Quantum State of $^4$He Confined in Nanocages of Na-Y Zeolite

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Abstract. We have studied the heat capacity of $^4$He adsorbed in Na-Y zeolite down to 70 mK. The Y-type zeolite has void cages 1.3 nm in diameter connected through narrow apertures 0.8 nm in diameter. After the first solid layer of adsorbed $^4$He is completed at 10.3 atoms/cage (about 37% of full pore), the pore apertures are considered to be so narrow that $^4$He adatoms in the second layer are confined in each cage at low temperatures, and form a cluster of several atoms. After the first layer completion, the low-temperature heat capacity isotherm has two peaks around 13.7 and 17.0 atoms/cage (about 50 and 63%), between which quantum-statistical differences from those of $^3$He appear. From the peaks in the heat capacity isotherm, the quantum region for $^4$He adatoms in Na-Y zeolite was determined.

1. Introduction

Helium atoms adsorbed on substrates have realized low-dimensional quantum fluids different from bulk liquid helium. Using flat substrates or Vycor glasses with pore diameters of about 10 nm, superfluid onsets in $^4$He films have been extensively studied for several decades [1, 2]. The onsets are explained in terms of the Kosterlitz-Thouless theory [3, 4]. In one-dimensional (1D) tunnels of 1.8–2.8 nm in diameter, we observed 1D-2D crossovers of phonon heat capacities in $^4$He fluid film [5, 6] and of heat capacities for $^3$He Boltzmann gas [7]. Of such varied restricted geometries, the most extreme dimension is that of several helium atoms confined inside cages in a nanometer scale. At low temperatures, the confined atoms likely form quantum “fluid” in zero dimension, i.e. the quantum cluster state, where their de Broglie waves overlap in each cage. The cluster state was examined for helium adsorbed in Y-type zeolites [8]. These zeolites have void cages of 1.3 nm in diameter connected through narrow apertures 0.8 nm in diameter. At the first layer completion of solid He films, apertures are considered to be sufficiently narrow to confine several He atoms in each cage. Previous heat capacity measurements for Na-Y zeolite above 0.2 K have shown that low-temperature heat capacities of $^4$He at coverages above the first layer completion are qualitatively different from those of $^3$He [9, 10]. The quantum-statistical difference between $^4$He and $^3$He adatoms suggests that quantum fluid is formed in the second layer. A tetrahedral cluster model was used in an attempt to explain the experimental results at some coverages [11].

To verify whether the quantum fluids observed in Na-Y zeolite are clusters of helium, we have to examine the heat capacities characteristic of the quantum cluster states, for example, drastic

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changes when one atom is added in each cage. Therefore, we have extended the heat capacity measurement for helium adatoms in Na-Y zeolite to lower temperatures down to 70 mK. In this article, preliminary results for $^4$He are shown, and the quantum region for the adsorbed $^4$He is determined from the results.

2. Experimental

The framework of the substrate Na-Y zeolite, $\text{Na}_{56}[\text{AlO}_2]_{56}(\text{SiO}_2)_{136} \cdot 250\text{H}_2\text{O}$, is made of alminosilicate including $\text{Na}^+$ cations which compensate negative charges of $\text{AlO}_2^-$ [12]. This is schematically shown in Fig. 1(a). After dehydration treatment, void cages 1.3 nm in diameter are left, which are connected in a diamond structure through apertures with a diameter of 0.8 nm.

![Figure 1. Schematic drawings of Na-Y zeolite. (a) Framework made of alminosilicate. (b) Adsorbed $^4$He atoms after the first layer completion. The apertures are narrowed by the solid layer and adatoms in the second layer are likely confined in each cage.](image)

Measurements of vapor pressure for adsorption clarified that, in the first layer of adsorbed $^4$He, the isosteric heat for sorption is 135–170 K depending on distances from the $\text{Na}^+$ sites on the surface of cages [13]. Due to this strong adsorption potential, the first layer of adatoms is solidified. As shown in Fig. 1(b), assuming that the thickness of the solid layer is 0.3 nm, apertures are narrowed to 0.2 nm. Thus, $^4$He atoms in the second layer are probably confined in each cage and form $^4$He clusters. From the isosteric heat for sorption and the heat capacity, coverages of the completed first layer $n_1$ and full pore $n_{\text{full}}$ were estimated to be about 10.5 and 27.5 atoms/cage, respectively [13].

For heat capacity measurements down to 70 mK, Na-Y zeolite powder was mixed with silver powder and sintered on silver disks, for good thermal contact against the body of the sample cell. The sample was dehydrated in vacuum at 300 °C for 8 hours. The dehydrated sample zeolite includes void cages of 0.207 mmol, the number of which was estimated from the maximum amount of $\text{N}_2$ adsorbed at 77 K. The heat capacity was measured by the heat pulse method. The heat capacity of adsorbed $^4$He was derived as a difference between the total heat capacity and that of the empty sample cell with Na-Y zeolite.

3. Heat Capacities and Quantum Region of $^4$He in Na-Y Zeolite

Isotherms of the $^4$He heat capacity $C$ divided by temperature $T$, where $C$ is for 1 mol of cages in Na-Y zeolite, are plotted in Fig. 2. The first layer completion of adsorbed $^4$He is indicated by a sharp dip around $n_1 = 10.3$ atoms/cage, which agrees with previous results (about 10.5 atoms/cage [10, 13]). Above $n_1$, the isotherms below 1 K increase with coverages $n$, and then start to decrease around 13.5 atoms/cage. Above this coverage, qualitative differences between heat capacities of $^4$He and those of $^3$He were observed in previous measurements [9]. Similar behavior is observed for $^4$He adsorbed on the other substrates such as FSM-16 or HMM-2 [14].
The porous materials FSM-16 and HMM-2 have 1D pores 2.8 nm in diameter and a 3D network of 2.7 nm pores, respectively. In these substrates, an apparent quantum-statistical difference between $^4$He and $^3$He is indicated by a peak of the $^4$He heat capacity isotherms at a coverage a little larger than $n_1$, where the $^3$He heat capacity increases with $n$ contrastively. The peak of the isotherm for $^4$He is attributed to an onset of the Bose quantum fluid phase, especially, superfluid phase in the case of HMM-2. Thus, above the isotherm maxima around 13.5 atoms/cage, $^4$He adsorbed in Na-Y zeolite is considered to enter a Bose quantum region. Above 15 atoms/cage, the $^4$He heat capacity isotherms below 0.7 K have the second peaks around 17 atoms/cage. The second peak is not observed in FSM-16 or HMM-2 [14]. In either substrate, $^4$He in the second layer remains fluid up to the full pore coverage $n_{\text{full}}$, because $^4$He inside pores can move to the outside easily through open ends of pores. On the other hand, near $n_{\text{full}}$ in Na-Y zeolite, $^4$He atoms are too closely packed in each cage to exchange sites with each other, as shown by the small heat capacities of $^3$He as well as $^4$He. Therefore, the quantum region in Na-Y zeolite is likely to have another boundary at the second peak of 17 atoms/cage.

Thus, from two peaks of the isotherms of $^3$He heat capacity, we can define boundaries of the quantum region for $^4$He adsorbed in Na-Y zeolite. The boundaries $n_{c1}$ and $n_{c2}$ were provisionally determined as two points of contact when a common tangent line to both peaks in a heat capacity isotherm was drawn. The derived phase diagram is shown in Fig. 3. The coverages of the quantum region, from $n_{c1} \simeq 13.7$ to $n_{c2} \simeq 17$ atoms/cage, correspond to 50–62% of $n_{\text{full}}$. The high-temperature boundary of the region is observed around 1.2 K. Recently internal energies of several atoms confined in a nanometer-scale cage were calculated by the path-integral Monte Carlo simulation [15]. The calculations suggest that the internal energy of 3 or 5 quantum $^4$He Bosons becomes lower than that of classical $^4$He atoms below about 2 K. The onset of the quantum effect is consistent with the observed high-temperature boundary of the quantum region, considering the ambiguity of the determination method of the boundary.

The temperature dependences of the heat capacities have qualitative differences between the quantum region and the other regions, which can be seen in the $C/T$ isotherms in Fig. 2. From $n_1$ to $n_{c1}$, the isotherms from 0.4 to 1 K collapse into the same curve, indicating that the heat capacities below 1 K are almost proportional to $T$ except for a steep decrease at low temperatures. Similarly, above the second peak around $n_{c2}$, the isotherms at 0.4–1 K tend to...
coincide again, indicating nearly linear $T$-dependence. In contrast, in the quantum region from $n_{c1}$ to $n_{c2}$, the heat capacities decrease with $T$ more rapidly than $T$-linear. This suggests that a quantum effect appears in this region.

4. Summary
We have studied the heat capacity of $^4$He adsorbed in 1.3 nm cages of Na-Y zeolite, where atoms in the second layer are likely to be confined in each cage, and form the cluster state. After the first layer completion of adsorbed $^4$He, the heat capacity isotherm below 1 K has two peaks. Between coverages of these two peaks, the quantum state of adsorbed $^4$He is likely to appear, where the temperature dependence of the heat capacity is steeper than the linear dependence observed outside the quantum region. The high-temperature boundary of the quantum region is observed to be around 1.2 K, which is consistent with a theoretical simulation for a $^4$He cluster.

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