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H⁻ Impurity States and Nuclear Magnetic Relaxation*

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It is shown that a hydrogenic impurity will bind a second electron in high magnetic fields, because of contraction of the electron wave functions about the lattice sites. The binding energy of the second electron exceeds kT for semiconductors at helium temperatures when $\gamma = \hbar\omega_c/2 \text{ Ry} \gg 1$. This H⁻ ion may then provide a new density of states $g^+(E)$ for electrons with spin "up" ($\sigma=1$). Nuclei which relax by mutual spin-flip processes with conduction electrons have a relaxation rate $1/T_1$ proportional to $g^+(E)$. In the last Landau state $n=0$, $\sigma=-1$, the conduction electron $g^+(E)$ vanishes so the additional $g^+(E)$ from the H⁻ state can produce a large change in T_1 . The magnitude of this effect is estimated for InSb and comparison is made with the experiments of Bridges and Clark, with some success. Alternative explanations involving plasma modes are investigated and found wanting. The presence of H⁻ impurities in concentrations on the order of one-tenth of the conduction electron concentration may also affect the negative magnetoresistance and the theory of scattering from localized spins.

I. INTRODUCTION

THE contact interaction with conduction electrons is a well-known nuclear-spin-relaxation mechanism in metals, semimetals, and semiconductors. At low temperatures in InSb it is dominant until the temperature exceeds $\approx 10^\circ\text{K}$, at which point phonon relaxation coupling through the nuclear quadrupolar moment becomes more favored.

In order for nuclear relaxation to proceed via the contact interaction, there must exist a density of states for the final electron eigenstate. During the relaxation process, the electron and nucleus "flip" their spin (conserving the total spin of the system), so the final density of states for electrons must be of opposite spin from the initial state. This paper deals with the possibility that additional densities of states may arise in semiconductors, due to the formation of hydrogenic states which bind *two* electrons in a high magnetic field.

We shall limit ourselves to consideration of a strongly degenerate conduction electron gas in a solid having a simple nondegenerate energy band with an isotropic, quadratic dispersion law, within the effective-mass approximation. The conduction electron fluid is in equilibrium. The applied magnetic field is taken to be so strong that quantization of the electron motion (Landau quantization) is important. Generally, the phenomena we treat will only be important when the electrons all occupy the lowest Landau level and the lowest spin state within that level. In Sec. II, we give a short review of electron dynamics in high fields.

This work was originally prompted by the experi-

ments of Bridges and Clark¹ (hereafter referred to as BC), which determined the nuclear relaxation times of InSb nuclei in high magnetic fields. Before describing our work, we therefore briefly summarize the BC results. This is done in Sec. III. Feher² has suggested that the BC experiments in very high fields may be explicable in terms of plasma effects in the conduction electron gas. In Sec. IV, we discuss various plasma modes which have been proposed, and the schemes necessary for them to relax nuclear spins in a semiconductor. We conclude that all the mechanisms thus far advanced fail to agree qualitatively with experiment.

In Secs. V and VI, the possibility of additional densities of states in semiconductors is examined, and the binding energy of the high field H⁻ ion is calculated. The formation of this ion makes a new density of states available for conduction electrons with spin index $\sigma=1$. It is then possible for this new state to participate in relaxation of neighboring nuclear spins by making energetically possible a spin-flip process between conduction electrons and nuclei. The relaxation rate due to this impurity is estimated in Sec. VII.

A He-like ion could also contribute a $\sigma=1$ density of states. We consider the binding energy of this impurity in Sec. VIII. We compare our model with the BC experiments in Sec. IX.

Although the BC work is the only data currently available for comparison, it should be noted that our theory applies to any semiconductor in which the H⁻ binding energy may exceed kT . (This will usually mean the dielectric constant $K \gg 1$.)

The important point of this work is that formation of the H⁻ state for high fields ($\gamma > 1$) does occur, and it may have important consequences in many areas of current interest, such as the theory of scattering from

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¹ F. Bridges and W. G. Clark, *Phys. Rev.* **182**, 463 (1969).

² G. Feher (private communication).

localized spins and the appearance of negative magnetoresistance. We have dealt here with implications in nuclear relaxation in InSb, primarily because there appears to be some hope of explaining a specific experiment in terms of our model. However, this should not obscure the fact that wider applications may be possible.

II. FREE-ELECTRON STATES

The eigenvalue problem for an electron in a magnetic field may be solved in the free-electron approximation so that at the end we simply replace m by the effective mass m^* and g by an effective g^* . This leads to the usual Landau levels, with energy eigenvalues for the electrons

$$E_{n,P_z,\sigma} = (P_z^2/2m) + \frac{1}{2}\sigma g\mu_B H + (n + \frac{1}{2})\hbar\omega_c, \quad (1)$$

where n is the number of the Landau level and σ is the electron-spin index.

The density of states in a magnetic field is changed drastically from the field-free case. If the number of electrons occupying states up to energy E is N , then the density of states is³

$$g(E) = dN/dE$$

$$= \frac{V}{2(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sum_{n=0}^{n_{\max}} \sum_{\sigma=-1}^1 \left[E - (n + \frac{1}{2})\hbar\omega_c - \frac{g\mu_B H \sigma}{2} \right]^{-1/2}$$

$$= \sum_{\sigma} g^{\sigma}(E), \quad (2)$$

where $n_{\max}$ is the largest integer for which the square root is real. Since $\sigma = \pm 1$, there are two square-root singularities for each Landau level n . The total number of electrons is

$$n_0 = \sum_{\sigma=-1}^1 \int g^{\sigma}(E) f(E) dE, \quad (3)$$

where $f(E)$ is the Fermi distribution

$$f(E) = \{1 + \exp[(E - E_F)/kT]\}^{-1}, \quad (4)$$

$$n_0 = \frac{\hbar\omega_c}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \times \sum_{n=0}^{n_{\max}} \sum_{\sigma=-1}^1 [E_F - (n + \frac{1}{2})\hbar\omega_c - \frac{1}{2}\sigma g\mu_B H]^{1/2}. \quad (5)$$

This is the equation relating E_F and n_0 , the electron concentration. For $H=0$, we have simply

$$E_F = (\hbar^2/2m)(3\pi^2 n_0)^{2/3}.$$

³ L. M. Roth and P. N. Argyres, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic Press Inc., New York, 1966), Vol. 1, p. 159.

FIG. 1. Electron density of states $g^{\pm}(E)$ versus E . The quantum limit is shown in which all electrons are in the $n=0$, $\sigma=-1$ state. The two-step process of Gunther *et al.* (Ref. 6) is indicated, whereby an electron absorbs a plasmon, gaining energy $\hbar\omega_p$, and then undergoes a mutual spin flip with a nucleus.

Equation (5) means that E_F decreases monotonically as H is increased, with some oscillations in the rate of decrease. For the extreme case (the "extreme quantum limit") of $n=0$, $\sigma=-1$,

$$E_F = \frac{1}{2}mv_F^2 = a_0^4 n_0^2 [(2\pi^2 \hbar)^2/m], \quad (6)$$

where now energy is measured from the bottom of the band [i.e., $\frac{1}{2}\hbar(\omega_c - \omega_s)$ is not included], and where

$$a_0^2 = \hbar/m\omega_c. \quad (7)$$

The Fermi velocity

$$v_F = (2\pi\hbar/m)a_0^2 n_0 \quad (8)$$

falls rapidly as H is increased in the extreme quantum limit. This is because the density of states increases with H , as may be seen by using Eq. (2). A plot of $g^{\sigma}(E)$ versus E is given in Fig. 1.

All equations in this section are valid in the free-electron approximation for a crystal lattice if m^* and g^* are substituted for m and g . We also write for convenience

$$g\mu_B H = \hbar\omega_s. \quad (9)$$

III. RELAXATION AT LOW FIELDS

The problem of nuclear relaxation through the contact interaction has been studied theoretically and

experimentally for some time.^{4,5} The coupling of the nuclear moment to the electron-spin moment for *s* states, the so-called contact interaction, is governed by the Hamiltonian

$$\mathcal{H} = (8\pi/3)\gamma_e\gamma_N\hbar^2(\mathbf{I}\cdot\boldsymbol{\sigma})\delta(\mathbf{r}). \quad (10)$$

Here, γ_e and γ_N are the electron and nuclear gyromagnetic ratios, $\gamma_e = g\mu_B/\hbar$, $\gamma_N = \mu_N/\hbar$. The Hamiltonian is only effective when the electron and nuclear wave functions have an appreciable overlap. One assumes a point nucleus for convenience.

Only *s* electrons contribute because of cubic lattice symmetry. We can write the dot product of the nuclear spin $\mathbf{I}$ and the electron spin $\boldsymbol{\sigma}$ as

$$\mathbf{I}\cdot\boldsymbol{\sigma} = I_z\sigma_z + \frac{1}{2}(I_+\sigma_- + I_-\sigma_+), \quad (11)$$

where $I_{\pm} = I_x \pm iI_y$ and $\sigma_{\pm} = \sigma_x \pm i\sigma_y$ are spin raising and lowering operators. Thus the Hamiltonian yields a process in which a mutual spin flip takes place between nuclei and electrons. Since the nuclear-spin energy is negligible compared with $\hbar\omega_s$, the electron kinetic energy must absorb or supply the energy for the transition. The transition rate for this process is proportional to the product of the number of electrons in the initial energy state and the number of available states in the final energy state. Korringa⁴ has investigated this process and finds an expression for $1/T_1$ when the electrons are degenerate:

$$1/T_1 = (64/9)\pi^3\gamma_e^2\gamma_N^2\hbar^3|\psi(0)|^4g^+(E_F)g^-(E_F)kT. \quad (12)$$

Here, $g^{\pm}(E_F)$ is the density of states for spin up or down, and $\psi(0)$ is the value of the electron wave function at the nucleus.

The product $|g^+(E_F)g^-(E_F)|$ is oscillatory in H . The other terms in Eq. (12) are at best very weak functions of H , so $1/T_1$ should oscillate in magnetic field.⁴ This behavior has been verified in InSb by Bridges and Clark.

However, as we enter the lowest spin level of the lowest Landau level ($n=0, \sigma=-1$), $g^+(E_F)$ must vanish so $(1/T_1)$ should fall rapidly. Bridges and Clark do not observe any such sudden decrease. Instead, at high fields two peaks in $(1/T_1)$ appear. This is shown qualitatively in Fig. 2.

The first peak which cannot be ascribed to the oscillatory factor $|g^+(E_F)g^-(E_F)|$ is called by Bridges and Clark the *A* peak. This peak has been observed in samples in the concentration range 10^{14} to 10^{16} electrons/cm³. The second or *B* peak was found for samples in the range 1 to 7×10^{14} electrons/cm³. (Limitation of the external field to 20 kG prevented investigation at higher concentrations.) Both peaks occur at magnetic fields which obey a relation

$$H_{A,B} = C_{A,B}n_0^{1/2}(1 + d_{A,B}T), \quad (13)$$

⁴ J. Korringa, *Physics* **16**, 601 (1950).

⁵ G. E. Gugenishvili and G. R. Khutsishvili, *Fiz. Tverd. Tela* **7**, 1335 (1965) [English transl.: *Soviet Phys.—Solid State* **7**, 1078 (1965)].

FIG. 2. Nuclear relaxation rates $(1/T_1)$ versus magnetic field, as found by Bridges and Clark (Ref. 1). The low-field oscillations are caused by the Landau levels. *A* and *B* peaks have T_1 of order 10^4 – 10^6 sec.

where the $d_{A,B}$ are constants of order 0.1, C_A and C_B are constants, and $C_B > C_A$.

Most of the *A* peaks occur at fields such that the conduction electron distribution is degenerate. For the *B* peaks, though, $kT/E_F \geq 1$, so the conduction electron statistics are not described by a zero-temperature Fermi distribution or a Boltzmann distribution. We shall assume in our work that the electrons are degenerate, and comment on corrections later.

The heights of the *A* and *B* peaks were found to be almost completely independent of temperature.

The relation $H \approx n_0^{1/2}$, Eq. (13), is true only for $T = 1.3^\circ\text{K}$. As T increases, the exponent of n_0 declines until at $T = 4.2^\circ$, $H \approx n_0^{0.4}$. We shall treat the $T = 1.3^\circ$ case extensively in this paper because it more nearly approaches a degenerate electron distribution.

The *A* peaks in particular occur at the point at which the conduction electron spin frequency equals the plasma frequency $\omega_s = \omega_p$ at $T = 1.3^\circ$. It was this fact, as well as the $n_0^{1/2}$ dependence of Eq. (13), which prompted the suggestion by Feher² that plasma effects might provide an explanation.

There are two clear approaches to the explanation of the *A* and *B* peaks. One is to find a source of additional density of states $g^+(E_F)$, which could be employed in Eq. (12). The other is to introduce an entirely new relaxation mechanism, perhaps due to plasma effects. We have followed both paths, and, in Sec. IV, we describe our conclusions regarding plasma mechanisms. In the remainder of the paper we consider an additional density of states arising from impurities in the solid.

IV. PLASMA-MODE MECHANISMS

It is well known that the degenerate electron gas in a solid may support collective oscillations. In general, there will exist oscillating electric and magnetic fields due to these plasma waves. The nuclear magnetic dipole moment will couple to the oscillating magnetic fields, and the nuclear quadrupole moment will interact with any electric field gradients.

A fundamental frequency which characterizes plasma motion is the familiar plasma frequency

$$\omega_p = (4\pi ne^2/Km^*)^{1/2}, \quad (14)$$

where K is the dielectric constant. This longitudinal electrostatic oscillation exists in the absence of a magnetic field, and indeed defines the lower limit for electrostatic oscillations if $\mathbf{H} = 0$.

Gunther *et al.*⁶ have considered the presence of the elementary quanta of frequency ω_p (plasmons) and their effect on the nuclear relaxation. Their theory discusses the A peak as being due to plasmon absorption and emission by electrons, as an intermediate step in the mutual electron-nucleus spin-flip process governed by the Korringa relation, Eq. (12). They obtain a logarithmic singularity in $(1/T_1)$ at $\omega_s = \omega_p$. Figure 1 gives a schematic illustration of the process. As one would expect, the final expression for $(1/T_1)$ obtained is proportional to the number of plasmons present at the beginning of the process, since an electron must absorb a plasmon and rise above the Fermi sphere until its energy is at least $\hbar\omega_s$, as measured from the bottom of the band. The number of plasmons is given by the Bose-Einstein distribution,

$$n(\omega) = (e^{\hbar\omega_p/kT} - 1)^{-1}. \quad (15)$$

For the samples considered by Bridges and Clark, the ratio $\hbar\omega_p/kT$ is at least 10. Therefore, $n(\omega)$ will be an exponentially decreasing number as temperature is lowered, and $(1/T_1)$ should reflect this property. This means a change from 1 to 2°K would reduce the peak by a factor $e^{-5} \approx 150^{-1}$. Bridges and Clark found that the peak height scarcely changed at all as a function of T .

The approach of Gunther *et al.*⁶ neglected the presence of the magnetic field. When H is applied, plasma oscillations have frequency $\sim \omega_p$ only along H . In general, their frequency is

$$\omega = (k_z/k)\omega_p[1 + (kL_s)^2]^{1/2}, \quad (16)$$

where $\mathbf{k}$ is the wave vector and L_s is the screening length. The effect of plasmons with this dispersion relation will be to considerably broaden the peak found by Gunther *et al.*

There are many other modes of a quantum plasma in a magnetic field, leading to a wide range of phenomena, but they are generally of higher frequency than ω_p and therefore, not excited in the experiments of Bridges and Clark, since $kT \ll \hbar\omega_p$. Direct relaxation of nuclei by helicons stimulated by an applied rf field has been observed when the frequency of the circularly polarized magnetic field of the helicon equals the nuclear Larmor frequency.⁷ It has also been proposed that helicons may be important in electron spin relaxation at low temperatures.⁸

For $\omega_c\tau \gg 1$, where τ is the electron momentum relaxation time, the helicon damping is small. The helicon has circularly polarized electric and magnetic fields, propagating along H with frequency

$$\omega = c^2\omega_c q q_z / (\omega_p^2 + c^2 q^2) \quad (17)$$

and wave vector $\mathbf{q}$. The direction of rotation of the fields is determined by the sign of the charge carrier—in this case, the electrons. (The condition $\omega_c\tau \gg 1$ is unusual, since for most waves supported by an electron plasma the condition is $\omega\tau \gg 1$. The requirement $\omega\tau \gg 1$ means the wave must persist for at least one oscillation in the face of electron momentum collisions. Such collisions usually disturb the momentum of the electrons sufficiently to destroy the “phase memory” of the wave. The reason helicons do not follow this rule is that the wave “information” is carried through the $\mathbf{E} \times \mathbf{B}$ drift of the electrons, i.e., not superimposed on the ordinary momenta as they would exist without H . The condition that the $\mathbf{E} \times \mathbf{B}$ drift of the carriers be meaningful is precisely that $\omega_c\tau \gg 1$.)

Consider Eq. (17) for $q_z \gg q_\perp$. If $qc \ll \omega_p$, $\omega \approx n_0^{-1}$. Setting $\omega = \omega_N$, where ω_N is the Larmor frequency of a nuclear spin, we obtain $H \approx 1/n_0$, which is quite different from the BC result $H \approx n_0^{1/2}$. If we do the same with $qc \gg \omega_p$, there is no resonant condition on n_0 . If $q_z \ll q_\perp$, the helicons are heavily damped unless $\omega_c\tau$ is very large. Even then the same dependences as above are found. Thus, it appears that the helicon cannot yield even the qualitative form of the BC resonant condition for nuclear relaxation.

Finally, we have considered in detail relaxation by coupling of the nuclear quadrupole moment to plasma waves obeying the dispersion relation of Eq. (16). Simple emission or absorption of one such plasmon affords too small a portion of the plasma wave spectrum. A two-plasmon (Raman) process yields relaxation times of the correct order of magnitude to explain the BC results. However, electron momentum relaxation times are too short to allow such plasma waves to have sharp frequencies, so that a resonant condition cannot result from a nuclear relaxation which employs two plasmons. (A more detailed outline of this work will be given at a later date.)

It appears, then, that relaxation through plasma modes does not allow an explanation of the BC experiments, though some other processes may give observable relaxation times. We next turn to mechanisms based on the possibility of an additional density of states in semiconductors in high magnetic fields.

V. HYDROGENIC MODEL

The success of the Korringa relation, Eq. (12), in describing the magnetic field dependence of the nuclear T_1 for fields such that $E_F > \hbar\omega_s$, leads one to consider using it for even higher fields. The Korringa process describes a mutual spin flip of electrons and nuclei, so

⁶ L. Gunther, M. Revzen, and A. Ron, *Physics* **3**, 115 (1967).

⁷ B. Sapoval, *Phys. Rev. Letters* **17**, 241 (1966).

⁸ G. Benford, *Phys. Letters* **26A**, 199 (1968).

that a density of states for both spin orientations of electrons must be available in order for the process to proceed. But as may be seen in Eq. (12), the density of states for $\sigma=1$, $g^+(E_F)$ is nonzero only for $E_F > \hbar\omega_s$. This is an outcome of the fact that we have used the Landau density of states for the conduction electrons; without the introduction of a new assumption we cannot gain any additional $g^+(E)$.

The Landau wave functions represent conduction electrons which move freely through the solid. As the external magnetic field increases, however, the cyclotron radii of the electrons become smaller. If they are circling about a positively charged impurity, they will fall further into the potential well of the impurity, and eventually the magnitude of their binding energy will exceed their kinetic energy. At this point, such electrons occupy bound states and cannot conduct. It is these bound states which may contribute a new density of states and augment the nuclear relaxation.

An approximate model for these slightly bound electrons is that of a hydrogenic atom in a magnetic field. Yafet *et al.*⁹ treated this problem in 1956. In the absence of a magnetic field we have the well-known case of a hydrogenic impurity of charge Z with a Bohr radius given by

$$a_B = \hbar^2 K / m^* Z e^2 \quad (18)$$

and ionization energy

$$E_0 = 13.6 (m^* / m K^2) \text{ eV}, \quad (19)$$

where K is the static dielectric constant. In InSb, an electron bound to a hydrogenic impurity has a Bohr radius equal to hundreds of lattice spacings, since $K=16$. The Rydberg, $m^* Z^2 e^4 / 2 \hbar^2 K^2$, is 6.9×10^{-4} eV at $n=10^{14}$ electrons/cm³.

With the introduction of a magnetic field, one must rely on a perturbative treatment to find the ionization energy. Yafet *et al.* considered fields so high that the ratio of cyclotron energy to the Rydberg energy, $\gamma = \hbar\omega_c / 2 \text{ Ry}$, was large. As γ grows, the ground-state wave function becomes distorted. Along the magnetic

FIG. 3. Binding energy of a hydrogenic impurity versus magnetic field, as calculated by Yafet *et al.* (Ref. 9).

⁹ Y. Yafet, R. W. Keyes, and E. N. Adams, J. Phys. Chem. Solids **1**, 137 (1956).

FIG. 4. Best values of a_1 , a_{11} , b_1 , and b_{11} versus $\gamma = \hbar\omega_c / 2 \text{ Ry}$; a_0 is the spatial extent of the free-electron wave function.

field, it is found that a slight contraction occurs, while in the plane perpendicular to H the wave function is considerably contracted. The charge cloud surrounding a fixed positive impurity gradually deforms from a sphere into an ellipsoid of revolution.

When $\gamma=1$, a perturbation treatment will not work, but as γ grows we might expect to treat the Coulomb potential energy as a small effect relative to the magnetic energy $\frac{1}{2}\hbar\omega_c$. The Landau wave functions in the $n=0$ Landau level are of the form $\psi(r) \approx e^{-r^2}$, so for high magnetic fields Yafet *et al.*⁹ assumed a trial wave function

$$\psi(r) = \frac{1}{(2^{3/2} a_1^2 a_{11} \pi^{3/2})^{1/2}} \exp\left(-\frac{x^2 + y^2}{4a_1^2} - \frac{z^2}{4a_{11}^2}\right),$$

where a_1 and a_{11} are variable parameters. The dimensionless Hamiltonian which governs the motion is

$$\mathcal{H}/1 \text{ Ry} = -\nabla^2 + \gamma L_z + \frac{1}{4}\gamma^2(x^2 + y^2) - 2/r,$$

where x , y , r are dimensionless lengths and ∇ is the dimensionless gradient operator in these variables. The quantity L_z is the operator for the component of angular momentum along the magnetic field. Yafet *et al.*⁹ carried out a variational estimate of the ground-state binding energy E_I as a function of γ , and their results are shown in Fig. 3. The values of a_1 , a_{11} which correspond to the minimum values of E_I are given in Fig. 4.

We wish to obtain some density of states as shown in Fig. 5. A peak in $1/T_1$ should occur when this density of

FIG. 5. Location of the H⁻ impurity density of states.

states intersects the Fermi surface of the conduction electrons and allows spin-flip encounters to take place with nuclei of the lattice. To be located at such a spot in the energy diagram, Fig. 5, we would expect the isolated electrons to have spin up ($\sigma=1$). A moment's consideration shows that the theory of Yafet *et al.* as it stands cannot yield such a state.

Suppose when $E_F < \hbar\omega_s$ there are N_1 donor ions which are isolated so their electrons do not enter the conduction band. In equilibrium, these electrons should occupy the $\sigma=-1$ state, since this is energetically preferred. Thus, all the isolated donor impurities are occupied and no $\sigma=1$ states are available, for a hydrogenic atom holds only one electron. A density of states *does* exist for $\sigma=-1$, and at sufficiently high fields the Fermi level will lie at the very bottom of the conduction band, since a large number of electrons would be "frozen out" onto the isolated impurities.

VI. H^- ION

The crucial point in the above argument is that a hydrogenic atom will hold only one electron. But we know that even in the absence of a magnetic field, hydrogen will bind a second electron to produce the H^- ion.

This ion appears only in diffuse gases—notably, in the upper atmosphere and in the sun.¹⁰ In solids, the perturbations due to neighboring lattice sites are sufficient to make the model of an independent atom break down for the very small binding energies of the H^- ion.

The lowest energy state for the isolated H^- ion finds the electron charge clouds centered on points which lie

on opposite ends of a line through the nucleus. This reduces their mutual repulsion to a minimum and allows a slight binding energy of 0.0555 Ry.

In a semiconductor, the influence of nearby lattice sites will easily overcome the small H^- binding energy at zero magnetic field. Now consider the effect of raising the field.

As H is increased from zero, the electrons move in tighter and tighter cyclotron orbits. Those circling about singly charged impurities will draw closer to the impurity sites and fall further down into its Coulomb potential. This enhancement of the wave function near the impurity can make up for the deficiency in nuclear charge and permit a two-electron bound state. Whether such a state is permitted depends on the balancing out of the mutual electron-electron repulsion versus the energy gained by drawing the electrons closer about the region where the impurity potential is large.

For a hydrogenic impurity in InSb, the thermal energy kT will exceed the H^- binding energy at $H=0$. Our problem is to find when the binding energy rises above kT as H is increased, and thus, allow a second electron to occupy a hydrogenic site.

A two-parameter variational calculation for this begins with the Hamiltonian

$$\begin{aligned} \mathcal{H}/1 \text{ Ry} = & -\nabla_1^2 - \nabla_2^2 + \gamma(L_z^1 + L_z^2) \\ & + \frac{1}{4}\gamma^2[(x_1^2 + y_1^2) + (x_2^2 + y_2^2)] \\ & - \gamma(\omega_s/\omega_c)(\sigma_z^1 + \sigma_z^2) \\ & - 2/r_1 - 2/r_2 + 2/r_{12}. \end{aligned} \quad (20)$$

Here, the m and g which appear in ω_s and ω_c are understood to be those of any system describable by a hydrogenic model. We take as a wave function

$$\psi(r_1, r_2) = \frac{\exp-(x_1^2 + y_1^2 + x_2^2 + y_2^2)/4b_1^2 \exp-(z_1^2 + z_2^2)/4b_{11}^2}{[(2\pi)^{3/2}b_1^2b_{11}]^{1/2}}, \quad (21)$$

since the free-electron wave functions in high fields take the form $\psi \approx e^{-r^2}$, and employ b_1 , b_{11} as our parameters. (This is identical, of course, to assuming a different screening charge Z in the perpendicular and parallel directions.) A trial value for the energy is

$$\begin{aligned} E_{II} = & \frac{1}{b_1^2}(1 + \epsilon^2/2) + \gamma^2 b_1^2 \\ & - \frac{(2\sqrt{2}-1)\epsilon}{\pi^{1/2}b_1(1-\epsilon^2)^{1/2}} \ln \left[\frac{1+(1-\epsilon^2)^{1/2}}{1-(1-\epsilon^2)^{1/2}} \right], \end{aligned} \quad (22)$$

where $\epsilon = b_1/b_{11}$. Minimizing E_{II} with respect to ϵ and b_1 , we obtain two equations relating ϵ , b_1 , and γ :

$$\epsilon + \frac{(2\sqrt{2}-1)}{\pi^{1/2}b_1} \left\{ \frac{2}{1-\epsilon^2} - \frac{1}{(1-\epsilon^2)^{3/2}} \ln \frac{1+(1-\epsilon^2)^{1/2}}{1-(1-\epsilon^2)^{1/2}} \right\} = 0 \quad (23)$$

¹⁰ S. Chandrasekhar, Rev. Mod. Phys. 16, 301 (1944).

and

$$\begin{aligned} & -2(1 + \epsilon^2/2)/b_1^3 + 2\gamma^2 b_1 \\ & + \frac{(2\sqrt{2}-1)\epsilon}{\pi^{1/2}b_1(1-\epsilon^2)^{1/2}} \ln \left[\frac{1+(1-\epsilon^2)^{1/2}}{1-(1-\epsilon^2)^{1/2}} \right] = 0. \end{aligned} \quad (24)$$

Numerical solution of these equations is straightforward, though tedious. Figure 6 shows E_B as a function of γ for the best values of b_1 , b_{11} obtained through Eqs. (23) and (24). E_B passes through zero at $\gamma \approx 0.15$. Beyond $\gamma=4$ its magnetic field dependence is somewhat weaker than that of the one-electron impurity (Fig. 3).

Figure 4 shows the variational results for b_1 and b_{11} as well as a_1 and a_{11} from the Yafet *et al.* theory. For $\gamma > 6$, a_1 and b_1 are virtually identical fractions of a_B . The charge clouds are contracted equally in the plane perpendicular to H . Along H , however, where we would expect the results to be more in accord with the zero-

FIG. 6. Binding energy of one electron in the H⁻ ion as a function of magnetic field.

field case, $b_{11} \approx 1.25a_{11}$, so the electrons are not as tightly grouped about the impurity. Also shown is $a_0 = (ch/eH)^{1/2}$, the spatial extent of the wave function of a free carrier in the magnetic field. Note that a_0 approaches a_1 and b_1 at large γ .

For $T = 1^\circ\text{K}$, $E_B > kT$ when $\gamma > 2$. Thus, the H⁻ impurity will begin to bind electrons from the conduction band at this field strength.

In the semiconductor InSb, this corresponds to $H > 6$ kG when $n_0 \approx 10^{15}$ electrons/cm³. Above this field strength, the H⁻ impurities may begin to play an important role in transport and relaxation properties of the solid.

(It should be noted that optical detection of the H⁻ state would be difficult, because the transition from the H⁻ level, which lies below the Fermi level, to a higher cyclotron state would be masked by the much larger number of conduction electrons which could make the same transition.)

VII. RELAXATION OF NUCLEI

The H⁻ ion provides the additional $g^+(E_F)$ needed for relaxation of the nuclear spins through the contact interaction. The H⁻ lattice sites must be present in appreciable numbers, however, in order to produce a measurable effect.

The samples of BC were produced by nuclear irradiation,¹¹ so that the positively charged impurities which donate conduction electrons are randomly distributed. One would expect that there will be a small fraction of the impurities which are separated from their neighbors by a distance larger than the average separation $N_I^{-1/3}$, where N_I is the density of impurities. If an impurity is sufficiently removed from its neighbors, there will be no overlap of wave functions between them, and the impurity will be isolated and unable to participate in the conduction process. How large this separation must be depends upon the exact nature of the impurity wave functions.

Suppose we wish to place N_I impurities in N lattice sites. If we isolate an impurity so that the nearest-neighbor impurity is s_1 lattice spacings away perpendicular to H and s_{11} spacings away along H , we must exclude $2\pi s_1^2 s_{11}$ sites. It is easy to show that the number of impurities so isolated is

$$N_1 = N_I \exp(-2\pi c_1^2 c_{11}/a_I^3), \quad (25)$$

where $a_I^3 = 1/N_I$, $c_1 = s_1 a$, $c_{11} = s_{11} a$, and a is the lattice constant.

We do not know precisely what separation of impurities is necessary to ensure that they will not participate in some form of impurity band conduction. In what follows we shall take the extent of the electron wave functions to be given by b_1 , b_{11} as shown in Fig. 4. We then assign an overlap parameter δ , defined by

$$N_1 = N_I \exp(-2\pi\delta b_1^2 b_{11}/a_I^3). \quad (26)$$

Therefore, δ measures (in Bohr radii) the separation necessary to achieve isolation.

Just as was the case for the Korringa relation when $E_F > \hbar\omega_s$, our picture of the A peak phenomenon assumes that conduction electrons will be able to undergo spin-flip processes when a density of states with spin up ($\sigma = 1$) intersects the Fermi level. As illustrated in Fig. 5, this occurs when

$$\hbar\omega_s(g^*) - E_B(m', g') = E_F(m^*, n_0). \quad (27)$$

The binding energy E_B is a function of m' and g' , the m and g values for the isolated impurity (as we shall see, $g' \neq g^*$, $m' \neq m^*$). The expression for the Fermi energy, Eq. (7), must be modified to include the fact that as electrons freeze out on the isolated impurities, they leave the conduction band. Equation (26) gives (in terms of δ) the number of isolated impurities holding two electrons each, so the number of electrons taken from the conduction band is (since we take $n_0 = N_I$)

$$2n_0 \exp(-2\pi\delta b_1^2 b_{11}/a_I^3).$$

Accordingly we modify the Fermi energy,

$$\begin{aligned} E_F(m^*, n) &= (\hbar^2/2m^*)^{1/4} (2\pi a_0)^4 n_0^2 \\ &\quad \times [1 - 2 \exp(-2\pi\delta b_1^2 b_{11}/a_I^3)] \\ &= \hbar\omega_s(g^*) - E_B(m', g'). \end{aligned} \quad (28)$$

Note that if E_B , g' , and N_1 were independent of H , Eq. (28) would give $H \approx n_0^{2/3}$ at the peak in $(1/T_1)$. It is the modification of these three quantities by H which leads to the relation $H \approx n_0^{1/2}$.

The relaxation time T_1 of the InSb nuclei may be calculated in the same manner as the Korringa process. At a Landau peak (subscript L), the Korringa expression for T_1 is

$$(1/T_1)_L \propto g^+(E_F) g^-(E_F) |\psi(0)|^4, \quad (29)$$

where $\psi(0)$ is the wave function of the conduction electron at the relaxing nucleus. For the peak due to

¹¹ W. G. Clark and R. A. Isaacson, J. Appl. Phys. 38, 2284 (1967).

relaxation with H^- sites, we will have

$$(1/T_1)_A \propto g_A^+(E_F)g^-(E_F)|\psi(0)|^2|\psi_A(r_N)|^2. \quad (30)$$

Here, $g_A^+(E_F)$ is the (unknown) density of states for the isolated H^- impurity electrons, defined by

$$n_A = \int g_A^+(E)f(E)dE = N_I \exp - (2\pi\delta b_{11}^2 b_{11}/a_I^3), \quad (31)$$

where $\psi_A(r_N)$ is the value of the bound H^- electron wave function at the nucleus at which the nuclear relaxation occurs. This will have a different value for each lattice site, since the H^- wave function is spread over many thousands of lattice spacings. In $1/T_1$, we take an average of this quantity over the nuclei

$$|\langle\psi_A(r_N)\rangle|^2 = \frac{1}{V} \int \sum_i |\psi(\mathbf{x}-\mathbf{x}_i)|^2 d\mathbf{x}_i = N_1. \quad (32)$$

The full expression for the Korringa $(1/T_1)$ is proportional to the square of the g value of the electrons. However, as Bridges and Clark¹ note, for both a Landau peak and relaxation by bound states the proper value to use in a Korringa-type process is $g=2$. Thus neither the conduction electron $|g^*|=50$ or the H^- impurity g' enters into the relaxation time.

Equations (28)–(32) may be used to find the location and height of the peak in $(1/T_1)$ due to relaxation of conduction electrons with local H^- sites. These equations are functions of m' , g' , $g_A^+(E_F)$, and δ .

Thus far, we have considered m' and g' , the mass and g value of the H^- electrons, to be independent quantities. For the conduction electrons in InSb, a relation exists between m^* and g^* , the so-called Roth equation^{12,13}

$$g^* = 2[1 - (m/m^* - 1)\Delta/(3E_g + 2\Delta)], \quad (33)$$

where E_g is the energy difference between the upper edge of the valence band and the lower edge of the conduction band in InSb, and Δ is a measure of the spin-orbit coupling which exists between conduction and valence bands and which produces the unusual m^* and g^* . The Roth relation is based on the assumption that the electrons move over many lattice sites. Since the electrons bound to the H^- impurities still have orbits extending over many hundreds of lattice spacings, they should obey Eq. (33). We will use this equation to eliminate m' from Eq. (28), taking the experimentally determined values for E_g and Δ .¹³

We may estimate the g value of the second H^- electron by Fourier analyzing the impurity wave function, Eq. (21). We find

$$g' = \int_{-\infty}^{\infty} dk_z g^*(k_z) e^{-2(k_z b_{11})^2} / \int_{-\infty}^{\infty} dk_z e^{-2(k_z b_{11})^2}, \quad (34)$$

where $g^*(k_z)$ is the conduction electron g factor as a function of the electron wave number k_z , for high fields ($\gamma \gg 1$). In the quantum limit,

$$k_F = (2\pi^2 ch/e)(n_0/H). \quad (35)$$

The experiments on InSb of McCombe *et al.*,¹⁴ and, earlier, Pidgeon *et al.*,¹⁵ yield a curve of $g^*(n, H)$ versus H up to $H=100$ kG, where n is the Landau level number. Their work is least accurate for the $n=0$ level of concern to us, since they have assumed that exciton and impurity effects do not figure in the difference between the energies of transitions, and this approximation is least valid for the $n=0$ level. Their experiments show that $g^*(0, H)$ falls as H increases. Taking $g^*(k_z) = g^*(k_F)$ when the Fermi level intersects the H^- density of states, we can see that the average shown above for g' will acquire contributions of low $g^*(k_z)$ from regions of low k_z . A numerical integration using the data of Refs. 14 and 15 yields $|g'| = 36$. The value of $|g^*|$ at $H=0$, by comparison, is 50. For a free electron, $g=2$.

For convenience, we may take the H^- density of states, $g_A^+(E_F)$, to be a very narrow function of energy. By using Eqs. (29)–(32) we can compare the experimentally determined ratio of $(1/T_1)_L$ and $(1/T_1)_A$, and find δ . Because of the inaccuracies of experiment this ratio is not very well known, but it can be used for a rough estimation.

Thus, it appears that all the parameters which appear in our model can be fixed and a comparison with experiment made.

VIII. HELIUMLIKE ION

It is natural, having considered H^- impurities as a source of a density of states for $\sigma=1$ electrons, to study a He-like ion. Such a doubly charged impurity will bind a second electron much more strongly and thus, will be auto-ionized at higher magnetic fields than a $Z=1$ impurity.

A $Z=2$ (He) impurity may be simulated by two singly charged impurities which are only a few lattice spacings apart. To an electron moving in a Bohr orbit of hundreds of lattice spacings, the two ions will appear to a good approximation as a He-like atom with its charge shielded by the dielectric constant of the medium K . If faults or slippages exist in the sample, there may be an appreciable number of these closely grouped configurations.

Since the second electron will be strongly bound to a $Z=2$ impurity, the intersection of the Fermi level with the $Z=2$ density of states [Eq. (28)] will occur at magnetic fields higher than is the case for the H^- ion. The quantity $g^-(E_F)$ is proportional to H^2 , and $(1/T_1)$

¹² L. M. Roth, B. Lax, and S. Zwerdling, Phys. Rev. **114**, 90 (1961).

¹³ O. Madelung, *Physics of III-V Compounds* (Wiley-Interscience, Inc., New York, 1964), p. 74.

¹⁴ B. D. McCombe, S. G. Bishop, and R. Kaplan, Phys. Rev. Letters, **18**, 748 (1967).

¹⁵ C. R. Pidgeon, D. L. Mitchell, and R. N. Brown, Phys. Rev. **154**, 737 (1967).

$\approx g^-(E_F)$. This means the number of $Z=2$ impurities can be smaller than the number of H⁻ impurities, and still produce a large peak in $(1/T_1)$.

A calculation of the He-like impurity binding energy in high fields follows much the same program as the $Z=1$ case. We take a trial wave function

$$\psi(r_1, r_2) = \frac{\exp[-(x_1^2 + y_1^2 + x_2^2 + y_2^2)/4d_1^2] \exp[-(z_1^2 + z_2^2)/4d_{11}^2]}{[(2\pi)^{3/2} d_1^2 d_{11}]^{3/2}}, \quad (36)$$

which gives a trial value for the energy

$$E_{II} = \frac{Z^2}{d_1^2} \left(1 + \frac{1}{2}\epsilon^2\right) + \frac{\gamma^2 d_1^2}{Z^2} - \frac{(2Z\sqrt{2}-1)Z\epsilon}{\sqrt{\pi}d_1(1-\epsilon^2)^{1/2}} \ln \left[\frac{1+(1-\epsilon^2)^{1/2}}{1-(1-\epsilon^2)^{1/2}} \right], \quad (37)$$

where $Z=2$. The equations minimizing E_{II} with respect to $\epsilon=d_1/d_{11}$ and d_1 ,

$$\partial E_{II}/\partial \epsilon = 0; \quad \partial E_{II}/\partial d_1 = 0, \quad (38)$$

may be solved numerically with a resulting binding energy E_B as shown in Fig. 7. Using the trial function, Eq. (36), the zero-field binding energy of the second electron to a $Z=2$ impurity is $E_B=1.20$ Ry. The experimental value is 1.808 Ry. However, as before, we expect our values of E_B to become much more accurate above $\gamma=1$.

If the He-like configuration is due predominantly to the close grouping of $Z=1$ sites, it may be that a molecular H-like model is more appropriate to describe it. Such a model may be worked out in the above manner.

IX. COMPARISON WITH EXPERIMENT

The experiments of Bridges and Clark¹ give the only data for comparison at present. In Sec. VII, the three unknown quantities g' , $g_A^+(E_F)$, and δ figure prominently in calculating $(1/T_1)$ and in the relation which fixes the magnetic field at which a peak in relaxation

FIG. 7. Binding energy of the second electron to a $Z=2$ impurity versus magnetic field. The dot at $\gamma=0$ indicates the observed binding energy at zero magnetic field.

time will occur, Eq. (28). If we take $g_A^+(E_F)$ to be a narrow function of energy, the resultant estimation of δ is not sufficiently accurate for our purposes. Therefore, we have followed a somewhat simpler scheme; we regard g' and δ to be independent parameters, and plot the right- and left-hand sides of Eq. (28) over the range of interest in g' and δ . We know from Eq. (24) that g' lies near 36.0 and the data of Bridges and Clark fix δ to be of order 1.

Figure 8 shows such a plot for a BC sample with $n_0=3.34 \times 10^{15}$ electrons/cm³. Intersections of the curves exist at many field strengths scattered about the point at which the A peak is observed by BC. A similar plot results when another BC sample of $n_0=7.65 \times 10^{14}$ electrons/cm³ is considered. These curves show that the estimated $|g'| \approx 36$ and δ on the order of one are values consistent with the BC experiment.

We find, in fitting the BC results for samples with concentrations between 7.65×10^{14} and 1×10^{16} electrons/cm³, that we can obtain $H = C_A n_0^{1/2}$ for the A peak locations, to within the accuracy of the experiment, with $g' = 34.0 \pm 4.0$, $m'/m_e = 0.021 \pm 0.002$.

We must also consider the temperature dependence of the A peaks found by BC. Temperature does not enter into the hydrogenic Hamiltonian, so the ionization energy of the H⁻ impurity will be temperature-independent. The electron plasma is not strongly degenerate, so the temperature shift in the Fermi energy around the A peak is

$$E_F(n_0, T) \cong E_F(n_0, 0) + kT. \quad (39)$$

The shift in location of the A peak found by BC is about 2.5 kG between 1 and 4°K. The above change in the

FIG. 8. Solution of Eq. (28) for $n_0=3.34 \times 10^{15}$ electrons/cm³. A family of curves for the Fermi level $E_F(H)$ is shown for a range of δ . The right-hand side of Eq. (28) is labeled with a range of values of g' , the H⁻ impurity g value.

Fermi energy, when substituted in Eq. (28) yields 1 kG. This seems to be satisfactory agreement, considering that Eq. (39) is approximate.

The population of the H^- level should vary slowly with T if $E_B > kT$, so we would expect the height of the peak in $(1/T_1)$ to be quite insensitive to temperature, in agreement with the data of BC.

A difficulty arises, however, when we consider the concentration of H^- impurities required to produce $(1/T_1)$ peaks of the height required by experiment. We find that $N_1 = 0.08n_0$. Since two conduction electrons "freeze out" on each H^- impurity, the conduction band must have lost 16% of its electrons before the Fermi level intersected the H^- density of states. Isaacson¹⁶ has performed Hall-effect measurements on the BC samples, and he does not find a density oscillation of this size at the fields where the A peaks occur. (His work measures changes in concentration of 8% or greater.)

It should be noted, though, that Isaacson's interpretation of his data is based on the low-field expression for the Hall coefficient. A theory for the Hall effect in the extreme quantum limit, and in the presence of impurities like the H^- ion, has not yet been given.

We now turn to the comparison between our theory of the He-like impurity and the BC data for the B peak. We can carry out a curve-plotting procedure as in Fig. 8, using the binding energy of the $Z=2$ impurity. Because the B peaks have been observed only in samples of low concentrations, the Fermi energy is small. The right-hand side of Eq. (28) is therefore relatively insensitive to δ , the overlap parameter.

For the BC sample with $n_0 = 1.78 \times 10^{14}$ electrons/cm³, we find that a peak will appear at the observed position, 11 kG, if $g' \approx 33.5$. This agrees with a numerical calculation based on Eq. (34). Similarly, we find that a fit to the B peaks gives $H = C_B n_0^{1/2}$ for the B peak locations, within the accuracy of the experiment with $g' = 33.5 \pm 1.0$.

Fitting the height of the peak found by BC to the number of $Z=2$ impurities, we find that on the order of 10^{12} /cm³ are necessary. Bridges and Clark estimate that their samples contain as many as 10^{15} /cm³ unknown impurities.

Because the degeneracy ratio kT/E_F is of order 50 in the region of H , where the B peaks occur, the simple analysis given here does not describe well the behavior of the (Boltzmann) electrons as they intercept the density of states due to doubly charged impurities. The peak will be extensively broadened because the Boltz-

mann distribution does not have a sharp discontinuity in momentum. Bridges and Clark do in fact find widths of approximately 8–12 kG for their B peaks.

The above considerations give us reason to believe that our He-like impurity model qualitatively describes the B peaks of Bridges and Clark.

X. CONCLUSIONS

We have shown that H^- impurities with binding energy $> kT$ may be expected to form in a semiconductor when $\gamma = \hbar\omega_c/2 \text{ Ry} \gg 1$. Such an H^- state contributes a new density of states to the semiconductor, which then makes possible a relaxation mechanism of the Korringa type, in which electrons undergo mutual spin-flips with nuclei.

Comparison of our theory with the BC experiments on InSb has shown general agreement. A difficulty arises, however, from the fact that more H^- impurities are required for agreement than it presently seems likely from Hall-effect measurements. Hopefully, a treatment of the Hall effect in the extreme quantum limit will clarify this point.

Similarly, we have hypothesized that $Z=2$ impurities in semiconductors may provide another source of the needed density of states. Here, our calculations compare qualitatively with the InSb BC experiments.

Further experiments at higher fields would prove quite useful in testing the validity of our model. Particularly, our work predicts that the relation $H = C n_0^{1/2}$ will continue to hold to much higher fields than those presently used by Bridges and Clark ($H \geq 20$ kG).

There are other consequences of the formation of an H^- state in high fields. The magnetoresistance of semiconductors may begin to show the effects of scattering from the H^- state, which is spread out over a large volume around the impurity when $\gamma > 1$. There may also be changes necessary in the theory of scattering from localized spins, and of the negative magnetoresistance in InSb.

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¹⁶ R. A. Isaacson (private communication).