

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,

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

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.

¹ E. A. Long and L. Meyer, Phys. Rev., preceding letter.

² S. Brunauer, *The Adsorption 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 show¹ permanent changes in their electrical properties: the resistivity of P-type germanium decreases, indicating the production of acceptors² 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 content² 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. 1a).

N-type material shows a decrease in conductivity which reaches a minimum, and then increases steadily with continuing bombardment (Fig. 1b). Hall effect measurements² 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 shows³ 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

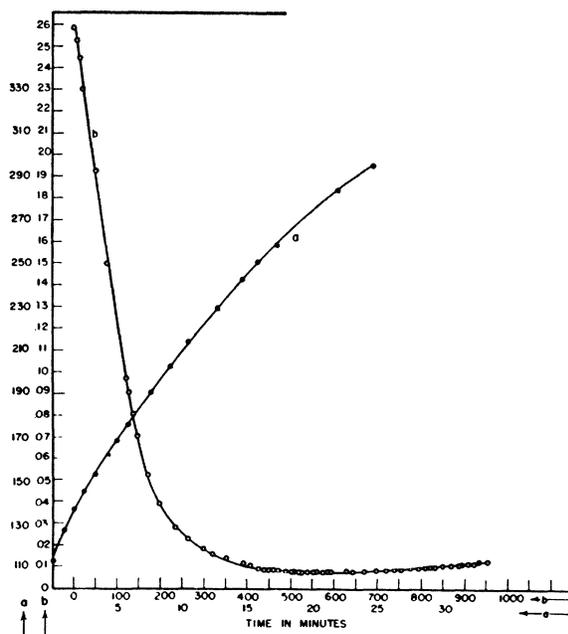


FIG. 1. Curve a: conductance of high resistance P-type germanium as a function of the time of irradiation. Curve b: conductance of N-type germanium as a function of time of irradiation.

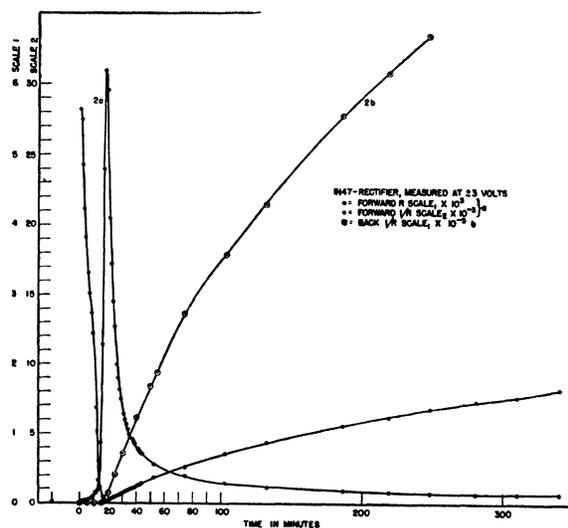


FIG. 2. Resistivity behavior in the forward and backward direction of a contact rectifier as a function of the time of irradiation.

(Fig. 2a). At forward bias of less than 0.18V and for bias in the back direction the resistance is determined primarily by the barrier resistance of the rectifier and since this barrier in an N-type rectifier is transparent for holes a decrease of resistance is expected and is actually observed (Fig. 2b).

The rectifier shows after prolonged irradiation ohmic behavior, but when reassembled with an aluminum point shows the behavior of a P-type rectifier.

When exposed in cadmium shields, the samples reach the point of minimum conductance at larger nvt values than in a graphite torpedo. Heat treatment reproduces the original behavior observed before neutron irradiation as in the case of deuteron and alpha-bombardment.

Silicon samples both N- and P-type show an increase in resistivity in a similar way, as has been observed with deuteron bombarded silicon samples. Heat treatment restores the original resistivity values; it also shows that deep lying traps of about 0.5 ev above the full band are produced, removing electrons and holes, thus producing poorly conducting material.

Preliminary experiments on Si-rectifiers (IN 21) Cu₂O semiconductors in bulk and rectifiers, Se bulk material and rectifiers, all show a behavior similar to the one observed for silicon samples discussed above.

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† Lark-Horovitz, Bleuler, Davis, and Tendam, Phys. Rev. **73**, 1256 (1948).

‡ We are indebted to members of the Purdue Semiconductor Laboratory: V. Bottom, J. W. Cleland, R. E. Davis, and J. C. Thornhill, for the preparation of the samples and the Hall effect measurements before and after irradiation.

§ Davis, Johnson, Lark-Horovitz, and Siegel, Phys. Rev. **74**, 1255 (1948); ARCD 2054 (1948).

Nuclear Magnetic Moments from Microwave Spectra: I¹²⁷ and I¹²⁹

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THE effects of a magnetic field on the hyperfine structure of the $J=2 \rightarrow 3$ transition of CH₃I¹²⁷ and CH₃I¹²⁹ have been studied. The Zeeman components of several F transitions of these molecules were completely or partially resolved. Observations were made with a coiled wave guide cell in such a way that the magnetic field was parallel to the E vector of the radiation. This allowed detection of the p components, $\Delta M_F = 0$ transitions, without complications from the s components, $\Delta M_F = \pm 1$ transitions. The field strengths used in the study ranged from 1160 gauss to 3700 gauss.

The nuclear magnetic moment of I¹²⁷ has already been determined by Pound,¹ using the nuclear resonance method, to a greater accuracy than can be reached by the present method. The remeasurement of this moment, however, helps to evaluate the accuracy obtainable with the microwave method. In Table I are listed the results obtained on different CH₃I¹²⁷ transitions. The average value for $\mu(I^{127})$ from these data is 2.792, which, when corrected for diamagnetic effects² of the extranuclear electrons of the iodine, is 2.810. The mean deviation from this value is 0.062, or 2.2 percent. The value obtained by Pound is 2.8122 ± 0.003 .

In Table I are also given results on two transitions of CH₃I¹²⁹, one of which is shown in Fig. 1. When diamagnetic corrections are made, our preliminary values*** for the I¹²⁹ nuclear g -factor and magnetic moment are 0.783 and 2.74, respectively. We believe these to be accurate to about five percent. The major factor

TABLE I. Nuclear magnetic moments as calculated from several observed Zeeman effects in the CH₃I spectrum, $J=2 \rightarrow 3$.

Isotope	K	F transition	H gauss	Separation Mc	μ^a nuclear magnetons
I ¹²⁷	0	1/2 \rightarrow 1/2	1160	4.07	2.878
	0	1/2 \rightarrow 1/2	2320	7.70	2.723
	0	1/2 \rightarrow 1/2	3010	10.17	2.773
	1	1/2 \rightarrow 1/2	3010	10.47	2.853
	1	1/2 \rightarrow 1/2	3180	10.64	2.745
	0	3/2 \rightarrow 3/2	2600	5.22 ^b	2.743
	1	3/2 \rightarrow 3/2	2600	5.19 ^b	2.728
	0	5/2 \rightarrow 5/2	3000	4.28 ^a	2.89
Average					2.792
I ¹²⁹	1	9/2 \rightarrow 9/2	3700	2.25 ^c	2.78
	1	7/2 \rightarrow 7/2	3700	2.64 ^a	2.66
	Average				

^a These values are not corrected for diamagnetic effects.

^b These separations represent the total spacing of the multiplet.

^c These separations are for peaks containing unresolved components (see Fig. 1).

limiting the accuracy is the incomplete resolution of the transitions used. Small errors may also arise from the measurement of the strength of the magnetic field. The 3/2 \rightarrow 1/2 transition, since it splits into a wide doublet, should be more favorable for these determinations. Unfortunately, this line, though detectable, was too weak to be measured when split by the magnetic field. We hope, with later improvements of the spectrometer, to measure the magnetic moment of I¹²⁹ to an accuracy of one percent.

So far as we know, this is the first determination of an unknown nuclear magnetic moment with the microwave method.*** This method, though not so precise as the molecular beam method or the nuclear resonance method, is particularly well suited to the study of rare or radioactive nuclei. Less than 10^{-5} g of I¹²⁹ was needed for each series of measurements. Previously, the Zeeman effect on the microwave spectrum of ammonia has been observed by Coles and Good³ and by Jen.⁴ The latter observer also studied the Zeeman effect in methyl chloride.⁴

The theory used for the Zeeman effect of the hyperfine structure is that developed for atomic spectra by Back and Goudsmit⁵ and previously applied to molecular spectra by Jen.⁴ In the present work, the effects caused by the molecular magnetic moment were considered to be negligible. The theory fits all observations satisfactorily except those for the $F=5/2 \rightarrow 7/2$ transitions of CH₃I¹²⁷. Here, an anomaly was detected which appears to result from a breaking down of the nuclear quadrupole coupling by the applied magnetic field.† This is being studied further.

The magnetic moment of I¹²⁹ with the previously measured spin⁶ of 7/2 allows an assignment of the state of the last proton in the I¹²⁹ nucleus as $5g^-$, according to the Nordheim⁷ scheme. The mag-

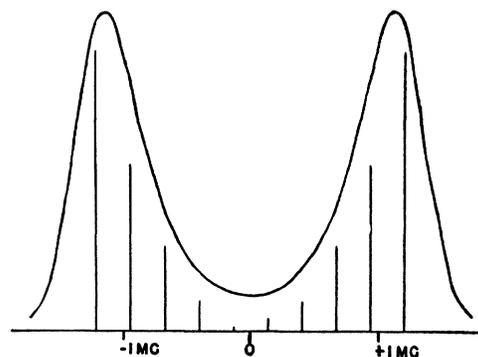


FIG. 1. Zeeman splitting of the hyperfine structure of the $J=2 \rightarrow 3$ transition of CH₃I¹²⁹, $F=9/2 \rightarrow 9/2$, $\Delta M_F=0$. Separation of the observed peaks is 2.25 mc/sec. $H=3700$ gauss. Bars represent calculated lines; curve represents the observed spectrum.