metallic density regions. Since Loucks and Cutler have shown that the surface potential results mostly from the step barrier and not from higher order terms in the gradient expansion, it is felt that in respect to retention of only the first-order terms in the screening length expansion, the high-density theory provides an adequate picture of laboratory systems.

The present intent in this paper has been to show that the exact theory for the dense electron gas can be extrapolated to realistic densities in which case the results obtained are still sensible and physically meaningful. The high-density theory does provide some useful insight into the physical world and it is with this thought in mind that the theory is offered.

ACKNOWLEDGMENTS

The author expresses appreciation to Dr. D. F. DuBois, Dr. R. Kikuchi, and Dr. R. G. Wilson for helpful and interesting discussions on various topics throughout the summer in which the present work was undertaken.

PHYSICAL REVIEW VOLUME 154, NUMBER 3 15 FEBRUARY 1967

Paramagnetic-Resonance Studies of S, Se, and Te Donor Impurities in GaP

REUBEN S. TITLE
IBM Watson Research Center, Yorktown Heights, New York
(Received 14 September 1966)

Resonances of electrons at neutral S, Se, and Te donors have been observed in GaP at 77°K. Within experimental error, the g values of the resonances are all in the range 1.9976 ± 0.0008. Each resonance consisted of a single broad line, 45 to 60 G wide and Lorentzian in shape. The results are discussed in terms of the effective-mass theory of Kohn and Luttinger.

INTRODUCTION

THE elements of column VI, S, Se, and Te, act as hydrogenic-donor impurities when they substitute for P in GaP. The depths of the donor energy levels below the conduction band, E_D, have been determined from the variation of the Hall constant with temperature.[1,2] The results are given in Table I. Also given in Table I are the results of optical determinations of E_D. Pair spectra which result from direct recombination between donors and acceptors are observed in GaP.[3–6] An analysis of the energies of the pair spectra gives the energy levels E_D of the donor impurities listed in Table I.

Since the donor ionization energies are of the order of 0.1 eV, the donor impurities are almost all electrically neutral at 77°K ($kT\sim0.1$ eV). The bound-donor electrons are paramagnetic. In this paper, paramagnetic resonance measurements on the bound-donor electrons of S, Se, and Te in GaP are reported.

EXPERIMENTAL METHOD

The crystals used in these studies were grown by L. M. Foster and J. E. Scardefield. The crystals were grown from solution with Ga as the solvent. The S, Se, and Te impurities were added in the form of S, ZnSe, and GaTe or ZnTe, respectively. The crystals were in the form of dendritic platelets. The impurity concentration in the crystals that were studied were in the range 10^{17}–2×10^{18} cm^{-3}.

Because of their conductivity at room temperature, the crystals loaded the microwave cavity heavily. There was no paramagnetic signal observable at room temperature. The electrons were frozen out at the donor sites at 77°K. The loading of the cavity disappeared and a resonance signal was observed. The strength of the paramagnetic signal was proportional to the donor-impurity concentration. The signal is attributed to the donor electrons. An example of the resonance signal observed is shown in Fig. 1 for a GaP:Se sample. The signal is typical of that obtained for all three donor

TABLE I. The depths of the donor-energy levels below the conduction band in GaP.

Donor	E_D (optical) eV	E_D (thermal) eV
S	0.110	0.089 ± 0.020
Se	0.109	...
Te	0.095	0.076 ± 0.020

[1] H. C. Montgomery and W. L. Feldman, J. Appl. Phys. **36**, 3228 (1965).
[2] D. N. Nasledov, V. V. Negreskul, S. I. Radautson, and S. V. Slobdchikov, Phys. Status Solidi **10**, 37 (1965).
[3] J. J. Hopfield, D. G. Thomas, and M. Gershenzon, Phys. Rev. Letters **10**, 162 (1963).
[4] D. G. Thomas, M. Gershenzon, and F. A. Trumbore, Phys. Rev. **133**, 269 (1964).
[5] M. Gershenzon, F. A. Trumbore, R. M. Mikulyak, and M. Kowalchik, J. Appl. Phys. **36**, 1528 (1965).
[6] F. A. Trumbore and D. G. Thomas, Phys. Rev. **137**, 1030 (1965).

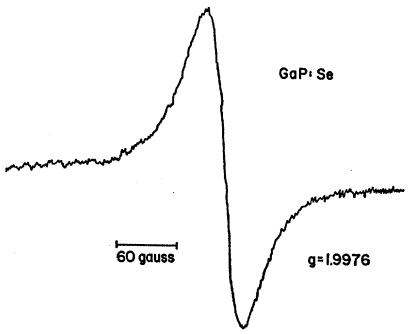

FIG. 1. The EPR signal of an Se-donor electron in GaP at 77°K.

impurities, S, Se, and Te. The resonance signal consists of a single line, Lorentzian in shape, and with no structure. The resonance signal is isotropic. The g values of the resonances for the three donors are, for GaP:S, 1.9975±0.0008; for GaP:Se, 1.9983±0.0007; and for GaP:Te, 1.9978±0.0010. The differences between the three g values are within experimental error and are not regarded as significant. The linewidth could be correlated with donor concentration, increasing from a width of about 50 G for concentrations around 5×10^{17} cm^{-3}, to 130 G for one sample doped with 2×10^{18} cm^{-3} S impurities.

DISCUSSION

The resonance results will be discussed in terms of the effective-mass theory of donor states of Kohn and Luttinger.[7] In semiconducting materials with high dielectric constants, the orbit of the donor electron is large. The properties of the donor electron, therefore, are mainly determined by the band structure and the dielectric constant of the lattice. In an indirect-band-gap material such as GaP, there are several conduction-band minima with which the donor may be associated. In this case, the wave function of the donor electron is given approximately by[7]

$$\psi_D=\sum_i \alpha_i F_i(\mathbf{r})\psi_i(\mathbf{k},\mathbf{r}). \quad (1)$$

The $F_i(\mathbf{r})$ are hydrogen-like envelope functions, and $\psi_i(\mathbf{k},\mathbf{r})$ are Bloch functions that are associated with the ith conduction-band minimum. The α_i are coefficients in the summation over the various conduction-band minima. From pressure measurements on GaP, it was shown by Edwards *et al.*[8] that the conduction-band extrema are in the ⟨100⟩ directions. The summation in Eq. (1), therefore, extends over the six minima in these directions.

The magnetic properties of a donor electron will, according to Eq. (1), be given by the magnetic properties of an electron at a conduction-band minimum. The problem has been considered by Roth.[9] She showed that the s-like character of the conduction-band minimum has admixed into it, via the spin-orbit interaction, some p-like character from other bands. The g factor of an electron at the conduction-band minimum will, because of the p-like admixture, depart from the value 2.0023 expected for an s state. If the spin-orbit interaction is treated as perturbation, the g factor is given by[10]

$$g_{ij}=2.0023(\delta_{ij}-\lambda\Lambda_{ij}), \quad (2)$$

where

$$\Lambda_{ij}=-\sum_{n\neq0}\frac{(0|L_i|n)(n|L_j|0)}{E_{0n}}. \quad (3)$$

λ is the spin-orbit-coupling parameter. E_{0n} is the energy difference between the ground state 0 and the admixed state n. Thus, the components of the g factor are related by (2) and (3) to matrix elements of the angular-momentum operators, L_i.

A significant contribution to the perturbation in Eq. (3) is from the nearby valence band which is p-like in character. In Ge,[11] InSb,[12] and GaAs,[13] for which the donor resonances have g values that depart significantly from 2.0023, the dominant contribution to the perturbation in Eq. (3) is, in fact, from the nearby valence band.

The effective-mass tensor is, like the g tensor, related to matrix elements of the angular-momentum operators. In cases where the dominant contributions to both the effective-mass tensor and the g tensor are from the nearby valence band, it is possible to express the components of the g tensor in terms of the components of the effective-mass tensor.[9,14] For example, the component of the g tensor, $g_{\parallel}$, parallel to the valley axis in an indirect-band-gap material, is related to the transverse effective mass m_t by[9]

$$\Delta g_{\parallel}=g_{\parallel}-2.0023\approx\tfrac{2}{3}(\Delta/E_{cv})[(m/m_t)-1]. \quad (4)$$

Δ is the spin-orbit splitting in the valence band at $k=0$, and E_{cv} the separation of the conduction band from the valence band at the position in k space at which the conduction-band minimum occurs. A similar expression relates $g_{\perp}$ to the longitudinal effective mass m_l. Equation (4) and a related one for $g_{\perp}$ are valid for an electron at one of the conduction-band minima. Since the wave function of an electron is a sum over all six minima [Eq. (1)], the observed g factor will be an average over these minima and is given by

$$g=\tfrac{1}{3}g_{\parallel}+\tfrac{2}{3}g_{\perp}. \quad (5)$$

[7] W. Kohn and J. M. Luttinger, Phys. Rev. **98**, 915 (1955); W. Kohn, Solid State Phys. **5**, 257 (1957).
[8] A. L. Edwards, T. E. Slykhouse, and H. G. Drickamer, J. Phys. Chem. Solids **11**, 140 (1959); A. L. Edwards and H. G. Drickamer, Phys. Rev. **122**, 1149 (1961).
[9] L. M. Roth, Phys. Rev. **118**, 1534 (1960); L. M. Roth, B. Lax, and S. Zwerdling, *ibid.* **114**, 90 (1959).
[10] M. H. L. Pryce, Proc. Phys. Soc. (London) **A63**, 25 (1950); A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).
[11] G. Feher, D. K. Wilson, and E. A. Gese, Phys. Rev. Letters **3**, 25 (1959).
[12] G. Bemski, Phys. Rev. Letters **4**, 62 (1960).
[13] W. Duncan and E. E. Schneider, Phys. Letters **7**, 23 (1963).
[14] L. Roth, B. Lax, and S. Zwerdling, Phys. Rev. **114**, 96 (1959).

An isotropic line is therefore observed. For direct-band-gap materials in cubic symmetry, the bottom of the conduction band is spherical, and is characterized by an effective mass m^*. Roth *et al.*[14] have derived a relation between g and the effective mass m^* for a spherical conduction band.

In cases where the departure of the g values from 2.0023 is large, as for donors in Ge,[11] InSb,[12] and GaAs,[13] excellent agreement is found between the g value calculated from (4) and that observed experimentally. For Si, on the other hand, the g values of the donor resonances are close to 2.0023,[15] and the Δg values calculated from Eq. (4) are three times larger than observed experimentally, and also have the wrong sign.[9,16] Liu[16] showed that the two-level approximation to the effective-mass and g tensors that is used in the derivation of Eq. (4) is not valid for Si. The summation in Eq. (3) has to be extended over levels other than the nearby valence band. Liu showed that the $2p$ core state, although some 80 eV below the conduction band in Si, contributed significantly to the g tensor because of the comparatively large spin-orbit splitting in the $2p$ state. Liu's calculation of the g tensor for donors in Si is in excellent agreement with the experimental results for P, As, and Sb donors.[15,17] The g value for the resonance of Bi donors in Si, however, is in comparatively poor agreement with the calculation.[15] A possible reason for the poor agreement in the case of Bi may be that the effective-mass theory for donors requires correction for donor states as deep as Bi (0.071 eV).

The resonance results obtained for S, Se, and Te donors in GaP will now be discussed in terms of the effective-mass theory of donors described above. Prior to the resonance measurements reported in this paper, an estimate of the g value at the conduction-band minimum was made from Zeeman studies of bound excitons in GaP.[18] A value 1.89 ± 0.10 was obtained. The resonance measurements on S, Se, and Te donors are in the range $g=1.9976\pm0.0008$. The departure from the free-electron value is -0.0047 ± 0.0008. In order to check whether the measured g value is in agreement with that predicted by Eqs. (4) and (5), it is necessary to know some of the details of the band structure of GaP.

There is less known concerning the band structure of GaP than, for example, Ge or Si. The conduction-band minima are along the [100] directions,[8] but their exact positions along these directions have not been determined. Zallen and Paul[19] assume them to be at the band edge. Along the directions in k space at which the conduction-band minima occur, the separation between a minimum and the valence band is 5.3 eV. This separation was determined from a study by Ehrenreich *et al.*[20] of the reflection spectrum of GaP. The spin-orbit splitting Δ of the valence band of GaP at $k=0$ has been determined[21] to be 0.127 eV from extrapolation of infrared-absorption measurements on p-type GaP-GaAs alloys. The values of the effective masses m_l and m_t are unknown. However, Moss, Walton, and Ellis[22] were able to determine an average effective mass $m^*=0.35m$ from infrared Faraday measurements in GaP. The average is related to m_l and m_t by

$$m^*=m_t(2m_l+m_t)/(2m_t+m_l). \tag{6}$$

Since a knowledge of both m_l and m_t is required to calculate g from Eqs. (4) and (5), the value of m^* alone cannot be used to calculate g.

Because of the incomplete knowledge of the band structure of GaP, any calculation of the g value from Eqs. (4) and (5) requires that some further assumptions be made. If one assumes that the spin-orbit splitting in the valence band at the position in k space of the conduction-band minimum is given by $\frac{2}{3}$ the spin-orbit splitting at $k=0$, as implied in Eq. (4), then for a wide range of m_l and m_t values consistent with an average $m^*=0.35m$ [Eq. (6)], a $\Delta g=-0.03$ is calculated from Eqs. (4) and (5). The calculated g value is close to 2, in excellent order-of-magnitude agreement with the experimental value 1.9976 ± 0.0008. The calculated Δg, although small, is however some six times the observed Δg. In view of the many assumptions made concerning the GaP band structure, it is difficult to determine whether the large discrepancy between the calculated and the observed Δg values is significant. In addition to the assumptions regarding the GaP band structure, the use of the two-level approximation to the effective-mass tensor implied in Eq. (4) may not be adequate for GaP. As noted above, the two-level approximation is not valid for Si, for which small Δg values are observed.

Another possible reason for the discrepancy may arise because effective-mass theory is no longer accurate for hydrogenic-donor impurities as deep as 0.1 eV below the conduction band. The orbital radius of a donor electron with an ionization energy of 0.1 eV in GaP (dielectric constant 10.2)[23] is 7 Å. Since this radius is only $1\frac{1}{2}$ times the lattice constant, Eq. (1) is not an accurate wave function to use for a hydrogenic-donor electron in GaP. The donor ionization energy E_D derived from the effective-mass wave function of Eq. (1) is given by

$$E_D=e^4m^*/2h^2\epsilon^2, \tag{7}$$

where ϵ is the dielectric constant, h is Planck's constant, and e is the charge on the electron. If the value of $m^*=0.35m$ measured by Moss *et al.*[22] is used in Eq. (7), a value of E_D of 0.046 eV is obtained, which is to be compared with the experimental values of 0.1 eV in Table I. A similar but smaller discrepancy between calculated and experimental donor ionization energies

[15] G. Feher, Phys. Rev. **114**, 1219 (1959).
[16] L. Liu, Phys. Rev. Letters **6**, 683 (1961).
[17] D. K. Wilson and G. Feher, Phys. Rev. **124**, 1068 (1961).
[18] D. G. Thomas, M. Gershenzon, and J. J. Hopfield, Phys. Rev. **131**, 2397 (1963); Y. Yafet and D. G. Thomas, *ibid.* **131**, 2405 (1963).
[19] R. Zallen and W. Paul, Phys. Rev. **134**, 1628 (1964).
[20] H. Ehrenreich, H. R. Philipp, and J. C. Phillips, Phys. Rev. Letters **8**, 59 (1962).
[21] J. W. Hodby, Proc. Phys. Soc. (London) **82**, 324 (1963).
[22] T. S. Moss, A. K. Walton, and B. Ellis, in *Proceedings of the International Conference on Semiconductors, Exeter* (The Institute of Physics and The Physical Society, London, 1962), p. 295.
[23] D. A. Kleinman and W. G. Spitzer, Phys. Rev. **118**, 110 (1960).

exists for Si ($\epsilon=12.0$). Kohn,[7] noting this discrepancy, corrected the effective-mass formalism for deep donor states. Formally, this was done by dividing the wave function into two parts, an outer region where the effective-mass formalism is still valid, and an inner region where, since the dielectric constant is no longer a good concept, a new wave function is required. Kohn, in addition, used the observed E_D rather than the calculated E_D in the effective-mass theory.

A recalculation of the g values with the corrected wave functions has not been carried out. However, the effect of the corrected wave functions on the g value can be considered qualitatively. Since the electrons of deep-donor impurities are less influenced by the lattice, a g value between that calculated from the uncorrected effective-mass theory [Eqs. (4) and (5)] and the 2.0023 expected for a tightly bound s-like state would be predicted. In the case of the donor resonances in GaP, the g values are indeed between these limits.

As a final note, a comment on the linewidth and shape will be made. The wave function of the donor electron will, even with a radius of 7 Å, overlap several neighboring Ga and P nuclei. Since all Ga and P isotopes have a nuclear moment, there is a resultant hyperfine interaction between the donor electron and every nucleus overlapped by the electron. If the individual lines resulting from these hyperfine interactions are not resolved, an inhomogeneously broadened line is obtained. The width of 45–60 G is not inconsistent with unresolved hyperfine interactions with several neighboring Ga and P nuclei. However, an inhomogeneously broadened line would be expected to have a Gaussian rather than the observed Lorentzian shape. The observed Lorentzian shape is probably due to motional effects caused by hopping of electrons between donor impurities. If one uses the criterion observed in Ge and Si, hopping begins to occur when the average separation between donors is about fourteen times the Bohr radius. With a Bohr radius of 7 Å, hopping would therefore occur when the total donor concentration N_D is the order of 10^{18} cm^{-3}. The net donor concentration in the samples used in the resonance experiments was of this order, and hopping would therefore be expected.

ACKNOWLEDGMENTS

I would like to thank L. M. Foster, J. E. Scardefield, and M. R. Lorenz, who provided the samples, W. Fitzpatrick for aid in the resonance experiments, and J. F. Woods for useful discussions.

PHYSICAL REVIEW VOLUME 154, NUMBER 3 15 FEBRUARY 1967

De Haas–Van Alphen Effect and Fermi Surface in Arsenic*

M. G. PRIESTLEY†
Institute for the Study of Metals and Department of Physics, University of Chicago, Chicago, Illinois

AND

L. R. WINDMILLER‡, J. B. KETTERSON, AND Y. ECKSTEIN
Argonne National Laboratory, Argonne, Illinois

(Received 15 July 1966)

A detailed and accurate study of the de Haas–van Alphen effect and Fermi surface of arsenic has been made by a vector-modulation technique. We find two sets of Fermi surfaces which together give the required volume compensation. The first set contains three closed, centrosymmetric pockets (β in our notation) which have a tilt angle (for the minimum area) of $86.4\pm0.1°$ from the trigonal axis. Their total volume is found to be $(2.12\pm0.01)\times10^{20}$ carriers/cm^3. The other set forms a single multiply connected surface of symmetry $\bar{3}m$ and consists of six α pockets (the Berlincourt carriers) which have a tilt angle of $37.25\pm0.1°$, and which are connected together by six long thin necks with a tilt of $-9.6\pm0.1°$. This is in excellent agreement with the recent pseudopotential calculation by Lin and Falicov if the β pockets are due to electrons at L and the multiply connected surface to holes around T. The multiplicities of the pockets are deduced from the experimental data and are supported by the consequent satisfactory agreement with the observed electronic specific heat.

I. INTRODUCTION

ARSENIC is a semimetal with the same $A7$ trigonal crystal structure as the other semimetals bismuth and antimony.[1] Recent theoretical work by Cohen, Falicov, and Golin[2] has shown that all their band structures are primarily a function of this crystal structure, and so these semimetals should have many

* Supported by the National Science Foundation, the Advanced Research Projects Agency, and the U. S. Atomic Energy Commission.

† This work was begun during the tenure of a National Science Foundation predoctoral fellowship in the Institute for the Study of Metals and the Department of Physics, University of Chicago, Chicago, Illinois.

‡ Present address: University of Bristol, Bristol, England.

[1] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1960), Vol. 1.

[2] M. H. Cohen, L. M. Falicov, and S. Golin, IBM J. Res. Develop. 8, 215 (1964).