SPECIFIC HEAT OF He^3 AND He^4 IN THE NEIGHBORHOOD OF THEIR CRITICAL POINTS

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Recently Bagatskiǐ, Voronel', and Gusak[1] showed that the specific heat at constant volume of argon exhibited what appears to be a logarithmic singularity at the critical temperature (T_c) for measurements taken at a density near the critical density. This singular behavior is in sharp contrast to the predictions of the traditional view of this phase transition by Landau and Lifshitz.[2] However, the behavior is precisely that to be expected for the so-called "lattice-gas" model for the liquid-gas transition. Lee and Yang[3] have shown that the partition function of a classical gas of particles moving on a discrete lattice with a repulsive force preventing double occupancy of any site and a nearest-neighbor attraction can be mapped precisely onto the partition function of an Ising model of a spin system in an external magnetic field. The specific heat for this Ising model in zero field exhibits a logarithmic singularity at the Curie point. The specific heat for the corresponding lattice gas on the critical isochore exhibits a logarithmic singularity at the critical point. The measurements on argon then indicate that for a real gas the specific heat behaves in a manner similar to that of a lattice gas. We have investigated this point further by studying the specific heat at constant volume (C_v) of both He^3 and He^4 at densities close to the critical density. We have done this for two main reasons. Firstly, to see whether the behavior observed for argon is also observed for helium, for which quantum effects should be important, and secondly, to investigate the detailed nature of the singularity in the pressure-density plane, not only on the critical isochore but also in its immediate neighborhood. Yang and Yang[4] have conjectured that the quantum effects would reduce the magnitude of the singular contribution to the specific heat in helium. Our results confirm this view.

The calorimeter was built of two OFHC copper parts. The helium was contained in the lower part in 50 slots each 0.3 cm deep and 0.01 cm wide. The large area of these slots facilitated good thermal contact between the helium and the calorimeter. The upper part was a lid, sealed to the lower section with an indium *O* ring. The lower part was wound with a Constantan heater and had a carbon resistor cemented and clamped to it. The calorimeter was supported on nylon threads in an evacuated chamber. Thermal contact to the bath was made with a mechanical heat switch. A stainless steel capillary 5 in. in length and 0.006-in. i.d. led from the calorimeter to a needle valve. The dead volume of the capillary was about $\frac{1}{2}\%$ of the total volume of the calorimeter. Helium was admitted to the calorimeter via a Toeppler pump which was used to measure the volume of the gas to an accuracy of about 0.2%.

A (1/10)-W Ohmite carbon resistor of nominal resistance 560 Ω was used as a secondary thermometer. Its resistance was measured with a 100-cps bridge using a lock-in amplifier. Temperature changes of about $2\times10^{-6}\,^\circ K$ at 5.2°K and $1\times10^{-6}\,^\circ K$ at 3.3°K could be observed. At the end of a run, exchange gas was admitted to the vacuum space and the resistor was calibrated against the vapor pressure of the He^4 bath from 2.9 to 5.15°K. A smooth resistance temperature relation was fitted, hence relative specific-heat measurements near the critical points are not sensitive to errors either in the vapor-pressure–temperature scale or in the calibration. Stray heat input to the calorimeter was measured before and after each data point was taken. The approach to temperature equilibrium of the calorimeter was observed after each heating interval. As T_c was approached, the equilibrium time increased from a few seconds to several minutes and became one of the limiting factors in this measurement.

For each run T_c was tentatively defined as the temperature at which C_v fell most abruptly. The final value of T_c was then chosen to give the best fit to

$$\frac{C_v}{R} = -a \ln\left(\frac{T_c - T}{T_c}\right) + b, \tag{1}$$

over the range $10^{-3}\,^\circ K < (T_c - T) < 10^{-1}\,^\circ K$. The adjustment involved was less than $3\times10^{-4}\,^\circ K$.

Figure 1 is a general view of the specific

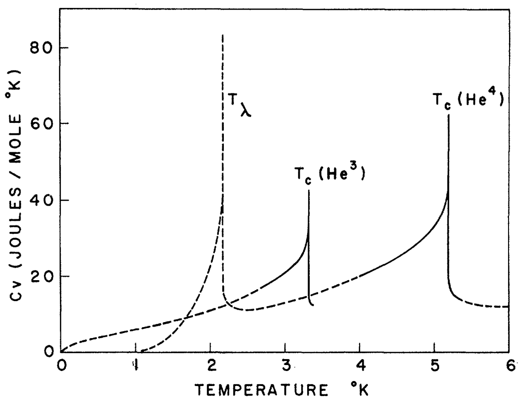

FIG. 1. C_v of He^3 and He^4 at their respective critical densities is plotted as a function of temperature. The solid curve is the present work.

heats at the critical volume of He^3 and He^4 at low temperatures.[5] We have indicated the temperature range covered by these measurements. In Fig. 2 we have plotted on both a linear and logarithmic scale measurements of C_v of He^4 at a density within 0.5% of the critical density. In the two-phase region below T_c, C_v clearly exhibits within 0.2°K of T_c, logarithmic behavior similar to that observed in argon[1] and oxygen.[6]

In the one-phase region above T_c two alternatives have been suggested. $C_v \propto \ln(T-T_c)$ has been suggested by an exact calculation on a two-dimensional Ising model,[7] by C_v measurements on argon[1] and oxygen,[5] and by velocity-of-sound measurements on helium four.[8] $C_v \propto (T-T_c)^{-\alpha}$ for some small positive α (such as $\frac{1}{5}$) has been suggested by Fisher[9] on the basis of an approximate calculation on a three-dimensional Ising model and his reanalysis of the argon and oxygen data. We do not believe the present data permit one to distinguish between these two alternatives.

In Fig. 3 similar plots are given for He^3 for a density of $0.98^5\rho_c$. Logarithmic behavior is again observed for $T<T_c$. The data for argon, oxygen, and both isotopes of helium expressed in the dimensionless form (1) are summarized in Table I. We see that the coefficient a decreases from argon to He^4 to He^3 in agree-

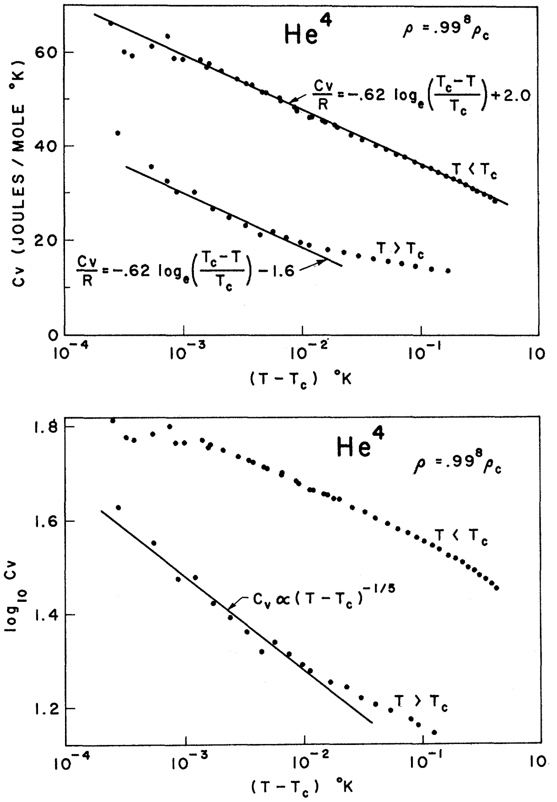

FIG. 2. C_v of He^4 is plotted against $|T-T_c|$ at a density of $0.99^8\rho_c$.

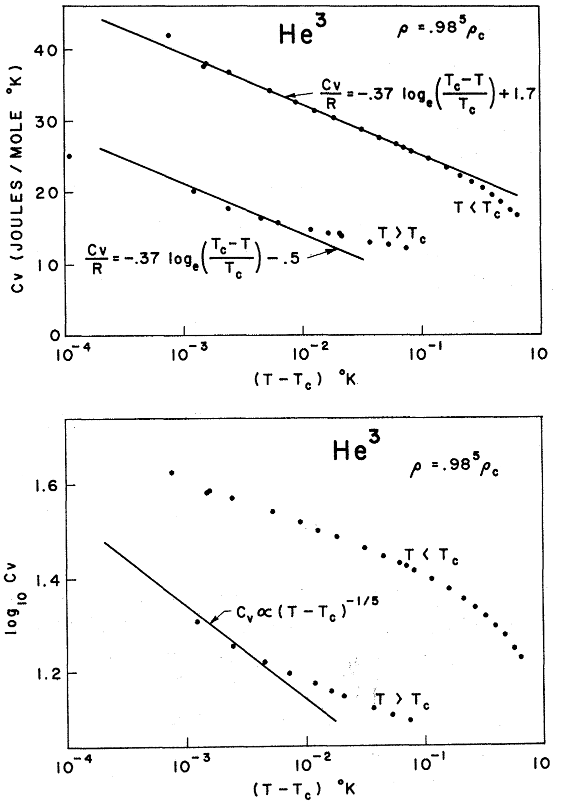

FIG. 3. C_v of He^3 is plotted against $|T-T_c|$ at a density of $0.98\rho_c$.

Table I. Coefficients a and b of Eq. (1) for Ar, O_2, He^4, and He^3.

Element	a	b $(T < T_c)$
Ar	1.8	8
O_2	2.4	10
He^4	0.62	2.0
He^3	0.37	1.7

ment with the conjecture of Yang and Yang.[4] We note that the coefficient 0.62 for He^4 is very close to that observed by Buckingham and Fairbank[5] for the specific heat along the saturated vapor curve at the λ point of He^4 (0.64) and may have particular significance in explaining the quantum transition.

Preliminary measurements of C_v for He^4 at densities not as close to ρ_c as the measurements presented above indicate that in the two-phase region $d^2\mu/dT^2$, where μ is the chemical potential, does not approach zero as T approaches T_c. This differs from the result of the two-dimensional lattice gas and supports the prediction of Yang and Yang.[4] The behavior of C_v in the one-phase region is a sensitive and complicated function of density. It will be discussed elsewhere.

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DIFFUSION OF TRIPLET EXCITONS IN ANTHRACENE*

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We have performed two types of experiments which indicate that the diffusion coefficient for triplet excitons in anthracene crystals is on the order of 0.4×10^{-2} to 2×10^{-2} cm^2 sec^{-1}. The results are particularly significant since they are compatible with coherent motion of triplet excitons (mean-free path greater than the lattice spacing) and give inconsistent results for the hopping or incoherent model of energy transfer unless present estimates of the hopping rate are grossly in error.

In a recent review article on excitons, Knox[1] pointed out that exciton diffusion by coherent motion has not been adequately demonstrated. Experimental observations on triplet excitons in anthracene[2,3] have shown that there was a very good possibility that diffusion effects could be observed in this system, and Avakian and Merrifield[4] have recently published results demonstrating this effect. Their results, how-