REVIEWS OF MODERN PHYSICS VOLUME 40, NUMBER 4 OCTOBER 1968

SESSION VI—HEAVILY DOPED SEMICONDUCTORS

Localization of Electrons in Impure Semiconductors by a Magnetic Field

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The magnetic-field-dependent activation energy required to explain the rapid increase in the Hall coefficient with decreasing temperature in *n*-type InSb from 2°–5°K and in fields of up to 15 kG, observed by Putley and other workers, is interpreted in terms of the energy gap between the two lowest donor levels. This gap appears to be rather insensitive to carrier screening. Further, the existence of a threshold magnetic field, below which no activation energy is found, is interpreted as evidence of a Wigner transition, in which the electrons in the lowest impurity band cease to conduct when the donor-wave-function overlap, or the effective mass for electron transport, reaches a critical value. Finally, the relation between the activation energy for conduction in the extreme high-field limit and the Yafet–Keyes–Adams ionization energy is briefly discussed. It is anticipated that this ionization energy will be more closely approached at high fields, but perhaps never quite attained in practice.

I. INTRODUCTION

Interest in the behavior of a hydrogenic impurity center in a semiconductor in a high magnetic field was first stimulated by the work of Yafet, Keyes, and Adams.[1] They demonstrated that the ionization energy of such a center increased with magnetic field, in the manner shown in the uppermost curve of Fig. 1. This curve is actually for *n*-type InSb, which is a particularly favorable case for discussing such magnetic-field-dependent effects. Here the ratio of the zero-point energy in a magnetic field, $eB\hbar/2m^*c$, to the effective Rydberg $m^*e^4/2K^2\hbar^2$, is unity when the magnetic field B is $\sim$2kG, since in this case the effective mass m^* is $0.013m$ and the dielectric constant K is 16. Fields much in excess of this value are easily achieved and we expect such high fields to markedly localize the wave functions around the donor impurities. However, since the effective Bohr radius in InSb is 5.7×10^{-6} cm, even in the purest specimens available substantial overlap of donor wave functions occurs at zero magnetic field, and isolated donor levels cannot therefore be studied when $B=0$.

Nevertheless, Hall-effect measurements of Putley[2] and Nad' and Oleinikov,[3] in the temperature range 2°–5°K, showed that, in magnetic fields up to 15 kG, there is a rapid increase in the Hall coefficient R with decreasing temperature. R was found to follow an exponential law and this established the existence of an activation energy for electrons to become conducting, provided the magnetic field exceeded some threshold value. Furthermore, for a fixed temperature, a marked rise in R was found to occur as the magnetic field was increased above this threshold value, indicating a magnetic-field dependence of the activation energy, in qualitative accord with the predictions of Yafet, Keyes, and Adams. However, Curves 1 to 4 of Fig. 1 show the derived activation energies for four compensated samples with the listed donor and acceptor concentrations N_D and N_A, respectively, and it is seen that the observed activation energies are smaller than the Yafet–Keyes–Adams energy by a large factor.

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[1] Y. Yafet, R. W. Keyes, and E. N. Adams, J. Phys. Chem. Solids **1,** 137 (1956).

[2] E. H. Putley, Proc. Phys. Soc. (London) **76,** 802 (1960); J. Phys. Chem. Solids **22,** 241 (1961); *Semiconductors and Semimetals,* R. K. Willardson and A. C. Beer, Eds. (Academic Press Inc., New York, 1966), Vol. 1.

[3] F. Y. A. Nad' and A. Y. A. Oleinikov, Fiz. Tverd. Tela **6,** 2064 (1964) [Sov. Phys.—Solid State **6,** 1629 (1965)].

II. ISOLATED DONOR LEVELS AND CARRIER SCREENING

To understand these results over the range of magnetic fields shown in Fig. 1, Durkan and March[4] have recently given a theory of the screening of charged impurities by free carriers, in which the cylindrically symmetric screening about the field direction, taken as the z axis, is accounted for from the outset. This screened potential depends on the electron density n_0, temperature T, magnetic field B, as well as on K and m^*. In the high-field limit and for the nondegenerate case the Fourier components $V(q)$ of the screened potential are

$$\tilde{V}(q)=\frac{4\pi e}{(2\pi)^{3/2}}\left\{Kq^2+4\pi e^2 n_0\beta\int_0^1 dy\,\exp-\left[\frac{q_z{}^2\hbar^2\beta(1-y^2)}{8m^*}\right]\exp-\left[\frac{(q_x{}^2+q_y{}^2)\hbar^2}{4m^*\mu_0{}^*B}\left(\coth\mu_0{}^*B\beta-\frac{\cosh\mu_0{}^*B\beta y}{\sinh\mu_0{}^*B\beta}\right)\right]\right\}^{-1}$$

$$\left(\beta=(k_BT)^{-1};\ \mu_0{}^*=\frac{e\hbar}{2m^*c}\right),\quad(1)$$

which reduce to the bare Coulomb potential when the carrier density n_0 is zero.

In this screened potential, variational calculations were carried out for the two lowest impurity levels, as a function of magnetic field, with trial wave functions given by

$$\psi_0=\exp(-r^2/a^2)\exp(-z^2/b^2),\qquad r^2=x^2+y^2,\quad(2)$$

for the ground state and

$$\psi_1=r\exp(-i\phi)\exp(-r^2/a^2)\exp(-z^2/b^2)\quad(3)$$

for the first excited state, ϕ measuring an angle around the magnetic field. Following earlier work, a^2 was taken equal to $4\hbar c/eB$, related to the classical magnetic radius, while b was varied to minimize the energy, and details are given by Durkan and March.[4]

The main conclusion is that while the individual levels are appreciably changed by screening, the energy difference between the ground state and the first excited state is quite insensitive to the detailed choice of n_0 over a wide range of densities. This energy gap (essentially the hydrogenic result) is shown in Fig. 1, and the magnitude of the observed activation energy accords semiquantitatively with this gap, over a substantial range of magnetic fields. We wish to stress that with the less-pure specimens studied by Sladek,[5] we expect the screening to be important and this is borne out by the experiments which give activation energies of magnitudes similar to those shown in Fig. 1, but at much higher magnetic fields. The threshold magnetic field is also much higher, and we return to this question in Sec. III.

The model then on which the Hall-effect measurements can be understood is one in which the impurity states higher than the ground state are broadened by overlap of the donor wave functions and eventually merge into a quasicontinuum with the InSb conduction band.

III. THRESHOLD MAGNETIC FIELD AND WIGNER TRANSITION

We wish now to comment on the interpretation of the threshold magnetic field required for an activation energy to be observed.

The first possibility suggested is that the carrier screening discussed in Sec. II is sufficient to suppress all bound states in the screened potential around a donor. This situation was discussed recently, with a rather less realistic screened potential than (1) by Fenton and Haering.[6] However, the criterion of Fenton and Haering needs some modification for, as the energy gap becomes very small, the donor wave functions become exceedingly diffuse and a great deal of overlap will occur. Thus, the impurity level has a bandwidth E_b say, and the criterion for conduction without an activation energy is that the energy gap E_g is $\sim\frac{1}{2}E_b$, rather than $E_g=0$. The criterion of Fenton and Haering for such conduction is rather too stringent.

However, in the case of the rather pure specimens considered in the present paper, the isolated donor levels do not appear to be greatly affected by screening. Our interpretation of the results of Putley[2] is that, below the threshold magnetic field, conduction is taking place in the lowest impurity band. Then, as the overlap of the donor wave functions is decreased by increasing magnetic field, we expect a transition to a nonconducting state, akin to the crystallization of electrons in a uniform background suggested long ago by Wigner,[7] as the electron density is lowered. This transition, to be distinguished from the Mott transition, can occur with much less than one electron/site, which is the case with the heavily compensated specimens

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[4] J. Durkan and N. H. March, Proc. Phys. Soc. (London) **1**, 1118 (1968).

[5] R. J. Sladek, J. Phys. Chem. Solids **5**, 157 (1958); **8**, 515 (1959).

[6] F. W. Fenton and R. R. Haering, Phys. Rev. **159**, 593 (1967). Similar considerations due to one of us (N.H.M.) have been briefly referred to by Putley (see Ref. 2).

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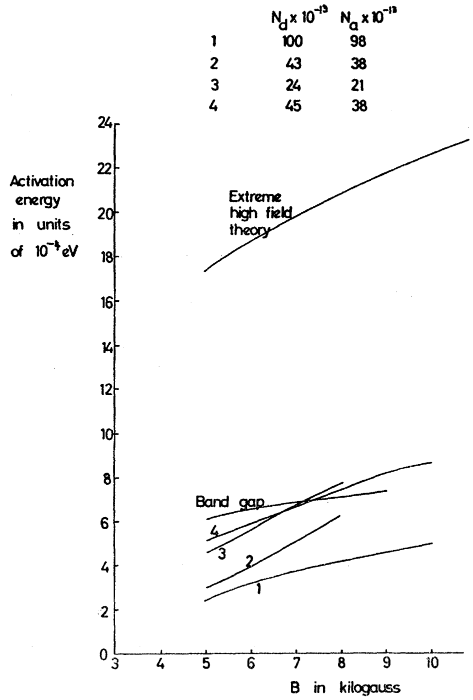

FIG. 1. Sample characteristics for specimens 1–4 are shown, along with the observed activation energies. The curve labeled "band gap" shows the separation between the ground and first excited isolated donor levels. The curve labeled "extreme high field theory" is the ionization energy of the hydrogenic impurity center as calculated by Yafet, Keyes, and Adams (Ref. 1).

considered here.[8] The long-range Coulomb interactions in such a low-density system of electrons are hardly screened and a primitive theory, extending that proposed by Wigner, would go as follows. Let the electron concentration be n, and define r_0 by

$$4\pi r_0^3/3 = 1/n. \tag{4}$$

According to Lindemann's criterion, used in his melting law, the transition will occur when the zero-point displacement is a fixed fraction of the inter-electronic spacing. If we assume, at high fields, that it is the magnetic field rather than the Coulomb repulsion which localizes the electrons, then we find

$$r_0^2 \sim a^2, \tag{5}$$

where, as we saw earlier, $a^2 \sim hc/eB$. This gives threshold fields of the order observed by both Putley[2] and Sladek,[5] but the approach has the drawback that it does not depend on the donor concentration N_D.

A second argument is that the Wigner transition occurs when the potential energy per electron is roughly equal to the kinetic energy associated with electron localization. This kinetic energy should reflect the width of the impurity band. Although it is difficult to estimate this for random impurities, it should be roughly proportional to N_D if overlap is appreciable. Suppose that the donor concentration which makes the bandwidth equal to the binding energy is N_0; then the criterion becomes

$$r_0 \sim N_D a_0 / N_0, \tag{6}$$

where a_0 is the effective Bohr radius of the hydrogenic impurity center. A plausible value for N_0 is given by

$$1/N_0 \sim 4\pi a_0^3/3. \tag{7}$$

However, in a magnetic field, one should replace a_0^3 by $b(hc/eB)$, where b is the extension of the orbit along the field direction, which also decreases with increasing B. In fact, $hc/eB \sim 10^{-8}\text{cm}^2$ for $B \sim 10$ kG and the critical fields observed by both Putley and Sladek fit in roughly if we take

$$r_0 = 3N_D a_0 / N_0. \tag{8}$$

The two estimates of the threshold fields are not very different in the present problem.

In spite of the disorder of the donors, an activation energy appears rather suddenly at a fairly well-defined threshold field according to Putley's measurements, and this seems to support our hypothesis that we are seeing here an example of a Wigner transition.

Finally, it is of interest to consider what will happen in the present model as the magnetic field is greatly increased beyond the range shown in Fig. 1. As the broadened first excited state is narrowed by the localization of the wave function (3) in the magnetic field, we expect an activation energy characteristic of the next excited state (or group of states) to be observed and so on. Thus, the Yafet–Keyes–Adams curve may be expected to become a rather better approximation to the observed activation energy in the extreme high-field limit, though, because of bunching of impurity levels below the bottom of the InSb conduction band, we do not expect the ionization energy ever quite to be reached in practice.

Discussion of March's Paper

R. W. Keyes (I.B.M.): I didn't understand why it was that you excluded the possibility that the difference between the observed ionization energy and the one Yafet, Adams, and I calculated isn't just due to screening.

N. H. March: No, there didn't seem to be a possibility of enough screening even if we said that the screening was due to all the available electrons. In the specimens which I talked about first, that never altered the ionization energy substantially. But now in the specimens of Dr. Sladek, where there are many more carriers, then of course, as you saw, the curves for the isolated levels began to decay away. Certainly there, the small activation energy shown in Fig. 1 for the impure specimens would be an ionization energy greatly reduced by screening. And so I think there are two mechanisms and I think that even for the threshold fields there could be two mechanisms. One I suggested was due to electron localization in the lowest impurity band, and the other one actually losing the bound state into the band by screening, but these are appropriate for very different conduction electron densities. The latter one is discussed in the recent paper by Fenton and Haering, as referred to in the

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[8] No doubt, the random fields of the acceptor centers will eventually have to be considered carefully in a definitive theory.

text. However, these authors did not refer to the very low-density case where the Wigner transition takes place.

H. Brooks (Harvard University): The real point is that you were dealing experimentally with very highly compensated samples so that the screening was minimized. I should point out one effect which would alter the screening although I don't think it will alter your explanation. That is that some years ago I showed that if you take into account in highly compensated samples the presence of both the donors and the acceptors and the fact that some of them can be populated and so on, there is an additional contribution to the screening due to the statistical population of the donors around another donor, so to speak, but this can double the screening but it can't change it in order of magnitude.

L. J. Neuringer (Massachusetts Institute of Technology): Magnetic freeze-out *has* been studied in the high-field region to 200 kG. In a recent paper [Phys. Rev. Letters **18**, 773 (1967)] by Hanamura, Beckman, and myself, we found that both the magnitude and magnetic-field dependence ($\epsilon_i \sim H^{1/3}$) of the ionization energy, determined from Hall-coefficient measurements on uncompensated, heavily doped specimens ($n \sim 10^{16}$ cm^{-3}), obeyed the Yafet, Keyes, and Adams theory. It would appear that our results have serious consequences for your theory with regard to the importance of screening and with respect to the magnetic-field dependence of the ionization energy which your theory would predict at high magnetic fields. It also appears that in deducing the ionization energy from the Hall coefficient data you have neglected the fact that there is present two-band conduction. With regard to the threshold magnetic field for freeze-out H_0, we found good agreement with experiment by simply equating the volume occupied by the electronic wave function in this high magnetic field to the volume occupied by a single impurity, as a result $H_0 \sim N_{\text{imp}}{}^{6/7}$. I would venture to say that magnetic freeze-out can best be studied at high magnetic fields using heavily doped, uncompensated samples because (a) one is free of the complications introduced by two-band conduction, and (b) the fluctuation in the electric field at the various donor sites in the crystal, produced by the compensating acceptors, does not play a role as it does in the compensated samples.

N. H. March: Well, I regret of course that I did not know about those results. They seem to agree satisfactorily with our prediction that the Yafet–Keyes–Adams ionization energy should be almost regained in very high fields.

REVIEWS OF MODERN PHYSICS VOLUME 40, NUMBER 4 OCTOBER 1968

Semiconductor-to-Metal Transition in *n*-Type Group IV Semiconductors*

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A synthesis is given of the most significant experimental features of the semiconductor-to-metal transition in group IV semiconductors. Two characteristic concentrations are discussed, the first being for a delocalization of electrons (the "Mott" transition), and the second being associated with the entry of the Fermi level into the conduction band of the host material. Experimental values are given for the two concentrations in several materials. Experimental data covering measurements of Hall coefficient, electrical resistivity and carrier mobility, NMR properties, magnetoresistance, magnetic susceptibility, and ESR properties are employed in arriving at values for the two characteristic concentrations. Si:P is taken as the model system because of the completeness of experimental measurements. Si:As is also briefly considered. Existing data for *n*-Ge are examined, as well as the more restricted evidence concerning *n*-SiC.

I. INTRODUCTION

Transitions from insulating to metallic behavior occur in a number of types of solid systems as some parameter of the system or some external variable is changed. It was recognized some time ago that increasing the concentration of shallow donors or acceptors in semiconductors could produce such a change,[1] and certain aspects of the theory were developed rather completely at an early stage.[2] A qualitatively new feature was injected into the picture by Mott,[3] who pointed out that this change might not be a continuous one, as implicitly assumed by the early workers. Mott proposed that the transition would be an abrupt one, smeared out only insofar as random positioning of impurity atoms leads to a distribution of local concentrations around a given average concentration. Mott also gives references to earlier work in those articles.

Mott showed, for a monovalent system such as that of donor or acceptor impurities in semiconductors, that as the interdonor atom spacing is reduced, free carriers will not appear until a critical concentration is reached, at which screening by the electrons of nearby atoms prevents binding by electron–hole pairs. That is, the activation energy for carrier production falls to zero,

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* This work partially supported by the U. S. Army Research Office (Durham), under Contract No. DA-31-124-ARO-D-407, Tech. Rept. No. 8.

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[3] N. F. Mott. Proc. Phys. Soc. (London) **62**, 416 (1949); Phil. Mag. **6**, 287 (1961); Advan. Phys. **16**, 49 (1967).