

Sound Measurements in Liquid and Solid He³, He⁴, and He³-He⁴ Mixtures*†

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Using the ultrasonic pulse technique at a carrier frequency of 10 Mc/sec, we have measured the longitudinal velocity of sound in liquid and solid He³, He⁴, and He³-He⁴ mixtures (0.0, 5.03, 25.0, 74.9, 98.00, 99.84% He³) in the temperature range from 1 to 4.2°K and the pressure range from 1 to 150 atm. An upper limit to the attenuation of sound in the region of the solid investigated is on the order of 0.3 to 0.7 cm⁻¹. Values of the adiabatic compressibility of the liquid along the melting curve of He⁴ are given. The discontinuity in the propagation velocity at a first-order phase boundary was utilized to locate the solidification curves of these samples and also to investigate the bcc-hcp crystallographic transition in solid samples, including pure He⁴, similar to that observed in pure He³ by Grilly and Mills. The triple points for this transition in He⁴ are given by $T_t = 1.449 \pm 0.003^\circ\text{K}$, $P_t = 26.18 \pm 0.05$ atm; $T_u = 1.778 \pm 0.003^\circ\text{K}$, $P_u = 30.28 \pm 0.05$ atm. The upper triple points for the mixtures lie on a straight line connecting He³ and He⁴ in temperature-pressure space. In addition, by observing the peak in the attenuation of sound, it was possible to measure the λ line in He⁴ and in the 5.0% and 25.0% He³ liquid mixtures. The upper λ point for pure He⁴ is given by $T_\lambda = 1.765 \pm 0.003^\circ\text{K}$ and $P_\lambda = 29.90 \pm 0.05$ atm. Comparison is made with existing data wherever possible.

I. INTRODUCTION

HELIUM, unlike all other substances, is greatly affected on a macroscopic level by quantum effects at low temperatures and pressures. One manifestation of this is the marked difference in the thermodynamic properties displayed by the two isotopes, He³ and He⁴. The properties of pure He³ and He⁴ have been studied in great detail, but much remains to be learned about mixtures of these two isotopes.¹

In order to gain some further insight into the behavior of such quantum mixtures, velocity-of-sound measurements have been made on liquid and solid He³-He⁴ mixtures. This type of measurement is of value not only because of the relation between the velocity of sound and the equilibrium properties of the mixture, but also because of its sensitivity to phase transitions. In particular the hcp-bcc transition, previously observed in pure solid He³, has been investigated in pure He⁴ and in several He³-He⁴ mixtures. In addition freezing curves and λ lines of several isotopic mixtures have been obtained.

This article is a detailed report of work reported earlier.²⁻⁴

II. APPARATUS

The objective of this research was to measure the longitudinal velocity of sound in liquid and solid He³-He⁴ mixtures in a temperature range from 1 to 4.2°K and a pressure range from 1 to 150 atm. Although the commonly used techniques for obtaining velocity measurements all yield approximately the same accuracy, the ultrasonic pulse technique was chosen over the acoustical interferometer and optical diffraction methods because it minimizes the heat input to the sample and is easily adapted to low-temperature and high-pressure investigations. There is some question of the validity of this method if the sample under investigation shows dispersion; however, for liquid helium this is not the case, there being less than $\frac{1}{2}\%$ change in the velocity over the frequency range 0.22 to 15 Mc/sec.⁵

The sound cavity used in the majority of the experiments is shown in Fig. 1. A two-transducer system was

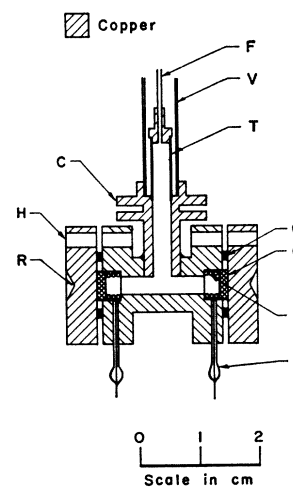


FIG. 1. Scale drawing of sound cavity showing how the quartz transducers (Q) are supported.

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¹ K. W. Taconis and R. de Bruyn Ouboter, *Progress in Low Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1964), Vol. 4, p. 38.

² J. H. Vignos and H. A. Fairbank, *Phys. Rev. Letters* 6, 265 (1961).

³ J. H. Vignos and H. A. Fairbank, *Bull. Am. Phys. Soc.* 7, 77 (1962).

⁴ J. H. Vignos and H. A. Fairbank, *Proceedings of the Eighth International Conference on Low Temperature Physics*, edited by R. O. Davies (Butterworths Scientific Publications, Washington, D. C., 1963), p. 31.

⁵ A. van Itterbeck, *Physica* 20, 133 (1954); A. van Itterbeck, G. Forrez, and M. Teirlinck, *ibid.* 23, 905 (1957).

chosen because it eliminates the decoupling problems in the electronics and reduces the restrictions due to ringing which arise when one uses the same transducer for transmission and reception. In determining the optimum operating frequency (f) and cavity dimensions, there are many factors which come into play: a workable volume for the sample cavity, limited by the capacity of the gas handling system (≈ 0.3 cc); the desired percentage error in the velocity measurements ($\frac{1}{4}\%$); the rise time of the sound pulses ($\approx 0.35 Q/f$, where $Q = f/\Delta f$); the Fraunhofer limit for spreading of the sound beam ($\approx r^2 f/c$, where c is the velocity of sound and r is the cavity radius); ringing of the crystal; and finally the over-all attenuation of the sound pulse ($\approx f^2 L$, where L is the length of the cavity). Optimization of these factors lead us to an operating frequency of 10 Mc/sec, a cavity radius of 5 mm and a cavity length of 20 mm. The two x-cut quartz crystals (Q), gold plated on both sides, were spring mounted (S) against the end caps in order to maintain the transducer alignment during solidification. Teflon inserts with a thickness of 2 mils were used to insulate the springs electrically from the cavity. Electrical contact was made to the transducers via the springs (S) through epoxy seals (E). These seals were made by first soldering a half-inch length of copper capillary (0.050 in. o.d.-0.012 in. i.d.) into the cavity. After etching and cleaning the outside end of the capillary, a 10-cm length of No. 40 formvar-covered copper wire was passed through it. The end was then sealed with epoxy resin⁶ and cured at room temperature for two days. These seals were found to be very reliable down to helium temperatures and up to 150 atm. The body of the cavity served as an electrical ground. In order to know the sample pressure during runs with solid helium, special precautions were taken to keep the fill line (F) open at all times. Plastic flow was then relied on to relieve any pressure gradients within the cavity. The CuNi fill line (0.030-in. o.d.-0.012-in. i.d.) was brought down through the vacuum jacket (V), thus allowing heat to

come down from the room-temperature end. This heat was then removed by the bath before reaching the sound chamber through the fins (C). The temperature gradient between the end of the fill line and the bath was determined primarily by the conductivity of the sample in the stainless-steel tube (T). In the event that this gradient would not be enough to maintain the solid-liquid interface within T, a small heater was wrapped around the flange connecting the fill line to the tube (T). It was found experimentally that this heater was unnecessary. In order to check whether there was any increase in cavity temperature due to the intentional heat leak, the freezing and λ curves of pure He⁴ were determined with and without the vacuum jacket (V). The results were identical. In order to eliminate echoes from the sound radiated in the back direction, conical cuts (R) were made in the end caps. The O-ring seals (O) used to seal the end caps were fabricated from 95% lead-5% antimony wire (diam.=0.015 in.).

The electronic circuitry employed is fairly standard and is shown for reference in Fig. 2. The pulsed 10-Mc/sec oscillator consists simply of a resonant circuit which is activated via a thyatron. The transmitted pulse (picked up by stray inductive and capacitive coupling) and the received signals are displayed together with a timing pulse on a Tetrionix 535 oscilloscope with a dual-trace plug-in unit. By making use of the delayed-sweep circuit in this scope, it is possible to measure the time-of-flight directly to an accuracy limited only by the rise times of the pulses. A sample of one of the better waveforms obtained in solid helium is displayed in Fig. 3. Under the best conditions with liquid helium, when as many as 20 echoes were visible, it was observed that the time between the transmitted and first received pulses was more than half the time between the first and second received pulses. This discrepancy (0.15 ± 0.05 μ sec) appears to stem from a delay incurred within the transmitting crystal in the conversion of electrical to mechanical energy and within the receiving crystal in the inverse process. For measurements between two successive echoes, the time of flight is not altered by this effect since all received pulses are delayed equally at the receiving crystal. A correction for this effect (always less than 0.7%) was applied to all measurements where applicable.

The cryostat, for maintaining the sound cavity at any given temperature between 1 and 4.2°K, is of standard design, consisting of an outer Dewar for liquid nitrogen and an inner Dewar for liquid helium. The sound cavity itself is immersed directly in the helium bath. The temperature of the bath was determined from its vapor pressure, using the T_{68} scale.⁷ To measure the vapor pressure, both a mercury and an oil manometer were used. Above the lambda point, a correction for the pressure head due to the liquid helium was applied. The error of our temperature measurement is

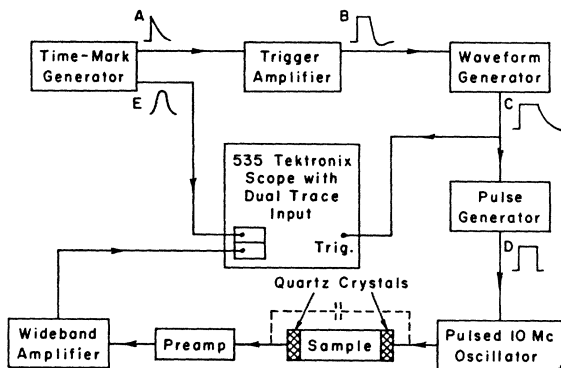


FIG. 2. Block diagram of the electronic circuitry.

⁶ Stycast 2850 GT (using Catalyst No. 11), Emerson and Cummings, Inc., Canton, Massachusetts.

⁷ F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Res. Natl. Bur. Std. (U. S.) 64A, 1 (1960).

estimated to be $\pm 0.001^\circ\text{K}$, except at temperatures below 1.25°K where the error begins to rise, reaching a value of $\pm 0.006^\circ\text{K}$ at 1.05°K . A mechanical pressure regulator, designed by Walker,⁸ was inserted into the pumping line to maintain the temperature of the bath at a constant value. Within the accuracy of the temperature measurement, this controller was able to maintain the temperature constant for several hours.

The gas-handling system consisted of a glass low-pressure system and a metal high-pressure system. The glass system, which contained two manually operated Toepler pumps, was designed for the handling and mixing of gaseous He³ and He⁴ at pressures up to about 2 atm. Volume calibrations of the Toepler pumps, between various fiducial marks and of all the glassware in the system, were made, so that mixtures of any desired concentration could be prepared. A stainless-steel Toepler pump was used to pressurize the sample to 150 atm. For measurements up to 50 atm a 0–50 atm Bourdon gauge with an accuracy of ± 0.50 atm was used, and from 50 to 150 atm a 0–200 atm gauge with an accuracy of ± 0.2 atm was used.⁹ These gauges were checked against a dead-weight gauge before the experiment and found to be within the quoted accuracy. Pressure was obtained from commercial high-pressure nitrogen tanks, which have a maximum pressure of approximately 160 atm. Since the pressure gauges were inserted on the high-pressure side of the Toepler pump, hydrostatic head corrections for the mercury column had to be made. The device used to locate the mercury levels for this correction was a differential transformer which sensed the position of a steel ball floating on the mercury surfaces. The accuracy in the head corrections using this mercury level indicator is in all cases ± 0.01 atm or better.

III. PROCEDURE

Over a good portion of the liquid region investigated, the attenuation of sound is large enough that the position of the foot of the second received pulse is difficult to locate. For accurate measurements this requires that the time-of-flight correction, mentioned before, be determined in the region of small attenuation, so that only the transmitted and first received pulses need be measured. Time-of-flight measurements in liquid helium were taken as a function of pressure at constant temperature.

The location of the lambda line was determined by noting the maximum in the sound attenuation as the pressure was varied at constant temperature.

The method of observing the pressure at which freezing or melting occurs (the temperature being held fixed), depends on whether the fill line is in contact with or isolated from the bath. In the former case there occurs at freezing a small disturbance in the time-of-

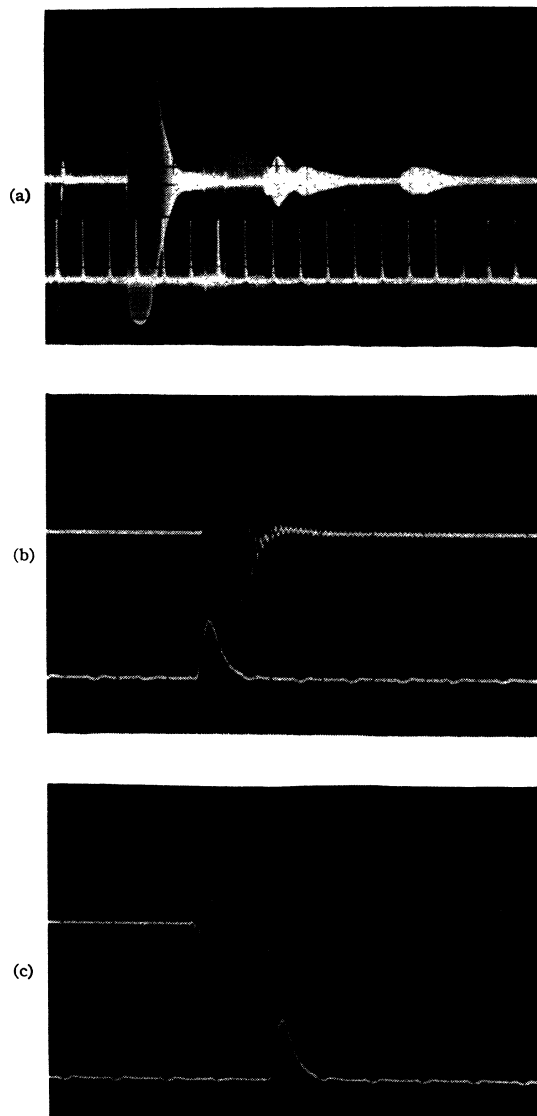


FIG. 3. Photographs of one of the better signals observed in solid helium. (a) Upper trace—transmitted and received pulses plus two echoes; lower trace—timing pulses 10 μsec apart. (b) Upper trace—enlarged view of transmitted pulse; lower trace—small timing pulses 1 μsec apart. (c) Upper trace—enlarged view of first received pulse; lower trace—small timing pulses 1 μsec apart.

flight, at which point the line blocks. Further increase in the pressure has no effect on the signal. Melting is observed in reverse order; a small disturbance occurs in the time-of-flight, after which the time-of-flight increases with decreasing pressure. In the case where the fill line is isolated from the bath, blockage does not occur in the line. Instead, when the freezing curve is reached, the signal starts to jitter in time and amplitude, and then finally disappears. After 5 to 30 min, if conditions are “right,” a new signal appears indicating the propagation of sound through the solid. The amplitude of this signal increases with time in an oscillatory

⁸ E. J. Walker, Rev. Sci. Instr. 30, 834 (1959).

⁹ Heise Bourdon Tube Company, Inc., Newtown, Connecticut.

manner, finally reaching a constant value which is not reproducible from run to run. It is not exactly clear what is taking place during the time when no signal is present. It is true, of course, that it takes a finite time to remove the heat of fusion and to get the additional mass into the cavity. This, however, judging from the few seconds it takes to go from a solid to a liquid signal, is not a factor here. Recently Sha'nikov¹⁰ made some interesting visual observations of the solidification of helium. He concludes that, without taking any special precautions, helium usually solidifies in the form of "snow" or "hail." If this is true in the present experiment, then a reasonable explanation is that plastic flow is taking place, which allows good contact to be made gradually between the helium crystals (and possibly the growth of large single crystals) and also between the quartz transducers and the helium. Once a signal appears in the solid, the melting point is determined by lowering the pressure until the signal vanishes.

In the case of sound measurements in the solid, the sample was formed at a constant pressure by reducing the temperature from a point just above the freezing curve. Experimentation has shown that with the fill line isolated from the bath, as it was during these measurements, the line remained unblocked, hence ensuring pressure transmission to the solid. The time-of-flight was measured as a function of temperature, the pressure being held constant. A small correction, similar to that mentioned in the liquid case, was applied to the time-of-flight.

The crystallographic phase transition in solid helium was located by noting the discontinuity in the velocity of sound (4 to 12%) as the pressure was varied at constant temperature and vice versa.

IV. RESULTS AND DISCUSSION

1. Helium Concentrations

The six samples investigated in the course of this research are listed in Table I. The pure He⁴ was obtained from the Linde Company. Mixture *E*, which was supposed to be pure He³ from the Oak Ridge National Laboratory, was found to contain 2.0% He⁴ when analyzed mass-spectrometrically. Purification of this

TABLE I. Concentration analysis of samples investigated in this work.

Mixture	% He ³	% He ⁴
<i>A</i>	≤0.0001	100.000
<i>B</i>	5.03±0.05	94.97±0.05
<i>C</i>	25.0 ±1.2	75.0 ±1.2
<i>D</i>	74.9 ±0.2	25.1 ±0.2
<i>E</i>	98.00±0.02	2.00±0.02
<i>F</i>	99.84±0.01	0.16±0.01

¹⁰ A. I. Sha'nikov, Zh. Eksperim. i Teor. Fiz. **41**, 1056 (1961) [English transl.: Soviet Phys.—JETP **14**, 753 (1962)].

mixture by low-temperature distillation yielded sample *F*. The remaining three mixtures were obtained by mixing sample *A*, *E*, and *F*. For samples *B* and *D* the calculated and mass-spectrometric values agreed to within experimental error. Agreement was not found for mixture *C*, thus explaining the large error quoted in the table for this sample.

2. Velocity of Sound in Liquid Helium

The velocity measurements made in liquid He⁴ and mixtures of He³ and He⁴ are shown in Figs. 4–7. In Table II are listed smoothed values taken from these curves. With a high degree of confidence, it can be said that we were always able to see at least the second cycle of the received pulse, hence the absolute un-

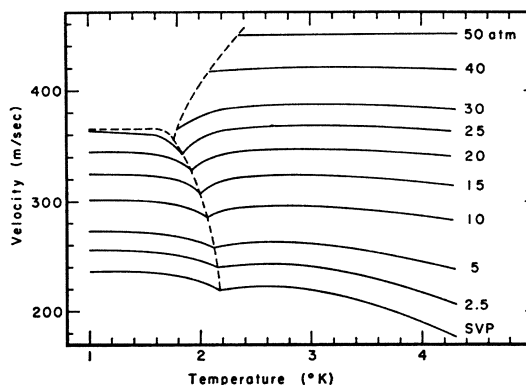


FIG. 4. Velocity of sound in pure liquid He⁴ as a function of temperature at various pressures. The freezing and lambda transitions are shown by dashed lines.

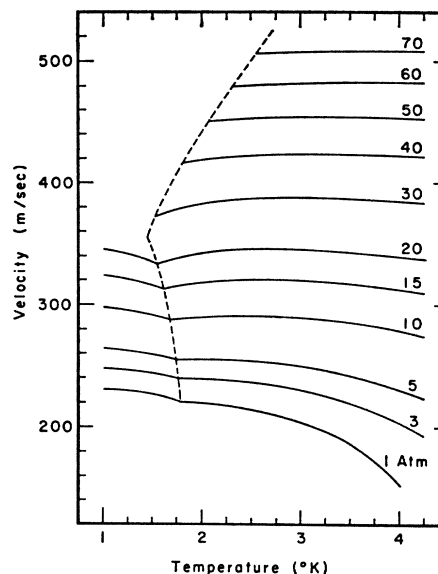


FIG. 5. Velocity of sound in a liquid mixture of 25.0% He³-75.0% He⁴. The freezing and lambda transitions are shown by dashed lines.

certainty in our time measurements is 0.1 μ sec. Within the region of the phase diagram explored, the time-of-flight for a 2-cm path is from 40 to 200 μ sec, thus the error is 0.05 to 0.25%. The path length which the sound travels is known to 0.05%, which, together with the above error in the time-of-flight, leads to an over-all error in the velocity of 0.1 to 0.3%.

Measurements of the velocity of sound in pure He⁴ have been made earlier by several investigators along

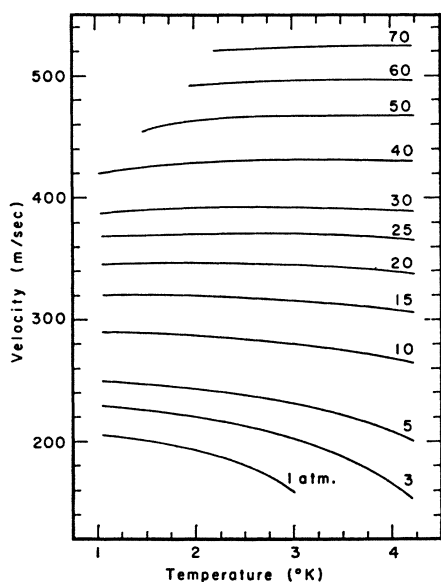


FIG. 6. Velocity of sound in a liquid mixture of 74.9% He³-25.1% He⁴.

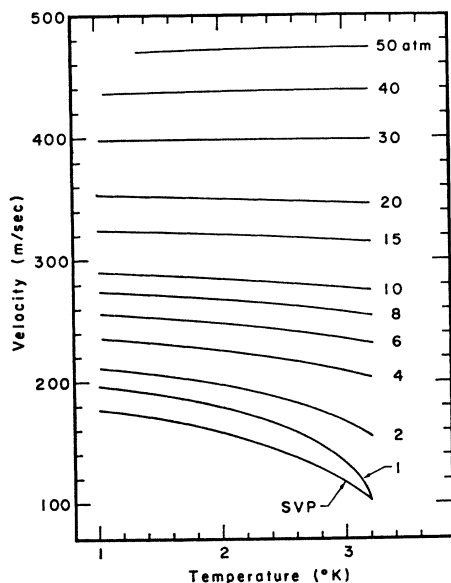


FIG. 7. Velocity of sound in a liquid mixture of 98.00% He³-2.00% He⁴.

TABLE II. The velocity of sound in liquid helium for various isotopic concentrations (smoothed values).

Pressure (atm)	Temperature (°K)						
	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Pure He ⁴							
SVP	236	235	226	222	218	207	190
2.5	255	254	245	243	240	232	217
5	272	271	262	262	261	255	245
10	301	300	288	295	295	292	286
15	324	323	307	322	323	321	317
20	344	343	333	346	346	346	343
25	363	360	355	366	368	367	365
30			376	385	386	386	384
40				419	420	420	419
50				450	450	450	450
25.0% He ³ -75.0% He ⁴							
1	230	226	219	214	204	186	152
3	248	244	239	236	230	219	203
5	264	260	255	254	249	242	230
10	298	291	290	290	289	285	278
15	324	316	318	320	320	317	312
20	345	335	342	346	345	343	340
30			382	387	388	387	385
40			418	422	423	423	422
50				453	454	454	453
60				480	482	482	482
70					507	508	508
74.9% He ³ -25.1% He ⁴							
1	206	201	193	180	159		
3	230	226	220	213	202	187	165
5	250	248	244	238	231	221	208
10	290	289	287	284	280	274	268
15	320	320	320	318	316	312	308
20	346	347	347	346	345	343	340
25	368	370	371	371	371	370	367
30	388	390	392	393	392	392	390
40	420	426	430	432	432	432	431
50		456	464	466	468	468	467
60			492	494	496	496	496
70				522	523	524	524
98.00% He ³ -2.00% He ⁴							
1	197	189	179	162	133	102 ^a	
2	212	206	198	186	167	156 ^a	
4	236	232	226	218	209	204 ^a	
6	256	253	248	243	236	232 ^a	
8	274	272	268	264	258	255 ^a	
10	290	288	285	282	278	275 ^a	
15	324	323	321	319	316	315 ^a	
20	353	352	351	349	347	346 ^a	
30	398	398	398	398	398	398 ^a	
40	436	437	438	438	439	439 ^a	
50		471	472	473	474	474 ^a	

^a This value is for $T = 3.2^\circ\text{K}$.

the vapor-pressure curve¹¹⁻¹³ and at higher pressures.^{14,15} Our data for pure He⁴ is in agreement with that of Atkins and Stassior¹⁵ to within their estimated error of 1% over the whole range of temperature and pressure. Measurements of the velocity of sound in pure He³ have been reported earlier by Laquer, Sydorik, and

¹¹ J. C. Findlay, A. Pitt, H. Grayson-Smith, and J. O. Wilhelm, Phys. Rev. **54**, 506 (1938).

¹² J. R. Pellam and C. F. Squire, Phys. Rev. **72**, 1245 (1947).

¹³ K. R. Atkins and C. E. Chase, Proc. Phys. Soc. (London) **A64**, 826 (1951).

¹⁴ J. C. Findlay, A. Pitt, H. Grayson-Smith, and J. O. Wilhelm, Phys. Rev. **56**, 122 (1939).

¹⁵ K. R. Atkins and R. A. Stassior, Can. J. Phys. **31**, 1156 (1953).

Roberts¹⁶ and by Atkins and Flicker¹⁷ at and near the saturated vapor pressure and at pressures up to 9 atm by Atkins and Flicker.¹⁸ Roberts and Sydoriak,¹⁹ have also made measurements of the sound velocity at saturated vapor pressure for several liquid He³-He⁴ mixtures over a wide range of temperature. Comparison of our data for nearly pure He³ (samples *E* and *F*) with the earlier measurements of Atkins and Flicker¹⁸ for pure He³ at elevated pressures show some clear discrepancies. For temperatures between 1 and 2°K and for pressures up to 9 atm the two sets of data are in satisfactory agreement. However, at higher temperatures the velocity values of Atkins and Flicker are consistently above ours (the concentration correction is in the opposite direction). Above 2°K and below 4 atm the disagreement is large. Since our data at 1 atm extrapolates to the value of the velocity at the normal boiling point,^{16,17} while that of Atkins and Flicker lies approximately 25% above, it must be assumed that their data is in error in this temperature and pressure region.

The expression for the velocity of sound in liquid He⁴ is $v^2 = V(\beta_s M)^{-1}$, where v is the velocity of sound, β_s the adiabatic compressibility, M the total mass of the He⁴ atoms, and V the volume of the system. In the region where the cohesive energy dominates the other contributions to the free energy, β_s and V will remain unchanged at constant pressure if we replace some He⁴ atoms with He³. If this replacement is done in a homogeneous fashion the above relationship is

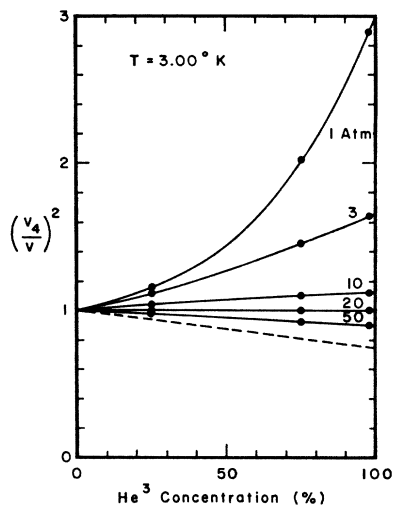


FIG. 8. The square of the ratio of the velocity of sound in liquid He⁴ to that in a He³-He⁴ mixture as a function of He³ mole concentration (x_3) for various pressures at 3.00°K. The dashed line represents the theoretical relation for a cohesive energy-dominated classical isotopic mixture of He³ and He⁴.

¹⁶ H. L. Laquer, S. G. Sydoriak, and T. R. Roberts, Phys. Rev. **113**, 417 (1959).

¹⁷ K. R. Atkins and H. Flicker, Phys. Rev. **113**, 959 (1959).

¹⁸ K. R. Atkins and H. Flicker, Phys. Rev. **116**, 1063 (1959).

¹⁹ T. R. Roberts and S. G. Sydoriak, Phys. Fluids **3**, 895 (1960).

TABLE III. The velocity of sound and adiabatic compressibility in liquid He⁴ along the freezing curve.

Temperature (°K)	Velocity (m/sec)	Molar volume (cm ³ /mole)	Adiabatic compressibility (atm ⁻¹)
1.024	364.8
1.065	364.8
1.156	364.8
1.242	364.8	23.09	4.391×10 ⁻³
1.329	364.8	23.05	4.383
1.446	365.4	22.97	4.353
1.517	365.4	22.90	4.340
1.576	364.8	22.81	4.337
1.643	364.1	22.68	4.329
1.693	362.1	22.54	4.350
1.725	360.2	22.42	4.373
1.748	356.4	22.33	4.448
1.777	360.2	22.19	4.328
1.798	366.7	22.09	4.157
1.846	379.2	21.96	3.864
1.947	397.1	21.76	3.492
2.042	411.7	21.51	3.211
2.155	426.4

still valid except that M , the total mass of the system, is now given by $n_3 A_3 + n_4 A_4$, where n_3 and n_4 are the number of moles of He³ and He⁴, respectively, and A_3 and A_4 their atomic weight. Thus

$$(v_4/v)^2 = M/M_4 = -x_3(1 - A_3/A_4) + 1$$

at constant pressure, where x_3 is the mole concentration of He³, v_4 is the velocity of sound in pure He⁴ and M_4 the total mass of the system if all the atoms are He⁴. This relation is represented by the dashed line in Fig. 8, which shows $(v_4/v)^2$ plotted as a function of He³ mole concentration for various pressures at 3.00°K. It is seen that the system approaches the above model as the pressure is increased; that is, as the cohesive energy begins to dominate the zero-point energy and thermal contributions to the free energy.

Accurate velocity measurements along the melting curve of He⁴ have been taken in order to calculate the adiabatic compressibility in this region. The results obtained, using the values given by Grilly and Mills²⁰ for the molar volume along the melting curve, are represented in Table III.

3. Lambda Line

The lambda lines for pure He⁴ and mixtures *B* and *C* were determined, as mentioned previously, by looking for the maximum in the attenuation of sound. It is known from experiment²¹ and theory²² that at saturated vapor pressure the maximum in the attenuation does not occur exactly at the lambda point, but is shifted to lower temperatures by about 5×10^{-4} °K at 10

²⁰ E. R. Grilly and R. L. Mills, Ann. Phys. (N. Y.) **18**, 250 (1962).

²¹ C. E. Chase, Phys. Fluids **1**, 193 (1958).

²² L. D. Landau and I. M. Khalatnikov, Dokl. Akad. Nauk. (U.S.S.R.) **96**, 469 (1954).

Mc/sec. Within the accuracy of this experiment, this shift can be neglected, provided, of course, that it does not change much with pressure or concentration. In all cases, it was possible to measure the minimum in the pulse amplitude to within the accuracy of the pressure gauge (± 0.05 atm). This data is presented in tabular form in Table IV and in graphical form in Fig. 9. The value of the upper lambda point for He⁴ is given by $T_s = 1.765 \pm 0.003$ °K and $P_s = 29.90 \pm 0.05$ atm.

Comparison of the He⁴ data was made with that of Lounasmaa and Kaunisto,²³ Elliott,²⁴ Swenson,²⁵ and Kierstead.²⁶ In the first three cases the present data overlap at low pressures, but deviate to higher pressures as the pressure is increased, reaching a maximum difference of about 0.3 atm at the melting curve. This is six times the uncertainty in our pressure measurements. Lounasmaa and Kaunisto, who have very precise data ($\Delta P = \pm 0.01$ atm, $\Delta T = \pm 0.001$ °K), made their measurements by observing the warm-up rate of an isolated calorimeter of He⁴. Essentially this amounts to measuring the temperature corresponding to the discontinuity in the specific heat, which is by definition the lambda point. The other measurements of the lambda line, including this work, have used indirect methods, that is, they have measured other physical quantities in the vicinity of the lambda line. Elliott's data ($\Delta P = \pm 0.2$ atm, $\Delta T = \pm 0.005$ °K) was derived from second-sound data, the lambda point coming at the temperature where the velocity goes to zero. Swenson's values were obtained by noting the change in the thermal conductivity at the lambda line. Within the accuracy of this experiment ($\Delta P = \pm 0.05$ atm, $\Delta T = \pm 0.001$ °K) there seems to be no intrinsic

TABLE IV. Lambda transition pressures and temperatures in liquid helium for various isotopic concentrations.

Temperature (°K)	Pressure (atm)	Temperature (°K)	Pressure (atm)
Pure He ⁴			
1.778	29.12	2.026	12.79
1.803	27.66	2.051	10.86
1.851	24.80	2.074	9.03
1.876	23.22	2.102	6.70
1.939	19.07	2.116	5.52
1.975	16.51	2.146	2.74
1.997	14.87		
5.03% He ³ -94.97% He ⁴			
1.724	27.94	2.001	9.10
1.801	23.26	2.066	3.48
1.896	16.77		
25.0% He ³ -75.0% He ⁴			
1.473	24.54	1.695	8.54
1.549	19.21	1.737	5.03
1.624	14.28		

²³ D. V. Lounasmaa and L. Kaunisto, Ann. Acad. Sci. Fennicae AVI, No. 59 (1960).

²⁴ S. D. Elliott, thesis, Yale University, 1958 (unpublished).

²⁵ C. A. Swenson, Phys. Rev. **89**, 538 (1953).

²⁶ H. A. Kierstead, Phys. Rev. **138**, A1594 (1965).

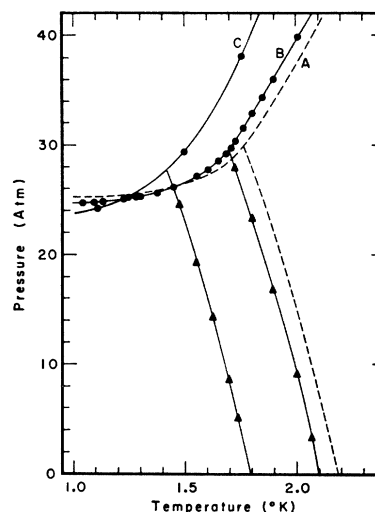


FIG. 9 The freezing curves (●) and the λ lines (▲) for: (A) pure He⁴, (B) 5.03% He³-94.97% He⁴, (C) 25.0% He³-75.0% He⁴.

reason why these methods should not all yield the same results. This discrepancy of approximately 1% in the pressure will be discussed again in the next section. Kierstead,²⁶ on the other hand, using an apparatus similar to Lounasmaa and Kaunisto, has recently determined the location of the upper lambda point to be at $T_s = 1.7633 \pm 0.0001$ °K and $P_s = 29.84 \pm 0.02$ atm. Within the quoted errors our measurement is in agreement with this determination of the upper lambda point. In the case of mixture B, Elliott's data ($\Delta P = \pm 0.2$ atm, $\Delta T = \pm 0.01$ °K) agree with the present data within experimental error.

4. Melting and Solidification Curves

The melting curve of He⁴ and the solidification curves of He⁴ and samples B, C, and D have also been investigated.

In Figs. 9, 14 and 16 and Table V will be found the melting-curve data for pure He⁴. These results differ from those of Grilly and Mills²⁷ and Swenson,²⁵ being shifted to higher pressures by 0.2 atm over the entire range from 1 to 2.3°K. All of the melting curve and lambda-line data were taken after the pressure gauge was checked against a dead-weight gauge. However, after these data were taken the gauge was accidentally subjected to an over pressure before it could be rechecked. A systematic error due to temperature measurements must be ruled out, since this would require the melting curve and lambda-line data to be shifted in temperature in opposite directions, contrary to observation. If there is a systematic error in the data it must lie in the pressure measurements.

Below the lambda point, as observed by Swenson, the freezing curve was the same as the melting curve, indicating no supercooling effects. Above the lambda

²⁷ E. R. Grilly and R. L. Mills Ann. Phys. (N. Y.) **8**, 1 (1959).

TABLE V. Freezing-point temperatures and pressures for various helium isotopic concentrations.

Temperature (°K)	Pressure (atm)	Temperature (°K)	Pressure (atm)
Pure He ⁴			
1.024	25.19	1.725	28.97
1.117	25.29	1.805	31.13
1.242	25.51	1.899	34.13
1.329	25.66	1.993	37.25
1.426	25.99	2.074	40.12
1.515	26.55	2.169	43.51
1.610	27.36	2.274	46.71
5.03% He ³ -94.97% He ⁴			
1.044	24.67	1.760	31.45
1.095	24.67	1.801	32.85
1.133	24.83	1.848	34.30
1.226	25.03	1.896	35.99
1.282	25.20	2.005	39.8
1.300	25.26	2.259	49.4
1.374	25.59	2.521	60.0
1.449	26.13	2.747	70.0
1.551	27.11	2.993	81.3
1.601	27.72	3.255	93.9
1.648	28.53	3.500	106.3
1.683	29.16	3.749	119.5
1.706	29.71	4.004	133.4
1.724	30.31	4.195	144.3
25.0% He ³ -75.0% He ⁴			
1.104	24.2	2.499	68.0
1.243	25.3	2.754	79.6
1.495	29.2	3.008	91.7
1.755	38.1	3.306	107.1
2.005	47.7	3.605	122.7
2.259	57.8		
74.9% He ³ -25.1% He ⁴			
1.152	34.2	2.269	79.6
1.172	35.4	2.557	94.0
1.351	41.1	2.862	109.9
1.649	52.3	3.158	125.2
1.945	64.6	3.496	143.5
99.84% He ³ -0.16% He ⁴			
2.701	111.6	2.995	127.6
2.905	122.5		

point supercooling was observed, giving rise to an upward shift in the freezing pressure of 0.2 atm.

In the case of mixtures it was possible to obtain reliable freezing curves but not melting curves. These data are presented in Figs. 9, 10, 15, and 16 and in Table V. It is expected that the freezing pressures are shifted slightly due to supercooling as for He⁴; however, no correction has been made for this effect. Measurements of the freezing curves of He³-He⁴ mixtures were first made by Esel'son and Lazarev²⁸ using the blocked capillary technique and recently by Bereznyak *et al.*²⁹ using a thermal-analysis method. The results of Bereznyak *et al.*²⁹ are included in Fig. 10.

²⁸ B. N. Esel'son and B. G. Lazarev, Dokl. Akad. Nauk. (U.S.S.R.) **95**, 61 (1954).

²⁹ N. G. Bereznyak, I. V. Bogoyavlenskii, and B. N. Esel'son, Zh. Eksperim. i Teor. Fiz. **45**, 486 (1963); [English transl.: Soviet Phys.—JETP **18**, 335 (1964)]. In these papers the values of the freezing pressures for pure He³, taken from Grilly and Mills (Ref. 27), are incorrectly plotted. They all lie about 6.6% higher than the published values. This error apparently arose in the conversion of units.

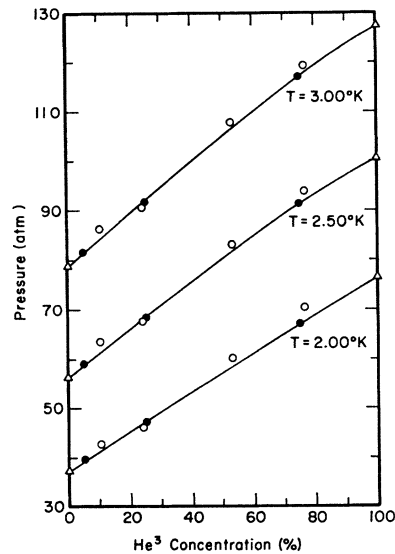


FIG. 10. Solidification pressure as a function of He³ mole concentration for various temperatures: (Δ) data of Grilly and Mills (Ref. 27) (\circ) data of Bereznyak *et al.* (Ref. 29); (\bullet) data from present work.

It is seen in Fig. 9 that the freezing curves for mixtures B and C at low temperatures fall below that for pure He⁴. This effect was first observed by Elliott.²⁴ Further investigation³⁰⁻³² of this effect in the temperature range below 1°K have shown the existence of a minimum in the solidification curves. Also, as was expected from entropy calculations, a minimum in the solidification curve for pure He⁴ has been observed.³³⁻³⁵ Le Pair *et al.*³⁰ have also made measurements on the change in slope of the solidification curve at the lambda line predicted by de Bruyn Ouboter and Beenakker.³⁶ This prediction was obtained by applying at the upper lambda point of a He³-He⁴ mixture the appropriate first- and second-order phase transition relations. In the case of a single-component system this discontinuity vanishes. A close examination of our data for the 5.0% He³-95.0% He⁴ mixture in Fig. 6 does give some indication of such a discontinuity.

5. Longitudinal Velocity of Sound in Solid Helium

The longitudinal velocity of sound was measured in pure solid He⁴ and in the mixtures B, D, E, and F.

³⁰ C. Le Pair, K. W. Taconis, R. de Bruyn Ouboter, and P. Das, Physica **28**, 305 (1962); Cryogenics **3**, 112 (1963).

³¹ H. Weinstock, F. P. Lipschultz, C. F. Kellers, P. M. Tedrow, and D. M. Lee, Phys. Rev. Letters **9**, 193 (1962); H. Weinstock, F. P. Lipschultz, C. F. Kellers, and D. M. Lee, in *Proceedings of the Eighth International Conference on Low Temperature Physics*, edited by R. O. Davies (Butterworths Scientific Publications Ltd., London 1962), p. 41.

³² K. N. Zinov'eva, Zh. Eksperim. i Teor. Fiz. **44**, 1837 (1963) [English transl.: Soviet Phys.—JETP **17**, 1235 (1963)].

³³ J. Wiebes and H. C. Kramers, Phys. Letters **4**, 298 (1963).

³⁴ C. Le Pair, K. W. Taconis, R. de Bruyn Ouboter, and P. Das, Physica **29**, 755 (1963).

³⁵ S. G. Sydoriak and R. L. Mills, *Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus Ohio, 1964*, edited by J. G. Daunt, D. V. Edwards, F. N. Milford, and M. Yaqub (Plenum Press, Inc., New York, 1965), p. 273.

³⁶ R. de Bruyn Ouboter and J. J. M. Beenakker, Physica **27**, 1074 (1961).

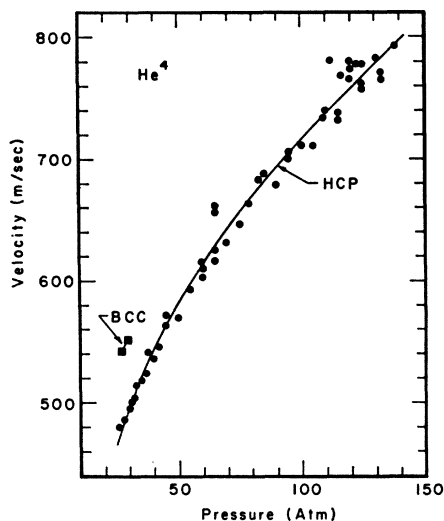


FIG. 11. Velocity of sound in pure solid He^4 . Circles—hcp phase. Squares—bcc phase.

This data, excluding mixtures *D* and *F*, is presented graphically in Figs. 11, 12, and 13.

For the most part this data represents the velocity of sound in the solid near the freezing curve. Within experimental error it was observed that the velocity did not vary with temperature, with one exception. Within a given pressure range, depending on the sample being investigated, there appeared at some temperature a discontinuity in the velocity. Below and above this temperature the velocity was independent of the temperature as long as the pressure was held constant. The locus of points in pressure-temperature space defined by this discontinuity has been interpreted as the boundary between two crystallographic phases in the solid. As will be discussed in Sec. 6, the high-pressure phase is hcp while the low-pressure one is bcc, similar to the transition observed in pure He^3 by Grilly and Mills.²⁷ Secondly it is to be noted that for a fixed pressure there is very little variation of the velocity with concentration.

Another interesting feature of the velocity versus pressure plots is the large scatter in the experimental points of up to 12%. Essentially every velocity point plotted in Fig. 8 is from a new sample, that is, one that has undergone a first-order phase transition (in most cases a liquid-solid transition) prior to measurement. The large variation of the velocity of sound in different samples at the same temperature, pressure and composition exceeds the uncertainty in velocity measurement by an order of magnitude or more and hence must be a reflection of real differences between samples. To begin with it is not known for sure whether the sample is polycrystalline, a number of large crystals, or a single crystal. Previous investigations of the structure of He^4 by Keesom and Taconis,³⁷ and Schuch,³⁸ using

³⁷ W. H. Keesom and K. W. Taconis, *Physica* 5, 161 (1938).

³⁸ A. F. Schuch, *Proceedings of the Fifth International Low*

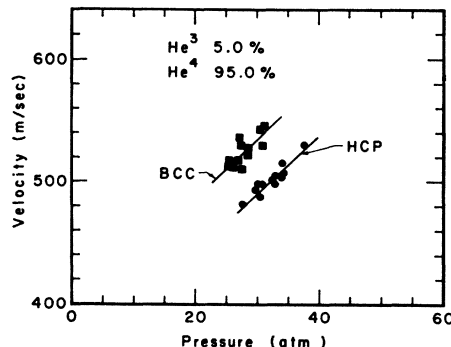


FIG. 12. Velocity of sound in a solid mixture of 5.03% He^3 -94.97% He^4 . Circles—hcp phase. Squares—bcc phase.

x-ray diffraction techniques, and Henshaw,³⁹ using neutrons, indicate that it has a tendency to form several large crystals when it solidifies. This being the case, the scatter in the velocity measurements can be interpreted as evidence for anisotropy in the velocity of sound in both the hcp and bcc phases of solid helium.

It is also possible that part of this scatter is due to the lack of pressure equilibrium, both within the sample and with the applied pressure. This means that in general the average pressure within the sample would not correspond with the applied pressure. Two facts indicate, however, that good pressure equilibrium was being attained. First there is the observation of only a small hysteresis in pressure (0.1 atm) in locating the solid-solid phase boundary in He^4 at constant temperature. Secondly, the change in velocity with pressure within the solid at constant temperature is the same as the variation of velocity with pressure along the melting curve, as found by solidifying at constant pressure.

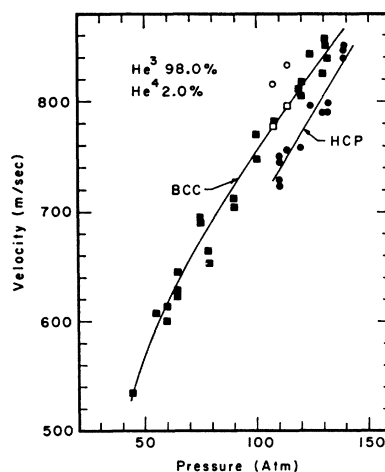


FIG. 13. Velocity of sound in a solid mixture of 98.00% He^3 -2.00% He^4 . Circles—hcp phase. Squares—bcc phase.

Temperature Conference, edited by J. R. Dillinger (University of Wisconsin Press, Madison, Wisconsin, 1958), p. 79.

³⁹ D. G. Henshaw, *Phys. Rev.* 109, 328 (1958).

In most cases as seen in Figs. 11, 12, and 13 the velocity of sound is greater (by 4 to 12%) in the lower pressure larger volume bcc phase than in the hcp phase, contrary to all expectations. However, it should be also noted that a few samples showed the opposite behavior (e.g., the open circles and squares in Fig. 13). This further strengthens the view that the solid is anisotropic in sound velocity and that our measurements are predominantly along preferred directions in the crystal. The solid lines in Figs. 11, 12, and 13 should therefore not be construed to be meaningful average velocities.

Recently Lipschultz and Lee⁴⁰ have reported measurements of the velocity of shear waves in solid He⁴ in both the bcc and hcp phase. These measurements show qualitatively the same behavior as was observed for longitudinal waves, i.e., the velocity in the bcc phase is greater than in the hcp phase at the same temperature and pressure and the observed scatter lies outside the limits of experimental error, indicating a fair degree of anisotropy in the elastic constants.

In a theoretical paper just received Nosanow and Werthamer⁴¹ have treated the solid helium problem using the time-dependent Hartree approximation, together with the results of variational calculations using correlated trial wave functions. Their calculated values of the sound velocity in hcp He³ and He⁴ and in bcc He⁴ show a large anisotropy of the order of 100 m/sec for the longitudinal modes and 150 m/sec for the transverse modes and give values that fall in the range of the experimentally observed velocities. The large anisotropy predicted by these calculations can not be confirmed in detail until measurements on oriented single crystal samples are made but our results and those of Lipschultz and Lee⁴⁰ are consistent with a sizable anisotropy in both the longitudinal and transverse sound modes. The variation of sound velocity with density calculated by Nosanow and Werthamer appears to exceed that observed in our measurements.

In order to calculate roughly the compressibility of solid helium, it was assumed that helium is an isotropic solid obeying the Cauchy relations. Under these conditions $\beta = 9/5\rho v^2$, where ρ is the density and v the longitudinal velocity. Over the pressure range from 25 to 150 atm the compressibility (β) went from 4 to 1×10^{-3} atm. This is of the same order of magnitude as the compressibility in the liquid phase along the melting curve.

6. Attenuation of Sound in Solid Helium

Rough values of the attenuation of sound at 10 Mc/sec in solid He³ and He⁴ were determined from the ratio of two successive amplitudes. The attenuation, measured over a wide range of pressure and tempera-

ture, was found to be on the order of 0.3 to 0.7 cm⁻¹. This is just slightly higher than that for liquid He⁴ at saturated vapor pressure, neglecting the attenuation peaks at the lambda point and at about 1°K. Because of the uncertainty in the condition of the sample (a single crystal, a few large crystals, or polycrystalline) and in the acoustical contact between the solid helium and the quartz transducers, these results must be considered as upper limits to the attenuation.

7. First-Order Phase Transition in Solid Helium

Both solid He³ and He⁴ are now known to exist at low temperatures in three different crystallographic phases (bcc, hcp, and fcc).⁴² Keesom and Taconis,³⁷ using x-ray diffraction techniques, were the first to identify the crystal structure of solid He⁴. In the medium pressure range which was investigated they observed the solid

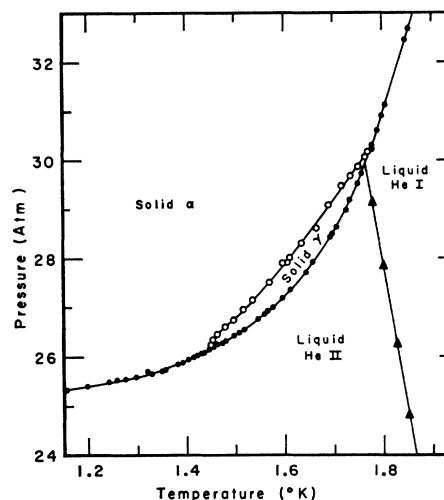


FIG. 14. Phase diagram of pure He⁴ from sound-velocity measurements (solid α —hcp, solid γ —bcc).

to be hcp. This work was later verified by Schuch³⁸ and Henshaw.³⁹ The high-pressure phase in He⁴, inferred by Dugdale and Simon⁴³ from their specific-heat measurements, was identified by Mills and Schuch⁴⁴ as fcc, while the low-pressure phase, observed by the authors,² was identified by Schuch and Mills⁴⁵ as bcc. In the case of solid He³, measurements of the molar volume²⁷ were the first to reveal a phase transition. Following this Schuch, Grilly, and Mills⁴⁶ determined that at low

⁴² In order to avoid confusion and to comply with the proposed nomenclature for helium allotropes the different phases will be referred to in terms of their crystal structure [cf. J. G. Daunt, A. F. Schuch and R. L. Mills, *Phys. Today* 17, No. 1, 50 (1964)].

⁴³ J. S. Dugdale and F. E. Simon, *Proc. Roy. Soc. (London)* A218, 291 (1953).

⁴⁴ R. L. Mills and A. F. Schuch, *Phys. Rev. Letters* 6, 263 (1961).

⁴⁵ A. F. Schuch and R. L. Mills, *Phys. Rev. Letters* 8, 469 (1962).

⁴⁶ A. F. Schuch, E. R. Grilly, and R. L. Mills, *Phys. Rev.* 110 775 (1958).

⁴⁰ F. P. Lipschultz and D. M. Lee, *Phys. Rev. Letters* 14, 1017 (1965).

⁴¹ L. H. Nosanow and N. R. Werthamer, *Phys. Rev. Letters* 15, 618 (1965).

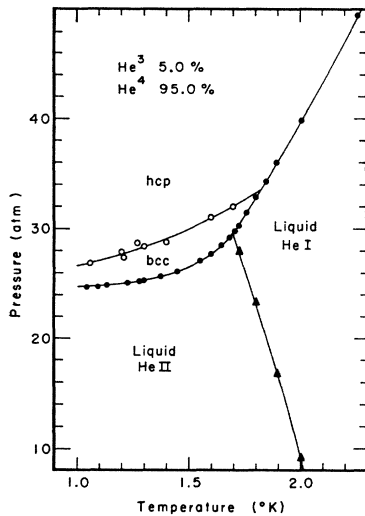


FIG. 15. Phase diagram of 5.03% He³-94.97% He⁴ from velocity of sound measurements.

pressures He³ is bcc and at medium pressures hcp. Prompted by their work on He⁴ Schuch and Mills⁴⁷ looked and found at high pressures a fcc phase in He³. The transition between this fcc phase and the adjacent hcp phase has been investigated by Franck.⁴⁸

The discontinuity in the velocity of sound in going from one crystal structure to another has been utilized to investigate the bcc-hcp phase transition in pure He⁴ and He³-He⁴ mixtures. The data for pure He⁴ and samples B, D, and F are displayed in Figs. 14, 15, and 16 and in Table VI. The data for sample E is not shown.

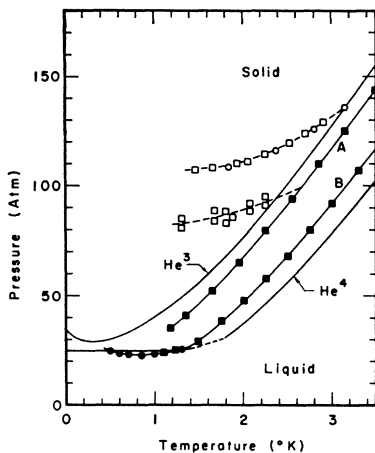


FIG. 16. Phase diagram of helium for (A) 74.9% He³-25.1% He⁴, (B) 25.0% He³-75.0% He⁴, "pure" He³ (99.84% He³-0.16% He⁴) and pure He⁴. The dashed lines are the hcp-bcc transition curves and the solid lines the freezing curves. The data from our sound-velocity measurements are shown by squares. The open circles are from the data of Grilly and Mills (Ref. 27) and the solid circles from that of Weinstock *et al.* (Ref. 31).

⁴⁷ A. F. Schuch and R. L. Mills, Phys. Rev. Letters **6**, 596 (1961).

⁴⁸ J. P. Franck, Phys. Rev. Letters **7**, 435 (1961).

TABLE VI. Pressure-temperature values for the bcc-hcp phase transition in helium for various isotopic concentrations.

Temperature (°K)	Pressure I ^a (atm)	Pressure D ^b (atm)
Pure He ⁴ ^c ($\Delta T = \pm 0.001^\circ\text{K}$, $\Delta P = \pm 0.05$ atm)		
1.448	26.22	
1.449	26.26	
1.449	26.35	
1.453	26.34	
1.462	26.45	
1.479	26.60	
1.494	26.70	
1.498	26.83	
1.515	26.95	
1.533	27.10	
1.568	27.49	
1.579	27.90	
1.606	28.00	
1.611	28.00	
1.636	28.31	
1.664	28.61	
1.689	29.07	
1.716	29.47	
1.734	29.67	
1.751	29.87	
1.765	30.07	
1.770	30.17	
5.03% He ³ -94.97% He ⁴ ($\Delta T = \pm 0.01^\circ\text{K}$, $\Delta P = \pm 0.2$ atm)		
1.06	27.3	26.5
1.20	28.3	27.5
1.21	27.9	27.0
1.30	28.5	28.3
1.40	29.0	28.5
1.60	31.3	30.6
1.70	32.2	31.8
74.9% He ³ -25.1% He ⁴ ($\Delta T = \pm 0.01^\circ\text{K}$, $\Delta P = \pm 0.6$ atm)		
1.31	83.9	80.9
1.68	88.6	83.9
1.80	87.4	83.4
1.93	...	86.1
2.07	91.9	88.9
2.26	93.9	92.5
98.00% He ³ -2.00% He ⁴ ($\Delta T = \pm 0.001^\circ\text{K}$, $\Delta P = \pm 0.2$ atm)		
2.562	119.3	
3.009	131.0	
99.84% He ³ -0.16% He ⁴ ^c ($\Delta T = \pm 0.001^\circ\text{K}$, $\Delta P = \pm 0.5$ atm)		
1.465 ^d	107.0	
1.665 ^d	107.9	
1.927 ^d	109.9	
2.046	111.0	
2.214	113.4	
2.234 ^d	114.1	
2.254 ^d	114.2	
2.496 ^d	118.7	
2.521	118.8	
2.706 ^d	123.7	
2.899 ^d	128.8	
2.905 ^d	128.6	

^a Pressure I is the transition pressure when pressure is increased at constant temperature.

^b Pressure D is the transition pressure when pressure is decreased at constant temperature.

^c Pressure D is equal to Pressure I within experimental error.

^d Temperature is being varied at constant pressure; $\Delta T = \pm 0.005^\circ\text{K}$, $\Delta P = \pm 0.2$ atm.

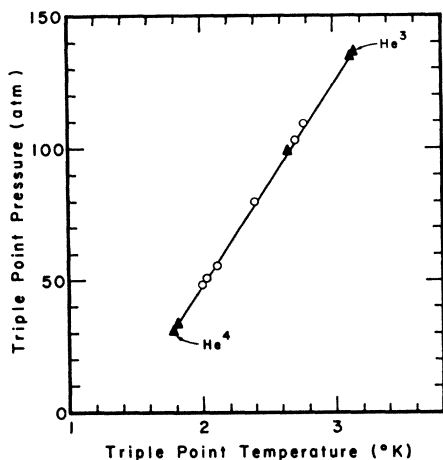


FIG. 17. The upper solid bcc-solid hcp-liquid triple points of pure He^3 , pure He^4 , and He^3 - He^4 mixtures. \blacktriangle —present work. \circ —data of Bogoyavlenskii *et al.* (Ref. 55).

It lies 0.9 atm below that for sample *F*. It was very difficult to produce and hold good signals in the 25.0% He^3 -75.0% He^4 sample, hence no reliable data on the transition were obtained.

The locations of the liquid-solid (bcc)-solid (hcp) triple points for pure He^4 are given by $T_l = 1.449 \pm 0.003^\circ\text{K}$, $P_l = 26.18 \pm 0.05$ atm and $T_u = 1.778 \pm 0.003^\circ\text{K}$, $P_u = 30.28 \pm 0.05$ atm. This is in fair agreement with the later work of Ahlers⁴⁹ and Kierstead,⁵⁰ but in poor agreement with Grilly and Mills.²⁰ The reader is referred to Ahlers for a more detailed comparison. Recently Bereznyak *et al.*²⁹ made measurements on this transition, however they reported no data close to the triple points.

Comparison of our data for the bcc-hcp transition in He^3 (99.84% He^3 -0.16% He^4) with that of Grilly and Mills²⁷ shows that our values lie approximately 0.6 atm above theirs, except at temperatures below 2.0°K where the deviation begins to increase. Signals were hard to maintain below 1.4°K, but on one occasion, with the pressure at 106.6 atm, the signal remained good down to 1.06°K. No transition was observed so it must be assumed that at 1.06°K the transition pressure must be greater than 106.6 atm. Heltemes and Swenson⁵¹ estimated from their specific-heat measurements that at 0.3°K the transition pressure is roughly 108 atm. This seems to be a little high, judging from the data of Grilly and Mills²⁷ and our work, unless the transition curve has gone through a minimum somewhere between 0.3 and 1.4°K. According to the work of Thomson *et al.*,⁵² the transition curve must lie between 98 and 110 atm in the temperature

TABLE VII. The upper solid (bcc)-solid (hcp)-liquid triple points of helium for various isotopic concentrations.

Mixture		Temp. (°K)	Press. (atm)
% He^3	% He^4		
	100.0	1.778	30.28
5.03	94.97	1.81 ^a	33.2 ^a
74.9	25.1	2.65 ^a	99 ^a
98.00	2.00	3.12	134
99.84	0.16	3.15	136

^a Extrapolated mean values.

range from 0.3 to 2.0°K. The only contradictory evidence to this behavior is the work of Reich,⁵³ who deduced from his nuclear-spin relaxation-time measurements that the transition curve starts to drop in pressure below 0.8°K and reaches about 90 atm at 0.6°K. This conclusion appears to be an incorrect interpretation of the data (see for example Beal *et al.*⁵⁴).

In the case of mixtures supercooling and/or superheating effects were observed (see Table VI: 5.03% He^3 -94.97% He^4 and 74.9% He^3 -25.1% He^4). In Table VI are listed the transition pressures on increasing (Pressure *I*) and on decreasing (Pressure *D*) the pressure at constant temperature. For the "pure" samples Pressure *I* is equal to Pressure *D*. In Fig. 15 (sample *B*) the mean value of Pressure *I* and Pressure *D* has been plotted. It should be mentioned that the observed supercooling and/or superheating effects could be accounted for by poor pressure equilibrium; however, the fact that it is a function of concentration, disappearing for the pure components, is not consistent with this assumption. It is also to be noted that the uncertainty in determining the transition pressure also increased as the samples approached a 50-50 mixture. A slight lack of pressure equilibrium at the higher pressures may account for some of this, but the greater part of it is most likely attributable to the sample being in a mixed phase region.

The upper triple points of the samples investigated (Table VII) found by extrapolation of the phase boundary to the solidification curve, have been plotted in pressure-temperature space in Fig. 17. For samples *B* and *D* the extrapolated mean values have been used. These values, along with the recently reported ones of Bogoyavlenskii *et al.*,⁵⁵ show that a linear relationship is obeyed. The theoretical significance of this, if any exists, is unknown to the authors.

Theoretically the high-pressure transition from a hcp to a fcc lattice structure can be understood on classical terms⁵⁶; however, this is apparently not the case for

⁴⁹ H. A. Reich, *Phys. Rev.* **129**, 630 (1963).

⁵⁰ B. T. Beal, R. P. Gifford, J. Hatton, M. G. Richards, and P. M. Richards, *Phys. Rev. Letters* **12**, 393 (1964).

⁵¹ I. V. Bogoyavlenskii, N. G. Bereznyak, and B. N. Esel'son, *Zh. Eksperim. i Teor. Fiz.* **47**, 480 (1964) [English transl.: *Soviet Phys.—JETP* **20**, 318 (1965)].

⁵² A. L. Thomson, H. Meyer, and D. N. Dheer, *Phys. Rev.* **132**, 1455 (1963).

⁴⁹ G. Ahlers, *Phys. Rev.* **135**, A10 (1964).

⁵⁰ H. A. Kierstead, *Bull. Am. Phys. Soc.* **10**, 1088 (1965).

⁵¹ E. C. Heltemes and C. A. Swenson, *Phys. Rev.* **128**, 1512 (1962).

⁵² A. L. Thomson, H. Meyer, and D. N. Dheer, *Phys. Rev.* **132**, 1455 (1963).

⁵⁶ T. H. K. Barron and C. Domb, *Proc. Roy. Soc. (London)* **A227**, 447 (1955).

the low-pressure bcc-hcp transition. Bernardes and Primakoff⁵⁷ had suggested earlier that perhaps nuclear spin effects might be responsible for the transition in He³. The later observation that the same transition exists in He⁴ eliminated this possibility. Bernardes⁵⁸ has more recently made an analysis of He³ which shows that the change in phonon entropy accounts for the total entropy change at the transition. This implies that the bcc-hcp transition is associated with the zero-point energy, since it dominates the thermal energy at these low temperatures.

V. SUMMARY

The longitudinal velocity of sound has been measured in liquid and solid He³-He⁴ mixtures and compared with existing data where possible. This investigation in

⁵⁷ N. Bernardes and H. Primakoff, Phys. Rev. **119**, 968 (1960).
⁵⁸ N. Bernardes, Phys. Rev. Letters **8**, 164 (1962).

the solid mixtures showed that the bcc-hcp transition observed by Grilly and Mills in He³ exists in He³-He⁴ mixtures and also in pure He⁴. Measurements of the solidification curves and λ lines were obtained and compared with known data. This comparison showed a discrepancy, our pressure values lying $\frac{1}{2}$ to 1% higher than values previously reported. Rough attenuation measurements obtained in solid samples of He³ and He⁴ yielded attenuation coefficients on the same order of magnitude as liquid He⁴ near the solidification curve, neglecting the peaks at the λ line and around 1°K.

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Measurement of Recombination-Rate Coefficient of He⁺⁺

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The rate of recombination of doubly ionized helium in the afterglow of a C stellarator discharge is deduced from measured light intensities of He II and He I, emitted by recombining He⁺⁺ and He⁺. The electron temperature and the He⁺⁺ and He⁺ and electron densities are determined from the Saha equations for the highly excited states and the condition of charge neutrality. The electron density is also measured directly with a 4-mm microwave interferometer. The rate of recombination of He⁺ is found to be in good agreement with previous measurements, at temperatures <0.25 eV. At higher temperatures, where He⁺ and He⁺⁺ are both present, the recombination rate is found to follow a Z³ relationship. The measurements appear to be in quite good agreement with the calculations of Bates, Kingston, and McWhirter over the entire range of measurement.

I. INTRODUCTION

IN our previous measurements¹ of the "collisional-radiative" recombination rate coefficient in the afterglow of the B-1 stellarator, a major problem was the very restricted range of available temperatures. For one reason or another, noted at that time, the range of electron temperatures in the afterglow did not exceed $0.3 > T_e > 0.1$ eV. In particular, we could not conclude anything definite about the recombination of multiple ions, except that He⁺⁺ appeared to recombine roughly an order of magnitude faster than He⁺.

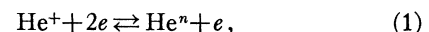
The C stellarator, with its improved particle confinement, allows a considerable extension of this available temperature range. In the present experiments we have been able to obtain simultaneous recombination data for both He⁺⁺ and He⁺ in the temperature range $1.0 > T_e > 0.25$ eV (and down to <0.1 eV for He⁺).

It appears possible to extend the range further, perhaps to 2 eV for He⁺⁺.

In the lower temperature range our present results are in good agreement with those reported previously.¹ The present paper therefore concentrates on the higher temperatures, and especially the differences between singly and doubly charged ions.

II. REVIEW OF THE RECOMBINATION PROCESS

Qualitatively, the recombination process may be described as two electrons colliding in the field ("sphere of influence") of an ion, during which one of the electrons loses sufficient energy to be unable to escape, i.e., it is transferred to a bound state. Symbolically (for helium)



where Heⁿ designates a helium atom in the *n*th quantum

¹ E. Hinnov and J. G. Hirschberg, Phys. Rev. **125**, 795 (1962).

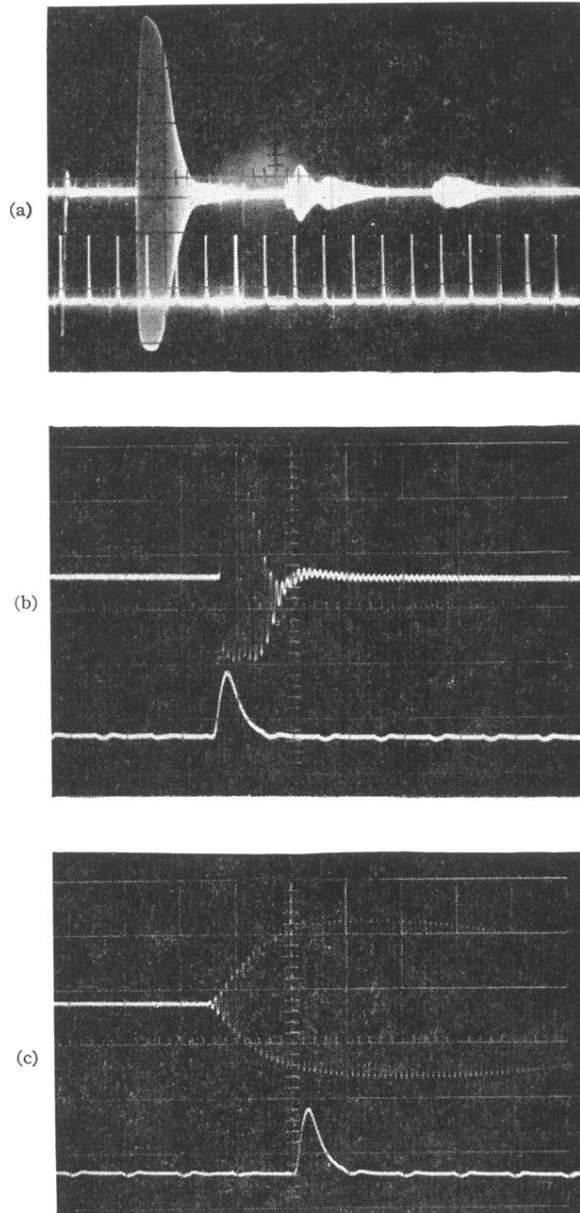


FIG. 3. Photographs of one of the better signals observed in solid helium. (a) Upper trace—transmitted and received pulses plus two echoes; lower trace—timing pulses 10 μ sec apart. (b) Upper trace—enlarged view of transmitted pulse; lower trace—small timing pulses 1 μ sec apart. (c) Upper trace—enlarged view of first received pulse; lower trace—small timing pulses 1 μ sec apart.