

Aluminum-doped silicon (3×10^{17} atoms/cc) was similarly unproductive.

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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 investigated¹ level at about 0.037 ev above the valence band, it has been reported that copper introduces another higher-lying acceptor level² 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 $1.5 \times 0.58 \times 0.27$ cubic centimeters and had about 1.2×10^{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 8×10^{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 $N_a \approx 8 \times 10^{14}/\text{cc}$, $2N_a - N_d \approx 4 \times 10^{14}/\text{cc}$, and at room temperature $p \approx 9 \times 10^{13}/\text{cc}$. 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 $T^{1.5}$, μ_H/μ as $T^{0.5}$,⁴ and μ as $T^{-2.3}$,⁵ where μ is the drift mobility, and μ_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.

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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).

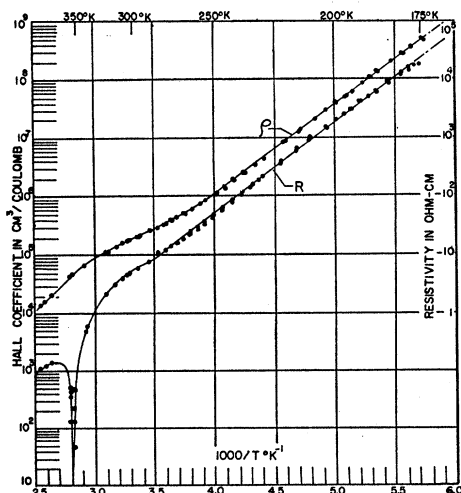


Fig. 1. Temperature dependence of Hall coefficient R and resistivity ρ for a germanium sample doped with 1.2×10^{15} arsenic atoms per cc and approximately 8×10^{14} copper atoms per cc.

Doppler Line-Width Reduction*

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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