

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.

\* This research was supported in part by the United States Air Force, through the Office of Scientific Research of the Air Research and Development Command.

<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 J. M. Smith and M. Lax, Progress Report, August 1, 1953 (unpublished).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Report No. 5, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, December 15, 1953 (unpublished).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\*

G. F. KOSTER† AND J. C. SLATER

Massachusetts Institute of Technology, Cambridge, Massachusetts

(Received April 15, 1954)

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above, a paper is being submitted to *The Physical Review*, containing material some of which has been presented in the unpublished Technical Report No. 5 of the Solid-State and Molecular Theory Group of Massachusetts Institute of Technology.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.

\* Supported in part by the U. S. Office of Naval Research, in part by the Army, Navy, and Air Force.

† Staff Member, Lincoln Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts.

<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

R. C. FLETCHER, W. A. YAGER, G. L. PEARSON, A. N. HOLDEN,  
W. T. READ, AND F. R. MERRITT

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received April 15, 1954)

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

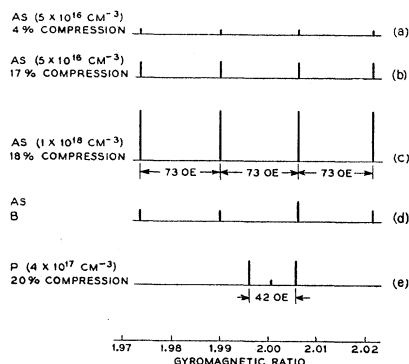


FIG. 1. The gyromagnetic ratio of the spin resonance absorption lines for various specimens of silicon.

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.