# Electron Shielding in Heavily Doped Semiconductors\*

I. B. KRIEGER

Physics Department, Polytechnic Institute of Brooklyn, Brooklyn, New York (Received 12 August 1968)

The ionization energy of an electron bound to a donor atom is calculated as a function of the number of electrons in the conduction band and the temperature assuming Thomas-Fermi screening. The results are compared with a previous numerical calculation performed for InSb. We also show that it is possible to induce a Mott transition by applying stress to a degenerately doped many-valley semiconductor, with a resulting change from a metallic to an insulating phase.

#### I. INTRODUCTION AND CONCLUSIONS

N the usual calculation of the energy levels of an l electron bound to a donor atom in a doped semiconductor,<sup>1</sup> the binding energy relative to the conduction-band minima is obtained for a single impurity atom in the crystal. However, it is well known experimentally that the binding energy of the electron decreases as the number of donors increases until at some critical impurity concentration there is no observed activation energy.<sup>2</sup>

A possible explanation of this phenomenon arises from the interaction between electrons bound on different impurity centers.<sup>3</sup> As the average distance between donors is decreased because of increasing impurity concentration, the wave functions of electrons on different donors will significantly overlap. For small overlap, the impurity levels will be broadened, but for strong overlap this electron-electron repulsion can destroy the bound state. However, it has been observed by Li et al.<sup>4</sup> that this effect cannot explain the fact that the electron binding energy vanishes for impurity concentrations as low as  $10^{14}$ /cm<sup>3</sup> for InSb. In order to account for this, these workers calculated, considering only S-wave scattering, the Hartree self-consistent field that an electron experiences due to the singly ionized impurity atom and the screening from conduction-band electrons. They calculate the ionization energy over a wide range of conduction-band electron concentrations and for several different temperatures. Most significantly, they find that for  $n \approx 6 \times 10^{13} / \text{cm}^3$ donors, the binding energy becomes zero.

In this paper we wish to point out that the latter result is a special case of a more general statement given by Mott,<sup>5</sup> developed in the course of his investigations on the insulator-metal transition. We have generalized Mott's calculation to obtain the ionization energy as a function of N (the concentration of conduction-band electrons) and the temperature, and find a different T dependence from that given by Li et al.,

besides finding a smoother N dependence near the critical concentration. Finally, we show that it is possible to induce a Mott transition by applying stress to a degenerately doped many-valley semiconductor with a resultant transition from the metal phase to the insulating phase.

#### **II. CALCULATION**

Instead of numerically calculating the self-consistent field, we note that, in the light of the variational principle for the ground-state energy, we expect that the binding energy will not be very sensitive to the exact form of the screening potential, but rather will depend on its general over-all variation. Consequently, we shall take, with Mott, the Thomas-Fermi potential as a good approximation to the potential of the singly charged donor screened by the conduction electrons, i.e.,

$$V(\mathbf{r}) = -\left(\frac{e^2}{\kappa r}\right)e^{-qr}$$

where  $\kappa$  is the static dielectric constant and q is the Thomas-Fermi inverse screening length. We note that in the limit of zero activation energy this approximation satisfies the Friedel sum rule<sup>6,7</sup> if the Born approximation for the scattering is valid, and it has been shown<sup>7</sup> that q need be changed by only  $\gtrsim 10\%$  from the Thomas-Fermi value in order for the Friedel sum rule to be satisfied when the phase shifts are calculated exactly.

We also note that, according to Li et al., a simple hydrogenic variational solution gives essentially the same binding energy as more complicated variational wave functions. Thus we seek the ground-state energy of the Schrödinger equation

$$-\frac{\hbar^2}{2m^*}\nabla^2\psi - \frac{e^2}{\kappa r}e^{-qr}\psi = \epsilon\psi$$

as a function of q, and hence as a function of the number of electrons in the conduction band. Then taking the variational solution as

$$\psi = (\alpha^3 / \pi)^{1/2} e^{-\alpha r}$$
,

<sup>\*</sup> Supported in part by NASA Research Grant NsG-589.
\* W. Kohn and J. M. Luttinger, Phys. Rev. 97, 869 (1955).
\* G. L. Pearson and J. Bardeen, Phys. Rev. 75, 865 (1949).
\* C. Hilsum and A. C. Rose-Innes, Semiconducting III-V Compounds (Pergamon Press, Inc., New York, 1961), p. 73.
\* S. P. Li, W. F. Love, and S. C. Miller, Phys. Rev. 162, 728 (1967). (1967).

<sup>&</sup>lt;sup>6</sup> N. F. Mott, Phil. Mag. 6, 287 (1961).

<sup>&</sup>lt;sup>6</sup> J. Friedel, Phil. Mag. 43, 153 (1952). <sup>7</sup> J. B. Krieger and S. Strauss, Phys. Rev. 169, 674 (1968).



FIG. 1. Graph of the binding energy  $\bar{\epsilon}$  versus the inverse screening length q, in terms of dimensionless quantities.  $\epsilon_0$  is the magnitude of the binding energy for zero screening, and  $a_0$  is the radius of the first Bohr orbit in the semiconductor.

we obtain

$$\bar{\epsilon}/\epsilon_0 = \beta^2 - 8\beta^3/(2\beta + \gamma)^2, \qquad (1)$$

where  $\epsilon_0 \equiv m^* e^4/2\hbar^2 \kappa^2$  is the magnitude of the binding energy for q=0 and the dimensionless quantities  $\beta$  and  $\gamma$  are defined by

$$\beta \equiv a_0 \alpha, \quad \gamma \equiv a_0 q,$$

where  $a_0 \equiv \hbar^2 \kappa / m^* e^2$  is the radius of the first Bohr orbit. Minimizing the energy with respect to  $\beta$  gives

$$(2\beta + \gamma)^3 - 12\beta(2\beta + \gamma) + 16\beta^2 = 0.$$
 (2)

Case (a): 
$$\bar{\epsilon}=0$$

Setting the right-hand side of Eq. (1) equal to zero, solving for  $2\beta + \gamma$  in terms of  $\beta$ , and substituting the result into Eq. (2) immediately gives

$$\gamma = 1, \qquad (3)$$

which is Mott's result. For a single-valley conduction band at T=0, this can be written as

$$a_0 k = \frac{1}{4}\pi, \qquad (4)$$

where we have used

$$q^2 = (4\pi e^2/\kappa)g(\epsilon_F), \qquad (5)$$

where  $g(\epsilon_F)$  is the density of states at the Fermi energy and k is the Fermi wave number. For InSb,  $a_0=0.64$  $\times 10^{-5}$  cm,<sup>4</sup> and using  $N=k^3/3\pi^2$ , we obtain from Eq. (4)  $N=6.2\times 10^{13}$ /cm<sup>3</sup> as the density necessary to make the binding energy equal to zero, which is precisely the result of Li *et al.* 

#### Case (b): $\epsilon \neq 0$

Here it is convenient to treat Eq. (2) as a quadratic equation in  $\beta$  with  $2\beta + \gamma$  given. Thus, for a definite  $2\beta + \gamma$ , we immediately obtain  $\beta$ , and hence the  $\gamma$  corresponding to that  $\beta$ . Retaining only those solutions having physical significance, i.e.,  $\beta$ ,  $\gamma > 0$ , we obtain  $\bar{\epsilon}/\epsilon_0$  from Eq. (1). Figure 1 is a graph of the results. We can again relate these results to the corresponding Fermi wave number and the temperature, for T much less than the degeneracy temperature  $T_D$ , by noting that  $q^2 = q_0^2 [1 - (\pi^2/12)(T/T_D)^2]$ ,<sup>8</sup> where  $q_0$  is the zero-temperature result. Thus,

$$a_0q = [(4/\pi)a_0k_0]^{1/2}[1-(\pi^2/24)(T/T_D)^2],$$

where  $k_0$  is the Fermi wave number at T=0.

## III. DISCUSSION OF RESULTS

Our results are significantly different from those of Li *et al.* in three respects when applied to InSb. First of all, they predict a much smaller change in the binding energy in the low-N case. Their results are probably more accurate than ours in this regime, because in this case the wavelength of conduction-band electrons is long compared to the Bohr radius of the bound electron, and thus the conduction electrons are scattered from a weak and relatively well-localized center, thus satisfying their assumption that only S-wave scattering is important. The Thomas-Fermi approximation really neglects the presence of the bound electron and thus attributes too large a screening effect to the conduction electrons.

Secondly, they predict that, for a given number of electrons in the conduction band, the magnitude of the binding energy decreases as the temperature is increased, whereas we find the opposite using Thomas-Fermi screening. We believe, however, that any realistic theory of screening must yield the results that as the temperature increases, the average kinetic energy of a conduction-band electron increases, and consequently the screening due to these electrons must decrease because they cannot be made to "linger" about the impurity center as easily as when they moved more slowly. This effect, however, is difficult to observe experimentally because experiments are not performed with constant N and variable T but are performed with constant number of donor atoms and variable T, and as T increases more donors are ionized, giving rise to higher densities in the conduction band.

Finally, Li *et al.* find that the ionization energy goes to zero extremely sharply at the critical density, whereas we find a much smoother variation of the binding energy as a function of N. It is difficult to understand how one might obtain such a rapid variation of the binding energy for small change in the conduction-band concentration, since the screening is a

<sup>&</sup>lt;sup>8</sup> R. Mansfield, Proc. Phys. Soc. (London) 69B, 76 (1956).

slowly varying function of N. In fact, if N changes by 1%, then the screened potential changes by  $\approx 1\%$  on the average, and if  $\phi_N$  is the exact solution for the wave function for N electrons/ $cm^3$  in the conduction band, then by the variational theorem the expectation value of H in the state  $\phi_N$  overestimates the energy when H corresponds to the system containing  $N + \Delta N$  electrons/cm<sup>3</sup> in the conduction band. Thus, if N changes by only 1%, then the change in  $\epsilon$  is less than the average change in V, which is less than 1% of V, which is thus of the order of 1% of  $\epsilon_0$ . Thus a slow variation of V with N leads necessarily to a slow variation of  $\epsilon$  with N. One should not, however, infer from this argument that the Mott transition is not sharp as a function of the number of donor atoms. The supposed sharpness of the Mott transition is due to the fact that as the number of donors is increased, the density of conduction-band electrons increases very much more rapidly. In fact, if the donor density is 1% of the density necessary to produce zero ionization energy, then the broadening of the impurity levels is not sufficient to raise more than a small fraction of the donor electrons into the conduction band at T=0. However, when the dopant density is raised by a factor of 100 to the level of degenerate doping, all the electrons move into the conduction band and thus N increases by many factors of 100. In general, N increases more rapidly than the number of donors until degenerate doping is achieved, because the decrease in the electron binding energy is a cooperative effect, i.e., as more electrons are detached, there is more screening, which tends to produce more free electrons, etc. Experimentally one could observe whether the binding energy is a slowly varying function of the number of conduction-band electrons by measuring the ionization energy as a function of the Hall constant for crystals having different donor densities.

In conclusion, we note that it may be possible to observe the Mott transition by applying stress to a degenerately doped many-valley semiconductor, with a resulting transition from the many-valley metallic state to the single-valley insulator state. This follows from Eq. (5), where

### $g(\epsilon_F) = \frac{3}{2}N/\epsilon_F.$

If stress is applied,<sup>9</sup> it is possible to lower the energy of one valley with respect to the other valleys, with the consequent emptying of all the electrons into the lowest valley. When this happens, q decreases because  $\epsilon_F$ increases by a factor of  $\nu^{2/3}$ , where  $\nu$  is the number of originally equivalent valleys. Thus if the donor density were only slightly larger than that required to make the many-valley semiconductor degenerate, it would not be sufficient to maintain degeneracy after stress was applied, and a transition to the insulating state would be observed; or, if not all electrons would become bound on donor sites, at least some would, and an ionization energy would be observable. This result, although obtained by assuming Thomas-Fermi screening, is really independent of that assumption, its validity depending only on the fact that when all the electrons are moved into one valley, the exclusion principle requires that they occupy higher energy states, and fast electrons do not screen as effectively as slow ones.

<sup>&</sup>lt;sup>9</sup> P. J. Price, Phys. Rev. 104, 1223 (1956).