

next eigenvalue that  $\lambda(p_1)$  has been shifted relative to  $E(p_1)$ . Since  $\cot\pi\epsilon$  covers the range from infinity to zero as  $\epsilon$  changes from zero to one-half, the eigenvalues are never shifted more than half an interval.

Application of the above techniques to vibrations of imperfect lattices will be discussed in more detail later.

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<sup>1</sup> J. M. Smith and M. Lax, Progress Report, August 1, 1953 (unpublished).  
<sup>2</sup> J. C. Slater, Technical Report No. 5, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, December 15, 1953 (unpublished).

<sup>3</sup> M. Lax, J. Chem. Phys. 20, 1351 (1952).

### Wave Functions for Impurity Levels\*

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UNDER the title above, a paper is being submitted to *The Physical Review*, containing material some of which has been presented in the unpublished Technical Report No. 5 of the Solid-State and Molecular Theory Group of Massachusetts Institute of Technology. Further material on the same subject will be incorporated in two further papers. These treat the technique of handling the motion of electrons in perturbed periodic lattices, by expanding the perturbed solutions in terms of Wannier functions, and setting up and solving the equations for the coefficients of the Wannier functions, which take the form of difference equations. Previous treatments of this problem<sup>1</sup> have usually approximated the difference equations by differential equations, thereby leading to the concept of an effective mass. This approximation, though sometimes satisfactory, is not rigorous, and we feel that the difference equation method is preferable.

Our attention has now been called by Professor Melvin Lax to the fact that he and a student of his, Mr. James H. Smith, of Syracuse University, have been independently using similar mathematical methods for handling problems in the vibrations of a lattice containing local impurities and imperfections. Lax describes these methods in an accompanying Letter to the Editor. The purpose of the present letter is merely to point out that our work, and that of Lax and Smith, were carried out independently, both leading to a mathematical technique which appears to have wide applicability, in problems of quantum theory of solids in the mathematical theory of difference equations. The application to the vibrations of a lattice, which Lax and Smith are treating, had also occurred to us as a useful application of the method, but we have not made wide use of this application.

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<sup>1</sup> G. Wannier, Phys. Rev. 52, 191 (1937); J. C. Slater, Phys. Rev. 76, 1592 (1949); and various other papers. See, however, for instance, P. Feuer, Phys. Rev. 88, 92 (1952), in which the difference equations are treated directly.

### Spin Resonance of Donors in Silicon

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RESONANCE absorption believed associated with the spin of electrons bound to Group V donor atoms has been observed in several different samples of silicon. The absorption was measured on a Zeeman modulation spectrometer operating at a frequency of 24 000 Mc/sec. The samples were cut from single crystals in the form of bars 0.420 in.  $\times$  0.170 in.  $\times$  0.030 in. They

were mounted on the narrow side of a rectangular resonant cavity kept at a temperature of 4.2°K.

The first resonances were observed in arsenic-doped silicon which had been plastically deformed by compression at 1000°C.<sup>1</sup> Four fairly sharp absorption lines (ca 10 oersteds between inflection points) appeared, equal in amplitude and spaced uniformly 73 oersteds apart. These are shown schematically in Fig. 1(a), (b), (c), where a line roughly indicating relative magnitude is plotted against its gyromagnetic ratio ( $g$ ). The gyromagnetic ratio was determined by introducing diphenyl picryl hydrazyl into the system and comparing its resonance absorption line ( $g=2.0036^2$ ) with the newly observed lines.

These four lines did not appear in undoped silicon (10 ohm-cm,  $p$  type at room temperature) either compressed or uncompressed. Neither did they appear in an arsenic-doped sample ( $5 \times 10^{16}$  atoms/cm<sup>3</sup>) which had not been compressed. In all of these samples, however, one weak line was observed with a  $g=2.006$ , approximately coinciding with one of the four strong lines previously observed. This line was strongly affected by etching and is thus presumably associated with the crystal surface.

Four lines with the same separation and appearance as the ones described above have also been found in silicon in which the

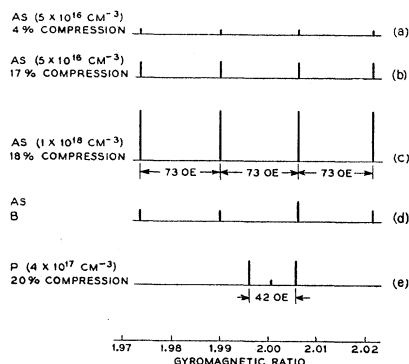


FIG. 1. The gyromagnetic ratio of the spin resonance absorption lines for various specimens of silicon.

arsenic donors have been compensated with boron acceptors [Fig. 1(d)]. In this sample the lines were fairly weak, and the line with  $g=2.006$  was larger and broader than the other three. This is probably caused by the presence of the same single weak line observed in the control samples.

In this compensated crystal the lines only showed up in that part of the crystal where the arsenic concentration exceeded the boron concentration. In addition the four lines were observed in an uncompressed silicon sample with  $10^{18}$  arsenic atoms/cc. These observations lead us to believe that the lines are associated with neutral arsenic atoms. Why the compression enhances the lines is not understood.

The presence of four lines associated with arsenic strongly suggests that this is hyperfine structure caused by the  $As^{75}$  nucleus of spin 3/2. In order to verify this suggestion, phosphorus was used to replace the arsenic as the donor material. Phosphorus has the single isotope  $P^{31}$  with a nuclear spin of 1/2 and thus should give a twofold hyperfine splitting. A sample containing  $4 \times 10^{17}$  cm<sup>-3</sup> phosphorus atoms was plastically deformed and measured. Two strong lines of about equal amplitude appeared with a separation of 42 oersteds [Fig. 1(e)]. This supports the interpretation that we are observing hyperfine splitting. In addition to the two strong lines there was a slight suggestion of a weak line midway between them, as shown in the figure. At the present time we are not certain whether this is real or not.

We have also examined  $p$ -type silicon with  $10^{17}$  boron atoms/cc, both compressed and uncompressed. No lines were observed.

Aluminum-doped silicon ( $3 \times 10^{17}$  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.

<sup>1</sup> C. J. Gallagher, Phys. Rev. **88**, 721 (1952).

<sup>2</sup> 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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**I**N addition to the much investigated<sup>1</sup> level at about 0.037 ev above the valence band, it has been reported that copper introduces another higher-lying acceptor level<sup>2</sup> 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,<sup>3</sup> and Finn,<sup>4</sup> 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.<sup>5</sup>

The sample for which data are shown in Fig. 1 was  $1.5 \times 0.58 \times 0.27$  cubic centimeters and had about  $1.2 \times 10^{15}$  Group V donors per cc. It was copper plated, held at  $630^\circ\text{C}$  for about ten days in an argon atmosphere, then quenched rapidly to room temperature

to try to introduce about  $8 \times 10^{14}$  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  $355^\circ\text{K}$ . 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  $T^{0.5}$ ,<sup>4</sup> and  $\mu$  as  $T^{-2.3}$ ,<sup>5</sup> 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.

<sup>1</sup> 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).

<sup>2</sup> 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).

<sup>3</sup> C. S. Fuller and J. D. Struthers, Phys. Rev. **87**, 526 (1952); G. B. Finn, Phys. Rev. **91**, 754 (1953).

<sup>4</sup> E. M. Conwell, Bull. Am. Phys. Soc. **29**, No. 3, 18 (1954).

<sup>5</sup> F. J. Morin, Phys. Rev. **93**, 62 (1954).

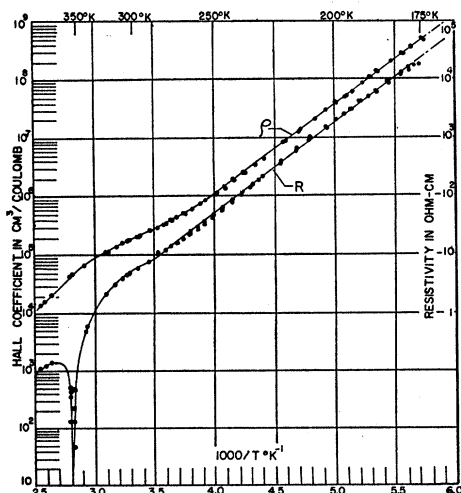


Fig. 1. Temperature dependence of Hall coefficient  $R$  and resistivity  $\rho$  for a germanium sample doped with  $1.2 \times 10^{15}$  arsenic atoms per cc and approximately  $8 \times 10^{14}$  copper atoms per cc.

### Doppler Line-Width Reduction\*

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**W**E 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.<sup>1</sup> 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.<sup>2</sup> 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