Theory of ferromagnetism in carbon foam

Daniel C. Mattis
Department of Physics, University of Utah, 115 S. 1400 E., #201 Salt Lake City, Utah 84112-0830, USA
(Received 7 January 2005; revised manuscript received 7 February 2005; published 27 April 2005)

An explanation is proposed for spontaneous magnetism in the material, "carbon nanofoam," in terms of random ferrimagnetism. Wherever a carbon nanotube branches out, an electron trap is created at the junction. Electrons occupying neighboring junctions align their spins antiparallel. Given that there are more sites on sublattice A than on the interpenetrating sublattice B, the net result is $M=m_{\rm o}|N_A-N_B|\neq 0$. Ultimately, some excess charge (and concomitant magnetism) is expected to dissipate into the atmosphere.

DOI: 10.1103/PhysRevB.71.144424 PACS number(s): 75.75.+a

INTRODUCTION

In view of the fact that most carbon-based solids such as graphite are resolutely nonmagnetic (Curie temperatures of, at most, a fraction of 1 K) it is amazing, unusual, and unexpected that any undoped carbon network, having only paired s and p electrons at its disposal, should exhibit substantial, cooperative, ferromagnetism. However, such is the case in a polymer of C_{60}.[1]

Leaving regular lattices aside, the more recent discovery of transient or possibly permanent *ferromagnetism*[2] in a *random* material, "carbon nanofoam,"[3] seems to support a fairly general theoretical model that the author has been independently researching for the past two years.[4] The present paper proposes to explain the ferromagnetism of carbon foam in the light of this theoretical model.

The four principal ingredients in the present explanation for nanofoams are simply:

(1) the presence of channels that allow electrons to move or communicate — the clusters have typical lengths of some 6 nm,

(2) the formation of bound states localized at the branching points (known as "tetrapods") of the nanotubes, capable of trapping electrons,

(3) the *anti*ferromagnetic correlation of any two electrons trapped on neighboring tetrapods, and

(4) unequal number of sites $N_A\neq N_B$ on the interpenetrating A and B sublattices that contain electrons of spin up and down, respectively.

These points are totally sufficient to explain the phenomena. However, because the foam is a random material, the explanations will perforce be more qualitative than quantitative, although we hope they are persuasive.

The first point is clear, the second is somewhat controversial (we shall address several possibilities there), the third is rigorously provable, and the last is surprising. Let us therefore start with this last, topological, feature.

FERROMAGNETISM OUT OF ANTIFERROMAGNETIC BONDS

In 1989, Elliott Lieb[5] presciently proved a theorem dealing with the possible ferromagnetism of interacting electrons on a "Hubbard model" type lattice. The premises that underpin this theorem are as follows: repulsive interactions U restricted to pairs of electrons that occupy a same site; a bipartite lattice (i.e., a lattice that can be decomposed into two, where sites on the A sublattice connect only to sites on the B sublattice and vice versa); and a number N_{el} of electrons that approximately equals the number of sites N capable of accommodating an electron, where $N=N_A+N_B$ (i.e., near "half-filling").[6] Once these conditions are satisfied, Lieb's theorem states that the ground state magnetic moment of the lattice is $M=m_o|N_A-N_B|$. Here, m_o, the intrinsic magnetic moment of an electron spin, is just the Bohr magneton. It is my belief that the carbon foam of Rode *et al.*[2,3] inherently satisfies most or all the conditions under which the theorem is valid.

It is possible to understand this ferromagnetism qualitatively without delving into any mathematics. As we shall show, states are localized within the energy gap at every tetrapod [the junction where the nanotubes branch out (see Fig. 1)]. Because double occupancy of these low-lying states is suppressed by an energy gap of $O(U)$ against charge fluctuations, electrons that are trapped at a tetrapod retain their spin degrees of freedom at half-filling, if not the ability to move.[7] Because nearest-neighbor electrons generally have lower energy if their spins are antiparallel, this electronic system maps onto a Heisenberg antiferromagnet.

In an earlier work,[8] Lieb and this author discussed a more general bipartite *spin lattice* of this type, in which N_A spins S_A of an A sublattice are antiferromagnetically coupled to neighboring spins S_B on the B sublattice. We proved the ground state includes states of *maximum* total spin angular momentum S_{tot} — a quantity that can vanish *if and only if* $N_AS_A=N_BS_B$. It follows that the ground state for arbitrary N_A, N_B generally exhibits a macroscopic magnetic moment.

In the special case that $S_A=S_B=$spin 1/2 of a localized electron, *both* the aforementioned study of the Heisenberg model *and* Lieb's theorem for a Hubbard model with an occupation number of one electron per site, predict the very same ferromagnetic[9] ground state on a bipartite lattice with $N_A\neq N_B$, regardless whether the structure is perfectly ordered or as random as a foam. Ultimately, we shall ask, and then answer, why N_A would differ from N_B in a foam. However, first let us deal with some details.

TOPOLOGICAL ISSUES

The magnetism and spatial structure of a carbon nanofoam was originally discussed in a study by N. Park *et al.*[2] in

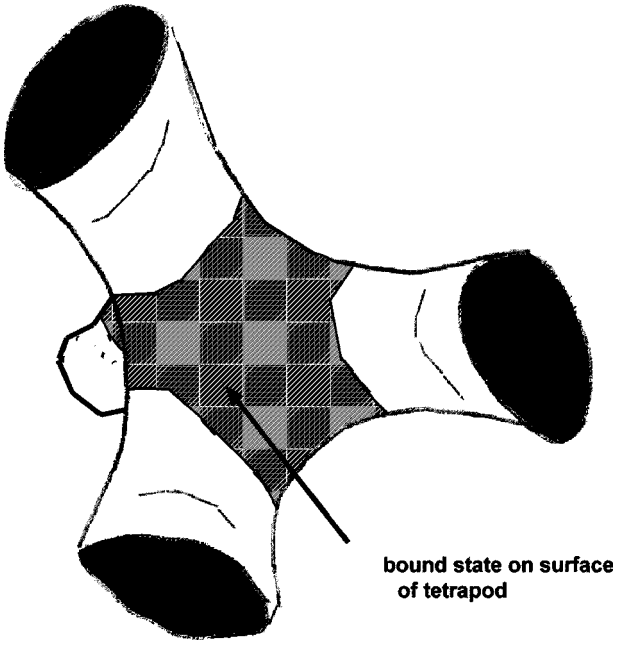

FIG. 1. Wherever a nanotube branches into two or more, pseudo-donor or pseudo-acceptor bound states form. Their wave functions (roughly in the shape of a diaper) are carved out as a linear combination of the Bloch states in the respective bands of the semiconductor (the single-walled carbon nanotube).

which extra spins were assigned to unpaired chemical bonds at the junctions where one nanotube branches out into three,[10] as in their Fig. 1 (cf. our Fig. 1) In the latest paper by Rode *et al.*,[11] the material and the valence-band states at the tetrapods are again described in some detail. However, as this picture yields four uncompensated spins per tetrapod, it is difficult to see how such a theory could produce anything other than a *locally nonmagnetic* state once the antiferromagnetic interactions among nearest neighbors *within* each tetrapod are taken into account — unless the two-body Coulomb interaction rendered it unprofitable for more than one electron to occupy the dangling bonds at each tetrapod. This we shall have to assume.

The present theory is not all that different. Some, perhaps all, the electrons that participate in ferromagnetism are loosely bound in a bound-state linear combination of the *conduction* band states of the nanotubes, and are therefore not part of the stable network of bonding electrons that populate their *valence* bands. Our tight-binding calculations (admittedly cruder than the density functional approach taken in ref. 3) yields just one bound state dropping below the conduction band at each tetrapod and, by symmetry, a bound state above the valence bands at each tetrapod. According to *any* theory, the *branching* is the essential ingredient in the formation of bound states in the energy gap.

WHERE DO EXCESS ELECTRONS COME FROM?

One supposes that in the cataclysm that creates the foam[2,3,11] electrons are easily stripped from the constituent materials and redistributed. Indeed, the ease with which semiconducting single-walled carbon nanotubes can accept charge was recently demonstrated by Lee, Gip, and Heller[12] who, by electrostatically charging such nanotubes (a few nanometers in diameter and micrometers in length), created *reversible p-n* or *n-p* junctions. Their experiment is evidence that electrons or holes are easily introduced into the conduction or valence bands of the single-walled nanotubes and is also strong evidence for the existence of a finite *semiconducting energy gap* (rather than metallic behavior).

We assume that any surplus of electrons that pervades the negatively charged foam drops from the lowest energy levels in the conduction bands into bound states that lie even lower: the bound state created at each tetrapod by the branching geometry.

FORMATION OF BOUND, LOCALIZED STATES, AND THEIR INTERACTIONS

What is the nature of these bound levels? If the surplus electrons were confined to the "vacuum" *inside* the cylinders and subject to the boundary conditions $\psi=0$ at the surfaces, a bound state[13] *would* drop below the continuum at each bulge, bend, or branch. (The boundary condition $\psi=0$ would be used to ensure that the trapped particles do not violate the Pauli principle when they reach the carbon network at the surface of the cylinders.) In such a scenario, one electron could be physically confined to the interior of each tetrapod.[14]

Given the Lee, Gip, and Heller experiments[12] in which *either* electrons *or* holes[15] were easily and symmetrically introduced into the Bloch bands of the virgin material, it is more reasonable to hypothesize that the excess electrons in carbon foam live as linear combinations of states within bands *on* the skin of the tubes and that a localized bound state acting as a pseudo-donor level, condenses within the energy gap, below the continuum, at each tetrapod junction. The probability function $|\psi|^2$ of this bound state would take the form of a "diaper" covering the intersection of the nanotubes, as in Fig. 1.

The band structure calculations that would be required to prove that a bound state occurs at each tetrapod (even in hexagonal tight-binding approximation often used to simulate the band structure of single-layered graphite),[16] all are too difficult for the task. Therefore we resorted to a simplified tight-binding model that may be viewed as an "existence theorem" that illustrates the desired result. In reality, the details do not matter — as long as we agree that a bound state is created at each and every tetrapod.

Figure 2 illustrates two neighboring tetrapods in the minimalist simple quadratic tight-binding version that we shall adopt (instead of the "exact" hexagonal texture). At each lattice point, a Wannier orbital constructed out of a given band is connected to its four nearest neighbors by a matrix element t. For the lowest *transverse* mode on each infinite cylinder (circulating around a cylinder) the *lowest-lying continuum* of propagating states has a minimum at $\varepsilon_o=-4t$ and maximum at $\varepsilon=0$. [For higher transverse modes, higher-lying overlapping continua are found at $-2t<\varepsilon_{\pm 1}(q)<+2t$ and $0<\varepsilon_2(q)<4t$.] Equating the bandwidth $(8t)$ to the conduction bandwidth of graphite[16] ($\approx$9 eV) yields $t\approx 1.1$ eV.

We construct the bound-state wave function at a given tetrapod by tridiagonalization; i.e., by reduction of the Schrödinger equation to a set of concentric waves originating at the intersection of four cylinders. In this manner, we easily determined the existence of a bound state, associated with and caused by the geometry which has a maximum amplitude at the intersection and decays exponentially at distances $n \times a_0$ from the origin (a_0 being the lattice parameter) as $\psi_n \propto \exp -|n|\lambda$, where $\exp(-\lambda)=(\sqrt{3}-1)=0.7132$. The energy of this bound state is $\varepsilon_B=-2t(1+\cosh\lambda)=-4.098\,08t$. It lies $0.098\,08t$ below the conduction-band continuum. We call this state the "pseudo-donor" level, "pseudo" because it is associated with geometrical constraints on the conduction-band states and not the orbital state of a donor atom. Neither is it a "dangling bond" caused by disorder or ionic mismatch.

Note that the same situation obtains for the valence band, for if one uses the appropriate valence-band Wannier orbitals, one finds a pseudo-*acceptor* state lying *above* the top of the valence-band continuum at each tetrapod, in an amount also $0.098\,08t$ (the t should be similar for the two bands) which may or may not be occupied depending on the position of the Fermi level. In the event that the energy gap E_g is not too large, i.e., that $E_g < 0.196\,16t = 0.2$ eV, the pseudo-acceptor level could actually lie *above* the pseudo-donor level, so that any excess electrons would populate the pseudo-donor level first. However, that would not affect the conclusion. In both cases, the two-body Coulomb interaction — which is of little consequence in extended states — is quite sufficient to prevent double occupancy of a localized level extending over only a few nanometers. Thus, as a minimum assumption, we postulate that only one, unpaired, electron can occupy each tetrapod.

CALCULATION OF THE EXCHANGE SPLITTING

As is the case for the two electrons of a H_2 molecule, it can be proved rigorously that the two electrons living on *nearest-neighbor pods* prefer a *joint singlet* state over the spin triplet, by an amount defined as J.[17] The spin dynamics of bound-state electrons is expressed by an Heisenberg Hamiltonian consisting of the sum over all nearest-neighbor, spin-spin bonds $H_{i,j}=J_{ij}\boldsymbol{S}_i \cdot \boldsymbol{S}_j$, where each $J>0$. (As in any *ferri*magnet, we find, paradoxically, that the explanation of spontaneous spin magnetism proceeds from the *antiferromagnetic* correlations of nearby sites) Next, by exact diagonalization of the two-tetrapod geometry of Fig. 2, we find *bonding* states connecting neighboring tetrapods $n=3$ lattice parameters apart, and that they lie $0.225t$ below the continuum.[18]

The "effective" hopping matrix element t_{eff} connecting a state on one tetrapod to the next at a distance n atomic spacings is either $1/2\times$ the energy splitting between the continuum and the bonding state or $1/2\times$ the energy splitting between the bonding state and the *antibonding* state (where it exists). Thus, $t_{eff}=1360k_B$ at $n=3$; at $n=6$ it is $t_{eff}=385k_B$, and at $n=8$ it drops to $t_{eff}=17k_B$ Hubbard's "U" is independent of n and is estimated at $U \approx 1500k_B$. Combining these results, we obtain in second-order perturbation theory: $J=4t_{eff}^2/U$; i.e., $J=1360k_B$ if $n=3$, $J=395k_B$ for $n=6$, and $J=1k_B$ for $n=8$. To explain the experimental value of J as deduced below from the experimental data, we shall determine that the average separation between tetrapods n should range between 6 and 8. In a random foam, of course, there exists a range of values and we can only deal with their averages.

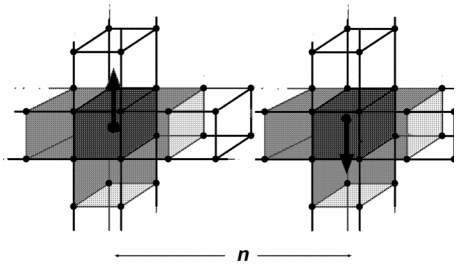

FIG. 2. Shows relative spin orientation of two electrons bound at two neighboring "tetrapods," in a discretized "tight-binding" version. A Wannier function of the conduction band is centered at each point of the gridwork and connects to its nearest neighbors by a "hopping integral" t estimated from band structure calculations (see Ref. 16) The exchange parameter J of the two bound electrons at a distance $n=7$ is calculated to be approximately $J=170k_B$ (in temperature units) leading to a Curie temperature $\approx O$ (100 K), in qualitative accord with experimental findings (see text).

WHY DO THE *A* AND *B* SUBLATTICES DIFFER?

Now, let us show by example that, absent some hidden symmetry considerations, the numbers of sublattice sites N_A and N_B in an arbitrary array will *always* differ by a nontrivial amount. Figure 3 shows a Cayley cluster of branching number 2. Half the sites are at the surface. In such a case, $N_A=2N_B$ regardless how large N_B may be, and the magnetic moment is $M=m_0N_B$. As described by its inventors,[2,3,11] *carbon nanofoam* has an open-weave structure in which each channel branches out into three, in which case, $N_A=3N_B$ and the total magnetic density should be higher: $M=2m_0N_B$.

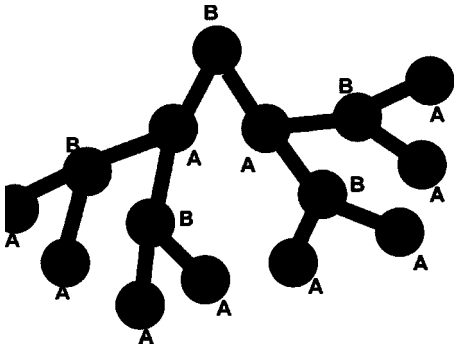

FIG. 3. Three generations of a "Bethe lattice" nearest-neighbor antiferromagnet with bifurcation are shown; coupling constant J, branching number 2. If each of the ten sites marked A contains an electron with its spin "up" and each of the five sites B contains one with its spin "down," the ground state belongs to total $S_{tot}=5/2$. Elimination of the B's results in Bethe lattices of A's that are *ferromagnetically* coupled (the coupling constant is $-J^*$, a function of J and kT) and a branching number 4. Given J and T, Fig. 4 shows the calculated ferromagnetic couplings J^*/kT as a function of J/kT.

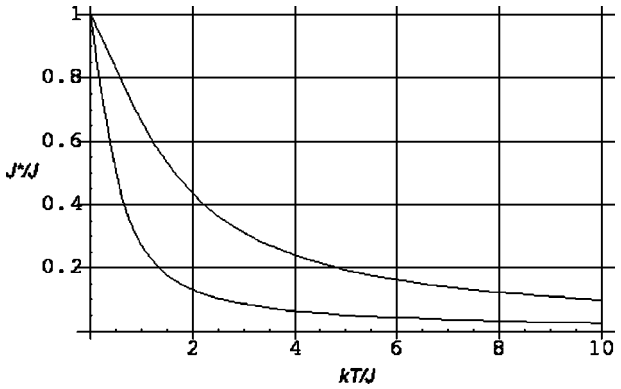

FIG. 4. Effective ferromagnetic coupling constant J^* vs kT, both in units of J. Upper curve is for the Ising model [Eq. (2)], lower curve for the spin-1/2 Heisenberg model [Eq. (3)].

RENORMALIZED COUPLING CONSTANTS

Given the *antiferromagnetic* A, B couplings J, we obtain an order-of-magnitude estimate of the renormalized *ferromagnetic* coupling constant J^* between spins on *next*-nearest-neighbor pods by the following approximate but qualitatively correct scheme.

Supposing the A's to be the majority sites, we eliminate any B's that separate the closest pairs of A's. Ising-like bonds provide a simple example. One evaluates $\langle \exp -JS_B(S_{A1}+S_{A2})/kT\rangle_B$ averaging over the values of the intervening B spin $S_B=\pm 1$. This yields a simple formula

$$\langle e^{-JS_B(S_{A1}+S_{A2})/kT}\rangle_B = \cosh^2(J/kT) + S_{A1}S_{A2}\sinh^2(J/kT) = (\sqrt{\cosh 2J/kT})e^{+K^*S_{A1}\cdot S_{A2}} \quad (1)$$

where $\tanh K^*=\tanh^2 K$, and $K^*=J^*/kT$ and $K=J/kT$. The ratio J^*/J is a function of T:

$$\frac{J^*}{J}=\frac{\log(\cosh 2K)}{2K}, \quad (2)$$

which is the Ising model.

The ratio J^*/J decreases from a maximum 1 (at low T) to 0 (at high T) as shown in Fig. 4. Heisenberg bonds are more realistic but also more complicated to evaluate; therefore, we just quote the final result. Setting $\hbar=1$, we write each spin 1/2 in the form $\vec{S}=(\sigma_x,\sigma_y,\sigma_z)/2$, where the σ's are the three Pauli matrices. The average $\langle \exp -J\vec{S}_B\cdot(\vec{S}_{A1}+\vec{S}_{A2})/kT\rangle_B$ over states of B have to be re-expressed in the form $C(K)e^{K^*\vec{S}_{A1}\cdot\vec{S}_{A2}}$. After some algebra, one obtains

$$\frac{J^*}{J}=\frac{\log\varphi(K)}{K} \quad (3)$$

(the Heisenberg model), where $\varphi(K)\equiv(e^K+2e^{-K/2})/3$ and $C(K)=[\varphi(K)]^{3/4}$. This too is plotted in Fig. 4. Finally, we note it is an empirical fact that *all* the regular three-dimensional (3D) geometries (cubic, hcp, etc.) yield a Curie temperature $kT_c\approx 0.75zJ^*$ for a lattice of Ising spins[19] $|S|=1$, where z is the coordination number of the lattice of ferromagnetic bonds J^*. In the more relevant case of Heisenberg ferromagnets of spins 1/2, one estimates a similar $kT_c\approx 0.5zJ^*$ for all regular 3D geometries.

For the purposes of our estimate, it is only necessary to assume the three-dimensional foam does not deviate substantially from this common range of values. Supposing the experimental T_c to be O (100 K) as experimentally observed and setting $\langle z\rangle=3$ (somewhat arbitrarily, but z is not a sensitive parameter), one inverts Eq. (3) numerically[20] to *infer* the order of magnitude of the original, "physical," antiferromagnetic coupling J that links nearest-neighbor spins. Our calculation for the Heisenberg model yields $J/k_B=T_c/0.6\approx 167$ K. According to the preceding calculations, this corresponds to interpod separations n in the most reasonable range: $6\leqslant n\leqslant 8$.

Once the A spins order ferromagnetically at temperatures below T_c, the B's follow, albeit antiparallel to the A's. Thus, a spontaneous moment M proportional both to $m_0|N_A-N_B|$ and to an order parameter $\sigma\equiv 2\langle|S_{j,z}|\rangle$, with $0\leqslant\sigma\leqslant 1$, persists at all $T<T_c$.

COMPARISON WITH EXPERIMENT AND CONCLUSION

How sturdy is the predicted ferromagnetism, in light of the facts? Experimental observations of ferromagnetism with a Curie temperature of $\approx$100 K and its subsequent disappearance in some samples after a few hours, suggest it to be an evanescent phenomenon.

We favor a picture in which localized charges are initially adequate to sustain the ferromagnetism in some regions of the carbon foam. However, as electrons at the periphery are repelled by the overall negative charge and escape into the atmosphere, the ferromagnetic regions are ultimately reduced to those few clusters from which electrons are unable to escape. If in any region the filling factor of the localized states drops substantially below unity, a paramagnetic (i.e. nonferromagnetic) Fermi liquid will replace the ferromagnetic phase. Whether the ferromagnetic foam will then exhibit ordinary metallic behavior relates to a simpler question, of whether the connectivity of the electron liquid lies below or above the percolation threshold of this random lattice. Regardless, the ac conductivity (i.e., microwave or *IR* Drude absorption) should then exhibit metallic characteristics.

In summary, we have a simple explanation for the ferromagnetism of carbon nanofoam, in terms of unpaired electrons loosely localized on the tetrapods. These particles populate shallow bound states carved out of Bloch bands as the result of bends and bifurcations of networks of nanotubes. A "Coulomb barrier" prevents dual occupancy of such states; hence, each localized particle carries an uncompensated spin. On a branching network the antiferromagnetic interactions of the localized spins with their neighbors results in a net, macroscopic, magnetic moment. This magnetic moment disappears once the Fermi level drops below the bound-state energy, the localized states are no longer all occupied, and charge transport is allowed. In this way we can explain both the existence and disappearance of the magnetism that has been observed.

ACKNOWLEDGMENTS

The author thanks Dr. A.V. Rode for emails, reprints, and for forwarding me the preprint of Ref. 11, is deeply grateful to Dr. Sam Bader (ANL) for pointing out this phenomenon as reported in the New York Times (see Ref. 2), and thanks Dr. Elliott H. Lieb and Dr. Oleg Starykh for their helpful remarks.

[1] For weak ferromagnetism observed in graphite at low temperatures, after bombardment by protons, see P. Esquinazi, D. Spemann, R. Höhne, A. Setzer, K.-H. Han, and T. Butz, Phys. Rev. Lett. **91**, 227201 (2003). Weak room-temperature ferromagnetism was first observed in polymerized C_{60}: T. L. Makarova, B. Sundqvist, R. Höhne, P. Esquinazi, Y. Kopolevich, P. Scharff, V. A. Davydov, L. S. Kashevarova, and A. V. Rakhmanima, Nature (London) **413**, 716 (2001).

[2] N.Y. Times, 6 April 2004: "… the newest form of carbon … will stick to a refrigerator for a couple of hours …". N. Park, M. Yoon, S. Berber, J. Ihm, E. Osawa, and D. Tománek, Phys. Rev. Lett. **91**, 237204 (2003).

[3] A. V. Rode, S. Hyde, E. Gamaly, R. Elliman, D. McKenzie, and S. Bulcock, Appl. Phys. A: Mater. Sci. Process. **69**, S755 (1999).

[4] D. C. Mattis, J. Stat. Phys. **116**, 773 (2004); D. C. Mattis (unpublished).

[5] E. H. Lieb, Phys. Rev. Lett. **62**, 1201 (1989); Phys. Rev. A **62**, 1927 (1989).

[6] As a condition for this theorem to apply, there is no requirement that the lattice structure exhibit either short- or long-range order nor that $N_A = N_B$. $U > 0$ is not required to be large; however the "filling factor" is required to be one electron per site or thereabouts.

[7] According to the fluctuation-dissipation theorems or to the Kubo formulas, there can be no dc electrical conduction without charge fluctuations, so that at half-filling when the Coulomb repulsion discourages motion from site to site, these electrons are not metallic but form a "Mott insulator."

[8] D. C. Mattis and E. H. Lieb, J. Math. Phys. **3**, 749 (1962)

[9] Some might call it *ferri*magnetic by analogy with magnetism in the ferrites.

[10] However, given that chemical bonds are generally stable and overall neutral, it is somewhat difficult to reconcile the explanation in Ref. 2, couched in terms of magnetic moments arising from carbon–carbon *s-p bonding* orbitals, with their observations that the virgin ferromagnetic material is initially negatively charged and that in the course of a few hours it may lose both charge and magnetic moment.

[11] A. V. Rode, E. G. Gamaly, A. G. Christy, J. G. Fitz Gerald, S. T. Hyde, R. G. Elliman, B. Luther-Davies, A. I. Veinger, J. Androulakis, and J. Giapintzakis, Phys. Rev. B **70**, 054407 (2004). *Carbon nanofoam* is a material "… consisting of carbon nanotubes clusters of diameter 6–9 nm randomly interconnected into a web-like random foam … [having] the lowest gravimetric density (~ 2 mg/cm^3) ever reported for a solid and a large surface area … of 300–400 m^2/g." Otherwise put, one gallon weighs less than 1/4 ounce.

[12] J. U. Lee, P. P. Gipp, and C. M. Heller, Appl. Phys. Lett. **85**, 145 (2004).

[13] Not a "donor level" according to the usual definitions, as it is not carved out of the conduction-band states but lives in the interior of the cylinders. This is the picture we originally envisaged for a geometrically structured semiconductor (e.g., intrinsic silicon) in D. C. Mattis, Ref. 3.

[14] The simple explanation is: electrons localized at a wide enclosure, such as in the interior of a tetrapod, do not have sufficient kinetic energy to travel freely down the narrower waveguides that are the nanotubes. Some early references: R. C. T. da Costa, Phys. Rev. A **23**, 1982 (1981); P. Exner and P. Seba, in *Stochastic Methods in Mathematics and Physics*, edited by R. Gielerak and W. Karwowski (World Scientific, Singapore, 1989), pp. 375–384; U. Fano, in *Semiclassical Descriptions of Atomic and Nuclear Collisions*, edited by J. Bang and J. deBoer (Elsevier, Amsterdam, 1985); J. Goldstone and R. L. Jaffe, Phys. Rev. B **45**, 14 100 (1992); J. C. Charlier, Acc. Chem. Res. **35**, 1063 (2002) and Ref. 4, all treat the problem of wave function localization at singularities in channels.

[15] As "missing" electrons ("holes") can only exist within the occupied valence bands of the material of the skin, we must assume, by symmetry, that *additional* electrons also live within the Bloch bands of the surface network; i.e., on the skin and not within the hollows.

[16] See T. Enoki, M. Suzuki, and M. Endo, *Graphite Intercalation Compounds and Applications* (Oxford University Press, New York, 2003), pp. 143ff.

[17] E. H. Lieb and D. C. Mattis, Phys. Rev. **125**, 164 (1962).

[18] Antibonding states disappear into the continuum at this separation but appear when neighboring tetrapods are $n=6$ lattice distances apart or greater. At $n=6$ the energy splitting is $0.07t$, and at $n=8$ the energy splitting is $0.033t$ (and drops exponentially by an additional factor ≈ 0.71 for every additional point of separation).

[19] From high-T series expansions: see D. C. Mattis, *The Theory of Magnetism* (Springer-Verlag, New York, 1985), Vol. II.

[20] The interested reader can similarly invert Eq. (2), as can be done analytically.