Ground State of the Helium-Atom-Graphite-Surface System

R. L. Elgin,[(a)] J. M. Greif, and D. L. Goodstein
California Institute of Technology, Pasadena, California 91125

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We report the first results of a thermodynamic analysis of data for ^{3}He adsorbed on Grafoil. The ^{3}He-graphite binding energy is in excellent agreement with a prediction made on the basis of ^{4}He-graphite atomic scattering data.

In a recent Letter, Boato, Cantini, and Tatarek[1] have reported the energies of the four lowest-lying bound states for a ^{4}He atom interacting with a graphite surface. These values were deduced from the bound-state resonances of an atomic beam of ^{4}He scattered from the basal plane of a graphite crystal. The ground-state energy of the system was found to be in agreement with a value for the zero-kelvin binding energy of the helium-graphite system, reported by Elgin and Goodstein,[2] which resulted from a detailed analysis of thermodynamic data. In particular, Boato, Cantini, and Tatarek report a ground-state energy of -11.7 ± 0.3 meV, which is equal to -136 ± 3 K. Frankl,[3] who has recently repeated the scattering experiment, has found for the ground state -12.08 ± 0.1 meV, or equivalently 140 ± 1 K. Thermodynamic analysis gave 143 ± 2 K.

Carlos and Cole[4] have subsequently made use of the energy levels reported in Ref. 1 to deduce the form of the graphite-helium potential. With that potential they then predicted the bound-state energy levels of the ^{3}He-graphite system. In this Letter we wish to report the first results of a thermodynamic analysis of the ^{3}He-graphite system similar to that applied previously to ^{4}He. The 0-K binding energy of ^{3}He-graphite is found to be in excellent agreement with the prediction of Carlos and Cole.

Since the procedure used to perform the thermodynamic measurement and analysis has been reported in detail elsewhere,[2] we shall only outline it briefly here. The substrate, the same as that used in the ^{4}He work, is a commercial product called Grafoil.[5] Data from different laboratories may be combined since the Grafoil surface area in each sample is self-calibrating. At a coverage corresponding to one helium atom for every three carbon hexagons in the graphite basal planes that the Grafoil presents for adsorption, a sharp heat-capacity peak, called the ordering peak, appears at about 3 K. By measuring the coverage at which this peak occurs, the surface area of each sample of Grafoil may be accurately calibrated. The data presented in this paper are given in terms of N/N_c, where N is the amount adsorbed and N_c the amount at the ordering peak. For orientation, N_c corresponds to approximately $\frac{2}{3}$ of a complete monolayer.

The measured quantities which go into the combined analysis are the heat capacity of the adsorbed film at constant coverage, C_N, and the vapor pressure in equilibrium with the film, P, both as functions of the temperature, T, and the coverage, N. The vapor-pressure measurements are most accurately made at relatively high T and N; the heat-capacity measurements at relatively low T and N. If the two sets of data have a region of overlap, a complete thermodynamic description of the system may be constructed.

In this Letter we shall be particularly interested in the chemical potential, μ, of the adsorbed helium at 0 K. To construct the quantity, the starting point is the chemical potential at finite temperatures, which is easily deduced from $P(N, T)$. The chemical potential measured at 4.169 K is shown in the figure. By integrating data for C_N/T, a complete table of the entropy $S(N, T)$ may be constructed.[6] Thermal contributions to the chemical potential are then determined using the Maxwell relation

$$-(\partial\mu/\partial T)_N = (\partial S/\partial N)_T. \tag{1}$$

In this way, $\mu(N, T=0)$ may be deduced from $\mu(N, T)$ (errors due to extrapolating from the lowest-temperature data to $T=0$ are very small except at the lowest coverages). The chemical potential at 0 K is also shown in the figure.

At very low coverages, $\mu(N, 0)$ is dominated by inhomogeneities, and at high coverages, it varies as a result of effects which have been discussed at length for ^{4}He, and will be further examined elsewhere for ^{3}He. There is, however, a range of N for which $\mu(N, 0) \approx -136$ K and is nearly constant. It is this result which is to be compared to the ground-state energy that would be found in an atomic scattering measurement.

More concretely, a model was presented in connection with the ^{4}He results[2] according to which the inhomogeneities were due to corners where Grafoil platelets came together. Ignoring all other effects, this yielded the form

$$-\mu(N,0)=E_b\left[1+\left(1+\frac{N/N_c}{N_0/N_c}\right)^{-3}\right], \qquad (2)$$

where E_b is the binding energy on a uniform graphite surface, and N_0 is a parameter crudely equal to the number of sites within one atomic spacing of a second graphite surface. The data for ^{4}He fitted this form with $E_b = 143$ K and $N_0/N_c = 0.039$. We find that the data for ^{3}He also fitted this form, as shown in Fig. 1, with $E_b = 136$ K and $N_0/N_c = 0.036$. The small change in N_0 is to be expected because of the larger zero-point energy of ^{3}He, and correlates well with the fact that monolayer completion occurs at slightly lower N for ^{3}He than for ^{4}He. Undoubtably, the inhomogeneities of a Grafoil surface include defects such as crystallographic bends, exposed edge planes, pits, and so on.[7] However, Eq. (2) remains a useful empirical formula showing that only a small fraction of the surface has a binding energy different from that of a uniform basal plane.

In comparing the thermodynamic and atomic scattering results, two small corrections should be kept in mind. The chemical potential at 0 K is given by

$$\mu(N,0)=(\partial E/\partial N)_{T=0},$$

where E is the energy of the system, and N the number of atoms adsorbed. The measured value therefore includes not only the helium-graphite interaction, but also the interaction between helium atoms adsorbed on the surface. In the case of ^{4}He, the low-density phase at 0 K is expected to be a self-condensed medium with an estimated binding energy of 0.6 K.[8] Thus the measured value of μ is approximately 0.6 K lower than the ^{4}He-graphite binding energy. The atomic scattering data on the other hand are reduced, assuming the helium in the bound state to be a free particle in two dimensions. In fact, however, the periodic nature of the graphite potential leads to a tunneling band, the bottom of which is estimated to be 1.6 K below the bottom of the assumed free-particle spectrum.[9] The net result is that the thermodynamic result should be expected to be roughly 2 K below the scattering result for the ground-state energy. While these corrections are small, if they are applied, the agreement between the thermodynamic and scattering data, cited in the first paragraph, becomes remarkable indeed.

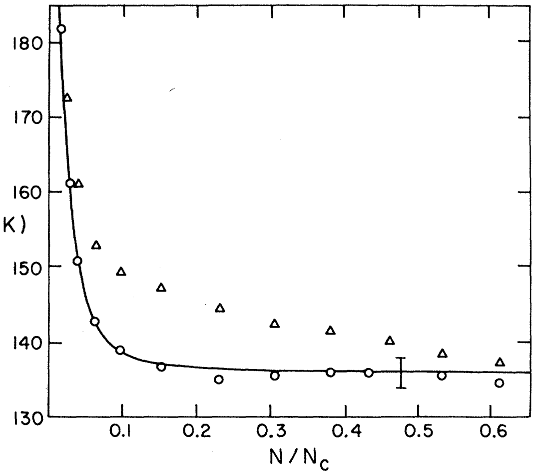

FIG. 1. The chemical potential (in kelvins) vs coverage (in units of the ordering coverage). Triangles give the chemical potential at 4.169 K, the circles give the values corrected to 0 K, and the curve is a plot of Eq. (2) of the text with $N_0/N_c = 0.036$ and $E_b = 136$ K. The error bars show the cited uncertainties of ± 2 K in E_b. Because of a lack of very-low-temperature heat-capacity data, the circles below $N/N_c = 0.1$ in coverage require a larger extrapolation to $T = 0$ than those at higher coverage.

The cited uncertainties in the thermodynamic E_b of ± 2 K in both ^{4}He and ^{3}He are of the same order of magnitude as the difference between the two values. However, as may be seen from the error bar in the figure, these uncertainties arise principally out of systematic errors, which should be the same in both cases (the measurements were made using identical procedures and apparatus, including the same samples of Grafoil). Thus the difference between the two values is more significant then the cited uncertainties would imply.

At first glance, the value −136 K seems surprisingly close to the −143 K reported for the binding energy of ^{4}He to the same surface. By way of comparison, the latent heats of vaporization of ^{3}He and ^{4}He differ by roughly a factor of 2. However, the physical reason why the binding energies are so nearly equal is not hard to understand. The zero-point energy, which is just the difference between the ground-state energy and the depth of the potential well, goes roughly as $m^{1/2}$, where m is the ^{3}He or ^{4}He mass.[10] It is because the well is deep that the 15% difference in $m^{1/2}$ between ^{3}He and ^{4}He introduces much smaller difference in binding energy. In particular, Carlos and Cole predict[4] for the ^{3}He ground-state energy −11.2 meV from their potential designed to agree with the ^{4}He ground-state energy of −11.7 meV reported by Boato, Cantini, and Tatarek.[1] The quantity of interest to compare to the thermodynamic results is the ratio $11.2/11.7 = 0.95$. The observed ratio is $136/143 = 0.95$.

We should like to end by pointing out our conviction that, given the conceptual and technical differences between these two kinds of measurement, the close agreement between the atomic-scattering and thermodynamic results[11] for ^{4}He is extraordinary. This agreement, we think, serves to emphasize the considerable power of both techniques, and is also emblematic of the rapidly increasing precision and sophistication of this area of surface physics. We hope that comparable scattering data for ^{3}He will soon be available.

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[a] Current address: 45 Sparks Street, Cambridge, Mass. 02138.

[1] G. Boato, P. Cantini, and R. Tatarek, Phys. Rev. Lett. 40, 887 (1978); G. Boato *et al.*, to be published.

[2] R. L. Elgin and D. L. Goodstein, Phys. Rev. A 9, 2657 (1974). The ^{3}He analysis, like the ^{4}He analysis before it, combines our own data with others from different laboratories. We have used data from the following sources: M. Bretz, J. G. Dash, D. C. Hickerwell, E. D. McLean, and O. E. Vilches, Phys. Rev. A 8, 1589 (1973), and 9, 2814(E) (1974); S. V. Hering, thesis, University of Washington, 1974 (unpublished); S. V. Hering, S. W. Van Sciver, and O. E. Vilches, J. Low Temp. Phys. 25, 793 (1976). These same authors have provided us with tabulated data.

[3] D. Frankl, private communication.

[4] W. Carlos and M. W. Cole, Surf. Sci. 77, L173 (1978).

[5] Manufactured by the Union Carbide Corporation.

[6] The entropy is derived by using one of the Maxwell relations [Eq. (1)] at high temperatures, where the chemical potential is measured, to find $(\partial S/\partial N)_T$, and this is integrated upward from $N = 0$ to give entropies at high temperature. The heat capacity is integrated downward in temperature from these starting points. This avoids the difficulty of integrating upward from zero temperature in regions where, at the lowest temperatures for which heat capacities are measured, there are still disordered nuclear spins, and hence a heat-capacity peak unmeasured at lower temperatures. In fact, this procedure provides reliable values of the residual spin entropy at low temperatures.

[7] J. G. Dash, private communication; M. B. Dowell, private communication to J. G. Dash.

[8] C. E. Campbell and M. Schick, Phys. Rev. A 3, 691 (1971).

[9] M. W. Cole, private communication.

[10] Since the form of the gas-graphite potential is assumed to be the same for ^{3}He and ^{4}He, the only way the mass enters is in the kinetic energy that balances the potential energy. The dependence on the square root of the mass can be easily derived by approximating the well by a harmonic-oscillator potential near the minimum, and equating the curvature of the well to $m\omega^2$, where ω is the oscillator frequency. Since the curvature is the same for the two isotopes, the frequency (and hence the zero-point energy) is proportional to $m^{-1/2}$. In fact, fitting a harmonic-oscillator potential to the ground and first excited states of ^{4}He from the scattering data to determine well depth and oscillator frequency yields the same ground-state energy for ^{3}He as reported by Carlos and Cole (Ref. 4) when the oscillator frequency is changed by the square root of the ^{4}He/^{3}He mass ratio.

[11] In addition to the ground-state energy, analysis of high-temperature heat capacities yielded an estimate from the thermodynamic data of the energy of the first excited state, 54 K above the ground state. Boato, Cantini, and Tatarek (Ref. 1) report a value of 5.6 meV or 65 K and Frankl (Ref. 3) 5.7 meV or 66 K. The thermodynamic result was somewhat model dependent, and we therefore believe that the agreement is reasonably good, and that the scattering results are the more reliable of the two.