Specific Heat of Liquid ^{3}He in Sintered Copper below 3 mK*

J. M. Dundon, D. L. Stolfa, and J. M. Goodkind
Physics Department, University of California, San Diego, La Jolla, California 92037

(Received 12 February 1973)

A nuclear cooling system consisting of copper wire was connected to a copper container inside of which a copper powder had been compressed and sintered. The heat capacity of the system without ^{3}He in the container was subtracted from the heat capacity with ^{3}He at pressures ranging from 0 to 29 atm. The difference shows a peak at 1.5 mK which decreases in magnitude as the pressure is reduced and a broad shoulder extending up to about 3 mK which is present at all pressures.

The search for a phase transition in liquid ^{3}He has been pursued for many years following the suggestion, on theoretical grounds, that there should be a superfluid phase.[1] One experiment[2] reported a specific-heat anomaly at 5.5 mK but was contradicted by other work,[3,4] and it was argued that it was an experimental artifact.[4] Recent work displayed two anomalies in the melting curve which were attributed to phase changes in the liquid.[5] A specific-heat anomaly[6] and increases in the sound attenuation in the liquid[7] have been observed more recently and appear to be associated with the higher-temperature anomaly in the melting curve. The absolute temperature at which these phenomena took place could only be estimated. We report here a specific-heat peak which occurs at 1.5 mK and a broad anomaly between 2 and 3 mK.

We used a nuclear cooling system similar to that reported earlier[8] except that the ^{3}He evaporator was replaced by a modest dilution refrigerator so as to reduce the heat leak to the paramagnetic salt. The nuclear cooling stage with sample holder is shown in Fig. 1. The container held 1.00 ± 0.05 cm^3 of liquid helium. The copper sponge was made from copper powder (particle size ~1 μm) with a surface area of approximately 1 m^2/g. The powder was pressed to 0.45 of the density of bulk copper and sintered at 450°C for 60 min in a hydrogen atmosphere. The resultant surface area was ~0.2 m^2/g as measured on a larger sample prepared in the same fashion. Hence, the surface area of this sample with 7.49 g of Cu powder was assumed to be 1.5 m^2 within a factor of 2.

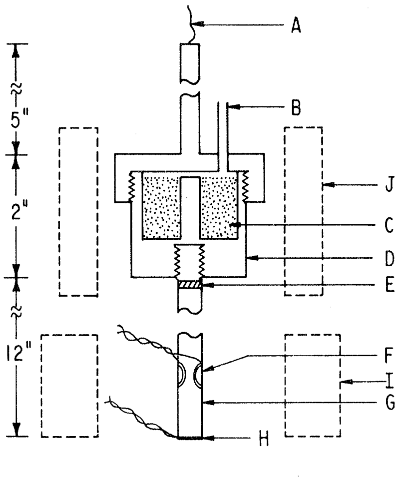

FIG. 1. Schematic drawing of nuclear cooling system and ^{3}He sample holder (not shown to scale). *A*, tin heat switch; *B*, fill capillary; *C*, sintered copper; *D*, copper container; *E*, weld; *F*, nmr coil; *G*, copper wires; *H*, heater; *I*, 70-kG magnet; *J*, magnetic shield coils.

The temperature was determined by measuring the NMR signal from the copper (see Fig. 1) and assuming that its nuclear susceptibility obeys Curie's law. In order to be certain that the temperature scale could be related to that of other work in the field, we normalized our specific-heat measurement at several points between 8 and 16 mK to those in which a cerium-magnesium-nitrate thermometer had been used.[3] The standard deviation of our heat-capacity measurements in this range was about 4% so that our stated temperatures should be accurate to that figure.

Heat-capacity measurements were begun 4 to 6 h after completion of the nuclear demagnetization, during which time the system had warmed from about 0.25 to 0.5 mK. Heat pulses containing between 20 and 60 erg were used employing power between $\frac{1}{4}$ and 1 erg/sec. The temperature was monitored by sweeping through the NMR signal once per minute (Fig. 2). It can be seen that the slope of $1/T$ versus time does not return to its steady-state value immediately after the heat pulses. This slow return was unaltered, within the resolution of our measurements, by the presence or absence of ^{3}He in the container.

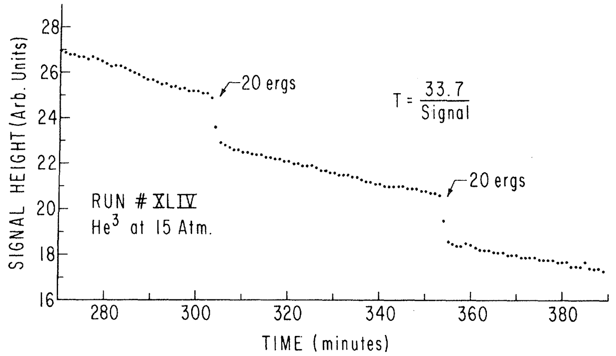

FIG. 2. NMR signal strength as a function of time with heat pulses applied as indicated.

We also measured the warmup rate, $\dot{T}$, as a function of temperature from the slopes of the curves between pulses and from the slope on runs in which the system was warmed only by the background heat leak. The heat capacities determined by dividing the heat leak by $\dot{T}$ agree with those obtained from heat pulses. The heat capacity of the system without ^{3}He was

$$C = (190 + 76 \ln T)/T^2 \text{ erg/mK}$$

with a 1100-G field on the copper wires. Thus, for example, at 1.5 mK and 29 atm the ^{3}He heat capacity was $\frac{1}{2}$ of the total.

Since we have not attempted to measure the temperature of the ^{3}He directly, indirect means for setting limits on the temperature have been devised. The information which is used for this purpose is as follows: The warmup rate, $\dot{T}$, with ^{3}He in the container is smaller in the region where the specific heat, measured with heat pulses, is larger; however, without ^{3}He, $\dot{T}$ does not show such minima and indicates a heat leak decreasing monotonically from 0.6 erg/min at 0.5 mK to essentially zero at 5 mK. The amount of heat required to heat the ^{3}He from 1 to 4 mK is in excess of that required for the extrapolated linear heat capacity regardless of whether it is heated at a steady rate of 1 erg/sec, or in widely separated pulses of 1 erg/sec, or $\frac{1}{4}$ erg/sec; or if it is heated only by the background heat leak of less than 0.01 erg/sec. The position and magnitude of the specific-heat anomalies is also the same under this variety of measuring conditions. The warmup rate between heat pulses divided into an inferred heat leak at the corresponding temperature yields the same heat capacity as the other measurements. There is no observable difference in the recovery of the warmup rate after heat pulses when ^{3}He is present and when it is not. The boundary impedance was measured in earlier work[9] to be $\leq 4\times 10^6/AT^3$ mK sec/erg at 3 mK, where A is the surface area in square centimeters and T the temperature in millikelvins. From the known value of the Korringa constant for copper and the Korringa relation, it can be shown that the temperature of the conduction electrons can be, at most, $(12.7\dot{Q}+1)T_N$, where T_N is the temperature of the copper nuclei in millikelvins and $\dot{Q}$ is the background heat leak in ergs per second entering the electrons.

We argue that the ^{3}He must be less than 0.2 mK above the measured T_N as follows: A measured increase in the heat capacity of the system with ^{3}He implies that the conduction electrons of the copper must be hotter than the ^{3}He during heat input in order to transfer heat into the ^{3}He. If the system consisted only of pure copper, for $T_N = 1.5$ mK the electron temperature would be 20 mK for 1 erg/sec heating power and 1.72 mK for 0.7 erg/min. (This assumes the validity of the Korringa relation for our copper in a field of 1 kG at a temperature of 1.5 mK.) In practice the heat capacities of the system, other than the nuclear-spin heat capacity, further reduce these computed electron temperatures. Since the measured heat capacity did not observably depend on the power used, we conclude that $T_{^3\text{He}} < T_N + 0.2$ mK.

A lower limit is set on $T_{^3\text{He}}$ by assuming that the thermal impedance measured at 3 mK can be extrapolated to lower temperatures. Even in the regions of maximum ^{3}He heat capacity the copper continues to warm up between heat pulses or when no heat pulses are applied. Therefore, during these times the heat input to the ^{3}He is at most some fraction of background heat leak. If we assume that half of the 0.6-erg/min maximum observed heat leak is going into the ^{3}He then for $T_N = 2$ mK, $T_{^3\text{He}} = 1.67$ mK. The low-temperature boundary impedance indicated by the time spent cooling the ^{3}He is apparently somewhat lower than the assumed extrapolation so that the temperature difference is even smaller than that computed above. The coefficient which we measure for the T^{-3} law is smaller than previous measurements and almost independent of pressure.[9] Thus, it appears that a mechanism other than the phonon-phonon transfer is dominant. Since the ^{3}He temperature could lag the thermometer during the warmup, sharp anomalies such as a possible first-order transition at 1.5 mK could be smeared out in our data.

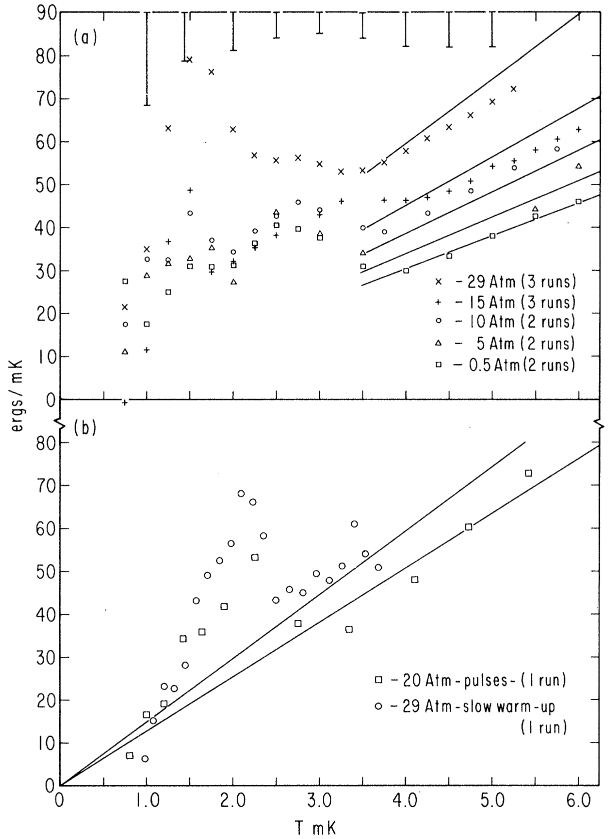

FIG. 3. Heat capacity of liquid ^{3}He. (a) Averaged curves from measurements with heat pulses; error bars represent 2 times the average of the standard deviation of all runs. (b) Different behavior observed on two individual runs. Straight lines represent low-temperature extrapolation of data of Ref. 4.

TABLE I. Total heat content, U, and excess, ΔU, over degenerate Fermi fluid value at pressure P in atmospheres, between temperatures indicated.

T (mK)	P (atm)	U (erg)	ΔU (erg)
1–2	29	67	45 ±8
	25	60	39 ±12
	15	35	18 ±8
	10	37	22 ±8
	5	34	21 ±8
	0.5	28	16 ±8
2–3.75	29	97	22 ±6
	25	94	39 ±21
	15	72	15 ±6
	10	73	24 ±6
	5	66	23 ±6
	0.5	62	24 ±6
1–2.5	20	56	23

If we separate the heat anomaly into two parts, the heat content in excess of the extrapolated Fermi fluid curve (straight lines in Fig. 3) between 1.0 and 2.0 mK and between 2.0 and 3.75 mK is shown in Table I. The excess heat capacity between 2 and 3 mK does not show any clear dependence on pressure but was apparently not a surface effect, since it was gone when we removed 90% of the ^{3}He from the container. One run at 25 atm measured a value for the heat capacity between 1 and 3.5 mK systematically larger than all other runs and could be explained by an incorrectly recorded heater power.

Two runs, shown in Fig. 3(b), revealed qualitatively different behavior from all of the others. One of them was at 20 atm and used heat pulses. The other was at 29 atm and used only the background heat leak to warm the system. Both show a sharp decrease in the heat capacity at 2.4 mK similar to that reported elsewhere[6] but the larger anomaly at 1.5 mK is missing. This could be interpreted as evidence that it is possible to supercool below 1.5 mK without a change of phase. This would be consistent with the identification of "B" as a first-order transition.[5] Since we have not observed the sharp decrease in specific heat at 2.4 mK on runs which display the peak at 1.5 mK it may be that a different phase occurs between 2 and 3 mK when the system has been in the new phase below 1.5 mK. A curious feature of the results of Fig. 3(a) is that the entropy of the liquid below 3 mK is substantially greater than that inferred by extrapolating the linear heat capacity to absolute zero.

Perhaps this feature as well as the qualitative differences between these results and those of Ref. 6 can be explained by the fact that the pore sizes in the sintered copper were of the order of 1 μm, 10 or 100 times smaller than those of Ref. 6. Therefore, this work may not have measured the heat capacity of bulk ^{3}He. Other differences between the experiments were that the surface-to-volume ratio of the ^{3}He was much greater in this work, the surface was copper rather than cerium magnesium nitrate, and the ^{3}He was cooled to substantially lower temperature in this work.

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*Work supported by the National Science Foundation.

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Direct Comparison of Core-Electron Binding Energies of Surface and Bulk Atoms of Ti, Cr, and Ni[†]

J. E. Houston, Robert L. Park, and G. E. Laramore
Sandia Laboratories, Albuquerque, New Mexico 87115
(Received 4 December 1972)

A direct comparison has been made of electron-excited soft–x-ray appearance potentials, which are surface sensitive, and photon-excited Auger-electron appearance potentials, which are more characteristic of bulk atoms. A single tungsten emitter served as a reference for both measurements. The "surface chemical shifts" thus obtained for the $2p_{3/2}$ levels of Ti, Cr, and Ni are in reasonable agreement with predictions based on a muffin-tin approximation of overlapping one-electron potentials.

Atoms in the outermost layer of a metal reside in a different chemical environment from their bulk counterparts simply by virtue of their reduced coordination. The resulting modification of the atomic potentials should produce a "surface chemical shift" in the core levels of the atoms. This has been invoked[1,2] to account for the fact that threshold energies for core-level excitation by electron bombardment[1-4] are consistently lower than tabulated x-ray energy levels.[5] The differences are, however, of the same order as the uncertainties in the determination of absolute binding energies. In this paper we present the first direct experimental evidence of a "surface chemical shift" for Ti, Cr, and Ni, and demonstrate that this shift is in reasonable agreement with calculations based on overlapping effective one-electron potentials. These materials span the spectrum of properties of the $3d$ transition metals: Ti is hcp and nonmagnetic, Cr is bcc and antiferromagnetic, and Ni is fcc and ferromagnetic.

When atoms come together to form a solid, the effective atomic potentials overlap appreciably, resulting in a drastically modified potential as seen by the higher-lying electronic states. The deep-lying core levels, however, see a potential only slightly changed in shape and thus essentially are just shifted in energy relative to their free-atom positions. The size of this shift is determined primarily by the superposition of the potentials centered on nearby sites. Since a surface atom has fewer neighbors at any given distance than an atom in the bulk, its core levels experience a smaller shift relative to their free-atom positions. Hence we expect a "surface chemical shift" between bulk- and surface-atom core levels.

We can obtain a theoretical estimate of the magnitude of the "surface chemical shift" from the same potential construction techniques as used in the calculation of the bulk electronic properties of solids. Specifically, we use the muffin-tin approximation as specified by Loucks. Relativistic free-atom charge densities[7] are overlapped and an average constant potential, V_0, is determined in the neighborhood of a particular atom. The "best" effective local atomic potential is determined relative to V_0 in the usual way.[8] The Slater local exchange approximation[9] is used throughout with the exchange parameter being set equal to the Kohn-Sham[10] value of $\alpha = \frac{2}{3}$. We then determine the position of the core level relative to V_0 by numerically solving the radial Dirac equation.[7,11] The calculated chemical shift for a surface atom is then given by

$$\Delta = (V_0 + E_c) - (V_0' + E_c'), \tag{1}$$

where E_c denotes the position of the core level relative to V_0 and the primed quantities refer to