between valence and conduction bands in silicon.[5]

We are extending these studies to irradiation with extrinsic polarized light, with which similar effects are expected. This experiment was suggested by Professor I. Solomon and we wish to thank him for his constant interest in this work. The help of Professor C. Benoit à la Guillaume and his group at the Ecole Normale Supérieure, Paris, is gladly acknowledged.

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ZERO-POINT BUBBLES IN LIQUIDS*†

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Bubbles due to the zero-point motion of positronium atoms in liquid He, H_2, Ne, and Ar have been observed and their sizes determined.

Many years ago Ferrell[1] proposed that the long lifetime of positronium atoms in liquid helium was due to the fact that the positronium atoms were trapped in a "zero-point bubble" in the liquid. The argument is that any very light free particle cannot be confined in a small space because of the pressure of its zero-point motion. Indeed many observations of positron annihilation in liquids and dense gases have been discussed in terms of the zero-point motion picture. One of the most recent of these experiments, that of Roellig and Kelly,[2] has even determined some of the conditions of density and temperature for the formation of these zero-point motion bubbles, or "cavities," in the gaseous state.

Because of the strong repulsive interaction with He atoms, an electron is also known to form a zero-point bubble in dense He gas and liquid. Discussions of the mobility of electrons in helium have often been based upon this bubble idea. Recently Northby and Sanders,[3] in an interesting experiment, have observed the photoejection spectrum of electrons in the bubble state. From the photoejection energy they deduce that the potential well (assumed square) seen by an electron has a depth of about 1.0 eV and a diameter of about 42 Å.

In this Letter we present a direct measurement of the bubble size in He and other liquids when the entrapped particle is a positronium atom. The principle of the measurement is simple. The motion of the positronium atom is observed by the small departure from 180° of the angle between the annihilation gamma rays. The width of the momentum distribution of annihilation photons (and hence of positronium atoms) is inversely proportional to the size of the bubble.

The experiment was done in the usual long-slit angular-correlation apparatus for positron annihilation experiments. See Fig. 1. The source-detector distance was 250 in. and the slit width 0.050 in., subtending an angle at the source of 0.20×10^{-3} rad. For some higher resolution runs the angle was decreased to 0.15×10^{-3} rad. The angle was varied by moving one detector and coincidences were automatically recorded as a function of angle. As shown in Fig. 1, the source of positrons was two copper foils each mounted parallel to the long slit detectors and about $\frac{1}{16}$ to $\frac{1}{8}$ in. apart. The liquid specimen was defined by a fixed lead slit close to the cryostat with a gap of about 0.025 in. for all liquids and of about 0.050 in. for some He runs. On the other side of the cryostat, the corresponding slit was always slightly larger than the fixed specimen-defin-

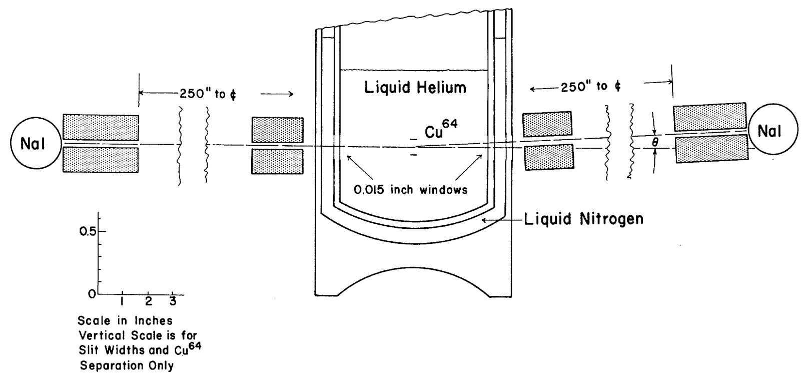

FIG. 1. Schematic drawing of the experimental arrangement.

ing slit in order that the volume of the specimen did not change with angle. All data were taken at the normal boiling points of the liquids except one low-temperature run in helium.

The experimental results are shown in Fig. 2. The lines through the points have been drawn by eye; the dashed lines, with imagination. It is clear that these data imply two momentum distributions; and it is the narrow one, which we attribute to singlet positronium atoms annihilating in the bubble state, that is of primary interest here. There are two comments to be made before discussing the narrow component. First, the width of the broad component is comparable with the width of the momentum distributions of the outer electrons of the various atoms or molecules. This component is thus attributed to the annihilation of very

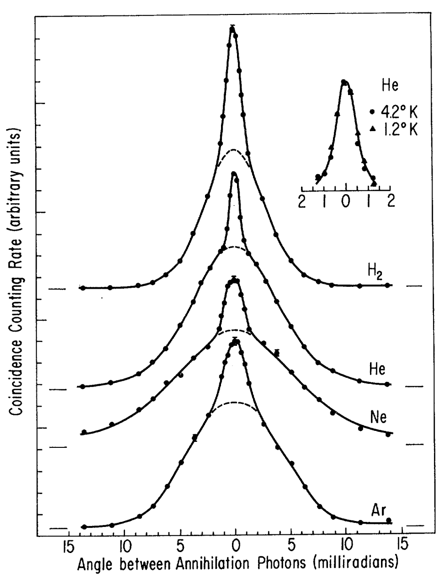

FIG. 2. The angular correlation of photons from positrons annihilating in various liquids.

slow positrons with the outer orbital electrons. A quantitative analysis will be made later. Second, the intensity of the narrow component measures the fraction of positrons which decay from the ${}^1S_0$ state, presumably in this system $\frac{1}{4}$ of all positronium formed. The intensity of the narrow peak we observe in He, 5%, agrees well with several measurements[4] of 20% total positronium atom (Ps) formation. However, our figures for the other liquids (peak area in H_2, 12%; in Ne, 5.3%; and in Ar, 7.3%) do not agree very well with Paul's[5] determination of 9.3% total Ps in Ar or with the determination of Liu and Roberts[6] of 7.3% total Ps in Ar and 24% in H_2. There are no comparative figures for Ne. While it is possible that O_2 contamination in Ar might have influenced some results, it is unlikely that our measurement of the narrow peak in H_2 is in error by anything like a factor of 2.

Concerning the narrow component: We follow the simple picture that a bubble is formed by the repulsive interaction between a Ps atom and the atoms of the liquid. The size of the bubble can be determined by minimizing the Gibbs' free energy of the system with respect to the radius R:

$$G = 4\pi(R-Z_0)^2\sigma + P\tfrac{4}{3}\pi R^3 + E_{ZP} + G_{SP} + G_{BT}.$$

The surface tension is denoted by σ, the radius of the surface of tension by $R-Z_0$, and the pressure of the bulk liquid by P. E_{ZP}, G_{SP}, and G_{BT} are the zero-point energy of the center-of-mass motion of the positronium atom, the contributions to the free energy from the surface phonons of the bubble, and the translational motion of the whole bubble with the Ps atom, respectively. In this Letter we consider only the first three terms and neglect Z_0 compared with R. The effect of the finite value of Z_0 on the calculated R will be noted briefly at the end of this Letter. Further investigation on the neglected terms will be reported later. In the formula, the free energy is measured from the hypothetical state in which the liquid is uniformly distributed and the Ps atom is in the lowest energy delocalized state. First we assume an infinite spherical well potential for which

$$E_{ZP} = (\hbar^2/2m)(\pi/R)^2.$$

Minimization of G under the above approximations yields values of R given by the equation

$$R^4 = (\pi\hbar^2/8m\sigma)[1 + (PR/2\sigma)]^{-1},$$

where m is the mass of a Ps atom. The calculated values of radii are listed in Table I. Also, using the infinite-spherical-well potential we can obtain a formula relating the radius to the momentum distribution. This is

$$R = (16.60 \times 10^{-3}/\theta_{1/2})\ \text{Å},$$

where $\theta_{1/2}$ is full width at half-maximum measured in radians. Radii calculated from this formula and the experimental data are also shown in Table I.

Secondly, we have taken a finite potential well for Ps atoms in the liquid helium. The depth of the potential well, 1.63 eV at 4.2°K and 2.05 eV at 1.7°K, was determined from a Wigner-Seitz-model calculation under the assumption that a helium atom can be represented by a hard sphere of radius 1.11 Å, which is the scattering length calculated by others.[7] The lack of information on the positronium scattering lengths of other atoms and molecules prevented us from carrying out similar theoretical calculations for other gases Since the ground-state energy in He is so low (~0.1 eV), the depth of the potential well is not very critical. In argon, however, the positronium kinetic energy may be $\frac{1}{2}$ eV, so more care must be used in finding a suitable potential. The potentials used and the bubble radii obtained are also shown in Table I.

In view of the approximations involved, agreement between the experimentally deduced bubble size and the calculated values is remarkable.

We note the sensitivity of the calculated value of the bubble radius R to the value of Z_0 by pointing out that Z_0 has to be 4.3 Å in order for the calculated value (16.5 Å for $Z_0 = 0$) to increase to the experimental value 21.0 Å at 1.7°K. This estimate is made from the simplified Tolman formula for the relation between the surface tension and Z_0.[8]

Finally it should be mentioned that this experiment has observed positronium atoms in the singlet state, $^1S_0$, decaying by two-photon emission in $\sim 10^{-10}$ sec. Since the simple picture seems to fit bubble sizes fairly well over the wide range of liquid densities from Ar to He, it appears that they can arrive at an approximate equilibrium radius in 10^{-10} sec or less. The dynamics of bubble formation will be investigated further.

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Table I. Bubble radii from calculation and experiment.

			$V=\infty$		$V\neq\infty$	
Liquid	Surface tension σ (dyn/cm)	Full width at half-maximum $\theta_{1/2}$ (10^{-3}rad)	From energy minimization (Å)	From measured narrow-peak width (Å)	Potential well (eV)	From energy minimization (Å)
He(4.2°K)	0.095	0.79 ± 0.05	18.8	21.0 ± 1.0	1.63	18.2
He(1.7°K)	0.325	0.79 ± 0.05	16.5	21.0 ± 1.0	2.1	15.8
H_2	1.91	$1.3^{+0.2}_{-0.1}$	10.5	13^{+2}_{-1}		
Ne	4.78	$1.7^{+0.2}_{-0.1}$	8.4	$9.8^{+0.9}_{-0.5}$		
Ar	10.94	$2.1^{+0.2}_{-0.1}$	6.8	$8.0^{+0.7}_{-0.4}$		

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SPECIFIC HEAT OF XENON NEAR THE CRITICAL POINT*

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We report measurements of the specific heat of xenon near the critical point. Good accuracy and temperature resolution are achieved with a semiautomatic system permitting direct recording of the heat capacity. From analysis of the results allowing for the effects of gravity, we conclude a value for the exponent α of about 0.08, although a value between 0 and $\frac{1}{8}$ cannot be ruled out. A symmetric logarithm is not consistent with the results.

We have measured the specific heat of xenon at constant critical density in the neighborhood of the critical temperature. Thermodynamic analysis[1] shows that in equilibrium under gravity the specific heat $C_{V,g}$ possesses a high but smooth peak instead of the singularity expected in $C_{V,0}$. Our measurements fully resolve this peak for a sample height of 1 cm.

The xenon (99.94% purity) was sealed at a density of 1.099 ± 0.003 g/cc in a volume consisting of 180 interconnected vertical holes, 1.00 cm high and 0.08 cm in radius, drilled in a copper block wound with two independent heaters and with miniature thermistors mounted in recesses cavities. This calorimeter, silver plated on the outside, was suspended in vacuum inside a massive (5.2 kg) chromium-plated copper cylinder, stage 1, possessing heaters and thermistors. This in turn was supported in a second similar stage equipped in addition with a thermoelectric heat sink, the whole being buried in insulating material (Vermiculite).

The temperature of stage 2 was controlled by a servomechanism having both mean temperature and gradient feedback. The temperature drift rate of stage 1 could thereby be held below 5×10^{-9} deg sec^{-1} for periods of 1 and 2 h without need for manual adjustment. Temperatures were measured with a 21-cps transformer ratio-arm bridge and lock-in amplifier having an rms noise corresponding to 10^{-5} deg with 1-cycle bandwidth. Absolute temperatures were determined to within ±2 mdeg using a platinum resistance thermometer. In the principal mode of operation a constant power is supplied to stage 1 whose temperature rises linearly with time, the temperature of stage 2 being maintained close to that of stage 1 throughout. Constant power is supplied to one of the heaters in the calorimeter, the other receiving the power output of a servomechanism operating to maintain temperature equality with stage 1. Under these conditions the total power supplied to the calorimeter is the product of its heat capacity and the rate of temperature rise; thus the servo power, which is recorded directly, is proportional to the total heat capacity less a constant, and it is therefore possible to record directly the heat capacity of the xenon alone as a function of temperature. The system is very flexible and it is possible to operate with the temperature decreasing with time or to perform more conventional step-by-step measurements. Results obtained by the latter method are shown in Fig. 1 together with measurements of the intrinsic thermal time constant τ of the calorimeter. While we can readily follow transient changes and thus observe the thermal response of the calorimeter, it is difficult to obtain accurate values of τ, particularly where it is changing rapidly with temperature.

Very near the critical temperature the rapid rise in τ results in distortion of the observed heat capacity when $\tau\dot{T}(dC/dT)$ is not small compared with C itself; the lowest convenient value of the ramp rate $\dot{T}$ was 3×10^{-6} deg sec^{-1}.