong & Schuele (1967) ^g	Pulse echo	298	3.181	16.42 ^(c)	4.398	3.370	4.87
Ho & Ruoff (1967) ^h	Pulse echo	296	3.1795	16.484 $\pm$.008	4.458 $\pm$.006	3.377 $\pm$.003	4.88
Elcombe & Pryor (1970) ⁱ	Model average			16.48 $\pm$.01	4.46 $\pm$.01	3.38 $\pm$.01	
Present work		297	3.1795				
	Pulse echo			16.49 $\pm$.01	4.52 $\pm$.05	3.386 $\pm$.002	4.86
	Optical, CW			16.56 $\pm$.1	4.62 $\pm$.05	3.396 $\pm$.02	4.88
	Optical, pulse			16.55 $\pm$.1			

a) W. Voigt, Lehrbuch der Kristall Physik, (Teubner, Leipzig, 1919), p. 744.

b) S. Bhagavantam, Pro. Ind. Acad. Sci., A41, 78 (1955).

c) No error stated.

d) L. Bergman, Der Ultraschall, (Hirzel, Zurich, 1949).

L. Bergman, Z. Naturf., 12a, 229 (1957).

e) D. R. Huffman and M. H. Norwood, Phys. Rev., 117, 709 (1960).

f) S. Haussuhl, Phys. Stat. Solidi, 3, 1072 (1963).

g) C. Wong and D. E. Schuele, J. Phys. Chem Solids (GB) 28, 1225 (1967).

h) P. S. Ho and A. L. Ruoff, Phys. Rev., 161, 864 (1967).

i) M. M. Elcombe and A. W. Pryor, J. Phys. C; Solid St. Phys. 3 492 (1970);
this paper gives phonon dispersion data from neutron scattering.

APPENDIX II: DIFFRACTION OF LIGHT EXPERIMENT ON SOLID KRYPTON

The technique of measuring the velocity of sound in solids by diffraction of light from ultrasonic waves is particularly useful because the technique is independent of the geometry of the solid, single grains are necessary only where the light beam penetrates the solid, and both longitudinal and transverse waves can be observed simultaneously.

Although this technique was successfully employed with the calcium fluoride crystal several problems were encountered in attempting the diffraction of light experiment in solid krypton. The experience however, has suggested modifications which may make the experiment feasible. Fig. (23) shows the typical krypton cell used. The main problems encountered were in maintaining single crystal growth in the region of the optical windows, in distortion of the diffracted beam due to bulging windows, in exciting ultrasonic waves capable of diffracting the light beam, in preventing heat input to the specimen from CW oscillations and finally, in maintaining transducer bonding while the crystal is cooled.

The thermal conductivity k of Kapton and glass are of the same order of magnitude near the triple point of krypton (115.78 K). The value of k is 0.006 watt/cm K. The glass windows are about 25 times thicker than the Kapton and therefore the thermal conduction is approximately 25 times greater in the glass. This larger thermal conduction apparently prevents proper temperature gradients from being established along the sides of the tube wall resulting in the nucleation of solid on the glass windows during crystal growth.

As the solid-liquid interface approaches the optical windows during crystal growth the edges turn up sharply, making the interface distinctly

Figure 23. Krypton cell used for diffraction of light experiments. Under the low temperature conditions necessary for growing the krypton specimens distortion of the system optics occurred, due to bulging windows caused by the high vapor pressure of liquid krypton. This distortion could not be corrected at low temperatures as it was for the same system at room temperature. a: Copper block which was cemented to the Kapton tube.²⁰ b: Glass windows 0.75 mm thick, 12 mm on each side. c: Hole, 5 mm diam, cut in Kapton tube for laser beam. d: Quartz transducer. e: Kapton tube 0.05 mm thick, 4.5 cm long overlapping copper blocks at top and bottom of specimen tube.

concave toward the liquid. Attaching heaters around the edges of the glass windows would keep the sides of the crystal warm and might keep the sides of the crystal from growing ahead of the central core. Maintaining this convex configuration of the liquid-solid interface is important as it prevents nucleation of small crystals along the Kapton or glass walls which would ruin the single crystal property of the specimen.

Cutting holes in Kapton with a 0.05 mm wall thickness and cementing²⁰ glass windows to the Kapton was proven feasible with respect to the problem of maintaining a vacuum seal inside the specimen chamber under the vapor pressure of condensed krypton (triple point pressure about 0.7 bar) in the specimen tube. But windows thicker than the 0.75 mm thick windows used here would be necessary in order to minimize distortion in the optical system. The distortion is caused by pressure inside the specimen tube bending the glass windows.

Before any attempt to grow a krypton specimen in a specimen tube with glass windows, tests were made to determine the effects of such bulging windows on the system optics. A specimen tube was filled with water (index 1.33) and pressurized to nearly 0.6 bar. A significant amount of astigmatism was found to be present. The focal length of the horizontal line was about 250 cm and of the vertical line about 130 cm. The normal focal length of the unpressurized system was about 181 cm.

In order to correct for the astigmatism, two cylindrical lenses of +0.125 and -0.250 diopters were placed between the focusing lens and specimen cell. When the lenses were properly aligned the astigmatism was essentially corrected. Nevertheless, under the low temperature condition present for growing the krypton specimen the distortion present with liquid krypton [unclear] ...

(index 1.3)⁵⁰ in the cell was much worse and could not be corrected. The difference might have been due to pronounced temperature dependence of the elasticity of Kapton. Information on such properties became available⁵³ only after the present work was directed to pulse-echo methods.

If we assume the pressure inside the specimen tube causes a simple bowing of the window, the radius of curvature can be related approximately (for small displacements) to the displacement of the center of the glass window from its flat configuration. If x is the displacement of the center of the window then one can write, if $x \ll$ than the length of one side of the window

$$R \propto 1/x. \quad (\text{AII-1})$$

As described by Timoshenko,⁵¹ the displacement x is proportional to the cube of the thickness of the glass h :

$$x \propto 1/h^3. \quad (\text{AII-2})$$

Then one has

$$R \propto h^3. \quad (\text{AII-3})$$

For a simple lens the radius of curvature is proportional to the focal length so:

$$f \propto h^3. \quad (\text{AII-4})$$

If the lens distortion is small enough to cause the focal length of the specimen tube under pressure to be greater than about 1000 cm, the net effect of the bulging windows on the system optics would be negligible. The focal length observed with liquid krypton in the specimen tube was about 20 to 30 cm. A window thickness of 3 mm (4 times the present thickness used) would therefore substantially eliminate the distortion of the system optics due to bulging specimen tube windows. Thicker windows would also be more convenient since it would be easier to make them optically flat.

During the present work, scattering from CW oscillations was observed in liquid krypton but the window distortions prevented accurate velocity measurements from being made. Diffracted light was observed from the liquid even after some solid had grown over the transducer, yet when the solid-liquid interface has reached the glass windows the attenuation in the solid was great enough to prevent diffracted spots from being observed.

Serious attenuation problems near the base of the crystal may be caused by dislocations arising from differential thermal contraction between transducer and the crystal during crystal growth.

The top of the crystal may be a more desirable place to generate CW oscillations. In addition to eliminating the problem of attenuation near the base of the crystal there is the advantage of having a shorter path to the windows and therefore much less attenuation resulting in a stronger acoustic wave to diffract the laser beam.

The high heat input to the specimen during CW operation is most easily avoided by using lock-in amplifier techniques as described in Appendix I. Short pulses and low repetition rates will decrease the heat input to the specimen to a practically negligible amount.

The problem of maintaining transducer bonding as the crystal temperature is lowered is also present in pulse-echo techniques. Experiences of this work and results and comments of other experimenters⁷ strongly indicate that the problem may be solved by first growing the crystal on a flat substrate and then imbedding the transducer into the top surface of the crystal.

Using thicker windows, keeping the windows warm during crystal growth, imbedding the transducer into the top of the crystal and using lock-in techniques to minimize specimen heating are all improvements which would increase the possibility of observing the optical diffraction pattern from acoustic waves in the noble gas crystals.

APPENDIX III. COMPUTER PROGRAM FOR DETERMINING SINGLE CRYSTAL ELASTIC CONSTANTS

A search for compatability of the earlier work by Moeller and Squire⁹ on the elastic constants of solid argon with the bulk modulus results of Urvas et al.²⁴ was carried out. It used a program developed to determine the adiabatic elastic constants of a cubic crystal from the single crystal velocity data and a given orientation by scanning direction cosines (l,m,n) in the irreducible portion of the Brillouin zone with the given velocity data. For the measurements of Moeller and Squire an orientation was sought, different from the $\langle 110 \rangle$ orientation they arbitrarily assumed, which would result in elastic constants giving the bulk modulus estimated from the work of Urvas et al. (see Section IV.C).

The solution to the problem defined above requires finding the roots of the secular equation for a cubic crystal. This involves finding a solution to the following expression:

$$(\rho v^2 - c_{44})^3 - (c_{11} - c_{44}) \cdot (\rho v^2 - c_{44})^2 + \quad (\text{AIII-1})$$

$$[(c_{11} - c_{44})^2 - (c_{12} + c_{44})^2] \cdot (\rho v^2 - c_{44}) \cdot (\ell_m^2 + m_n^2 + \ell_n^2) -$$

$$(c_{11} - c_{12} - 2c_{44})^2 \cdot (c_{11} + 2c_{12} + c_{44}) (\ell_{mn})^2 = 0$$

Setting for simplicity:⁵²

$$a = c_{11} - c_{44} \quad (\text{AIII-2})$$

$$b = c_{12} + c_{44} \quad (\text{AIII-3})$$

$$H = \rho v^2 - c_{44} \quad (\text{AIII-4})$$

$$\Sigma = \ell^2 m^2 + m^2 n^2 + \ell^2 n^2 \quad (\text{AIII-5})$$

$$\pi = (\ell mn)^2 \quad (\text{AIII-6})$$

one has

$$H^3 - H^2 a + (a^2 - b^2)(\Sigma)H + (a-b)^2(a+2b)\pi = 0 \quad (\text{AIII-7})$$

which is a set of three equations (one for each of the three acoustic waves) cubic in c_{11} , c_{12} , and c_{44} .

Given the three velocities v_ℓ , v_{t_1} , v_{t_2} , the density ρ , the polar and azimuthal angles θ and ϕ , and initial guesses for c_{11} , c_{12} , and c_{44} a solution to equation (AIII-1) can be found by using a modified Newton-Raphson method of iteration. The computer program solves equation (AIII-1) for 120 points in the irreducible portion of the Brillouin zone for each set of velocities, given initial guesses for the elastic constants. The method of iteration is described next.

From expression (AIII-1) there are three equations, one for each of the three velocities. If $x = c_{11}$, $y = c_{12}$, $z = c_{44}$ these three equations can be written:

$$F(x,y,z) = 0$$

$$G(x,y,z) = 0 \quad (\text{AIII-8})$$

$$H(x,y,z) = 0$$

Expanding each expression in a Taylor series yields, for example:

$$\begin{aligned} F(x,y,z) = & F(x_o, y_o, z_o) + (x-x_o) \left. \frac{\partial F}{\partial x} \right|_o \\ & + (y-y_o) \left. \frac{\partial F}{\partial y} \right|_o + (z-z_o) \left. \frac{\partial F}{\partial z} \right|_o, \end{aligned} \quad (\text{AIII-9})$$

where x_o, y_o, z_o , are the initial guesses for the elastic constants. We want $F(x,y,z) = 0$,

so then

$$\Delta x F_x + \Delta y F_y + \Delta z F_z = -F, \quad (\text{AIII-10})$$

and similarly

$$\Delta x G_x + \Delta y G_y + \Delta z G_z = -G \quad (\text{AIII-11})$$

$$\Delta x H_x + \Delta y H_y + \Delta z H_z = -H, \quad (\text{AIII-12})$$

where the subscripts indicate partial derivatives and

$$\Delta x = x_{K+1} - x_K$$

$$\Delta y = y_{K+1} - y_K$$

$$\Delta z = z_{K+1} - z_K,$$

where k indicates the k^{th} iteration. Equations (AIII-10,11,12) are solved for Δx , Δy , Δz which results in new guesses for x , y , and z . This process is continued until $\frac{\Delta x}{x}$, $\frac{\Delta y}{y}$, $\frac{\Delta z}{z}$ are all less than 10^{-4} .

This program works best for directions not close to the principal crystal directions $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$.

Figure (24) shows the entire computer program.

Figure 24. Computer program for determining the second-order elastic constants from a given set of velocity measurements on a crystal of arbitrary orientation. Initial guesses for c_{11} , c_{12} , c_{44} are required. For each set of velocity measurements the elastic constants are determined for 120 points in the irreducible Brillouin zone where the direction of wave propagation is expressed in terms of the polar and azimuthal angles theta and phi. For both input and output, velocities are in units of 10^5 cm/sec, densities in gm/cm^3 , elastic constants in 10^{10} dynes/cm², compressibility in 10^{-10} cm²/dyne, angles in degrees. The output gives the angles theta and phi, elastic constants, adiabatic compressibility XI, deviation from the Cauchy relation DL and the inverse of the anisotropy AN.

```

      GO
      FASTRAN
      DIJMP
      DIJNCH OBJECT
      ARGON      RODEG KELVIN
      CALCULATE C11,C12,C44, FROM VT1,VT2,VL      GIVEN THETA AND PHI
      C IN UNITS OF 10EXP10 DYNES/CM**2
      XI IN UNITS OF 10EXP-10 CM**2/DYNE
      A,B,C, = RHO*VFL**2
      FFUNCF(X,Y,Z)=(A-Z)**3-(X-Z)*((A-Z)**2)+(((X-Z)**2)-((Y+Z)**2))*S*
      1(A-Z)-((X-Y-2.0*Z)**2)*(X+2.0*Y+Z)*P
      GFUNCF(X,Y,Z)=(B-Z)**3-(X-Z)*((B-Z)**2)+(((X-Z)**2)-((Y+Z)**2))*S*
      1(B-Z)-((X-Y-2.0*Z)**2)*(X+2.0*Y+Z)*P
      HFUNCF(X,Y,Z)=(C-Z)**3-(X-Z)*((C-Z)**2)+(((X-Z)**2)-((Y+Z)**2))*S*
      1(C-Z)-((X-Y-2.0*Z)**2)*(X+2.0*Y+Z)*P
      DFDXF(X,Y,Z)=-((A-Z)**2)+2.0*(A-Z)*(X-Z)*S-2.0*(X+2.0*Y+Z)*(X-Y-2.
      0*Z)*P-((X-Y-2.0*Z)**2)*P
      DFDYF(X,Y,Z)=-((B-Z)**2)+2.0*(B-Z)*(X-Z)*S-2.0*(X+2.0*Y+Z)*(X-Y-2.
      0*Z)*P-((X-Y-2.0*Z)**2)*P
      DFDZF(X,Y,Z)=-((C-Z)**2)+2.0*(C-Z)*(X-Z)*S-2.0*(X+2.0*Y+Z)*(X-Y-2.
      0*Z)*P-((X-Y-2.0*Z)**2)*P
      DGDYF(X,Y,Z)=-((B-Z)**2)+2.0*(B-Z)*(X-Z)*S-2.0*(X+2.0*Y+Z)*(X-Y-2.
      0*Z)*P-((X-Y-2.0*Z)**2)*P
      DGDZF(X,Y,Z)=-((C-Z)**2)+2.0*(C-Z)*(X-Z)*S-2.0*(X+2.0*Y+Z)*(X-Y-2.
      0*Z)*P-((X-Y-2.0*Z)**2)*P
      DHDYF(X,Y,Z)=-((C-Z)**2)+2.0*(C-Z)*(X-Z)*S-2.0*(X+2.0*Y+Z)*(X-Y-2.
      0*Z)*P-((X-Y-2.0*Z)**2)*P
      DHDZF(X,Y,Z)=-((C-Z)**2)+2.0*(C-Z)*(X-Z)*S-2.0*(X+2.0*Y+Z)*(X-Y-2.
      0*Z)*P-((X-Y-2.0*Z)**2)*P
      DIMENSION Q(20,3),P(20),DETERM(1)
65      RIT 7,75,RHO,VL,VT1,VT2,GESC11,GESC12,GLSC44
75      FORMAT(7F10.0)
      DO 50 K=1,15
      TH=(3.141593/2.0)-(((2.0*3.141593)/120.0)*FLOATF(K-1))
      X=GESC11
      Y=GESC12
      Z=GESC44
      L=(16-K)
      DO 50 J=1,L
      CALL TIMIRS
      FI=(3.141593/4.0)-(((2.0*3.141593)/120.0)*FLOATF(J-1))
      W=COS(TH)
      CFI=COS(FI)
      U=(SORT(1.0-W**2))*CFI
      TT=(1.0-U**2-W**2)
      IF (TT) 50,51,51
51      V=SQRT(TT)
      THETA=(TH/(2.0*3.141593))*360.0
      PHI=(FI/(2.0*3.141593))*360.0
      S=(U**2)*(V**2)+(V**2)*(W**2)+(U**2)*(W**2)
      P=(U**2)*(V**2)*(W**2)
      A=RHO*(VL**2)
      R=RHO*(VT1**2)
      C=RHO*(VT2**2)

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5.   TIME=TIMIRD(0)
      IF (TIME-180.0) 6,50,50
6.   Q(1,1)=DEDXF(X,Y,Z)
      Q(1,2)=DEDFYF(X,Y,Z)
      Q(1,3)=DEFDZF(X,Y,Z)
      Q(2,1)=DGDXF(X,Y,Z)
      Q(2,2)=DGDYF(X,Y,Z)
      Q(2,3)=DGDZF(X,Y,Z)
      Q(3,1)=DHDXF(X,Y,Z)
      Q(3,2)=DHDYF(X,Y,Z)
      Q(3,3)=DHDZF(X,Y,Z)
      R(1)=-FFUNCF(X,Y,Z)
      R(2)=-GFUNCF(X,Y,Z)
      R(3)=-HFUNCF(X,Y,Z)
      CALL MATINV(Q,3,R,1,DETERM)
      X=X+R(1)
      Y=Y+R(2)
      Z=Z+R(3)
      TESTX=ARSF(P(1)/X)
      TESTY=ARSF(P(2)/Y)
      TESTZ=ARSF(P(3)/Z)
      AX=ARSF(X)
      AY=ARSF(Y)
      AZ=ARSF(Z)
      IF (AX-1.0E+04) 2,50,50
2.   IF (AY-1.0E+04) 3,50,50
3.   IF (AZ-1.0E+04) 4,50,50
4.   IF (TESTX-1.0E-04) 10,5,5
10.  IF (TESTY-1.0E-04) 20,5,5
20.  IF (TESTZ-1.0E-04) 30,5,5
30.  XI=3.0/(X+2.0*Y)
      DL=(Z-X)/X
      AN=(X-Y)/(2.0*Z)
      WOT6,40,THETA,PHI,X,Y,Z,XI,DL,AN,DETERM
40.  FORMAT( /,1X,6HTHETA=,F6.3,2X,4HPHI=,F6.3,8X,4HC11=,F8.4,2X
1,4HC12=,F8.4,2X,4HC44=,F8.4,6X,3HXI=,E9.3,4X,3HDL=,F7.4,4X,3HAN=,F
27.4,1X,F12.4)
50.  CONTINUE
      GO TO 65
      FND

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