Aluminum-doped silicon ($3\times10^{17}$ atoms/cc) was similarly unproductive.

We are indebted to W. H. Brattain for stimulating discussion, to N. B. Hannay and E. D. Kolb for the special silicon crystals, and to P. Breidt and W. F. Flood for preparing the silicon samples.

[1] C. J. Gallagher, Phys. Rev. **88**, 721 (1952).
[2] Holden, Kittel, Merritt, and Yager, Phys. Rev. **77**, 147 (1950).

## Energy of the High-Lying Acceptor Level in Copper-Doped Germanium

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In addition to the much investigated[1] level at about 0.037 ev above the valence band, it has been reported that copper introduces another higher-lying acceptor level[2] in the forbidden energy gap of germanium. If this is the case, the level should make itself very evident in Hall and resistivity data at room temperature and below if it can be arranged that the lower-lying level is substantially completely populated and the higher level is partially populated at these temperatures. This requires the Fermi level to be within a few $kT$ of the upper level and will lead to an exponential variation of carrier density in the temperature region where the carrier concentration of a sample doped only with Group III and Group V atoms is approximately constant.

This situation may be achieved by diffusing copper into an originally $n$-type sample of Group V impurity concentration $N_d$. If a density of copper atoms, $N_a$, between $\frac{1}{2}N_d$ and $N_d$ is introduced, the lower copper level will be entirely filled and the upper level partially filled with the Group V donor electrons. The solid solubility of copper in germanium as a function of temperature may be estimated from the work of Fuller and Struthers,[3] and Finn,[3] and the time necessary to achieve a reasonable approximation of solid solubility may be estimated from a knowledge of the diffusion coefficient as a function of temperature.[3]

The sample for which data are shown in Fig. 1 was $1.5\times0.58\times0.27$ cubic centimeters and had about $1.2\times10^{15}$ Group V donors per cc. It was copper plated, held at 630°C for about ten days in an argon atmosphere, then quenched rapidly to room temperature to try to introduce about $8\times10^{14}$ copper atoms/cc. Room-temperature measurement following this treatment showed the sample to be high-resistivity $p$ type.

The condition for electrical neutrality in this semiconductor at room temperature and below requires that $p+p_a=2N_a-N_d$, where $p$ is the hole density in the valence band and $p_a$ is the density of empty upper copper levels. This may be written as

$$N_v\exp[-(F-E_v)/kT]+N_a/\{1+\exp[(F-E_a)/kT]\}=2N_a-N_d,$$

where $N_v$ is the effective density of states in the valence band, $F$ is the Fermi energy level, $E_v$ is the energy of the top of the valence band, and $E_a$ is the upper copper energy level. For the sample measured $N_a\simeq8\times10^{14}$/cc, $2N_a-N_d\simeq4\times10^{14}$/cc, and at room temperature $p\simeq9\times10^{13}$/cc. Thus for values of $p$ smaller than the room-temperature value, the Fermi level should coincide with the upper copper level to within an energy of the order of $kT$, and $p=N_v\exp[-(E_a-E_v)/kT]$.

Hall and resistivity data are shown in Fig. 1. The curves exhibit a temperature dependence below the intrinsic range which is consistent with the premise of a partially populated level at about 0.3 ev above the valence band. Both Hall coefficient and resistivity curves show a very steep activation energy below room temperature where $F$ and $E_a$ coincide. Both curves go into the usual intrinsic line above room temperature, and the Hall curve exhibits a reversal of sign at about 355°K. The activation energy for the upper copper level is 0.304 ev from the Hall curve and 0.308 ev from the resistivity curve if other temperature dependences in these expressions are neglected. If it is assumed that $N_v$ goes as $T^{1.5}$, $\mu_H/\mu$ as $T^{0.5}$,[4] and $\mu$ as $T^{-2.3}$,[5] where $\mu$ is the drift mobility, and $\mu_H$ the Hall mobility, a plot of $\rho T^{-0.8}$ or $RT^{1.0}$ *versus* $1/T$ should be proportional to $\exp[(E_a-E_v)/kT]$. Using this procedure the Hall data give $E_a-E_v=0.285$ ev and the resistivity data $E_a-E_v=0.315$ ev.

The authors wish to give thanks to Robert Carye for help in preparation of the samples and taking of the data.

[1] See for instance F. J. Morin and J. P. Maita, Phys. Rev. **90**, 337 (1953); W. C. Dunlap, Bull. Am. Phys. Soc. **29**, No. 3, 21 (1954).
[2] W. Kaiser and H. Y. Fan, Phys. Rev. **93**, 977 (1954); J. A. Burton *et al.*, J. Phys. Chem. **57**, 853 (1953); W. C. Dunlap, Bull. Am. Phys. Soc. **29**, No. 3, 21 (1954).
[3] C. S. Fuller and J. D. Struthers, Phys. Rev. **87**, 526 (1952); G. B. Finn, Phys. Rev. **91**, 754 (1953).
[4] E. M. Conwell, Bull. Am. Phys. Soc. **29**, No. 3, 18 (1954).
[5] F. J. Morin, Phys. Rev. **93**, 62 (1954).

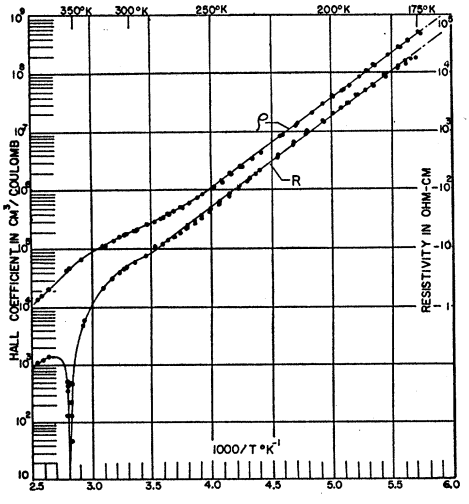


FIG. 1. Temperature dependence of Hall coefficient $R$ and resistivity $\rho$ for a germanium sample doped with $1.2\times10^{15}$ arsenic atoms per cc and approximately $8\times10^{14}$ copper atoms per cc.

## Doppler Line-Width Reduction*

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(Received April 13, 1954)

We have succeeded in observing a large reduction in the Doppler width of a molecular absorption line by using a combination of microwave spectroscopic and molecular beam techniques.[1] This procedure, utilizing the effect of the matter on the electromagnetic radiation, solves the onerous detection problem encountered in the usual molecular beam experiments where the effect of the radiation on the matter is observed. The high resolution of molecular beam experiments afforded by the interaction of the radiation field and the transverse molecular beam is thus made available for microwave spectroscopic use.

In the exploratory study reported here the ammonia inversion absorption transition for the rotational state $J=3$, $K=3$ was observed with the microwave radiation propagated transverse to a beam of ammonia molecules. The radiation was detected and displayed by conventional techniques.[2] However, because of the resulting narrow line width the microwave oscillator was swept in saw-tooth fashion only over a region 80 kc/sec wide, centered at about 23 870 Mc/sec. Figure 1 shows the absorption signal of the

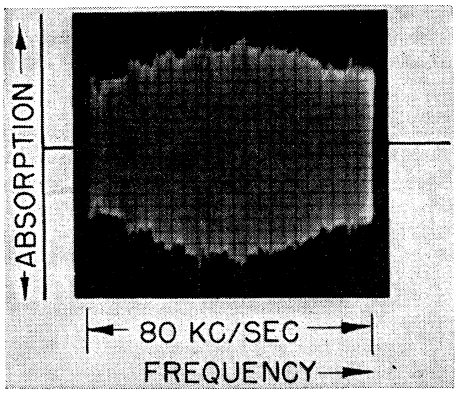


FIG. 1. The 23 870-Mc/sec $NH_3$ inversion absorption line exhibiting the limiting Doppler breadth with conventional observation ($2\Delta\nu = 72$ kc/sec).

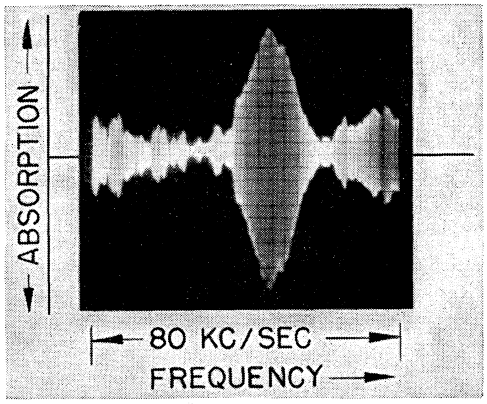


FIG. 2. The 23 870-Mc/sec $NH_3$ inversion absorption line exhibiting a large reduction in Doppler width from observation of a transverse beam.

ammonia inversion line ($J=3, K=3$) as observed in a conventional absorption cell of such dimensions and with the gas at such a pressure that essentially only the Doppler width ($\Delta\nu$ = half-power − half-width = 36 kc/sec) remains; i.e., the radiation is swept in frequency between the half-power absorption points. Figure 2 shows the simultaneous record of the absorption of the same radiation as observed transverse to an ammonia molecular beam of the same temperature. A reduction of the Doppler width by a factor of about six is apparent. Further line-width reduction will be accomplished in the future by available experimental means. The signal-to-noise ratio shown here is readily attained with a system noise band width of the order of 10 cps. An improved value for this transition frequency has not yet been obtained, since the possible precision afforded by this experimental arrangement is beyond our present frequency-determining facilities.

We feel that the use of these techniques will bring a large and new field of problems within the reach of microwave spectroscopic methods; e.g., spectra of the more refractory materials, the study of fine structure beyond present resolution, and the study of free radicals and substances of evanescent existence.

We wish to acknowledge the laboratory assistance of J. D. Kierstead.

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[1] For earlier work with different apparatus see H. R. Johnson and M. W. P. Strandberg, Phys. Rev. **85**, 503 (1952).

[2] M. W. P. Strandberg, *Microwave Spectroscopy* (Methuen Publishing Company, London, 1954).

## Magnetothermoelectric Behavior of Bismuth at Liquid Helium Temperatures

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THE previously observed anomalous magnetic properties of bismuth at low temperatures[1-3] suggested that the thermoelectric properties of this metal be studied in a magnetic field. Such magnetothermoelectric measurements have now been made on a single crystal of bismuth.

The crystal was grown from Cerro de Pasco Copper Company bismuth (99.99 percent pure) in a furnace described by Schubnikow.[4] It was a cylinder 57 mm long and 1.7 mm in diameter. The distance between the bismuth-copper thermoelectric junctions was 47 mm. By cleaving the crystal it was found that the trigonal axis was parallel to the crystal length to within 1.5°. The measurements were taken with the magnetic field, $H$, perpendicular to the crystal length (and heat current). The binary axes were located from magnetoresistance measurements. Thermoelectric data were obtained for two orientations of the field relative to a binary axis, parallel and perpendicular. Because of the more complicated nature of the results for the perpendicular orientation (due to beats resulting from more than one oscillating term) only the data for the parallel orientation will be discussed in this paper. Figure 1 shows the results for $H$ parallel to a binary axis. The graph gives the thermoelectric voltage observed as a function of $H^{-1}$ for a constant temperature difference of 0.0055°K ±0.0002°K between junctions (mean temperature 4.379°K). Temperatures at both junctions were measured with carbon resistance thermometers[5] throughout the entire experiment. In order to depict the oscillatory nature of the thermoelectric voltage more clearly, the differences, $\delta$, between the experimental points and the envelope curve are shown at the bottom of Fig. 1. Positions for maxima and minima in $\delta$ are indicated by arrows on the graph. In Fig. 2 the values of $H^{-1}$ corresponding to these positions are plotted against integers. The resulting straight line indicates that the thermoelectric oscillations are periodic in $H^{-1}$ as are the magnetic susceptibility (de Haas-van Alphen effect),[1] magnetoresistance[2] and Hall Coefficient.[3] From the slope of the line in Fig. 2 we obtain a value of $7.3\times10^{-5}$ gauss$^{-1}$ for $\beta^*/E_0$ (where $\beta^*$ is the double effective Bohr magneton and $E_0$ is the Fermi energy for the de Haas-van Alphen electrons). The calculated value of $\beta^*/E_0$ (from susceptibility data) for an orientation with $H$ perpendicular to the trigonal axis and parallel to a binary axis (within a few degrees of our orientation), using the parameters given by Shoenberg,[6] is $7.1\times10^{-5}$ gauss$^{-1}$. The good agreement

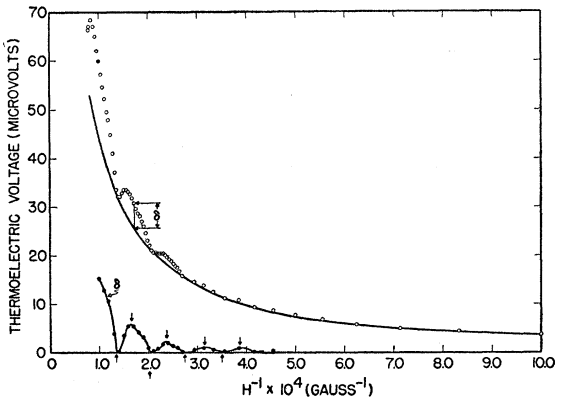


FIG. 1. Thermoelectric voltage of a bismuth single crystal as a function of $H^{-1}$ for a temperature difference of 0.0055°K between bismuth-copper junctions (mean temperature of 4.379°K). $\delta$ is the difference between the experimental points and the solid curve.

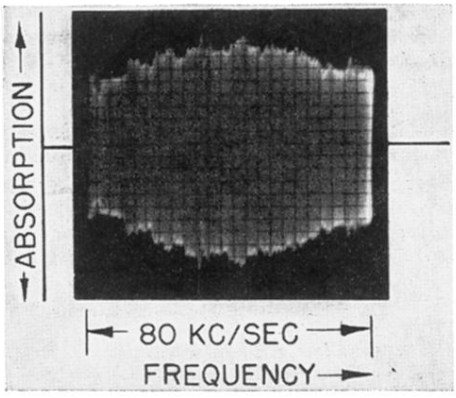


FIG. 1. The 23 870-Mc/sec $NH_3$ inversion absorption line exhibiting the limiting Doppler breadth with conventional observation ($2\Delta\nu = 72$ kc/sec).

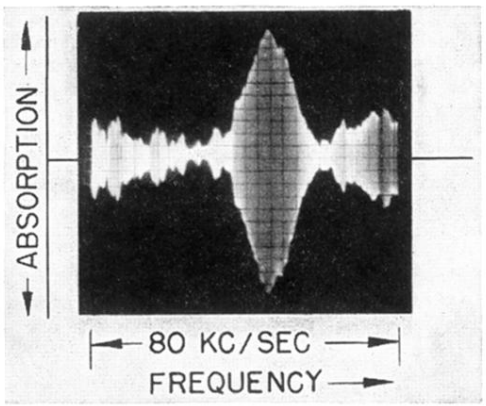


FIG. 2. The 23 870-Mc/sec $NH_3$ inversion absorption line exhibiting a large reduction in Doppler width from observation of a transverse beam.