

Electron Shielding in n -InSb*†

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The effect on bound electrons in donor levels by conduction-band electrons in n -InSb is investigated using a self-consistent calculation. Results of the calculations show that no bound state exists for impurity concentrations greater than $6 \times 10^{13} \text{ cm}^{-3}$. This shielding appears to be the predominant effect leading to the lack of impurity-binding energy.

I. INTRODUCTION

IT is well known that the binding energy relative to the bottom of the conduction band for electrons on substitutional impurities in semiconductors decreases as impurity concentration increases. Eventually this energy goes to zero at some concentration. One possible explanation for this effect is that increasing concentration causes a broadening of the impurity levels¹ due to bound-electron wave function overlap. For sufficient impurity concentration this could be an important factor. However, it is difficult to explain the lack of ionization energy in n -indium antimonide² at impurity concentrations of 10^{14} cm^{-3} by this mechanism, since the wavefunction overlap for bound electrons would be very small. Another possible explanation based on change of dielectric constant with impurity concentration³ should also not be important at a concentration of 10^{14} cm^{-3} . An alternate explanation for this effect discussed here was originally suggested by Pincherle,⁴ who did rough order of magnitude calculations for silicon. The argument is that if most of the impurity electrons are in the conduction band, there may be appreciable wave function overlap between these conduction band electrons and any bound electrons. This leads to a shielding of impurity centers and a decrease of the ionization energy.

For n -InSb it has been found experimentally that the effective mass is isotropic at the minimum of the conduction band⁵ with an effective mass⁶ m^* in terms of electron mass m_e of $m^* = 0.013m_e$ up to an impurity concentration of $2.6 \times 10^{15} \text{ cm}^{-3}$. The usual model of a substitutional impurity in a semiconductor is that of a hydrogen atom with the effective rather than electronic mass and coulomb potential reduced by a factor of the

reciprocal of the static dielectric constant κ . This dielectric constant for InSb is⁷ $\kappa = 15.7$. If there were no other impurities giving shielding electrons, this model would lead to a ground-state energy of the impurity relative to the bottom of the conduction band of $-6.7 \times 10^{-4} \text{ eV}$ in n -InSb. The corresponding Bohr radius is $0.64 \times 10^{-5} \text{ cm}$. For the calculations below, this model is used but with the addition of charges due to the other impurities. It will be assumed that the other impurities are ionized so that the number of electrons in the conduction band is essentially the same as the number of impurities. In his calculations for silicon, Pincherle⁴ assumed local thermodynamic equilibrium of conduction electrons near the impurity. However, for InSb because of the low expected ionization energies, to observe them one must have the temperature on the order of liquid-helium temperatures or lower. Thus the mean free path of electrons is large. Therefore, except for the effect of ionized impurities, no scattering will be assumed, and the statistical distribution function will be that for the crystal as a whole.

In considering the effect of ionized impurities on electrons, one may simply assume a positive-charge background far from the impurity on which the binding of an electron is being investigated. In the neighborhood of this impurity, however, the discreteness of the impurity centers must be taken into account. If the reciprocal of the impurity concentration is $1/N = 4\pi r_0^3/3$, then for a random impurity distribution one could assume that for any one impurity, there is a spherical region of radius comparable to r_0 centered on the impurity in which on the average there are no other impurities. The effect of nearby impurities on the electrons is then approximated by the following model. Outside of a sphere of radius Br_0 centered at the unionized impurity, there is a positive background of charge to give over-all neutrality. Here B is of the order-of-magnitude of one. Inside the sphere, there is only a single point impurity charge $|e|$ at the sphere's center. On the surface of the sphere is a surface charge density such that the surface charge plus the central impurity positive charge $|e|$ divided by $4\pi(Br_0)^3/3$ is equal to the uniform background-charge density. This surface charge may be thought of as approximating the effects of nearest-

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¹ C. Hilsum and A. C. Rose-Innes, *Semiconducting III-V Compounds* (Pergamon Press, Inc., New York, 1961), p. 73.

² E. H. Putley, Radar Research Establishment Memorandum No. 1512 1958 (unpublished).

³ G. W. Castellan and F. Seitz, *Semiconducting Materials* (Butterworths Scientific Publications Ltd., London, 1951).

⁴ L. Pincherle, Proc. Phys. Soc. (London) A64, 663 (1951).

⁵ G. Dresselhaus, A. F. Kip, C. Kittel, and G. Wagoner, Phys. Rev. 98, 556 (1955).

⁶ S. D. Smith, T. S. Moss, and K. W. Taylor, Phys. Chem. Solids 11, 131 (1959).

⁷ T. S. Moss, S. D. Smith, and T. D. F. Hawkins, Proc. Phys. Soc. (London) B70, 778 (1957).

neighbor ionized impurities. This model does not take into account the anisotropy introduced by the fact that the nearest impurity is discrete and is not distributed over a spherical surface. Also, because actual distance to the nearest impurity is variable, described by a distribution function, there will be a distribution of impurity binding energies for a given temperature and impurity density. However, it was found that the binding energies are fairly insensitive to the exact choice of B even for $B < 1$, and it is believed that this model gives good order of magnitude binding energies.

II. CALCULATIONS

In this section, the methods of calculation of the impurity ionization energy will be discussed. The problem consists of two main parts: (a) the calculation of the bound electron wave function with its corresponding charge density, and (b) the calculation of the conduction-band electron wave functions with their associated charge density. These calculations are repeated until the results are mutually consistent to within a few percent.

The bound electron is assumed to move in the Coulomb potential $-e/\kappa r$ of the positive impurity center combined with the potential $V(r)$ due to the conduction-band electron distribution and the positive-charge background of the other impurities. Here e is the negative electronic charge and κ is the dielectric constant. This potential is simply inserted in the Schrödinger equation for the bound electron. Correlation and exchange energies are neglected. The method of finding $V(r)$ will be discussed later. The Hamiltonian for the bound electron is then

$$H = (\hbar^2/2m^*) - (e^2/\kappa r) + V(r). \quad (1)$$

A variational approach was used to find the wave function of the bound electron. The normalized trial wave function used for the ground state was of the form

$$\psi(r) = a(1+br)e^{-cr}, \quad (2)$$

with

$$a = [\pi(c^2 + 3bc + 3b^2)/c^5]^{-1/2}$$

for normalization. The parameters b and c were varied to minimize the expectation value of H . In all the results, b was found to be quite small compared to c so that a simple exponential appears to be a good approximation to the ground-state wave function. The parameter c is comparable to 10^5 cm^{-1} , going to zero as the impurity density becomes large. Because $V(r)$ is not a simple function, this minimization was done numerically on a computer using a relaxation method. The potential V' due to the bound electron is then found from Gauss's law to be

$$\begin{aligned} V'(r) &= -\frac{e}{\kappa} \int_{\infty}^r \frac{dr'}{r'^2} \int_0^{r'} |\psi(r'')|^2 d\mathbf{r}'' \\ &= -(e/\kappa)e^{-2cr}(1/r + N_1 + N_2 r + N_3 r^2) + e/\kappa \quad (3) \end{aligned}$$

with

$$\begin{aligned} N_1 &= \frac{1}{2}\pi a^2(2c^2 + 8bc + 9b^2)/c^4, \\ N_2 &= \pi a^2(2bc + 3b^2)/c^3, \\ N_3 &= \pi a^2 b^2/c^2. \end{aligned}$$

To find the wave functions and charge density of the conduction-band electrons, it is assumed that each of the electrons sees the potential $-e/\kappa r$ due to the impurity, the potential $V'(r)$ due to the bound electron, and the potential $V(r)$ due to the other conduction-band electrons and the positive background of the ionized impurities. The contribution of any one conduction electron to $V(r)$ is negligible because of the large number of such electrons and, thus, this contribution need not be subtracted from $V(r)$ in the Schrödinger equation for a conduction-band electron. If the energy of a conduction-band electron is taken to be $\hbar^2 k^2/2m^*$, its Schrödinger equation is then

$$\{\nabla^2 + k^2 + (2m^*/\hbar^2)[(e^2/\kappa r) - eV(r) - eV'(r)]\} \times \phi_{\mathbf{k}}(\mathbf{r}) = 0. \quad (4)$$

To solve this equation, the method of partial waves is used. Here the behavior near $r=0$ is of interest rather than the asymptotic behavior used in scattering cross-section problems. Because of the low temperatures used in the calculations ($\leq 3^\circ\text{K}$), the average wavelength of the conduction-band electrons is about 10 times the size of the bound-electron Bohr radius and thus when the binding energy is of the order-of-magnitude of the unshielded binding energy, only the modification of the S -wave part of a plane wave solution need be considered. If there were no potential, for a volume Ω there would be a plane wave solution, $\Omega^{-1/2} e^{i\mathbf{k}\cdot\mathbf{r}}$, with an S -wave part $\Omega^{-1/2}(\sin kr)/kr$. Let $\phi_{\mathbf{k}S}(\mathbf{r})$ be an S -wave solution of Eq. (4). Then a modified plane wave solution in the S -wave approximation is

$$\phi_{\mathbf{k}} = \Omega^{-1/2}(e^{i\mathbf{k}\cdot\mathbf{r}} - [\sin kr]/kr) + \phi_{\mathbf{k}S}(\mathbf{r}). \quad (5)$$

The function $\phi_{\mathbf{k}S}$ was found by numerical integration of Eq. (4) out to an r large compared with all the various characteristic lengths involved. This was then matched at that r to a solution of the form $\Omega^{-1/2}[\sin(kr + \eta)]/kr$ to find the normalization. The total charge density of the conduction-band electrons is given by

$$\rho = (e\Omega/4\pi^3) \int |\phi_{\mathbf{k}}|^2 f_{\mathbf{k}} d\mathbf{k}, \quad (6)$$

where $f_{\mathbf{k}}$ is the Fermi-Dirac distribution function depending on the impurity density N . In the angular integration, the S -wave parts of $|\phi_{\mathbf{k}}|^2$ do not mix with the other parts. This leads to an effective $|\phi_{\mathbf{k}}|^2$ of $\Omega^{-1} + \{|\phi_{\mathbf{k}S}|^2 - \Omega^{-1}[(\sin kr)/kr]^2\}$. Outside a sphere of radius $B r_0$, the positive background contributes an additional charge density $-eN$. Inside the sphere no positive background is assumed. Also the surface

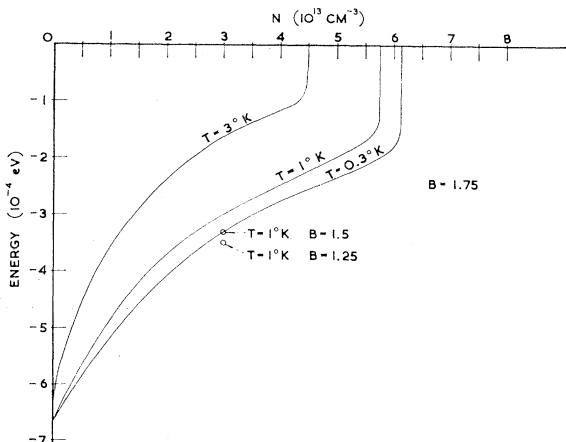


FIG. 1. Energy for an impurity electron in the ground state versus concentrations of conduction-band electrons for several low temperatures.

charge on the sphere discussed in the Introduction contributes to the potential. Numerical integration over \mathbf{k} together with numerical spatial integration using Gauss's law for the spherically symmetric charge distribution as in Eq. (3) for V' , give the potential $V(r)$ due to these various charge distributions. As mentioned above, these calculations were repeated until there was mutual consistency between the various wave functions and potentials. The potential $V(r)$ is somewhat Gaussian in shape with a characteristic width of about 2×10^{-5} cm which is very insensitive to B , concentration, and temperature. Well depth does depend on these quantities.

III. RESULTS OF COMPUTATION

The two independent variables of the problem are N , the concentration of conduction-band electrons and T , the temperature. For each set of N , T , the Fermi energy was found from published values.⁸ Calculations for several sets of N , T , have been carried out and the results are summarized in Fig. 1. The curves are for

⁸ J. McDougall and E. C. Stoner, Phil. Trans. Roy. Soc. London, A237, 67 (1938).

$B=1.75$, where Br_0 is the radius of the sphere outside of which there is uniform positive-charge background. Two points for $T=1^\circ\text{K}$ and $B=1.25, 1.5$ are shown to illustrate that the curves are not very sensitive to the exact choice of B .

It is seen from Fig. 1 that the ionization energy decreases with increasing electron density as one would expect. It is also seen that the ionization energy goes to zero rather sharply at a critical density N . However, the points where the ionization energy goes to zero at the various temperatures should be considered to be only rough approximations to the correct values because as the electrons become unbound, the approximations used, such as the S -wave approximation, no longer hold. As a result of the calculations, it appears that in n -InSb, electron shielding could be the principal mechanism that explains the absence of ionization energy for the usual impurity densities.

The mechanism discussed here is similar to that for the Mott transition.⁹ If the impurities were distributed uniformly, one would expect that application of an increasing magnetic field would lead to a sudden transition giving a decrease in conductivity at a critical field. This is because the magnetic field tends to give a larger ionization energy for impurities. For a field large enough to cause binding of some electrons on impurities, the decreased density of conduction-band electrons would increase the binding still further so that this cumulative effect would cause almost all the electrons to become bound on impurities at low temperatures. The fact that there is a statistical, nonuniform distribution of impurities with possible clustering at various imperfections leads to a less sharp transition so that the electrons should become bound to the impurities over a small range of magnetic fields. Some evidence for this has been seen by Wilson, Love, and Miller.¹⁰ This shielding effect in strong magnetic fields is at present being computed for quantitative comparison with experiment.

⁹ N. F. Mott, Trans. Faraday Soc. 34, 500 (1938).

¹⁰ J. H. Wilson, W. F. Love, and S. C. Miller, Phys. Rev. (to be published).