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1994 J. Phys.: Condens. Matter 6 2341

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Heat capacities of neon in one- and three-dimensional channels at low temperatures

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Received 16 July 1993, in final form 8 December 1993

Abstract. Heat capacities of Ne adsorbed in the one- and three-dimensional channels in the high-silica zeolites ZSM-23 and ZSM-5 have been observed in the temperature range from 2 K to 23 K for various concentrations of Ne. For lower concentrations of Ne, the low-temperature heat capacities for both the one-dimensional and the three-dimensional channels, both about 5.5 Å in diameter, are described by the Einstein model, which implies that Ne atoms are localized independently or construct clusters of minute size in the channels. However, for the higher concentration where channels are nearly filled with Ne atoms, the heat capacities of Ne reflect the difference between the topological channel structures of the two zeolites. In the case of three-dimensional channels, the heat capacity is revealed to be well reproduced by the Debye model for a continuous solid with the characteristic temperature $\Theta_D = 29$ K, which is unexpectedly smaller than the values $\Theta_{3D} \simeq 67$ K for the bulk solid Ne and $\Theta_{2D} \simeq 50$ K for the two-dimensional solid Ne. This suggests the possibility of an unusual softening effect of phonons in solid of Ne in the three-dimensional network of channels. While the heat capacity of Ne in the one-dimensional channels cannot be understood in terms of the one-dimensional Debye model, it can be explained using the Einstein model. These results for the classical Ne particle are significant when compared with the thermal behaviour of He in the same zeolites, which reflects the characteristic quantum effect at low temperatures.

1. Introduction

Recently, extensive studies have been made on quantum particles adsorbed in zeolites [1–4] or high-silica zeolites [5–7] in which the channel diameter is less than 10 Å. In these severely restricted geometries quantum degeneracy, such as the Fermi degeneracy of ^3He or the superfluidity of ^4He , is greatly affected by the channel size, or dimensionality, of the structure [2, 3, 5]. In the case of H_2 , the possibility of superfluid molecular hydrogen supercooled in a narrow channel [8] was examined [1, 4]. However, there are few experimental studies of classical particles in such severely restricted geometries at low temperatures. As for the thermal behaviour of Ne adsorbed in wider geometries, such as Vycor glass and graphite, several experiments have been carried out. Tell and Maris [9] measured the heat capacity of Ne in porous Vycor glass, with a pore diameter of 54 Å, and obtained qualitatively the same heat capacity as in the bulk phase, except that the freezing temperature in Vycor glass (20.7 K) was lower than that of the triple point of bulk Ne (24.5 K). For Ne adsorbed on a two-dimensional graphite system [10–12], the heat capacity reveals a sharp peak at a triple point of 13.5 K and shows the characteristic low-temperature

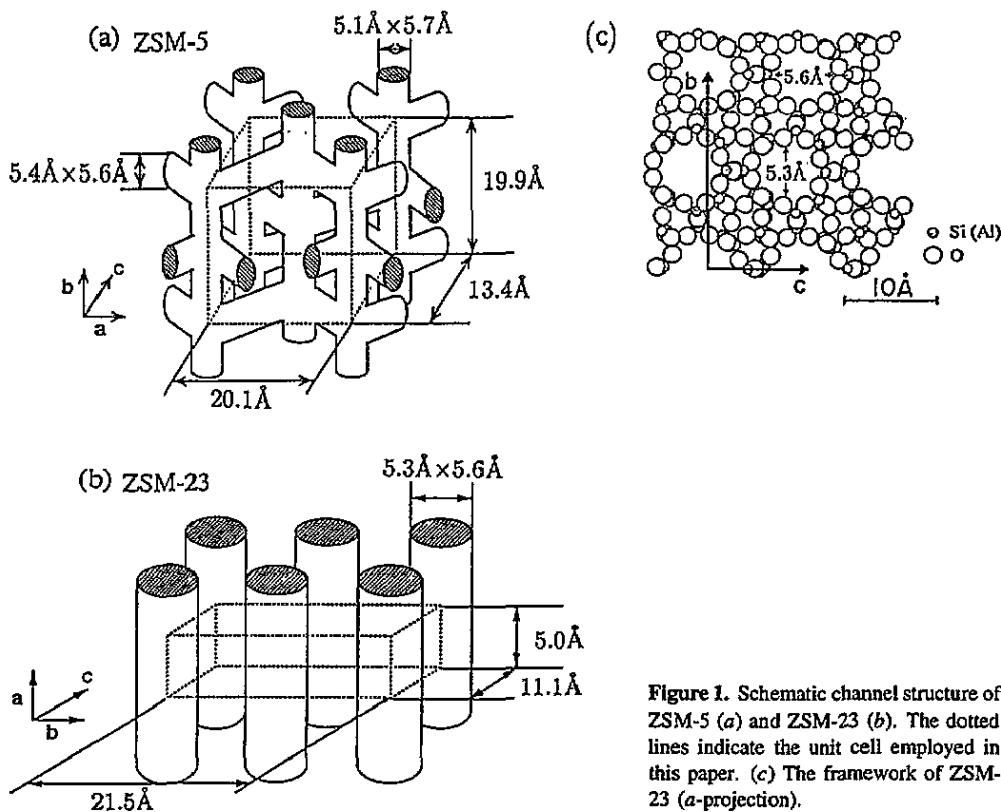


Figure 1. Schematic channel structure of ZSM-5 (a) and ZSM-23 (b). The dotted lines indicate the unit cell employed in this paper. (c) The framework of ZSM-23 (a-projection).

heat capacity expected for a two-dimensional Debye solid with a Debye temperature of $\Theta_{2D} \simeq 50$ K.

The purpose of this study is to clarify the low-temperature thermal behaviour of classical Ne particles in very restricted geometries, of the order of 5 Å, and to compare it with previous results for He with strong quantum effects [7].

2. Experiment

We use two types of high-silica zeolites, ZSM-23 [13] and ZSM-5 [14]; these specimens were used in previous work on a He system [7]. High-silica zeolites have a high value of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, which is a measure of electrical neutrality on the framework; the ratio for ZSM-23 used here is 63 and that of ZSM-5 is 1900. The channel structure of these high-silica zeolites is schematically shown in figure 1 [7]. The zeolite ZSM-23 has one-dimensional channels parallel to [100] enclosed by a ten-membered atomic ring of size $5.3 \text{ \AA} \times 5.5 \text{ \AA}$; its porosity is $0.21 \text{ cm}^3 \text{ g}^{-1}$. The zeolite ZSM-5 has a three-dimensional network of channels enclosed with ten-membered atoms, as shown in figure 1(c). Straight channels parallel to [010] have openings of size $5.4 \text{ \AA} \times 5.6 \text{ \AA}$, and zigzag channels along [100] have openings of size $5.1 \text{ \AA} \times 5.7 \text{ \AA}$. The porosity is $0.32 \text{ cm}^3 \text{ g}^{-1}$. In ZSM-23, direct positional exchange of Ne atoms is prohibited within the channels. In ZSM-5, however, the exchange is possible through the three-dimensional paths. The high-silica zeolites used here are powdered specimens with an average size of about $1 \mu\text{m}$.

The experimental apparatus and method are similar to those described in [7]. The sample cell with the zeolite, and the capillary tube for the gas inlet, were kept at temperatures around

the boiling point of Ne (27 K), and above 32 K, respectively; Ne gas was let into the sample cell. In the case that a certain number of Ne atoms have been adsorbed at one time, we point out that some adatoms may be adsorbed on the surface of the zeolite specimen [7]. We then repeated the adsorption of a small amount of Ne gas; the total adsorption time was more than 10 h. After annealing the sample system up to 35 K to prevent irregular distribution of adatoms, and cooling to 1 K, we measured the heat capacity by the conventional adiabatic DC pulse method. The measured data for the first run agree, within experimental error, with the data from the second run; this agreement may be due to the adsorption process and the annealing effect. The annealing effect in the heat capacity measurement was also observed for Ne adsorbed on graphite [12].

3. Results and discussion

3.1. Adsorption isotherms

We first checked the dependence of the isothermal pressure on the amount of adsorbent Ne gas in the two zeolites. The experimental results are shown together with those of helium for ZSM-5 (figure 2(a)) and for ZSM-23 (figure 2(b)). The data were taken at the boiling points for Ne (27 K) and He (4.2 K). The pressure was nearly constant until the amount of gas reached a critical value, N_c , above which the pressure increased abruptly. For amounts smaller than N_c , the gas is thought to be adsorbed mostly within the channel, as will be mentioned in section 3.2. The critical values for Ne are a little larger than those for helium. This may be responsible for the enhanced zero-point motion of helium atoms in a narrow channel [7]. From this figure, we estimate N_c for Ne to be 2.1 atoms per unit cell in the case of ZSM-23, which is rather smaller than the value of 3.5 atoms per unit cell calculated under the assumption that Ne atoms are hard-sphere particles with a diameter of about 3 Å. This indicates that Ne atoms are likely to be trapped on the wall of the channels and are unlikely to be closely packed within the one-dimensional channels in which the position of two atoms cannot be exchanged directly. For the case of ZSM-5, we get N_c for Ne to be 46 atoms per unit cell, almost the same as the calculated maximum value of 44 atoms per unit cell.

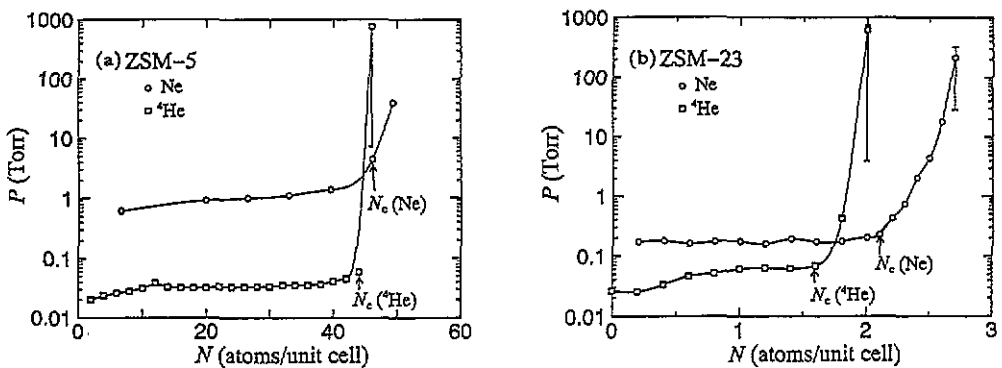


Figure 2. Adsorption isotherms of Ne and ^4He in ZSM-5 (a) and ZSM-23 (b). Measurements were made at 27 K for the case of Ne and at 4.2 K for ^4He . The full curves are to guide the eye.

Hereafter, we define the concentration n of Ne atoms in the high-silica zeolites as the ratio of the adsorbed number N to N_c : $n = N/N_c$.

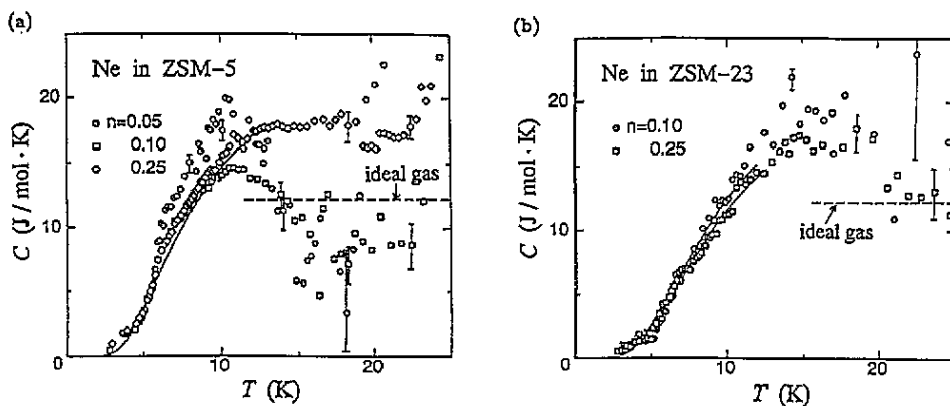


Figure 3. Heat capacities of Ne adsorbed in high-silica zeolites for the low concentration range. (a) ZSM-5: the full curve is the heat capacity of the Einstein model with $\Theta_E = 26$ K. (b) ZSM-23: the full curves are the heat capacities of two sets of the Einstein model ($\Theta_E = 25$ K and 35 K). The broken curve indicates the heat capacity of ideal gas.

3.2. Heat capacity

Measurements of the heat capacity were carried out for various concentrations of Ne. The heat capacity of Ne was obtained after subtraction of the contribution from high-silica zeolites and the sample cell [7]. The results are shown in figure 3 (lower concentrations) and figure 4 (higher concentrations) for ZSM-5 (a) and ZSM-23 (b). The data points have a large uncertainty for the lower concentration range at high temperatures. However, the experimental error becomes small with increasing concentrations. Above 23 K, the data points are unreliable, probably because Ne atoms begin to get out of channels of the zeolite; we therefore discuss only the results below 23 K. The temperature dependence of heat capacities for both zeolites are clearly different from that of the bulk Ne or two-dimensional solid of Ne. We see no anomalous peak, as observed for Ne adsorbed on graphite [11, 12], nor any jump related to the characteristic solid-liquid transition in bulk Ne. If a small amount of Ne atoms were adsorbed on the surface of the high-silica zeolites, it would be expected to form a two-dimensional solid at low temperatures and exhibit the sharp heat capacity peak around a triple point as observed at 13.5 K for submonolayer Ne on graphite [11]. Therefore, the contribution of Ne trapped on the surface is believed to be negligible in the present experiments.

First, we consider the heat capacities for lower concentrations. When $n < 0.25$ for ZSM-5 and ZSM-23, the Ne heat capacities increase abruptly, nearly independently of the concentration below 10 K, as in figure 3(a) and 3(b). Above 10 K, there appears the broad maximum around 11 K for ZSM-5 and 15 K for ZSM-23, although experimental error becomes large. For Ne in ZSM-5, the data below 10 K fit well the Einstein model with a characteristic temperature $\Theta_E = 26$ K. The data for ZSM-23 below 10 K are reproduced by a combination of two sets of the Einstein model, with $\Theta_E = 25$ K and 35 K, with equal numbers of effective oscillators in each mode. These results imply that Ne atoms are localized on a channel wall of the zeolites, or form minute clusters, giving a few dominant characteristic vibrational modes. We speculate no further here, and say only that at these concentration the low-temperature heat capacity cannot be fitted to a continuous-solid model.

Passing through the broad maximum above 10 K, the heat capacity seems to show a plateau or become smaller above 15 K as in figure 3(a) and 3(b), although the experimental error becomes large. For the three-dimensional channel structure, ZSM-5, the data points

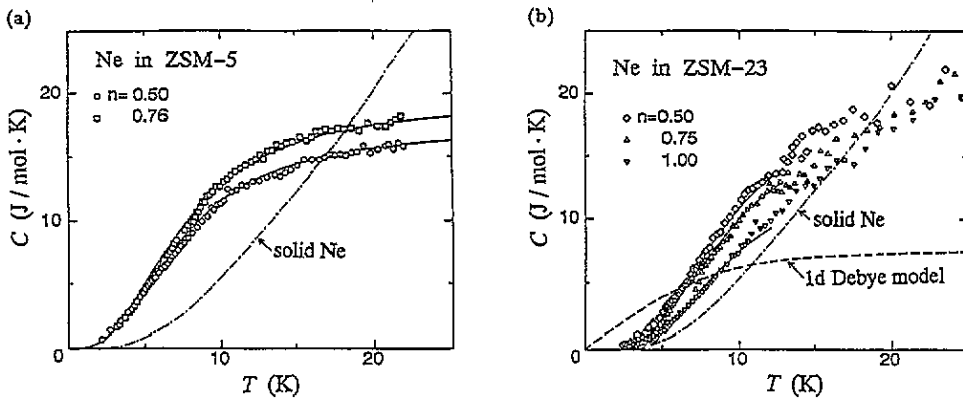


Figure 4. Heat capacities of Ne adsorbed in ZSM-5 (a) and in ZSM-23 (b) for the high-concentration range. The full curves in (a) are the heat capacities of the combination of the dominant three-dimensional Debye model with $\Theta_{3D} = 29$ K and the additive Einstein model with $\Theta_E = 32$ K. The full curves in (b) are examples of the heat capacities which are reproduced with two sets of the Einstein model ($\Theta_E = 25$ K and 35 K). The broken curve shows the heat capacity of the one-dimensional Debye model with $\Theta_{1D} = 30$ K. The chain curve shows the heat capacity of solid Ne.

for $n = 0.05$ and $n = 0.10$ fall below the value $3R/2$ for a classical three-dimensional gas. This may be because Ne atoms begin to behave like a gas in the restricted three-dimensional channels in ZSM-5 at high temperatures, and the restriction of kinetic space makes the heat capacity become smaller than $3R/2$ in the isotropic three-dimensional case.

In conclusion, for the lower Ne concentration, at low temperatures Ne atoms localize on a channel wall, or form minute clusters, but they may start to move in the restricted geometries at temperatures $T > 15$ K. The broad maximum of the heat capacity around $11 \sim 15$ K indicates an intermediate state of Ne atoms at the lower and higher temperatures.

Next, we discuss the heat capacity of Ne for higher concentrations, $n \geq 0.50$. The temperature dependence of heat capacity seems to be qualitatively the same in both zeolites. However, we can see an intrinsic and quantitative difference between them as follows. The heat capacity of Ne in the three-dimensional zigzag channels as in figure 1(a) can be well reproduced using the three-dimensional Debye function with a Debye temperature $\Theta_{3D} = 29$ K, as in figure 4(a). For the best fit with the data points, we need to add a small contribution from the Einstein function, with $\Theta_E = 32$ K. The additional heat capacity amounts to only $1/9.4$ and $1/14$ of the total heat capacity for $n = 0.50$ and $n = 0.76$, respectively, becoming smaller with increasing values of n . This suggests that Ne atoms may form a continuous solid even in the three-dimensional network of channels of size $5 \sim 10$ Å. The value of the heat capacity in the high-temperature limit does not reach $3R$. We believe this is because the vibrational modes are reduced by the anisotropic three-dimensional network of Ne atoms along the channels. It is remarkable that the value $\Theta_{3D} = 29$ K in the present case is much smaller than the value $\Theta_{2D} = 50$ K for the two-dimensional Ne solid [11] or the value $\Theta_{3D} = 67$ K for the bulk solid of Ne [15]. The large reduction of Θ_{3D} in this narrow space cannot be understood as the softening effect of phonons as in a system with a small number of particles [16], or in the amorphous state [17], where the value of the Debye temperature reduces by about 10% of the value for the bulk state. It is pointed out that theoretically the interaction between particles is weakened in the comparably narrow space of the particle size [18]. This may be a reason for the present reduction of Θ_{3D} .

The heat capacity for the higher concentration of Ne in the one-dimensional channels is shown in figure 4(b). The data points cannot be represented by the one-dimensional Debye function for the continuous solid (broken curve). The data points below 10 K can be represented by one or more Einstein functions. In figure 4(b), the theoretical values given by the combination of two Einstein models with $\Theta_E = 25$ K and 35 K, for example, are shown for each concentration. One-dimensional lattice dynamics gives the vibrational modes to be equal, at most, to the number of constituent particles. The experimental result shows that the number of modes will reduce, and some dominant modes may contribute the Einstein-type of heat capacity at low temperatures. It seems that Ne atoms in the channels may form minute clusters or be localized irregularly. On the other hand, Ne atoms may be trapped on a channel wall by van der Waals forces, again giving rise at low temperatures to an Einstein-type contribution to the heat capacity. Although we cannot deduce, from the heat capacity alone, the detailed behaviour of Ne atoms in the one-dimensional channels, it is an experimental fact that Ne atoms do not give a heat capacity of the one-dimensional Debye-function type.

These results for Ne are very different from those of He in ZSM-23 and ZSM-5 [7]. Heat capacities of He in high-silica zeolites did not show the temperature dependence given by the Debye or Einstein models. In ZSM-23, the heat capacity of helium depends linearly on temperature, which can be explained by the semi-quantum-liquid state caused by the large quantum effect. In ZSM-5, the heat capacity for the lower concentration of He shows a shoulder around 2 K, which can be explained by the enhanced energy levels of He in the severely restricted geometries. This interpretation is now supported by a comparison with the present results for Ne.

Acknowledgments

The authors would like to express their sincere thanks to Dr O Terasaki of Tohoku University and Dr S Ueda of Osaka University for supplying the high-silica zeolite samples. They are grateful to Professor T Haseda for his constant interest and valuable comments.

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