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Electron Shielding in Doped Semiconductors*

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The binding energy of an electron bound to two ionized impurity atoms is calculated as a function of the screening parameter δ, which occurs in the screened Coulomb potential. The binding energy is found to diminish with increase in δ, ultimately becoming zero at $\delta \approx 1.254$. The role played by such a system in the Mott transition is discussed.

I. INTRODUCTION

The binding energy of an electron, bound to a donor atom in a doped semiconductor, relative to the conduction-band minima is usually calculated[1,2] for a single impurity atom in the crystal. On the experimental side, it is known[3,4] that the binding energy of the electron decreases as the number of donors increases until at some critical impurity concentration there is practically no activation energy.

The theoretical problems associated with this phenomena can be conveniently discussed in terms of the potential of the singly charged donor screened by the conduction electrons[5,6]:

$$V(r) = -(e^2/\kappa r)e^{-qr} , \qquad (1)$$

where κ is the static dielectric constant and q is the Mott screening parameter defined by $q^2 = 4m^* e^2 n^{1/3}/(\kappa \hbar^2)$, n being the free-electron density.

The approximation that the electron is bound to a single ionized impurity is, however, no longer justified if there is considerable overlap between the wave functions of electrons bound to two neighboring impurity atoms. The occurrence of such a situation is governed by three factors: the static dielectric constant κ, the effective mass m^*, and the free-electron density n. The effect of κ and of m^* can be seen from the expression of the Bohr radius, $a_0 = \hbar^2\kappa/m^*e^2$; since in semiconductors, $\kappa > 1$ and $m^* < m$, this means a greater radius than that in the free space. An increase in the doping concentration acts in two ways: First, it decreases the average distance between impurities, and second, it increases the value of q, which in its turn leads to an increase in the average distance $\langle r \rangle$ between the electron and nucleus of the impurity atom.[7] An appropriate combination of these factors can lead to the situation such that $\langle r \rangle \simeq \frac{1}{2}d$, where d is the average distance between impurities. We may note here that such a condition can sometimes exist at fairly low impurity concentrations, e.g., for InSb it occurs at an impurity concentration of $\sim 10^{14}/\text{cm}^3$. As this limit is approached, there will be an increasing concentration of systems in which two or more impurity atoms are participating. In the present paper we investigate the stability of the simplest of these systems, consisting of two ionized impurity atoms and an electron. We shall represent this system by Im_2^+ in analogy with H_2^+.

II. CALCULATION AND RESULTS

As shown in Fig. 1, r_a and r_b represent the distances between the electron and the nuclei a and b, and R is the distance between the nuclei. We shall carry out the calculation in the following units: unit of energy $= m^*e^4/\hbar^2\kappa^2$, unit of length $a_0 = \hbar^2\kappa/m^*e^2$. Also $\delta = qa_0$.

The Hamiltonian of the system may be written

$$H = -\tfrac{1}{2}\nabla^2 - e^{-\delta r_a}/r_a - e^{-\delta r_b}/r_b + e^{-\delta R}/R . \qquad (2)$$

At this point, the reader may well raise the question whether it is justified to represent the poten-

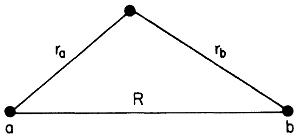

FIG. 1. Coordinates used for Im_2^+.

tial between two impurity ions by Eq. (1). The answer is in the affirmative. Alfred and March[8] (semiclassical arguments) and Corless and March[9] (wave-mechanical treatment) have shown that the potential between two ions embedded in the bath of conduction electrons is the same as that between an ion and an electron [Eq. (1)].

We obtain the energy of the system by the variation method, and for the trial wave function we choose[10]

$$\psi = a e^{-b\mu}(1 + c\nu^2) \; , \tag{3}$$

where a is a normalization constant and b and c are parameters. μ and ν are variables in confocal elliptical coordinates.

The evaluation of integrals involved in the calculation is lengthy, but can be analytically carried out. We merely quote here the final expression for the energy:

$$E = \frac{e^{-\delta R}}{R} + \frac{840b^3}{R^2[4b^2(35+14c+3c^2)+7(2b+1)(15+10c+3c^2)]}\left[\frac{1}{60b}[(2b+1)(15+10c+3c^2)+16c^2] - \frac{2Re^{-\delta R/2}}{\delta R+4b}\right.$$
$$\left.\times\left(1+\frac{2}{\delta R+4b}\right)[B_0(\tfrac{1}{2}\delta R)+2cB_2(\tfrac{1}{2}\delta R)+c^2B_4(\tfrac{1}{2}\delta R)] + \frac{2Re^{-\delta R/2}}{\delta R+4b}[B_1(\tfrac{1}{2}\delta R)+2cB_3(\tfrac{1}{2}\delta R)+c^2B_5(\tfrac{1}{2}\delta R)]\right] \; , \tag{4}$$

where

$$B_n(m) = \int_{-1}^{1} \nu^n e^{-m\nu}\, d\nu \; . \tag{5}$$

For a given δ, the minimized value of the energy and the optimum values of the parameters were obtained as follows. E was obtained at three values of R in the neighborhood of the minimum of the potential-energy curve ($R = R_e$) by minimizing the energy with respect to b and c at each distance. Assuming a parabolic relationship between E and R, $E = k_1 + k_2R + k_3R^2$, R_e was located. The procedure was iterated, with finer intervals between the 3 points, until R_e was accurately determined. Finally, at this R_e, the energy was minimized with respect to b and c. The optimized values of the parameters, for various values of δ, together with the corresponding values of R_e and E are shown in Table I. Also shown in the table is the "dissociation energy" D given by

$$D = -E(Im_2^+) + E(Im)$$

for the dissociation

$$Im_2^+ \rightarrow Im + Im^+ \; .$$

Values of E(Im) were taken from an earlier study.[7]

III. DISCUSSION

The binding energy is seen to diminish with increase in δ, ultimately becoming zero at a critical value $\delta = 1.254$. The trial wave function that we have used is known[11] to give very good results for H_2^+ (0.04% accuracy in E), and it would be reasonable to assume that for low values of δ our results are satisfactory. However, it is difficult to estimate the accuracy of our results at very high val-

TABLE I. Binding energy and optimized parameters as a function of screening parameter (unit of energy is $m^*e^4/\hbar^2\kappa^2$; unit of length is $=\hbar^2\kappa/m^*e^2$).

Screening parameter δ	Equilibrium internuclear distance R_e	b	c	E	D
0.0001	1.997	1.3522	0.4466	−0.602 29	0.102 39
0.0002	1.997	1.3522	0.4466	−0.602 19	0.102 39
0.0005	1.997	1.3522	0.4466	−0.601 89	0.102 39
0.001	1.997	1.3522	0.4466	−0.601 39	0.102 39
0.002	1.997	1.3522	0.4466	−0.600 39	0.102 39
0.0025	1.997	1.3522	0.4466	−0.599 89	0.102 38
0.005	1.997	1.3522	0.4466	−0.597 40	0.102 38
0.01	1.997	1.3522	0.4466	−0.592 45	0.102 38
0.02	1.997	1.3519	0.4467	−0.582 65	0.102 35
0.025	1.997	1.3517	0.4467	−0.577 79	0.102 33
0.03	1.997	1.3515	0.4468	−0.572 97	0.102 31
0.04	1.997	1.3510	0.4470	−0.563 42	0.102 25
0.05	1.997	1.3503	0.4472	−0.553 99	0.102 17
0.06	1.997	1.3495	0.4474	−0.544 68	0.102 08
0.07	1.998	1.3486	0.4477	−0.535 49	0.101 97
0.08	1.998	1.3476	0.4480	−0.526 42	0.101 85
0.09	1.998	1.3464	0.4483	−0.517 46	0.101 71
0.10	1.999	1.3451	0.4486	−0.508 61	0.101 55
0.20	2.005	1.3268	0.4533	−0.425 94	0.099 13
0.25	2.010	1.3145	0.4563	−0.388 28	0.097 36
0.30	2.016	1.3007	0.4595	−0.352 87	0.095 24
0.40	2.033	1.2690	0.4666	−0.288 34	0.089 98
0.50	2.056	1.2330	0.4740	−0.231 53	0.083 45
0.60	2.087	1.1933	0.4815	−0.181 77	0.075 69
0.70	2.126	1.1503	0.4887	−0.138 52	0.066 78
0.80	2.178	1.1036	0.4953	−0.101 32	0.056 73
0.90	2.244	1.0526	0.5010	−0.069 79	0.045 61
1.00	2.333	0.9961	0.5052	−0.043 60	0.033 44
1.05	2.389	0.9650	0.5066	−0.032 43	0.026 99
1.10	2.456	0.9312	0.5073	−0.022 53	0.020 33
1.15	2.539	0.8938	0.5073	−0.013 87	0.013 46
1.20	2.648	0.8509	0.5061	−0.006 48	0.006 07
1.25	2.803	0.7984	0.5031	−0.000 40	0.000 40

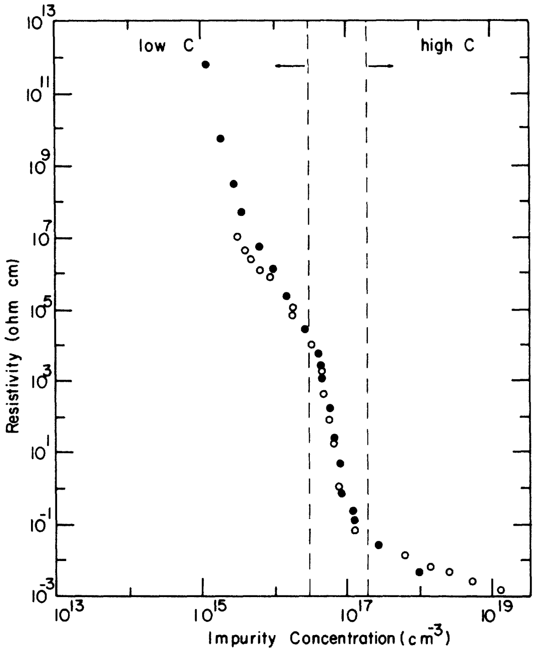

FIG. 2. Dependence of the resistivity at 2.5 °K on the impurity concentration (from Fritzsche, Ref. 13). Dots: *n*-type germanium, antimony doped; circles: *p*-type germanium, gallium doped.

ues of δ. In view of this, the critical value of δ quoted above is, more accurately, only a lower limit. It is of interest to note that in the case of an electron bound to a single impurity center, the critical value of δ at which the ionization energy becomes zero[12] is 1.19; thus there is a narrow region between $\delta = 1.19$ and 1.254 in which an electron cannot be bound to one ionized impurity, but it can be bound to two.

The "dissociation energy" D also decreases with increase in δ, but the rate of change is much smaller than that in the case of E.

There is some indirect evidence of the existence of systems such as Im_2^+ in doped semiconductors. Fritzsche[13] has measured the resistivity of germanium at 2.5 °K with different impurity concentrations. Antimony- and gallium-doped samples were used. His results are reproduced in Fig. 2. The dotted lines indicate the approximate borders between the three concentration ranges in which the resistivity showed a different behavior.

There is seen to be a sharp drop in the region between the two dotted lines. To the right of the drop the conductivity is independent of temperature. Mott[6,14] has interpreted this drop in terms of the Mott transition and has identified the onset of this transition with the situation when the binding energy of the electron in the impurity potential (1) becomes zero. This corresponds to

$$q > 1.19/a_0 .$$

The value 1.19 is from Rogers *et al.*[12] Mott actually took the approximate value 1.0; the same value was obtained by Krieger[15] from a simple hydrogenic variational solution. Our results show that even for impurity concentrations beyond $q > 1.19/a_0$, electrons will not be completely delocalized. There will exist Im_2^+ systems at least up to $\delta = 1.254$; as noted earlier this value is only a lower limit, probably $\delta \simeq 1.27$ would be a better value. Further, these results suggest that probably more complicated systems, such as Im_2 (2 ionized impurities + 2 electrons), might have a finite binding energy even for $\delta > 1.27$. From the foregoing considerations, we are led to the following picture: In the region $\delta = 1.19$ to ~ 1.4 (this value is very approximate) the electrons are no longer localized around individual impurities, but many of these are "partially" localized. This region corresponds to the transition region between the two dotted lines in Fig. 2. Beyond a certain value of δ, it is no longer possible for an electron to be bound to a cluster of impurity atoms and the electron is completely "delocalized," and this can be identified with the "high-*C*" region in Fig. 2.

If the above picture is valid, one expects that the activation energy should remain finite, though small, in the transition region, and ultimately diminish to zero in the neighborhood of the right-hand boundary of the transition region.

Mott and Twose[14] have remarked that what is happening in the transition region is not clear. In the foregoing we have attempted to give a plausible picture of the transition region. However, we may note here one possible difficulty. In the Mott transition, it is the same electrons that participate in the screening and conduction in the metallic state. In a formal many-body treatment of the transition it is possible that there may be a discontinuous change in the screening parameter from the Mott value ($\delta = 1.19$) to a value that exceeds the critical value for Im_2^+ binding and therefore could preclude the Im_2^+ intermediate phase.

Finally, we may note that the results presented here are also relevant to another field of physics, namely, the plasma physics. The potential around an ion in a plasma is also given by Eq. (1); the significance of q is, however, different. The results for Im_2^+ given here are also applicable to H_2^+, in a plasma.

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Optical and Electrical Properties of $AgGaS_2$ and $AgGaSe_2$

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From the results of low-temperature luminescence and reflectivity, both $AgGaS_2$ and $AgGaSe_2$ are determined to have a direct energy band gap. The values are 2.727 and 1.830 eV at 2 °K, respectively. The gap shifts to slightly higher energy at 77 °K, which is opposite to that observed in most semiconductors. Both crystals appear to contain shallow impurities or defects. However, the crystals are semi-insulating as-grown, and various annealing and diffusion procedures have failed to produce useful conductivity.

I. INTRODUCTION

Among the group of I-III-VI_2 ternary semiconducting compounds which crystallize in the chalcopyrite structure are $AgGaS_2$ and $AgGaSe_2$. $AgGaS_2$ has been shown to be potentially useful for nonlinear optics,[1,2] but the semiconducting properties of these materials have not been previously studied.[3] In the present paper, we present optical properties sufficient to determine the presence of a direct band gap, and in addition, describe some doping experiments.

As in our previous study of two I-III-VI_2 compounds, $CuGaS_2$ and $CuInS_2$,[4] we have observed low-temperature exciton reflectivity and near-band-gap sharp-line photoluminescence. The highest-energy luminescence coincides in energy with the reflectivity anomaly. From this result, we conclude that both $AgGaS_2$ and $AgGaSe_2$ have direct band gaps whose values are 2.727 and 1.830 eV at 2 °K, respectively. In addition, luminescence studies at 2 °K indicate that both materials have shallow defects or impurities with binding energies of several tens of millivolts. However, both crystals are semi-insulating "as-grown" and it has proven difficult to achieve useful conductivity of either *n* or *p* type. The inability to produce rapid and dramatic conductivity changes is in contrast to our previous work on the copper compounds.[4]

II. CRYSTAL GROWTH

$AgGaS_2$ and $AgGaSe_2$ crystallize in the chalcopyrite structure (symmetry $\bar{4}2m = D_{2d}^{12}$)[3] which is an ordered superstructure of the zincblende type. Both are grown from the melt. The starting materials were silver 99.999% pure, gallium 99.9999% pure, sulfur 99.9999% pure, and selenium 99.999% pure, according to spectrographic analysis. Equivalent amounts of sulfur and the metals were reacted in silica boats contained in evacuated silica ampoules. The melts were then cooled from 1050 °C ($AgGaS_2$) or 950 °C ($AgGaSe_2$) at a rate of 2 °C/h to below 950 °C for $AgGaS_2$ and below 750 °C for $AgGaSe_2$ and then cooled at a faster rate to room temperature. In many cases the silica boats were cracking due to the strongly anisotropic thermal contraction. Frequently the ingots contained crystals of several millimeters in dimension. The ingots of $AgGaS_2$ varied in color from light yellow to dark green. It appears that in the cases with both colors present the yellow material crystallized first and the green material crystallized later. There does not appear to be a sharp boundary between these regions. It is presumed that the color