Self-trapped states of carriers in antiferromagnets and amorphous semiconductors with dangling bonds

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Self-trapped states of charge carriers in $3D$ and $2D$ antiferromagnetic systems of the Hubbard-model type in a magnetic field are analyzed. One of these systems is a quasi-oscillator (or string), in which an electron is oscillating in space with respect to the center of the state, and there is a simultaneous oscillation of a deformation of the magnetic order. A system of equations corresponding to the Feynman version of quantum mechanics derived here for the paths of the electron motions is used to construct an effective wave equation. This wave equation makes it possible to find the energy of the string as a function of the parameters of the system within a factor on the order of unity. Another state of this type is a ferron (or large-radius magnetic polaron), in which an electron creates a microscopic ferromagnetic region and undergoes self-trapping there. Under the conditions considered here, the ferron is fundamentally different from that described previously (E. L. Nagaev, *Physics of Magnetic Semiconductors*, Mir, Moscow, 1983). The differences involve the nature of the ferron and the conditions under which it exists. Under certain conditions, a ferron may be preferable to a string from the energy standpoint in the absence of a field; a field will stabilize it. It is suggested that the anomalous field dependence of the electrical and optical properties of a-Se and a-Ge might be explained by the presence of pores with dangling bonds at their surfaces. This situation would cause these materials to behave as $2D$ antiferromagnets. Electrons or holes trapped by pores would form ferrons whose energy would depend strongly on the field.

The recent discovery of high T_c superconductors has breathed new life into the waning research on magnetic semiconductors. The reason is that most of the high T_c superconductors and related compounds are degenerate antiferromagnetic or nearly antiferromagnetic semiconductors (in the latter case, only a short-range antiferromagnetic order is observed instead of a long-range order). Antiferromagnetic semiconductors contain self-trapped states of charge carriers, with a disruption of the antiferromagnetic order near the point of carrier trapping.[1] Although the theory for such states dates back to the 1960s, it is by no means perfected. This theory is not only of independent interest; it is also pertinent to high T_c superconductivity: Several recent papers have proposed explanations for the properties of high T_c superconductors on the basis of self-trapped states (e.g., Refs. 2–4).

In this paper we would like to suggest that magnetic self-trapped states might be capable of explaining the anomalous behavior of such amorphous semiconductors as Ge and Si in a magnetic field. Experimental data, which we will discuss below, indicate that this behavior is similar to that of magnetic semiconductors. Although a-Ge and a-Si are generally only slightly magnetic, they do contain regions in which there may be a short-range antiferromagnetic order. These regions are the inner surfaces of the pores which are unavoidably present in large numbers in a-Ge and a-Si samples. Each atom at the surface of a pore has a single unpaired s–p bond, because there is no neighbor on the pore side. The orbits of neighboring atoms at the surface of pores overlap somewhat. The exchange interaction which arises between the unpaired electrons of these atoms should result in conversion of the pore surfaces into $2D$ magnets. These pores can serve as donors or acceptors. In addition, self-trapping of an electron or a hole trapped by these pores can occur there, by the same mechanism as in magnetic semiconductors. It would lead to a strong field dependence of the depth of the level associated with the pore.

Various models have been proposed for magnetic self-trapped states in antiferromagnetic semiconductors. De Gennes[5] has suggested that such a state arises from a deviation of the spin of one single electron from the direction of the moment of the corresponding sublattice. However, an analysis in Ref. 1 shows that such a state would not be possible at realistic values of the parameters of the crystal. In particular, the realization of such a state would require huge values of the atomic spins—far greater than anything which exists in nature.

A different model for the self-trapping of an electron in an antiferromagnetic semiconductor was proposed in Ref. 6: An electron creates a ferromagnetic region in the semiconductor and stabilizes this region by being trapped in it. The size of the region is found by minimizing the energy of the system. In materials such as EuTe and EuSe, in which the existence of such states is implied by experimental data,[1] the region may contain hundreds or even thousands of atoms. The results found in Ref. 6 were subsequently reproduced by many workers. The term "ferron" was used for such a state in Ref. 1, although the term "large-radius magnetic polaron" is often used for it in the current literature.[1)]

Bulaevskiĭ *et al.*[7] have proposed an entirely different model of a self-localized state. They considered a Hubbard model or the equivalent limit of narrow conduction bands in an s–f model. In this case the spin of a regular magnetic atom is 1/2; if there is a conduction electron at this atom, the spin of the atom is zero. When the conduction electron makes a transition to a neighboring atom, the spin of the atom which the electron leaves behind is directed opposite the angular momentum of the sublattice to which that atom belongs.

Consequently, the longer the path traveled by the electron, the greater the disruption of the antiferromagnetic order along the path, and the higher the energy of the magnetic order. Correspondingly, a quasielastic force arises and tends to move the electron toward a certain central atom—an atom in a configuration such that if the electron moves there the antiferromagnetic order will not be disrupted. As a result, the electron oscillates with respect to this atom, and the degree of disruption of the magnetic order oscillates along with the electron.

Subsequent papers on this topic have referred to this state not as a "quasi-oscillator," as proposed in Ref. 7, but as a "string." "String" is indeed a more convenient term. A string differs from a ferron not having a huge magnetic moment. According to Refs. 1 and 7, a string is described by electron-path equations which are in a sense analogs of the equations in Feynman's formulation of quantum mechanics. In contrast with the latter, however, the string equations cannot be reduced exactly to a wave equation. It was for this reason that reliable estimates of the string energy could not be found in Ref. 7 except in the case in which only short paths were important. A string in a magnetic field has not been studied; we do not even know whether a ferron might be preferable to a string from the energy standpoint.

In the present paper we take a new approach to the string problem. This approach leads to an effective wave equation for a string. This approach makes it possible to derive the nontrivial part of the string energy to within a factor of order unity and to find a lower estimate of this energy (an upper estimate can be found by a path method[1,7]). The equation derived below can be used to determine the behavior of the string energy as a function of the magnetic field.

We also calculate the energy of a ferron. A ferron in a Hubbard-type magnetic material is quite different from the ferrons, described in Ref. 1, in magnetic materials of other types. In this case the ferromagnetic region is not a potential well for electrons, and the formation of a ferron can be explained by saying that the motion of an electron in the ferromagnetic region is not accompanied by deformation of the magnetic structure. Correspondingly, the conditions for the existence of a ferron in this case are quite different than those given in Ref. 1. In contrast with Ref. 1, for example, a magnetic field stabilizes a ferron instead of destroying it.

It has been found that the string energy is small in comparison with the ferron energy by a factor proportional to the parameter $(I/B)^n$, where I is the exchange integral, and B is the Bloch integral. For the 3D case we would have $n = 4/15$, and for the 2D case we would have $n = 1/6$. As $I/B \to 0$, in the absence of a field, a string should thus be energtically preferable to a ferron. With increasing field, however, regardless of the value of I/B, the ferron becomes preferable to the string from the energy standpoint.

At the actual values of I/B, because of the small value of the power n with which I/B appears in the ratio of the string energy and the ferron energy, it may happen that these energies are approximately the same. There could even be a situation, particularly in the 2D case, in which a ferron is energetically preferable to a string even in the absence of a field. This circumstance might lead to an explanation of the anomalous behavior of amorphous semiconductors in a magnetic field.

EFFECTIVE WAVE EQUATION FOR A STRING

The concept of a string (or quasi-oscillator) can be explained most simply in the Hubbard model. We consider a situation in which a crystal initially has an ideal antiferromagnetic order. A second electron appears at one atom of the crystal, which we adopt as the central atom. [In the 1D case, the $(\uparrow)(\downarrow)(\uparrow)(\downarrow)(\uparrow)$ pattern is replaced by $(\uparrow)(\downarrow)(\uparrow\downarrow)(\downarrow)(\uparrow)$.] The extra electron can leave this central atom and go to a neighboring atom. Of the two electrons at the central atom, the one which makes the transition is that whose spin is opposite the spin of the neighbor [the pattern $(\uparrow)(\downarrow)(\downarrow)(\uparrow\downarrow)(\uparrow)$]. After the electron leaves the atom, the atom will thus be left with the "wrong" spin—a spin directed opposite the moment of the sublattice to which the atom belongs. The transition of the extra electron to the next atom gives rise to yet another wrong spin, again at the atom which the electron leaves. Consequently, wrong spins appear along the entire path of the electron. The higher the number of these wrong spins, the greater the increase in the magnetic energy of the system, i.e., the greater the force which tends to return the electron to the central atom. The disrupted antiferromagnetic order can be restored if the electron moves back toward the center along the same path which it took in moving away from the center. The electron must therefore oscillate with respect to the central atom.

In string calculations it is more convenient for technical reasons to use an s–f model instead of the Hubbard Hamiltonian. It was proved in Ref. 1 that the s–f model is equivalent to the Hubbard model in the particular case in which the f-spin S is 1/2, and the integral of the s–f exchange, A_{sf}, tends toward $-\infty$. In this limit one can use the spin-polaron representation described in Refs. 1 and 7. A spin-polaron is an s-electron whose spin is strongly coupled to the f-spin of the atom at which the electron is residing. In terms of the spin-polaron operators α_g^*, α_g (g is the site index), the Hamiltonian of the system is

$$\mathcal{H} = B \sum_{g,\Delta} F(\mathbf{S}_g, \mathbf{S}_{g+\Delta}) \alpha_g^* \alpha_{g+\Delta} - \frac{I}{2} \sum_{g,\Delta} \mathbf{S}_g \mathbf{S}_{g+\Delta} - h \sum_g S_g^z,$$

(1)

$$F_{g,g+\Delta} = (S+S_g^z)^{1/2}(S+S_{g+\Delta}^z)^{1/2} + (S+S_g^z)^{-1/2} S_g^+ S_{g+\Delta}^- (S+S_{g+\Delta}^z)^{-1/2},$$

$$S_g^\pm = S_g^x \pm i S_g^y, \qquad F_{g,g+\Delta} \equiv F(S_g, S_{g+\Delta}),$$

where S_g is the spin operator of atom g, $I < 0$ is the exchange integral for the exchange between nearest neighbors, which are connected to each other by the vector Δ, and h is the external magnetic field (expressed in energy units), which is directed along the z axis.

The quantity F incorporates the strong correlation between the spin of the carrier and the spins of the magnetic atoms. In the methods of Refs. 1 and 7, the atom at which the extra electron resides is also formally assigned a spin of 1/2; the singlet nature of the state of this atom is taken into account by assuming that its spin projection is fixed: $S_g^z = 1/2$. The first term in F describes transitions in which the spin of the atom which the electron leaves is parallel to the original spin of the atom to which the electron moves. The second term describes transitions in which these spins are in opposite directions. The expression for F given here includes a factor of 2 which was not present in Refs. 1 and 7. Because of this factor, the first term in (1) takes the same form as the

ordinary electron Hamiltonian when a ferromagnetic ordering occurs.

To find the energy of the string we use a variational principle. We write the wave function of the system as

$$\psi = \sum_{g} c_g(\{\theta_f\}) \psi_g(\{S_g^z\}) \alpha_g^* |0\rangle, \qquad (2)$$

$$\psi_g = \prod_{f \neq g} [\delta(S_f^z, \tfrac{1}{2}) \sin(\theta_f/2) + \delta(S_f^z, -\tfrac{1}{2}) \cos(\theta_f/2)],$$

where θ_f is the angle between the direction of the average spin of atom f and the z axis, $\delta(x,y)$ is the δ-function of discrete argument, and $|0\rangle$ is the vacuum wave function of the spin-polaron. Expressions (2) and (3) ignore minor quantum-mechanical effects which lead to zero-point vibrations of the spins and to the possibility that the center of the string will move through the crystal.[7]

Using (1)–(3), we find the equations of the Ritz method:

$$[E - E_g^M(\{\theta_f\})] c_g(\{\theta_f\}) = \sum_{\Delta} B_{g,g+\Delta} c_{g+\Delta}(\{\theta_f\}), \qquad (4)$$

$$E_g^M = -\frac{I}{2} \sum_{1,\Delta} (\psi_g, S_1 \cdot S_{1+\Delta} \psi_g), \qquad (5)$$

$$B_{g,g+\Delta} = B(\psi_g, F_{g,g+\Delta} \psi_{g+\Delta}) = B \cos \frac{\theta_g - \theta_{g+\Delta}}{2}.$$

We see from (5) that the matrix element $B_{g,g+\Delta}$ of the transition of the electron from the first atom to the second reaches a maximum when the spin direction at the first atom is the same as that at the second atom before the transition. Because of the strong inequality $|B| \gg |I|$ (B is a small quantity of first order, and I is one of second order, in the overlap of the orbitals of neighboring atoms), the electron transitions should occur in such a way that the quantity $|B_{g,g+\Delta}|$ is maximized. After a transition of an electron from a central atom (labeled 0) to a neighboring atom Δ_1, the angle between the spin of the central atom and the field becomes equal to the initial value (θ_{Δ_1}) of the angle between the spin of atom Δ_1 and the field. Correspondingly, after the electron leaves atom Δ_1 and goes to atom $\Delta_1 + \Delta_2$, the angle between the spin of atom Δ_1 and the field becomes equal to $\theta_{\Delta_1 + \Delta_2}$, instead of the original value θ_{Δ_1}.

It is suggested below (and the suggestion is supported by subsequent calculations) that an electron has only a minor effect on the value of the magnetic moment of the crystal. Under this assumption one can make the further assumption that, as in the absence of a conduction electron, the initial values of the angles are given by the following expression in a simple cubic 3D lattice or a simple square 2D lattice with a checkerboard antiferromagnetic order:

$$\theta_g = e^{iQg} \beta, \quad \beta = \arccos(h/2\mathcal{J}), \quad \mathcal{J} = zIS^2. \qquad (6)$$

Here z is the number of nearest neighbors, and Q is the antiferromagnetism vector ($Q\Delta = \pi$). As an electron passes through an atom, the sign of the angle between the spin of the atom and the field changes if the electron is at a distance from the center. When the electron undergoes the opposite transition, the angle recovers its original value.

We thus see that the distribution of the angles θ_g is determined unambiguously by the path of the electron, i.e., by the particular set of sites Δ_1, $\Delta_1 + \Delta_2, ..., \Delta_1 + ... + \Delta_n$, which the electron has visited and which satisfy the condition $\Delta_{n+1} \neq -\Delta_n$. The coefficients $c(\{\theta_g\})$ can thus be assumed to be functionals of the paths, and the Ritz equations (4) become ($\Delta_0 \equiv 0$)

$$[E - E^M(\Delta_0, ..., \Delta_n)] c(\Delta_0, ..., \Delta_n)$$

$$= B \left[\sum_{\Delta_{n+1} \neq -\Delta_n} c(\Delta_0, ..., \Delta_n, \Delta_{n+1}) + c(\Delta_0, ..., \Delta_{n-1}) \right]. \qquad (7)$$

If the path has no self-intersections or self-tangencies, the magnetic energy increases by an amount

$$f = |I| S^2 (z-2)(1 - \cos 2\beta) \qquad (8)$$

after each successive step (the first step is an exceptional case, in which the energy of the step is proportional to $z - 1$ instead of $z - 2$). Since there can be a huge number of paths without self-intersections or self-tangencies, we can assume that the magnetic energy is proportional to the number n of the steps in the path:

$$E^M(\Delta_0, ..., \Delta_n) \approx nf. \qquad (9)$$

We can use (9) to construct an effective wave equation for the string, which will replace the path equations (7). This approach is conceptually similar to the construction of the wave equation through a summation over particle paths in the Feynman formulation of quantum mechanics.[8] In the case at hand, however, there are some difficulties which were not present in Ref. 8, since even the simplified expression for the magnetic energy in (9) depends not on the final point of the path, $g = \Delta_0 + ... + \Delta_n$, but on the number of steps taken to reach this point. This number can be any number greater than $|g|$. It is thus not possible to construct a one-particle wave equation which is precisely equivalent to (7).

The effective wave function $\varphi(g)$ of the string is introduced by means of

$$\varphi(g) = \sum_n \varphi_n(g), \qquad (10)$$

$$\varphi_n(g) = \sum_{\Delta_1, ..., \Delta_n} c(\Delta_0, ..., \Delta_n) \delta(\Delta_0 + ... + \Delta_n, g).$$

Multiplying both sides of Eqs. (7) by $\delta(\Delta_0 + ... \Delta_n, g)$, and summing over all Δ_k and n, we find, using (9),

$$\left[f \sum_n n\varphi_n(g) - E\varphi(g) \right] + B \sum_{\Delta} \varphi(g+\Delta) = 0. \qquad (11)$$

Using the mean value theorem, we find

$$\sum_n n\varphi_n(g) = \bar{n}(g)\varphi(g), \quad \bar{n}(g) = |g| + \bar{\rho}. \qquad (12)$$

The only paths which contribute significantly to $\varphi(g)$ are those whose lengths are greater than the minimum possible length $|g|$ by an amount on the order of the radius ρ of the self-trapped state. The quantity $\bar{\rho}$ must therefore be on the order of this radius, which must itself be determined from a further calculation. (Strictly speaking, $\bar{\rho}$ may depend weakly on g, but we will ignore that dependence.)

As usual in an effective-mass method, we expand

$\varphi(\mathbf{g} + \Delta)$ in (11) in powers of Δ and use (12). We find the wave equation ($\hbar = 1$)

$$\mathscr{H}_{\mathrm{Ai}}^{(d)} \varphi(\mathbf{r}) = \eta \varphi(\mathbf{r}),$$

$$\mathscr{H}_{\mathrm{Ai}}^{(d)} = -\frac{1}{2m}\Delta + \frac{r}{a} f, \qquad (13)$$

$$\eta = E + z|B| - f\bar{\rho}/a, \qquad \frac{1}{2m} = |B|a^2, \qquad B < 0,$$

where a is the interatomic distance, $r = ga$, and d is the dimensionality of the system.

STRING ENERGY

Equation (13) can be solved exactly in the $3D$ case. The ground state of the string, in which we are interested here, is described by the wave function

$$\varphi(r) = r^{-1} \mathrm{Ai}(r/\rho - \eta/\rho f), \qquad \rho = (a/2mf)^{1/3}, \qquad (14)$$

where $\mathrm{Ai}(r)$ is the Airy function. The energy is found by requiring that $\varphi(r)$ remain finite at $r = 0$. Using the values of the zeros of the Airy function, which are given in Ref. 9, we find an expression for the quantity η. This quantity represents a lower estimate of the string energy, reckoned from the minimum electron energy zB:

$$\eta = L|I|^{2/3}|B|^{1/3}\sin^{4/3}\beta, \qquad L = \frac{2^{1/3}(9\pi)^{2/3}}{4}. \qquad (15)$$

The actual energy of the string, ε_s [i.e., the smallest eigenvalue of Eqs. (4)] is given by

$$\varepsilon_s = \eta + f\bar{\rho}/a = C\eta, \qquad (16)$$

where $C \sim 1$. In deriving this result we made use of the happy circumstance that the two terms in (16) depend in an identical way on the parameters of the problem at $\bar{\rho} \sim \rho$, according to (14). If the ratio $\bar{\rho}/\rho$ is between 1 and 3, the quantity C is between 1.34 and 2.02. The functional dependence of ε_s on the parameters of this system described by (15) and (16) is essentially exact.

To find an upper estimate $\bar{\eta}$ on the energy of the string, we can assume that as an electron moves away from the center it reaches atom g by a random walk. For this purpose, the electron must take an average of g^2/a^2 steps. Correspondingly, the potential energy of the string in a wave equation like (13) must be given by an expression $f(r/a)^2$, and $\bar{\eta}$ must be the same as the energy of the ground state of a 3D oscillator:

$$\bar{\eta} = 3(f|B|)^{1/2}. \qquad (15a)$$

With $h = 0$, according to (15) and (15a), we have a ratio $\bar{\eta}/\eta \approx (B/I)^{1/6}$. In other words, even in the case $I/B = 0.01$ this ratio is close to 2. We thus find that the upper and lower estimates of the string energy are not far apart.

To evaluate the accuracy of expression (6), which was used in deriving (14)–(16), we can assume that the angle between the spin of the atom and the field differs from β inside a sphere whose radius is that of the string in (14). Minimization of the total energy $E^M + \varepsilon$ with respect to this angle leads to a value for this angle which differs from that in (6) by an amount $\sim (I/B)^{2/3} \ll 1$.

In analyzing the $2D$ case, our first task is to formulate boundary conditions on the wave function $\varphi(r)$ at $r = 0$. It is

a simple matter to show that for any potential which vanishes at $r = 0$ the condition that $\varphi(0)$ remain finite is equivalent to the equation

$$\varphi'(r) = 0. \qquad (17)$$

To demonstrate the point, we note that as $r \to 0$ in this case Eq. (13) becomes

$$-\frac{d}{dr}\left(r\frac{d\varphi}{dr}\right) = K, \qquad K = 2m\eta\varphi(0).$$

A solution of this equation which satisfies the condition that $\varphi(0)$ remain finite is $d\varphi/dr = Kr/2$; hence (17).

In the $2D$ case, it is not possible to solve (13) exactly. Nevertheless, we can find a lower estimate η for the string energy:

$$\eta = \int \varphi \mathscr{H}_{\mathrm{Ai}}^{(1)} \varphi \, d^2r + \pi\varphi^2(0)/2m > \int \mathrm{Ai}(r) \mathscr{H}_{\mathrm{Ai}}^{(1)} \mathrm{Ai}(r) d^2r \equiv \eta_{\mathrm{Ai}}.$$

$$(18)$$

In writing (18) we used the equation $\varphi(\infty) = 0$ and the fact that the expectation value of $\mathscr{H}_{\mathrm{Ai}}^{(1)}$ in terms of the state $\varphi(r)$ is greater than the expectation value in terms of the eigenstate $\mathrm{Ai}(r)$ of this Hamiltonian.

As a lower estimate of the string energy ε_s we can thus use the quantity η_{Ai}. For the latter we find the result (15) with $L = 3.6$ by making use of boundary condition (17) and the zeros of the function $\mathrm{Ai}'(z)$, which are given in Ref. 9. To verify that the result for ε_s in the $2D$ case differs from (15) only by a factor ~ 1, in complete analogy with (16), we note that the Hamiltonian $\mathscr{H}_{\mathrm{Ai}}^{(2)}$ in (13) would be the same as $\mathscr{H}_{\mathrm{Ai}}^{(1)}$ if it were acting on a cylindrically symmetric wave function in the limit $r \to \infty$. Consequently, the asymptotic behavior of this function is $\mathrm{Ai}(r/\rho)$, with ρ from (14). In other words, the quantity ρ serves as the radius of the state again in the $2D$ case. According to the uncertainty principle, the ground-state energy must then be $\sim 1/m\rho^2$. In other words, it must be given by an expression like (16), but with a different constant.

We could reach the same conclusion by a different path—by examining corrections of arbitrary order in $\mathscr{H}_{\mathrm{Ai}}^{(2)} - \mathscr{H}_{\mathrm{Ai}}^{(1)}$. It turns out that all such corrections are on the order of (15). The term $f\bar{\rho}/a$, which also appears in the expression for ε_s, is on the same order of magnitude.

FERRON STATES IN THE SPIN-1/2 CASE

To determine whether a string is stable, we should compare its energy with the energies of ferron states. In contrast with the $S > 1/2$ case, which was studied in detail in Ref. 1, ferron states in the $S = 1/2$ case have several distinctive features if the s–f exchange integral has the behavior $A_{sf} \to -\infty$. That this is true can be seen from simply the circumstance that at such values of A_{sf} the microscopic ferromagnetic region is a potential well of depth $\sim [1 - (2S)^{-1/2}]$ for a conduction electron. With $S = 1/2$, the depth of the well vanishes. On the other hand, while an electron can move in the antiferromagnetic part of the crystal without disrupting the antiferromagnetic order in the $S > 1/2$ case, such motion would not be possible with $S = 1/2$. Consequently, the formation of a self-trapped state of some type or other is unavoidable in this case. The only question is the particular type of state. Correspondingly, the

conditions for the existence of a ferron state as given in Ref. 1 are not applicable here.

A ferron state is evidently stable if its energy is lower than that of a string. The reason why a ferron can be preferable from the energy standpoint is as follows: After magnetic-order energy is expended on the creation of a ferromagnetic region, there is no need for a further expenditure of magnetic energy in order to allow the electron to move in this region. Strictly speaking, an electron can go from the ferromagnetic part of the crystal into the antiferromagnetic part and move there by a string mechanism. However, the influence of this effect on the carrier energy could not be large, because the very existence of a ferron presupposes that the energy of the ferron is lower than that of a string. Of course the only way to determine what is preferred from the energy standpoint—a steady-state disruption of antiferromagnetic order, as in a ferron, or a disruption of this order which oscillates along with the electron, as in a string—is to carry out the corresponding calculations. Nevertheless, we can immediately assert that a magnetic field would lower the energy of a ferron, which has a huge magnetic moment, to a far greater extent than it would lower the energy of a string, which does not have such a huge moment.

To find an upper estimate λ of the ferron energy ε_f, it is sufficient to assume (a) that the ferromagnetic region is spherical in the $3D$ case and circular in the $2D$ case and (b) that the electron is entirely inside the ferromagnetic region, so its wave function vanishes at the surface of the region. In the presence of a field h, the loss of magnetic-order energy due to the replacement of the antiferromagnetic order by the ferromagnetic order is given (per atom) by the following expression, where we are using (6):

$$D = \left| \left(-\frac{\mathscr{I}}{2}\cos 2\beta - h\cos\beta \right) - (-\mathscr{I}/2 - h) \right| = 4|I|\sin^4(\beta/2).$$

(19)

In the $2D$ case, the electron component of the energy, $k^2/2m$, is determined by the first zero of the Bessel function $J_0(kR)$. We thus find the following upper estimate λ of the energy of a ferron with a ferromagnetic region of large radius R:

$$\lambda \approx 17|IB|^{1/2}\sin^2(\beta/2),$$

(20)

$$R/a \approx 0,8|B/I|^{1/4}\sin^{-1}(\beta/2) \gg 1.$$

(21)

In the $3D$ case, the corresponding qualities are given by

$$\lambda \approx \left(\frac{5}{3}\pi^{2/5} \right) |B|^{3/5}|6I|^{2/5}\sin^{4/5}(\beta/2),$$

(22)

$$R/a = |\pi B/I|^{1/5}\sin^{-2/5}(\beta/2).$$

(23)

As $I \to 0$, the upper estimates in (20) and (22) of the ferron energy become exact values of this energy. It follows from these expressions and (15) and (16) that in the limit $I/B \to 0$ the string is preferable to the ferron from the energy standpoint if there is no magnetic field. In the $2D$ case, in contrast, the string energy differs parametrically from the ferron energy only by a factor of $|I/B|^{1/6}$, which is of order unity even at $|I/B| \sim 10^{-2}$. With regard to the numerical factor in (20), we note that in the case $h = 0$, i.e., $\beta = \pi/2$, this factor is not much greater than the corresponding factor $L = 3.6$ in (15). At $h = 0$, the difference between ε_f and ε_s is

thus essentially masked by the error of the calculations. [Even in the $3D$ case, as we will show below, ε_s in (16) is greater than η in (15) by several tenths of η; in the $2D$ case, by virtue of (18), the difference between ε_s and η would apparently be even larger. The value of ε_f should be smaller than λ by an amount of the same order of magnitude in the case $|I/B| \sim 10^{-2}$, i.e., $R/a \approx 4$. This is the basis for the assertion above regarding the accuracy of the calculations.]

We thus see that we cannot draw a clear conclusion about the stability of a ferron in the absence of a magnetic field unless $|I/B|$ is very small. As the field increases, the ferron energy falls off far more rapidly than the energy of a string. Specifically, using (6), (15), and (20) we find

$$\varepsilon_f/\varepsilon_s \sim (1-x)^{1/3}(1+x)^{-2/3}, \quad x = h/2|I|.$$

Consequently, even before the sublattices collapse, the upper estimate on the energy of a ferron becomes smaller than the lower estimate on the energy of a string. The meaning here is that a ferron is definitely preferable to a string from the energy standpoint in such fields. The situation here is thus qualitatively the opposite of that in the $S > 1/2$ case, which was studied in Ref. 1: A magnetic field stabilizes a ferron, rather than destroying it.

Qualitatively the same arguments hold for the $3D$ case, although in that case the difference between the parametric dependence of the ferron energy, (23), and that of the string (15), is stronger ($\propto |I/B|^{4/15}$). For this reason, stability of a string in the absence of a field is more likely, although a string–ferron transition should occur again in this case as the field is strengthened.

It follows from (21) that with $|I/B| = 10^{-2}$ the ferromagnetic region of the ferron contains about 50 atoms and becomes larger with increasing field. If we speak in terms of a surface of finite dimensions, we see that as long as the ferron radius R is small in comparison with the pore radius r_V the r_V dependence of the ferron energy will be weak. When the entire surface becomes ferromagnetic, however, the energy will depend on r_V in the following way (the ferromagnetic region is a circle):

$$\varepsilon_f = 5,76|B|(a/r_V)^2 + 2\pi(r_V/a)^2(|I| - 2h).$$

(24)

Using (21), (6), and the condition $r_V > R$, we find the following upper estimate of the ferron energy in (24):

$$\varepsilon_f < 5,76|B|(a/r_V)^2 + \pi|BI|^{1/2} - 3\pi h(r_V/a)^2.$$

(25)

According to (25), this energy decreases with increasing pore radius. Its field dependence is the linear law in (24).

Let us compare the energy of a ferron with $r_V < R$ and that of a string with $r_V < \rho$, to represent the state of an electron at a small-radius pore. In this case the potential energy of the string in (13) can be treated by perturbation theory. For the string energy we find ($h = 0$)

$$\varepsilon_s = 5,76|B|(a/r_V)^2 + 32|I|(r_V/a).$$

(26)

It follows from a comparison of (24) and (26) that for $r_V/a < 5$ a ferron is preferable to a string from the energy standpoint even in the absence of a field. This result, of importance in its own right, also lends support to the assumption (made above) that ferrons are stable in the case $h = 0$ even at the surface of large-radius pores.

POSSIBILITY OF FERRON STATES IN AMORPHOUS SEMICONDUCTORS

In this section we take up the question of whether ferron states are possible at the surface of pores in amorphous semiconductors such as Ge and Si. These semiconductors have large numbers of pores, depending on the particular method by which the samples are prepared. In Ge and Si films grown by evaporation, for example, the number density of pores with radii $r_V < 10$ Å is in the interval 10^{19}–10^{17} cm^{-3} Å^{-1}, while the number density of pores with radii between 10 and 20 Å is in the interval 10^{17}–10^{16} cm^{-3} Å^{-1} (Ref. 10). At the surface of each pore with $r_V < 10$ Å there are several tens of atoms with dangling s–p bonds, while the number at the surface of each pore with $r_V > 10$ Å is several hundred. The orbitals of singly filled s–p states which are oriented into a pore overlap somewhat with those of the neighboring atoms. An exchange interaction thus occurs between them. The energy of this interaction is small in comparison with the energy of the chemical bond between atoms; i.e., it amounts to hundredths or tenths of an electron volt.

The exchange interaction between s–p orbitals is usually antiferromagnetic. This general rule appears to apply to the exchange between the surface atoms of pores. At any rate, there is no experimental indication of the existence of ferromagnetic layers at the surfaces of electrically neutral pores. Consequently, the magnetic order at the surfaces of pores should probably be a defective antiferromagnetic order, in view of the irregularity of the shape of the pores. We cannot at the outset rule out the possibility of a spin-glass state of the pores, but at this point we do not know whether such a state occurs in $2D$ systems of finite dimensions. On the other hand, the condition that the system be finite is sufficient for an antiferromagnetic order at sufficiently high temperatures.

Each pore can serve as either a donor or an acceptor, depending on its particular situation. Strictly speaking, the pore cannot be represented on an energy diagram of a semiconductor as a singly filled level inside a mobility gap, in the way that an individual dangling bond is represented. The reason is that the pore may be multiply ionized. This circumstance does not change the picture qualitatively, however, and the effects which stem from multiple ionization will not be discussed below.

If the pore acts as an acceptor, its ionization is accompanied by the appearance of an electron there. This electron should move among the surface atoms of the pore, occupying the same s–p orbitals as are occupied by the dangling-bond electrons. The situation essentially corresponds to the Hubbard model, and the theoretical results derived above can be applied to it: An electron can be in a ferron state at a pore. In accordance with the estimates of the preceding section of this paper, and in view of the relative insensitivity of R in (21) to the ratio B/I, we would expect that for $r_V \lesssim 10$ Å all the spins of the partially filled s–p shells of surface atoms would be in a ferromagnetic order. For $r_V \gtrsim 10$ Å, in the absence of a field, only the part of the surface of a pore where the electron is self-trapped could be ferromagnetic.

It follows from (6), (20), and (24) that, regardless of the pore size, the ferron energy will decrease with increasing field h. Because of the huge moment of a ferron, $\sim \min\{(R/a)^2 (r_V/a)^2\}$, the ferron energy will decrease to

a far greater extent than will that of an electron. The lowering of the ferron energy implies a decrease in the energy expenditure required for the transition of electrons from lower-lying levels (e.g., from the valence band) to the pore. Correspondingly, with increasing field there is an increase in the number of carriers, regardless of whether the charge is transferred by jumps of holes among normally filled low-lying local levels or by a motion of holes of a band mechanism. An increase in the number of carriers should be manifested by an isotropic negative magnetoresistance.

A ferron may form at a pore even after an electron leaves the pore to go to higher-lying levels, since the hole remaining at the pore can also render this pore partially or completely ferromagnetic. Correspondingly, the ferron energy is lowered in a magnetic field again in this case; i.e., there is a decrease in the energy expended on an upward transition of an electron. Consequently, a negative magnetoresistance could occur for a conductivity of either sign. A mechanism of this sort may also operate in the case of a spin-glass order, since ferron states are possible again in that case.[11] On the other hand, other magnetoresistance mechanisms could in general operate in amorphous semiconductors, so a competition among mechanisms might result in a fairly complex field and temperature dependence of the magnetoresistance.

Experiments show that negative magnetoresistance is indeed observed in amorphous Ge and Si, while in crystalline Ge and Si, in which there are no pores, the magnetoresistance is positive and anisotropic, in total agreement with band theory. According to Ref. 12, the magnetoresistance of a-Ge is always negative, while that of a-Si goes through a maximum at a temperature ~ 200 K and then falls off very sharply as the temperature is raised further. This maximum value is on the order of 1% at 25 kG. Kubelik and Tříska[13] state that the magnetoresistance of certain a-Si samples changes sign, from negative to positive, as the temperature is raised, while the absolute value decreases sharply. The effect of a magnetic field on the photoconductivity of a-Si and a-Ge was observed in Ref. 14. The sign of the effect was opposite that for the dark conductivity.

Although I do not know of other theories of negative isotropic magnetoresistance in a-Si and a-Ge, the qualitative agreement between the ferron theory derived here and experiment does not by itself prove that this theory is the only one possible. On the other hand, the extremely significant dependence of the luminescence intensity of these materials on very weak fields—at 10 K, a 30-G field changes the intensity by $\sim 1\%$ (Ref. 15)—is evidence that these materials acquire huge magnetic moments when charge carriers are excited. The energy of a ferron containing 100 atoms in such a field would be specifically 1% of the thermal energy, so the effect might be linked with an orientation of the ferron moments by the field. A qualitative change in the nature of the magnetoresistance upon a hydrogenization of samples, which would liquidate the dangling bonds, would be a convincing argument in favor of the magnetoresistance mechanism proposed here.

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[1] It is also common to find Ref. 5 or Ref. 16 erroneously cited as the original source instead of Ref. 6.

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