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Impurity Molecule and Concentration of Conduction Electrons in *n*-InSb in High Magnetic Fields*

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Nearby impurities in *n*-InSb in high magnetic fields are treated as hydrogen molecules. Because of the large g factor the electronic magnetic moments are all in the direction of the magnetic field, making the spin part of the wave function symmetric under electron exchange. The exclusion principle then gives an antisymmetric space part of the wave function, which decreases the ionization energy. The number of electrons in the conduction band is calculated and is found to be greatly increased by this effect at low temperatures.

I. INTRODUCTION

When a strong magnetic field is applied to a hydrogen-like atom, the ionization energy is increased. This has been discussed by Yafet, Keyes, and Adams (YKA).[1] If impurities in semiconductors are treated as hydrogen-like, then the results of YKA can be used to predict how far the energies of donor impurities lie below the conduction band in the presence of a magnetic field. Application of these results to donor impurities in indium antimonide leads to the conclusion that for magnetic fields above 5 kG the ionization energy is large enough so that at a temperature of 1°K the fraction of donor electrons left in the conduction band is negligible ($<10^{-4}$). However, recent experiments of Love and Phelan[2] have indicated that the fraction of electrons ionized even up to 30 kG at this temperature may be of the order of 10^{-2}. A partial explanation of this might be that the hydrogen atom model is not good for the impurities in indium antimonide. This is indicated by the fact that no ionization energy has been observed when no magnetic field is present even for very low impurity concentrations. Also experiments of Sladek[3] appear to give ionization energies with a magnetic field which are lower than the YKA theory predicts. However, these ionization energies are still large enough to make the fraction of ionized electrons small compared to 10^{-2} for fields greater than 10 kG.

A possible explanation of this lack of freeze-out is considered here. It is based upon the exclusion principle which becomes important for the electronic wave functions when two impurities are close together. Because of the large g factor of the electrons in indium antimonide,[4] there is a relatively large separation in energy between different spin states for fields of a few kilogauss, and the only states that need be considered at a few degrees Kelvin are those with all effective magnetic moments parallel to the magnetic field. Then the electronic wave function for two impurities close together has a symmetric spin part and, therefore, an antisymmetric space part. This tends to reduce the binding energy of the electrons. On the other hand if one of the electrons is ionized to the conduction band, the exclusion principle has little effect and this ionized state might have even lower energy than the unionized state.

The model that will be used in the next section is that of a hydrogen molecule for nearby impurities (though far apart compared with the lattice spacing); i.e., the potentials will be taken to be pure Coulomb potentials modified by the dielectric constant. The electronic effective mass will be assumed to be isotropic. A variational calculation will be made to find the energies.

II. CALCULATIONS

In this section, the calculation of the electronic energies for two impurities close together will be discussed and the results will be used to find the fraction of the impurity electrons which are in the conduction band.

The effective mass Hamiltonian for the unionized impurity combination with two donor electrons is assumed to be

$$\mathcal{H}=\sum_{i=1,2}\left[(\mathbf{p}_i+e\mathbf{A}_i/c)^2/2m^* +e^2(-r_{ia}^{-1}-r_{ib}^{-1})/\kappa\right]+e^2/\kappa r_{12}, \quad (1)$$

where the subscript i designates the electron, and the subscripts a and b denote the two impurities. The effective mass m^* will be taken to be 0.013 times the electron mass, and 16 will be used for the dielectric constant κ. The effect of spin will not be considered explicitly in the Hamiltonian. It will simply be assumed that all electronic magnetic moments are in the direction of the magnetic field $\mathbf{H}$. Calculation shows that for the temperatures ($T\leqslant 4°\text{K}$) and the fields ($H\geqslant 5$ kG) considered here, the energies are such that statistically this is a very good approximation. The gauge will be chosen such that

$$\mathbf{A}=\tfrac{1}{2}(\mathbf{H}\times\mathbf{r}). \quad (2)$$

The origin of the coordinate system will be taken midway between the two impurities. If the y axis is perpendicular to the magnetic field and to the line joining the impurities, the positions of the impurities will be

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

[2] W. F. Love and R. J. Phelan, previous paper, Phys. Rev. **133**, A1134 (1964).

[3] R. J. Sladek, Phys. Chem. Solids **5**, 157 (1958).

[4] L. M. Roth, B. Lax, and S. Zwerdling, Phys. Rev. **114**, 90 (1959).

designated by $\pm\frac{1}{2}\mathbf{r}_0$ with x and z components $\pm\frac{1}{2}x_0$ and $\pm\frac{1}{2}z_0$.

The Rydberg constant for a hydrogenlike atom with mass m^* and dielectric constant κ is

$$\tfrac{1}{2}m^*e^4/\kappa^2\hbar^2=0.69\times10^{-3}\text{ eV}$$

and its Bohr radius is

$$\hbar^2\kappa/m^*e^2=642\text{ Å}.$$

Expressed in these units of energy and length the Hamiltonian becomes

$$\begin{aligned}\mathcal{H}=\textstyle\sum_{i=1,2}[-\nabla_i^2+\gamma L_{zi}+\frac{1}{4}\gamma^2(x_i^2+y_i^2)\\ -2(r_{ia}^{-1}+r_{ib}^{-1})]+2/r_{12},\end{aligned}\quad(3)$$

where γ is the ground-state Landau energy $\frac{1}{2}\hbar eH/m^*c=\frac{1}{2}\hbar\omega_c$ expressed in rydberg units (3.2 for 5 kG) and $L_z=(\mathbf{r}\times\mathbf{p})_z/\hbar$. The magnetic field is taken in the direction of the z axis. The cylindrically symmetric ground-state wave function for a single electron in a magnetic field with no Coulomb interactions is proportional to[5] $\exp[-\frac{1}{4}\gamma(x^2+y^2)+ik_zz]$. This suggests that at high magnetic fields reasonable symmetric and antisymmetric variational wave functions might be

$$\psi_\pm=N_\pm[F(\mathbf{r}_1,\mathbf{r}_0)F(\mathbf{r}_2,-\mathbf{r}_0)\pm F(\mathbf{r}_2,\mathbf{r}_0)F(\mathbf{r}_1,-\mathbf{r}_0)],\quad(4)$$

where

$$\begin{aligned}F(\mathbf{r},\mathbf{r}_0)=\exp\{[(x-\tfrac{1}{2}x_0)^2+y^2]a^{-2}\\ +(z-\tfrac{1}{2}z_0)^2b^{-2}-\tfrac{1}{4}i\Gamma x_0y\},\end{aligned}\quad(5)$$

with the variational parameters a, b, and Γ. The term involving Γ gives a gauge transformation corresponding to a translation of coordinates perpendicular to the y axis. For large r_0, Γ approaches γ and this term corresponds to the coordinate translation of $-\frac{1}{2}\mathbf{r}_0$. In this limit the variational function is substantially the same as that of YKA. The Γ term can also be considered to take account of possible anisotropy in the xy plane when the impurities are close together. The normalization constant is given by

$$N_\pm^{-1}=2^{1/2}a^2b(2\pi)^{3/2}(1\pm\eta)^{1/2}\quad(6)$$

with

$$\eta=\exp[-\tfrac{1}{4}(a^{-2}+\Gamma^2a^2)x_0^2-\tfrac{1}{4}b^{-2}z_0^2].\quad(7)$$

The expectation value of the Hamiltonian for these functions is

$$\begin{aligned}\epsilon_\pm=\gamma^2a^2+a^{-2}+\tfrac{1}{2}b^{-2}+\tfrac{1}{8}x_0^2(\Gamma-\gamma)^2\mp\tfrac{1}{8}[x_0^2(a^{-2}-\gamma^2a^2)\\ \times(a^{-2}-\Gamma^2a^2)+z_0^2b^{-4}+2x_0^2(\Gamma-\gamma)^2]\eta/(1\pm\eta)\\ -4(2\pi)^{3/2}a^2bN_\pm^2\operatorname{Re}\{4\pi a^2\sigma^{-1}\ln[(1+\sigma)/(1-\sigma)]\\ +2G(1,0)-G(2^{-1/2},0)\mp G(0,2^{-1/2})\\ \pm4\eta^{1/2}G(\tfrac{1}{2},\tfrac{1}{2})\exp[-\tfrac{1}{8}(x_0^2/a^2+z_0^2/b^2)]\},\end{aligned}\quad(8)$$

where Re means real part,

$$\sigma=(1-a^2/b^2)^{1/2},\quad(9)$$

and

$$\begin{aligned}G(u,v)=\exp[-\tfrac{1}{2}(x_0^2/a^2+z_0^2/b^2)u^2]\\ \times\int_0^{2\pi}\int_0^{\pi}\alpha^{-2}\left[\tfrac{1}{2}+\beta\exp(\beta^2)\int_{-\beta}^{\infty}\exp(-w^2)dw\right]\\ \times\sin\theta d\theta d\phi\end{aligned}\quad(10)$$

with

$$\begin{aligned}\alpha^2=\tfrac{1}{2}[(\sin\theta/a)^2+(\cos\theta/b)^2],\\ 2\alpha\beta=u[(x_0\sin\theta\cos\phi/a^2)+z_0\cos\theta/b^2]\\ -ivx_0\Gamma\sin\theta\sin\phi.\end{aligned}\quad(11)$$

The energy ϵ_- corresponding to the antisymmetric function ψ_- will be taken as the energy of the unionized impurity molecule.

The case of the singly ionized impurity combination may be treated in a similar fashion. The Hamiltonian is the same as that of Eq. (3) but with the r_{12} term and the i subscript and summation dropped. If a wave function of the form

$$\Phi=AF(\mathbf{r},\mathbf{r}_0)+BF(\mathbf{r},-\mathbf{r}_0)$$

is assumed, a variational treatment shows that $A=\pm B$ so that

$$\Phi_\pm=N_\pm'[F(\mathbf{r}/\mathbf{r}_0)\pm F(\mathbf{r},-\mathbf{r}_0)].\quad(12)$$

The normalization constant is given by

$$(N_\pm')^{-2}=2a^2b(2\pi)^{3/2}(1\pm\eta^{1/2}).\quad(13)$$

To the expectation value of this Hamiltonian the Landau energy of the other electron should be added to obtain the total two-electron energy. The result is

$$\begin{aligned}\epsilon_\pm'=(2n+1)\gamma+k_z^2+\tfrac{1}{2}(\gamma^2a^2+a^{-2})+\tfrac{1}{4}b^{-2}\\ +\tfrac{1}{16}x_0^2(\Gamma-\gamma)^2\mp\{[x_0^2(a^{-2}-\gamma^2a^2)(a^{-2}-\Gamma^2a^2)\\ +z_0^2b^{-4}+2x_0^2(\Gamma-\gamma)^2]\eta^{1/2}/16(1\pm\eta^{1/2})\}-4(N_\pm')^2\\ \times\operatorname{Re}\{2\pi a^2\sigma^{-1}\ln[(1+\sigma)/(1-\sigma)]+G(1,0)\\ \pm2G(\tfrac{1}{2},\tfrac{1}{2})\exp[-\tfrac{1}{8}(x_0^2/a^2+z_0^2/b^2)]\},\\ n=0,1,2,\cdots.\end{aligned}\quad(14)$$

The G's and σ are as defined above in Eqs. (9) and (10). The first two terms on the right of this equation give the Landau energy with k_z the wave number in the direction of the magnetic field.

The energies $\epsilon_\pm$, $\epsilon_\pm'$ were found by calculations on an IBM 709 computer. In these calculations an approximate algebraic expression for the error integral in G, Eq. (9), was used with Simpson's rule giving the other two integrations. It was found that the energies are very insensitive to changes of Γ near the minimum of the expectation values of the energies. Therefore, the energies were minimized by first finding the a's and b's for which the partial derivatives of the energies with respect to a and b were zero by a relaxation method, and then finding the Γ's for which the partial derivatives of the energies with respect to Γ were zero. This was repeated until the energies did not change in the third

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[5] M. H. Johnson and B. A. Lippmann, Phys. Rev. **76**, 828 (1949).

TABLE I. The variational parameters, a and b, for $\theta=0$.

		ψ_-		Φ_+	
H (kG)	R	a	b	a	b
	$\frac{1}{2}$	0.49	0.74	0.40	0.44
5	3	0.49	0.72	0.47	0.58
	∞	0.43	0.62	0.43	0.62
	$\frac{1}{2}$	0.36	0.64	0.32	0.39
10	3	0.36	0.63	0.35	0.51
	∞	0.33	0.54	0.33	0.54
	$\frac{1}{2}$	0.27	0.56	0.25	0.34
29	3	0.27	0.54	0.26	0.44
	∞	0.24	0.47	0.24	0.47
	$\frac{1}{2}$	0.22	0.51	0.21	0.31
30	3	0.22	0.49	0.22	0.40
	∞	0.20	0.43	0.20	0.43

significant figure. These calculations were carried out for magnetic fields of 5, 10, 20, and 30 kG and for various impurity separations and orientations relative to H.

The variational parameters appear to be most simply given as functions of $R\equiv[(x_0/a_0)^2+(z_0/b_0)^2]^{1/2}$ and $\theta=\tan^{-1}(x_0/z_0)$, where a_0 and b_0 are the values of a and b, for r_0 approaching infinity. The resulting parameters, a and b, are given in Table I for x_0 zero for ψ_- and for Φ_+. The a's are almost independent of θ as is the b for Φ_+. The b for ψ_- and for $\theta=\frac{1}{2}\pi$ is 0.12 less than that for $\theta=0$ at $R=\frac{1}{2}$ and 0.06 less for $R=3$ for these fields and varies approximately linearly with θ. Also, between $R=\frac{1}{2}$ and $R=3$, a and b vary approximately linearly with R. The energies ϵ_+ and ϵ_-' were found only roughly, and thus the corresponding a's and b's are not tabulated. Also because the energies were so insensitive to Γ this parameter was rarely found very accurately. At $R=\frac{1}{2}$ the parameter Γ is about 15% greater than γ for ψ_- and 25% less than γ for Φ_+ near $\theta=0$.

The energies $\epsilon_--2\gamma$ and $\epsilon_+'-2\gamma$ for n and k_z zero, the energies relative to the lowest Landau level, are shown in Fig. 1 for various r_0 for $\theta=0$. The energy ϵ_- changes very slightly between r_0's of 140 Å and 1120 Å for $\theta=0$. For $r_0=140$ Å and $\theta=\frac{1}{2}$, $\epsilon_+'-2\gamma$ is slightly smaller in magnitude and $\epsilon_--2\gamma$ is about 20% greater in magnitude than for $\theta=0$. The difference between ϵ_+' and ϵ_- is the ionization energy. This is shown for $\theta=0$ and $\theta=\frac{1}{2}\pi$ versus magnetic field for various r_0 in Fig. 2 and is shown versus angle for a magnetic field of 10 kG in Fig. 3. Curves for other fields are qualitatively very similar to those of Fig. 3 with larger energies and smaller lengths for larger fields. It is seen that the binding energy of the electron is reduced considerably for close spacing of the impurities, especially where $\mathbf{r}_0$ and $\mathbf{H}$ are nearly parallel or antiparallel, and is, in fact, negative for some values of the parameters. One would expect this binding energy to be less for small θ than for $\theta=\frac{1}{2}\pi$, as shown in Fig. 3, because the magnetic field shrinks the single particle wave function primarily in directions perpendicular to the field. Thus, when $\mathbf{r}_0$ is perpendicular to $\mathbf{H}$, the exchange terms in the expectation value of the Hamiltonian will be less important than when $\mathbf{r}_0$ and $\mathbf{H}$ are parallel.

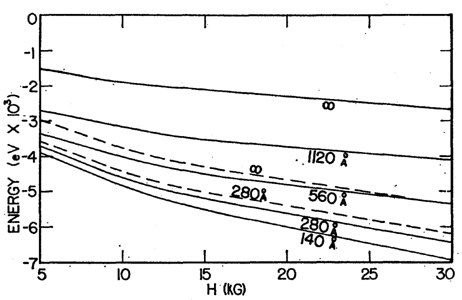

FIG. 1. Energies of the impurity molecule versus magnetic field for various r_0. The solid curves give $\epsilon_+'-2\gamma$ and the dashed curves give $\epsilon_--2\gamma$.

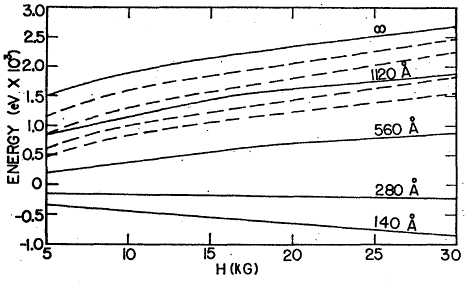

FIG. 2. Ionization energy $\epsilon_+'-\epsilon_-$ is given as a function of the magnetic field H for $\theta=0$ and for various r_0 (solid curves) and for $\theta=\frac{1}{2}\pi$ for the same r_0 (dashed curves).

The quantity ϵ_+ was roughly calculated simply to test the validity of neglecting states with antisymmetric spin functions, i.e., one magnetic moment antiparallel to $\mathbf{H}$. As mentioned above, it was found that these can be neglected in the statistical treatment for the fields considered. The energies ϵ_+' and ϵ_-' become equal for large r_0, and thus give equal contribution in the statistics. Therefore, it appeared necessary to calculate ϵ_-' in order to see if there is appreciable variation in $\epsilon_-'-\epsilon_-$ in the region where both ϵ_+' and ϵ_-' are important. It was found that $\epsilon_-'-\epsilon_-$ varied little from that for

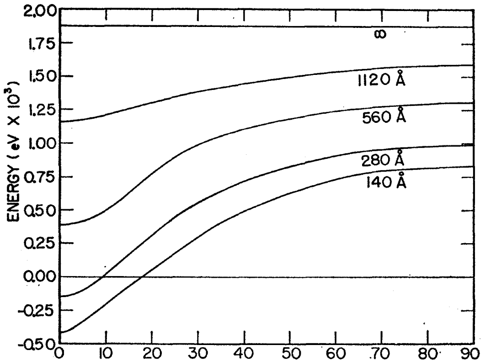

FIG. 3. Ionization energy $\epsilon_+'-\epsilon_-$ is given as a function of the angle θ between $\mathbf{r}_0$ and $\mathbf{H}$ for various values of r_0. The magnetic field is 10 kG.

infinite impurity spacing except for vary small r_0 where the levels corresponding to ϵ_+' would greatly predominate in the statistics. Therefore, $\epsilon_-' - \epsilon_-$ was simply set equal to its value (given by YKA) for $r_0 = \infty$ in the treatment below.

The calculation of the number of electrons in the conduction band will next be discussed. If it is assumed that the impurities can be separated into noninteracting pairs, the grand partition function is

$$Z = \prod_i \{1 + \exp[(2\mu - \epsilon_-)/kT] + \exp[(\mu - \epsilon_+'')/kT] + \exp[(\mu - \epsilon_-'')/kT]\}_i \times \prod_j \{1 + \exp[(\mu - E_j)/kT]\}, \quad (15)$$

where μ is the Fermi energy. The subscript i refers to an impurity doublet, and j, to a conduction band state. The quantities $\epsilon_\pm''$ are $\epsilon_\pm'$ minus the Landau energy, and E_j is the Landau energy in the conduction band. Here the states with magnetic moments antiparallel to the magnetic field are neglected along with excited states of the impurities. The assumption that the impurities can be treated in pairs raises the question as to how one could unambiguously do the pairing. A possible pairing procedure might consist of steps in which one selects as a pair the two closest spaced impurities, neither of which was chosen in a previous pairing step. In following this procedure one does not consider the possibility that three or more impurities might be close enough together so that simple pairing is not a reasonable way of treating the grouping. This difficulty is related to the other assumption above, that the pairs are not interacting. However, as the density of impurities decreases, possible interaction of three or more impurities becomes less and less important. Thus, the assumptions made above correspond to a low density approximation. This approximation appears to be justified at least up to densities of $10^{15}/\mathrm{cm}^3$ in indium antimonide for the fields considered here.

The average number of electrons bound to an impurity doublet is given by

$$f_i = -kT(2\partial/\partial\epsilon_- + \partial/\partial\epsilon_+'' + \partial/\partial\epsilon_-'')_i \ln Z. \quad (16)$$

When the exponents involving ϵ_-, ϵ_+'', and ϵ_-'' are large, as is true for the temperatures considered here, the one in the resulting denominator is small in comparison with the exponentials and can be dropped. Then

$$f_i = 1 + 1/\{1 + \exp[(\epsilon_- - \epsilon_+'' - \mu)/kT] + \exp[(\epsilon_- - \epsilon_-'' - \mu)/kT]\}. \quad (17)$$

The number of electrons in the conduction band due to one impurity is $2 - f_i$. The average number of electrons in a conduction band state is given by the usual Fermi function,

$$f_j = 1/\{1 + \exp[(E_j - \mu)/kT]\}. \quad (18)$$

In the Landau representation,[5] the state in the conduction band is characterized by the integer n and the propagation vector with components k_y and k_z. The component k_y, when multiplied by the square of the characteristic length

$$\lambda = (\hbar c/eH)^{1/2}, \quad (19)$$

is physically a translation of orbit center in the x direction. Then, for a cube with unit sides, the maximum range in k_y is $1/\lambda^2$. Since the energy does not depend on k_y, the number of electrons per unit volume in the conduction band is

$$N = \sum_{n,k_y,k_z} f_{n,k_z} = (2\pi\lambda^2)^{-1} \sum_{n,k_z} f_{n,k_z} = \sum_n (2\pi\lambda)^{-2} \int_{-\infty}^{\infty} (1 + \exp\{[(n+\tfrac{1}{2})\hbar\omega_c + k_z^2/2m^* - \mu]/kT\})^{-1} dk_z \quad (20)$$

in the usual units. For the values of H/T used in this paper only the $n=0$ term need be retained in the summation. Another expression for N is obtained by summing $2 - f_i$ over the impurity doublets. With ρ the number of impurities per unit volume, the probable number in a differential volume dV is ρdV. The probability that there are no impurities in the volume V is then

$$\prod (1 - \rho dV) = e^{-\rho V}.$$

The probability that there are no other impurities in a spherical volume V surrounding a given impurity, but that there is one between V and $V + dV$, is thus

$$dP = \rho e^{-\rho V} dV. \quad (21)$$

This will be used for the probability for a pair of impurities to occur a distance r_0 apart with the angle between $\mathbf{r}_0$ and $\mathbf{H}$ equal to $\theta = \tan^{-1}(x_0/z_0)$. This assumes that a given impurity is always associated with the next nearest impurity. This is a good approximation for impurities close together for low concentrations with the pairing procedure given above. Equation (21) may not be a good approximation for impurities with average spacing, but again for low density, these would largely have energies differing little from that for infinite spacing so that any properly normalized probability function could be assigned to them. The alternate expression for N is then

$$N = 2\pi(\tfrac{1}{2}\rho) \int_0^{\pi} \int_0^{\infty} [2 - f(\mathbf{r}_0, \theta)]\rho \times \exp(-4\pi\rho r_0^3/3) r_0^2 dr_0 \sin\theta d\theta \quad (22)$$

with $f(\mathbf{r}_0, \theta)$ given by Eq. (17). The Fermi energy μ is found by equating the two expressions for N in Eqs. (20) and (22). The necessary calculations were carried out on an IBM 1620 computer. These calculations consisted of performing the integrations numerically and using a relaxation method to obtain the equality of the expressions. The resulting N/ρ is shown in Fig. 4 for four fields and for $\rho = 10^{14}/\mathrm{cm}^3$. For comparison N/ρ is

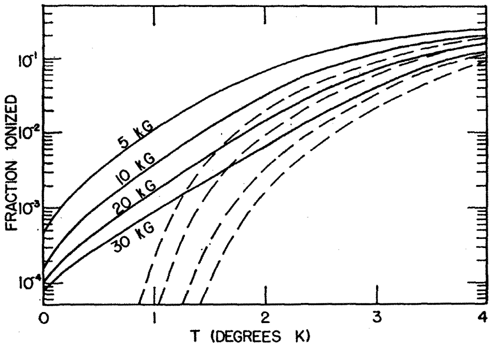

FIG. 4. The solid curves give the fraction of electrons in the conduction band as a function of temperature for four magnetic fields using the hydrogen molecule model. The dashed curves give this fraction for noninteracting impurities for the same fields.

also shown for the case where both ϵ_-'' and ϵ_+'' have the values for infinite spacing.

III. DISCUSSION

Figure 4 shows that the effect considered in this paper greatly increases the fraction of electrons in the conduction band near 1°K. However, at $H=30$ kG, the fraction is still an order of magnitude lower than the experiments of Love and Phelan[2] indicate. Also the effects of compensation were not taken into account above. Calculations show that if the compensation is comparable to the fraction of electrons of Fig. 4, the fraction is not greatly changed near 1°K, but when the compensation is more than three times as great, the fraction is greatly decreased. Several calculations with $\rho=10^{15}/\text{cm}^3$ were also made. This increased the fraction of electrons ionized by about a factor of three near 1°K over the results for $\rho=10^{14}/\text{cm}^3$.

There was no independent check to show how accurate the variational calculations were. However, it was observed that the energies, both total ϵ_+' and ϵ_- and their differences, changed only slightly from what was obtained if a, b, and Γ were simply chosen to be the values of these parameters a_0, b_0, and γ for infinite r_0. It is believed, therefore, that the results are fairly accurate.

This model does not appear to account completely for the observed number of electrons in the conduction band. However, as pointed out in Sec. I, there is some doubt as to the correctness of a hydrogen molecule model. If the binding of the electron were less, as indicated by experiment, the number of electrons in the conduction band could be greatly increased; firstly, because of the lower ionization energy compared to kT, and secondly, because the wave functions would have larger characteristic lengths so that r_0 need not be as small to give an appreciable effect. Also the calculations assumed a random impurity distribution. Any lack of randomness, e.g., impurities precipitating out on crystal imperfections, which gives more impurities close together than randomness would predict, would increase the effect discussed here. Therefore, this effect might account for the observed number of conduction electrons if these considerations were properly taken into account.