

interesting in view of the fact that the nearby superconducting transition metals, vanadium, niobium, and tantalum, usually exhibit very broad magnetic field transitions unless great care is taken to avoid contamination of these metals by small amounts of nitrogen and oxygen.^{5,6} The absence of such effects in rhenium may perhaps be due to the low solubility of nitrogen and oxygen in this metal; it may be noted that rhenium has a close-packed hexagonal structure in contrast to the more open, body-centered cubic structure of the group 5A metals.

In comparing the present data with previous results, it seems possible that the low transition temperature (0.95°K) reported by Aschermann and Justi may have been due to chemical impurities in their sintered rod, as evidenced by a rather high residual resistance, 0.017 of the ice-point value. However, the somewhat high transition temperature (2.4°K) reported for the powder specimens cannot be attributed to chemical impurities, as the materials were believed to be spectroscopically pure. In seeking the origin of this anomalous behavior, we have observed that untreated rhenium powder samples received from the University of Tennessee (reduced from ammonium perrhenate) undergo a superconducting transition which is spread out over the range from 2.4°K down to 1.7°K. However, after such samples have been compressed and heated for 12 hours at 1460°C, the entire superconducting transition takes place between 1.8° and 1.7°K, in good agreement with the behavior of the bulk metal. It seems likely that these effects are due to the existence in the untreated rhenium powder of appreciable amounts of very finely divided metal with transition temperatures higher than that of bulk rhenium, perhaps for reasons similar to those responsible for the elevated transition temperatures found by Buckel and Hilsch⁷ for thin films of tin condensed at low temperatures. The occurrence of such finely divided metal is possible because of the low temperature at which the ammonium perrhenate reduction takes place, 300°C, well below the melting temperature of rhenium, 3170°C. Annealing at quite high temperatures is necessary to permit the aggregation of metal fragments and the removal of imperfections so that crystals are produced with superconducting transition temperatures close to that of bulk rhenium.

I am grateful to H. Charbnaou and S. Foldes for assisting in the fabrication of the rhenium rod. A detailed account of the work will be published later.

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³ J. G. Daunt and T. S. Smith, *Phys. Rev.* **88**, 309 (1952).

⁴ Obtained from Professor A. D. Melaven, University of Tennessee.

⁵ A. Wexler and W. S. Corak, *Phys. Rev.* **85**, 85 (1952).

⁶ H. Preston-Thomas, *Phys. Rev.* **88**, 325 (1952).

⁷ W. Buckel and R. Hilsch, *Z. Physik* **132**, 420 (1952).

Localized Perturbations*

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THERE are many problems in physics characterized by a strong local perturbation on an otherwise solvable problem. One such problem that has been treated by Smith and the author is the vibration of a lattice in the neighborhood of an impurity center.¹ More recently, Slater² has treated the problem of electronic impurity levels using difference equations. Since many other applications are possible, it seems worthwhile to present the procedure used to solve such problems in its most general and abstract form.

We are required to find the eigenvector x and eigenvalues λ of the matrix $A+b$:

$$\sum_j (A+b)_{ij} x_j = \lambda x_i, \quad (1)$$

where the matrix $A=A_{ij}$ has elements $i, j=1, 2, \dots, N$, and all elements of the matrix b_{rs} vanish except b_{rs} for $r, s=1, 2, \dots, k$. It

is assumed that the eigenvectors S_p and eigenvalues $E(p)$ of A are known:

$$\sum_j A_{ij} S_{jp} = E(p) S_{ip}. \quad (2)$$

Equation (1) can be rewritten in the form $x = (\lambda - A)^{-1} b x$, or

$$x_i = \sum_{r,s} (\lambda - A)^{-1}_{ir} b_{rs} x_s, \quad (3)$$

expressing all elements x_i of the eigenvector in terms of the few components x_s associated with the localized perturbation. The latter components may be obtained by specializing i to any of the values $1, 2, \dots, k$ and solving k equations in k unknowns—a problem whose order is small if the perturbation is localized.

The reciprocal matrix elements in (3) can be obtained from (2) by regarding S as the matrix of a similarity transformation

$$\begin{aligned} (\lambda - A)^{-1}_{ij} &= [S(\lambda - E)^{-1} S^{-1}]_{ij} \\ &= \sum_p S_{ip} [\lambda - E(p)]^{-1} (S^{-1})_{pj} \\ &= \sum_p S_{ip} S_{jp}^* / [\lambda - E(p)]. \end{aligned} \quad (4)$$

In the last part of (4) we have utilized the fact that S will be unitary if A is Hermitian.

A particularly simple special case arises if the matrix b has only one nonvanishing element

$$b_{ij} = b_0 \delta_{i0} \delta_{j0}. \quad (5)$$

This case has particular usefulness for the vibration of a lattice one of whose atoms differs in mass from that of a pure lattice. In this case the $k \times k$ problem reduces to a single equation obtained from (3) by setting $i=0$ (and cancelling x_0):

$$1 = b_0 \sum_p |S_{0p}|^2 / [\lambda - E(p)]. \quad (6)$$

If the matrix A is cyclic, then S will have Bloch form,

$$S_{jp} = N^{-1/2} \exp(i\mathbf{p} \cdot \mathbf{R}_j), \quad (7)$$

where \mathbf{R}_j is the position of atom j in the lattice. For this cyclic case, Eqs. (4) and (6) reduce to those obtained by Slater.

Equation (6) can be rationalized to an algebraic equation of degree N for λ . The N roots for λ will interlace the unperturbed roots $E(p)$. For positive b_0 , each λ will exceed the corresponding $E(p)$, but not the next higher $E(p)$. The largest λ is not limited, however, and can separate from the other roots if b_0 is large enough. For the calculation of a separated root the sum in (6) can be replaced by an integral.

Each intermediate eigenvalue will differ by an amount of order N^{-1} from one $E(p)$. Thus one term in the sum (6) will be of finite size. Since unperturbed eigenvalues neighboring to $E(p)$ will differ from it by an amount of order N^{-1} in three dimensions and $N^{-1/2}$ in two dimensions, the neighboring terms in the sum will all be infinitesimal. It will therefore be possible to replace (6) by an isolated term plus a principal-valued integral. This procedure is similar to that used in the spherical-model saddle-point condition.³

In one dimension, the eigenvalue separation is of order N^{-1} , so that if λ differs from one eigenvalue $E(p_1)$ by an amount of order $O(N^{-1})$ its distance from the neighboring eigenvalues is similar. This difficulty may be overcome by considering separately the contributions to the sum for which $|\lambda - p_1| > N^{-1/2}$ and for which $|\lambda - p_1| < N^{-1/2}$. The former contribution may be replaced by a principal-valued integral since a symmetric interval about p_1 is excluded, and the terms now vary sufficiently slowly for the sum to be replaced by an integral. The latter contribution must be handled as a sum, but only the properties of $E(p)$ in the neighborhood of p_1 are involved. The number of terms in this sum (of order $N^{1/2}$) can then be allowed to go to infinity. Equation (6) can, for one dimension, therefore be written:

$$(b_0)^{-1} = (2\pi)^{-1} P \int_0^{2\pi} \frac{d\phi}{E(\phi) - E(p_1)} + \frac{N |S_{0p_1}|^2 \cot \pi \epsilon}{\pi dE/dp_1}, \quad (8)$$

where the eigenvalue $\lambda(p_1)$ has been written in the form

$$\lambda(p_1) = E(p_1 + 2\pi N^{-1} \epsilon), \quad (9)$$

so that ϵ is the fraction of the separation between $E(p_1)$ and the

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

³ 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 problem¹ 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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¹ 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.¹ 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 (5×10^{16} atoms/cm³) 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

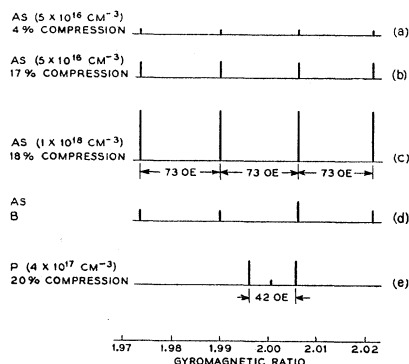


FIG. 1. The gyromagnetic ratio of the spin resonance absorption lines for various specimens of silicon.

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 4×10^{17} cm⁻³ 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.