(2) Application of the simple BET theory[5] shows that the volume adsorbed in the first layer (v_m) is much larger than that calculated from surface areas and the liquid density, as already shown by Schaeffer *et al.*[6] from their data for carbon black at 4.2°K. We find for v_m about 0.9 cc/m^2, four times the value calculated from the liquid density, and corresponding to an atomic spacing in solid He under several hundred atmospheres pressure. The data of Schweers[7] at small P/P_0 also fit a BET plot, giving about the same v_m on glass and O_2 below 2.5°K, and yield also the value of Schaeffer *et al.* ($v_m=0.57$ cc/m^2) at the b.p. It seems, therefore, certain that the first adsorbed layer on most surfaces is highly compressed.

Schweers' stated result, that the adsorption energy drops by *ca.* 50 cal./mole in building up the first four layers, must now be re-interpreted as representing the work of compression necessary to complete the mono-layer.[8]

(3) The He *II* isotherms show anomalously high adsorption, starting at $P/P_0 \sim 0.7$, and increasing enormously at high saturations. We reached the limiting value of 40 cc/m^2 with a distinctly lower equilibrium pressure than P_0. This value yields a minimum film thickness of ~160 atomic layers, on the reasonable assumption of liquid-type spacing (4A) for all but the first few layers.[9]

We consider this anomalous adsorption as due to the formation of the Rollin film. Previously widely differing results[10] on the film thickness are explainable because of the extreme sensitivity of the film thickness to percent saturation.

We observed some indication of slight hysteresis in desorption above $P/P_0=0.9$ below T_λ, whereas in all other parts of the isotherm the equilibrium pressures were identical in adsorption and desorption.

The isotherm at 2.45°K yields a $v_m=0.9$ cc/m^2, the same as below T_λ, but shows distinctly smaller adsorption above P/P_0 ~0.20, reaching saturation with ~30 layers adsorbed.

The two methods proposed by Harkins and Jura[11] for plotting adsorption data ($\log P/P_0$ *vs.* $1/v^2$, and the "film pressure" π *vs.* the area σ available per atom adsorbed) show a distinct break at $P/P_0 \sim 0.7$, in a manner which in their treatment would indicate a two-dimensional second-order transition. This, along with the disappearance of the effects above T_λ, suggests that the phenomenon is cooperative, and of the same character as the λ-point in bulk liquid He.

We plan to investigate in more detail the anomalous density of the first adsorbed layers, the "transition" at $P/P_0 \sim 0.7$ with the resulting high adsorption, and the entropy of the system as a function of the number of adsorbed layers.

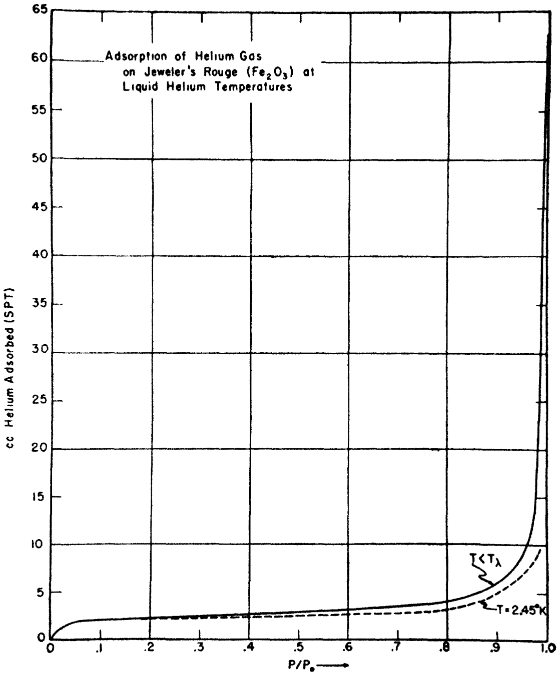

FIG. 1.

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[1] Measurements made in collaboration with Professor A. O. C. Nier and Mr. B. B. McInteer, Department of Physics, University of Minnesota.

[2] J. Kistemaker, Leiden Comm. No. 271-b.

[3] The He *II* results are in good agreement with unpublished data of H. P. R. Frederikse, Leiden, who kindly sent us his data on the isotherms between 1.39° and 1.99°K, up to 85 percent saturation. We are indebted to him for these data, and for the manuscript of his communication to Physica on the specific heat of adsorbed He on Fe_2O_3, prior to publication.

[4] H. A. Kramers, personal communication to L. M.

[5] Brunauer, Emmett, and Teller, J. Am. Chem. Soc. **60**, 309 (1938).

[6] Schaeffer, Smith, and Wendell, J. Am. Chem. Soc. **71**, 863 (1949).

[7] J. Schweers, Thesis, Leiden, 1941.

[8] Suggested by W. Band.

[9] Kistemaker's statement that the number of adsorbed layers does not increase over ~30 layers, above $P/P_0 \sim 0.9$, is due to his method of evaluation, only valid below $P/P_0 \sim 0.8$, as it assumes the number of adsorbed layers to be equal in the two adsorption bulbs he compares. His original data show the effect we observed.

[10] See W. H. Keesom, *Helium*, Elsevier Publishing Company, Inc., New York, 1942) pp. 292–308,

[11] See Geo. Jura and W. D. Harkins, J. Am. Chem. Soc. **68**, 1941 (1946).

Anomalous Adsorption of Helium at Liquid Helium Temperatures

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THE results reported recently[1] under the above title by Earl A. Long and Lothar Meyer raise the following question: The "Brunauer-Emmett-Teller" theory[2] assumes that the saturation number of atoms in each monolayer is a constant and should be roughly equal to the number to be expected from the interatomic spacing in the liquid phase. However, by applying the B.E.T. isotherm to their observed adsorption for helium, Long and Meyer find that in the neighborhood of the lambda-temperature the saturation number in the first monolayer is about four times that expected from the liquid density. Schaeffer *et al.*[3] similarly found about twice the expected number at the boiling point temperature. Can these results be considered real, or are they simply an indication that the B.E.T. theory breaks down completely?

The density of liquid helium is unusually low at these temperatures because of the zero point energy, and it is, therefore, physically reasonable to suppose that the potential energy of adsorption can compress the first, and perhaps partly also the second monolayer to be adsorbed. Moreover the measurements by Fredericke[4] on the specific heat of an amount of adsorbed helium that corresponds to the first (compressed) monolayer, are actually consistent with that of a two-dimensional Debye solid with a characteristic temperature of about 18°K. It is, therefore, reasonable to consider the film at low pressures as immobilized, and to apply the following generalization of the B.E.T. theory: Let the number of sites available to the second monolayer be only some fraction α_1 of the number of atoms adsorbed in the first monolayer, the number of sites available to the third monolayer be another fraction α_2 of the number of atoms adsorbed in the second layer, and so on. This problem can be solved by the methods introduced by T. L. Hill.[5] In the simplest case where only one anomalous monolayer is present, i.e., $\alpha_1<1$, while α_2 etc. are all $=1$, the resulting adsorption isotherm is a simple generalization of the B.E.T. equation.

$$(V_1/V)\{x/(1-x)\}=\{x+\beta_1(1-x)^{\alpha_1}\}/\{1-x(1-\alpha_1)\}, \quad (1)$$

where $x=P/P_0$ is the ratio between the gas pressure and the saturated vapor pressure, V is the volume (at *STP*) of gas adsorbed, V_1 is the volume of gas that would just fill the first monolayer at its saturation density, $\alpha_1 V_1$ is the saturation volume for the second monolayer and must equal the value calculated from the normal liquid spacing, β_1 is the usual function of the heat of adsorption of the 1st monolayer ϵ_1 and the heat of evaporation $-\epsilon_L$,

$$\beta_1=\exp\{-(\epsilon_1-\epsilon_L)/kT\}.$$

If x is sufficiently small compared with unity (1) reduces to the following first approximation,

$$(V_1/V)\{x/(1-x)\}=\beta_1+x(1+\beta_1-2\alpha_1\beta_1). \tag{2}$$

In practice β_1 is of the order 0.005, so that (2) is practically identical in form with the ordinary B.E.T. isotherm, but leaves V_1 free to be greater than the value given by the liquid density.

By admitting two anomalous monolayers, the isotherm becomes much more complicated, but it remains true that at small x it reduces practically to the same form (2). It may, therefore, be concluded that the anomalously high values of V_1 yielded by the ordinary B.E.T. plot are real, and indicate only that the B.E.T. theory requires generalization in the above manner.

The additional parameters present with two anomalous monolayers allow a much better fit between theory and observation in the case of the isotherms above the lambda-point, but do not reduce the discrepancy below T_λ, where the adsorption is already measurably greater than the maximum theoretical value at 20 percent saturation, or about four monolayers. A rough estimate of the order of magnitude of the cooperative energy ϵ_c required to account for this excess adsorption can be obtained as follows. If an attraction is included in the partition function of the assembly by means of a simple Boltzman factor for each monolayer, the adsorption isotherm is found to be the same as before, but on an x-scale reduced in the ratio $e^{\epsilon_c/kT}$. Such an isotherm would give formally an infinite adsorption at a pressure actually less than saturation, and if the cooperative energy is chosen about 0.07 cal. per mole it fits the data below T_λ at least as well as the corresponding isotherm (without the cooperative factor) fits the data above T_λ.

It is proposed to develop the above theory for isotopic mixtures, and details will be published later.

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[1] E. A. Long and L. Meyer, Phys. Rev., preceding letter.
[2] S. Brunauer, *The Absorption of Gases and Vapors* (Princeton University Press, Princeton, New Jersey, 1943).
[3] Schaeffer, Smith, and Wendell, J. Am. Chem. Soc. **71**, 863 (1949).
[4] See footnote 3 in reference 1 above.
[5] T. L. Hill, J. Chem. Phys. **4**, 263 (1946); **4**, 268 (1946); **15**, 767 (1947).

Neutron Irradiated Semiconductors

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GERMANIUM semiconductors after bombardment with deuterons or alpha-particles show[1] permanent changes in their electrical properties: the resistivity of P-type germanium decreases, indicating the production of acceptors[2] due to the bombardment, and N-type germanium becomes converted to P-type. The original state can be reproduced by heat treatment, indicating that the observed effects are not due to transmutations, but primarily due to lattice displacements, creating vacancies and interstitial atoms. If this explanation is correct, it is expected to find similar changes due to neutron bombardment.

Various samples of Ge semiconductors, with known impurity type and content[2] were exposed in the Oak Ridge reactor and the conductivity was measured during exposure as a function of irradiation: P-type samples show an increase in conductivity, as expected from the results of cyclotron irradiation (Fig. 1*a*).

N-type material shows a decrease in conductivity which reaches a minimum, and then increases steadily with continuing bombardment (Fig. 1*b*). Hall effect measurements[2] after bombardment indicate that the material has been converted to P-type. These experiments indicate also that neutron bombardment produces acceptors, creating additional holes; thus the conductivity of P-type material increases whereas the conductivity of N-type material first decreases, as electrons are removed from the conduction band, but increases again as hole conduction becomes prominent.

Exposure of germanium point contact rectifiers of the 1N34 and 1N38 type shows[3] that at 3 volt forward bias, where spreading resistance is primarily responsible for the resistance measured, the behavior is the same as the one observed for bulk resistivity

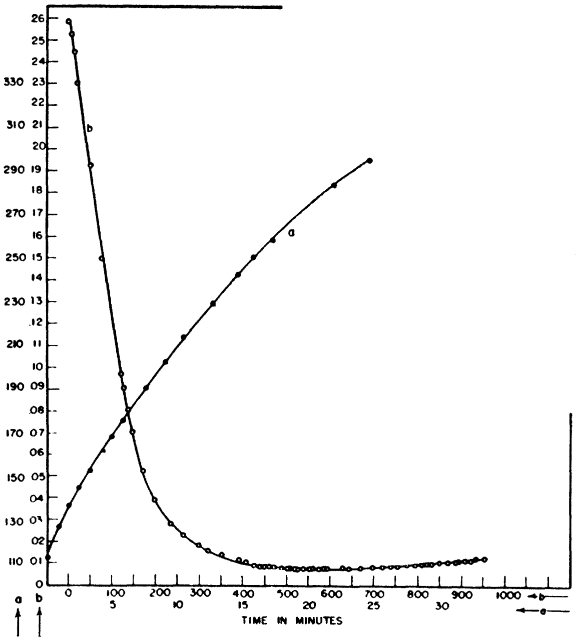

FIG. 1. Curve *a*: conductance of high resistance P-type germanium as a function of the time of irradiation. Curve *b*: conductance of N-type germanium as a function of time of irradiation.

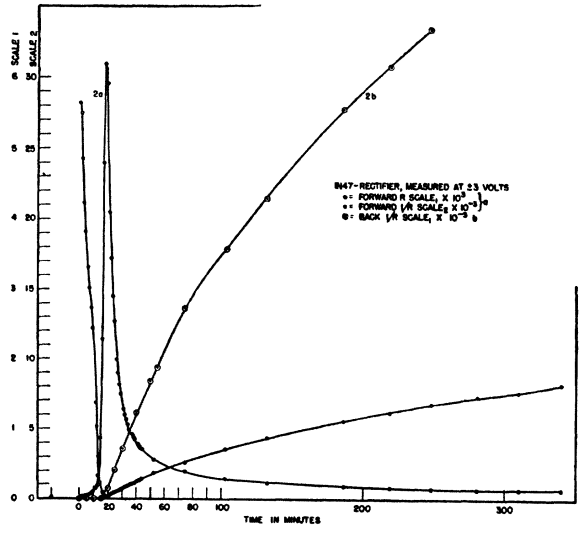

FIG. 2. Resistivity behavior in the forward and backward direction of a contact rectifier as a function of the time of irradiation.