Entropy and Magnetization Measurements Relating to the Nature of the Adsorbed Phases of Helium-3 Under Pressure*

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NMR and compressional cooling experiments have been carried out in Vycor porous glass immersed in liquid ³He in a Pomeranchuk cell at various temperatures and pressures. The expected nucleation of a solid phase near the substrate at a few bar does not take place, but compressional cooling occurs at about 2/3 bar below the melting curve. Modification of a simple statistical layer model to take into account the two-dimensional nature of the second layer gives better agreement with the observations, but other considerations show that the phase is probably fluid. These experiments therefore show the existence of a previously undiscovered high-density (>solid) disordered phase which is probably mobile. The NMR measurements show that the ferromagnetic interactions in the adsorbed ³He are larger than in bulk liquid, and increase with increasing pressure and decreasing temperature.

1. INTRODUCTION

Many experiments have been done to study the properties of ³He in the adsorbed state, using a number of different substrates. In previous work in this laboratory we have made extensive investigations of the thermal, magnetic, and flow properties of helium adsorbed in Vycor, which is a highly porous silica glass, at saturation pressure and below, and at temperatures between 30 mK and 4 K (see Ref. 1 for a review). These have shown a wide variety of phenomena associated with the effect of a strongly attractive wall or the confinement of helium to small dimensions—in the case of Vycor, to cavities which can be characterized by a size around 70 Å. The theoretical problem of calculating precisely the properties of helium in the large and

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rapidly varying potential provided by an irregular surface such as Vycor is not at present tractable, but several useful approximations have been attempted. Using a continuum approximation, Franchetti calculated the increase in pressure near the wall in a thick film and hence, using the measured properties of bulk helium, the variation of density with distance from the wall. He found that, because of the large helium-substrate van der Waals force and the high compressibility of fluid helium, the layer of atoms immediately adjacent to the wall was compressed to solid bulk density, and that the density increase was appreciable even at two atomic distances away. A similar approach was used by Atkins.

The statistical layer model extends the continuum approximation by including the atomic nature of the adsorbate. We outline some relevant aspects of it here; a fuller description has been given in a recent review. It arose out of a modification of the Brunauer-Emmett-Teller adsorption equation, which relates the mass of adsorbate to the interatomic spacing in the first layer and the relative pressure. When applied to helium it gives a very high first layer density, and the fit of the equation is poor. A better fit can be obtained by treating the tightly bound first layer as part of the substrate and applying the BET equation to the additional adsorption on top of it. The equation then gives a slightly enhanced density for the second real helium layer. The essential idea of the simplest form of this model, therefore, is that the continuous density variation calculated by Franchetti and Atkins is replaced by a succession of layers, the first of which is compressed to the density of bulk solid at about 400 bar and is probably localized, the second is compressed to the same interparticle spacing as bulk liquid near the melting curve, and the atoms further away are at a density close to bulk liquid at the saturation vapor pressure. The interparticle spacings in the first two layers, derived from low-coverage adsorption measurements of $^3$He and $^4$He on Vycor, are consistent with their average densities in a thick film calculated by Franchetti using the bulk helium PVT relations. Direct measurements of the average density of the adsorbate can be made by measuring the quantity of helium required to fill the known volume of the Vycor pores, and are in agreement with the statistical layer model to an accuracy of 1.5% for $^4$He over the temperature range 1.2–4.2 K. In $^3$He the temperature variation of the observed average density in Vycor is less than in bulk liquid and the agreement is not so good; the layer model parameters give an accuracy of 3% between 0.5 and 2.8 K, and 10% at 3.0 K.

The depth and narrowness of the potential binding the first layer suggest that there will be little mobility between the first and other layers, and that the first layer may form a two-dimensional array of localized atoms, though not necessarily a self-cohesive or crystalline solid. When not covered by additional layers, the monolayer does have properties consistent with such a hypothesis. For example, the specific heat of both $^3$He and $^4$He