Commensurate and modulated magnetic phases in orthorhombic AC$_{60}$

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Abstract

Competing magnetically ordered structures in polymerized orthorhombic AC$_{60}$ are studied. A mean-field theory for the equilibrium phases is developed using an Ising model and a classical Heisenberg model to describe the competition between inter- and intra-chain magnetic order in the solid. In the Ising model, the limiting commensurate one-dimensional and three-dimensional phases are separated by a commensurate three-sublattice state and by two sectors containing higher-order commensurate phases. For the Heisenberg model the quasi-1D phase is never the equilibrium state; instead the 3D commensurate phases exhibits a transition to a continuum of coplanar spiral magnetic phases.
Recent experiments have revealed that $AC_{60}$ (where $A$=K, Rb) undergoes a first-order structural phase transition from a high-temperature face centered cubic (fcc) structure to a low-temperature orthorhombic phase [1]. The structure of this new low-temperature phase is quite interesting since the lattice parameter along the polymer direction ($c$ axis) is only 9.1 Å. This distance implies a separation between nearest-neighbor molecules along this axis as small as $\sim$2 Å, and has led to the suggestion that the fullerene molecules in this phase polymerize to form an ordered crystalline array of quasi-one-dimensional (quasi-1D) chains, resembling a lattice of aligned “necklaces” of fullerene molecules. Moreover, below 50 K this orthorhombic phase undergoes a second electronic phase transition, which Chauvet et al. argue arises from a spin-density-wave instability within the quasi-1D chains [1].

More detailed electronic structure studies do not support this interpretation [2]. The conduction band calculated for the orthorhombic phase shows substantial dispersion for the doped carriers both parallel and perpendicular to the polymer direction. Furthermore, by treating the effect of a short-range repulsive potential on this paramagnetic state within the random-phase approximation (RPA), one finds that the metallic phase of this structure favors magnetic fluctuations to a three-dimensionally ordered two-sublattice state, with spin polarizations alternating on the corner and body-centered sites of the pseudo-body-centered orthorhombic cell [2]. Indeed, this spin structure is stable for quite modest values of the repulsion strength, and is likely associated with the 50 K transition observed experimentally.

However, it is plausible that a dilation of the interchain galleries, such as might be achieved by alloying the alkali donors with larger spacer molecules, could lead to the one-dimensional situation envisioned by Chauvet et al. If so, the transition of the magnetic structure from the three-dimensional ordered phase to the quasi-1D phase is of some importance, and is the subject of this paper. We study the transition from three-dimensional to one-dimensional magnetic structures using both an Ising model and a classical Heisenberg model to describe the spin dynamics. Interestingly, as we show below, the passage from the three-dimensional ordered structure to the quasi-1D structure is not an easy one. In fact, at $T = 0$ the quasi-1D modulated magnetic phase appears as an equilibrium phase in the
Ising model but not the Heisenberg model for this system. In the former case, the ordered quasi-1D magnetic structure is separated from the three-dimensional structure by an assortment of intervening modulated magnetic phases, and in the latter case it is preempted by a continuum of spiral magnetic phases.

The structure of the pseudo-body-centered orthorhombic (pseudo-bco) phase is sketched in Fig. 1(a). The measured lattice parameters (for RbC$_{60}$) are $a=14.23$, $b=10.11$, $c=9.14$ Å. There are two candidate orientational structures for the fullerene molecules on this Bravais lattice; the measured x-ray diffraction intensities at present are unable to distinguish between a model with fixed orientations (space group Pmnn) and a model with binary orientational disorder (space group Immm). For simplicity, we assume here a true bco Bravais lattice with a single orientation. The Brillouin zone for this bco cell is sketched in Fig. 1(b). In our model, each Bravais lattice site of this structure is presumed to localize a single electron, with the coupling between the sites described by the Hamiltonian

$$H = \frac{1}{2} \sum_{i,j} J_{ij} \left( S_i^z S_j^z + \frac{\lambda}{2} (S_i^+ S_j^- + S_i^- S_j^+) \right),$$

where $S_i^\pm = S_i^x \pm i S_i^y$. We consider the limiting cases of the Ising model ($\lambda = 0$) and the Heisenberg model ($\lambda = 1$), with the spins treated classically.

The sum in Eq. 1 runs over the first ten sites $j$ surrounding any lattice site $i$. This sum thus includes all the interactions $J_1$ between a reference site and its eight neighbors along the body diagonal of the bco cell, and the interaction $J_2$ to the two nearest neighbors along the polymer direction. Note that this spin Hamiltonian can be frustrated, since for the choices $J_1 > 0$ and $J_2 > 0$ antiferromagnetic correlations along the body diagonal must compete with antiferromagnetic correlations along the polymer chain. For the actual RbC$_{60}$ structure, our calculations within the RPA show that the system is in fact not frustrated, and that both of the effective interactions favor the two-sublattice structure discussed in Ref. [2], that is, we have a situation with $J_1 > 0$ and $J_2 < 0$. More distant interactions within each of the chains also favor ferromagnetic intrachain order. However, one can imagine that by reducing the size of the interchain hopping amplitudes one ultimately arrives in the
regime with $J_2 >> J_1 > 0$, which would then favor the quasi-1D spin configuration originally proposed by Chauvet et al [1]. In the following we label these two limiting commensurate reference states $C_{3D}$ (for the three-dimensional state) and $C_{1D}$ (for the one-dimensional state). Schematic representations of these spin configurations are shown in Fig. 2.

The general structure of the phase diagram for these colinear states, shown in Fig. 3(a), can be understood by comparing the free energies of the competing colinear states, $C_{1D}$ and $C_{3D}$, as we vary the interaction ratio $J_2/J_1$. Within the Ising model, mean field theory yields a multicritical line at $J_2/J_1 = 2$, which separates the $C_{3D}$ phase from the $C_{1D}$ phase. Each of these phases is in turn separated from the high-temperature disordered phase by a second-order phase boundary, denoted by solid lines. There are an infinite number of coexisting phases along vertical dashed line, since the line locates the critical interaction ratio where the creation energy vanishes for a domain wall which slips the stacking sequence of the laterally ferromagnetically ordered layers by one lattice spacing along the polymer axis.

The situation is more interesting if one allows for the possibility for a longer range modulation of the spin texture. Consider first the Ising limit, given by $\lambda = 0$. The mean-field inverse susceptibility in the paramagnetic phase of the model has the form $\chi^{-1}(q,T) = S_o^2 J(q) + kT$, where $S_o^2 = 1/4$ and $J(q) = \sum J_{ij} \exp(iq \cdot R_{ij})$. For a given value of $J_2/J_1$, we then seek the critical wave vector $q_c$ which minimizes $J(q)$. Examination of the evolution of $q_c$ reveals that this system exhibits four limiting instabilities from the paramagnetic phase: (a) For $J_2/J_1 < 1$, the dominant fluctuations are at the X point of the bco zone, $(2\pi/a, 0, 0)$; below the critical temperature, this leads to the $C_{3D}$ spin structure. (b) For $1 < J_2/J_1 < 2$, the ordering wave vector evolves continuously from the X point towards the G point, $(2\pi/a, 0, 2\pi/3c)$. (c) For $J_2/J_1 = 2$, the dominant fluctuation is obtained exactly at the G point. This leads to a commensurate three-sublattice antiferromagnetically ordered phase, $C_{3s}$, which will be briefly discussed below. (d) For $2 < J_2/J_1$, the modulated structure is again incommensurate, with the ordering wave vector evolving between the G point and the point, $(2\pi/a, 0, \pi/c)$. The one-dimensional limit of this problem corresponds
to a condensation at any wavevector on the plane $q_z = \pm \pi/c$.

For $0 < T < T_c$ we can investigate the properties of the low-temperature ordered phases by solving self-consistently the linear stability relations $\sigma_i = \sigma_o \tanh(\beta h_i)$, where the field is $h_i = -\sum_j J_{ij} \langle \sigma_j \rangle$. The resulting phase diagram is shown in Fig. 3(b). As one expects in the frustrated Ising model, the degeneracy along the original multicritical line is broken by the entropic contributions to the free energy $[4]$, and at finite temperature one finds that a $T = 0$ multicritical point branches into two sectors containing modulated incommensurate (actually, higher order commensurate) phases, $I$ and $I'$, and a locked commensurate threesublattice phase, $C_{3s}$. This intermediate commensurate phase is a modulated phase with the amplitude $\sigma_z(z) = \sigma_o \sin(2\pi z/3c)$. It thus consists of lateral planes of fullerene molecules ferromagnetically aligned within a layer, with antiferromagnetic ordering across isolated pairs of neighboring layers, leaving the third layer in the cell unpolarized; this is shown schematically in Fig. 2. The regions $I$ and $I'$ are themselves further partitioned into a denser set of higher order commensurate phases.

We now remove the scalar constraint on the spin degree of freedom, and treat the Heisenberg vector-spin model of Eq. (1) with $\lambda = 1$. The orientation of the spin on the $i$-th lattice site can be specified by an angle $\Omega_i$ locating a point on the surface of the unit sphere. Within the mean field theory, expanding around the disordered phase, we consider a normalized trial density matrix of the form $\rho(\Omega) = (1/4\pi) (1 + \sum_\alpha p_\alpha K_\alpha(\Omega))$ with $\alpha = x, y, z$ labeling the three real normalized vector harmonics $(K_x, K_y, K_z) = \sqrt{3/4\pi} (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$. The thermal average of the $\alpha$-th component is thus $\langle S_\alpha \rangle = \sqrt{1/12\pi} S_o p_\alpha$. The mean-field free energy per site in this model has the form

$$f = \frac{1}{2N} \sum_{ij,\alpha} J_{ij,\alpha} \langle S_{i\alpha} \rangle \langle S_{j\alpha} \rangle + \frac{kT}{N} \sum_{i,\alpha} \int d\Omega_i \rho(\Omega_i) \log \rho(\Omega_i).$$

To study the equilibrium magnetic states of the system, we minimize this trial free energy with respect to the coefficients $p_\alpha$. For $T \ll T_c$ the expansion in $K_\alpha$ is inadequate, and we replace it by an expansion in a set of gaussians uniformly distributed over the surface of the
unit sphere.

To quadratic order in the $p_\alpha$, the free energy in this vector model takes the form:

\[ f = \frac{1}{8\pi} \sum_{q,\alpha} p_\alpha(q) p_\alpha(-q) \left( \frac{S^2_\alpha J(q)}{3} + kT \right). \]  

(3)

The susceptibility thus diverges on the same locus as found above for the Ising model, and leads to the same high-temperature phase boundary as shown in Fig. 3(b). The vector character of the spin qualitatively changes the low-temperature behavior of the model, however. At $T = 0$ the commensurate $C_{3D}$ phase remains stable only up to the critical point $J_2/J_1 = 1$. This can be seen most directly by studying the long wavelength spin fluctuations around the ordered $C_{3D}$ state. To do this we adopt a semiclassical model, in which the equation of motion for a spin precessing on site $i$ is:

\[ \frac{dS_i}{dt} = S_i \times h_{\text{eff},i} \]  

(4)

where $h_{\text{eff},i\alpha} = -\langle \partial H/\partial S_{i\alpha} \rangle$, and the brackets denote a thermodynamic average. Eq. (4) is then solved by linearizing the spin, $S \approx \langle S \rangle + \sigma(t)$. The dependence of the equation of motion on the geometric structure of the parent spin state is expressed explicitly in Eq. (4). Expanding around the ordered $C_{3D}$ phase one finds that the competition between $J_1$ and $J_2$ renormalizes the spin-wave velocity. For $q \to 0$ the spin waves have the dispersion $\omega = 8(J_1(J_1-J_2))^{1/2} q_c c$, so that at $J_2/J_1 = 1$ the system is only marginally stable with respect to transverse fluctuations of the magnetization that are modulated along the $c$ direction.

For larger values of $J_2/J_1$, the system spontaneously develops a static transverse undulation of the ordered moment. This yields a helical phase modulated at a wave vector $q$ that can be tuned continuously by varying the interaction ratio. Indeed, for $J_2/J_1 > 1$ the equilibrium phase of the model is a coplanar spiral texture. This is seen by studying the zero-temperature internal energy per site, $u$. We assume that each spin is tipped with respect to the $c$ axis by a polar angle $\theta$, and that the transverse component of the magnetization advances by a uniform pitch $\phi$ between neighboring planes normal to the polymer direction. The energy per site then is then
\[ u = J_2 \cos^2 \theta + J_2 \sin^2 \theta \cos 2\phi + 4J_1 \sin^2 \theta \cos \phi. \] (5)

We see that this interaction energy is always minimized by a texture with \( \theta = \pi/2 \) and \( \phi = \cos^{-1}(-J_1/J_2) \). The dependence of \( \phi \) on \( J_2/J_1 \) is shown in Fig. 4. One sees that for \( J_2/J_1 \to 1^+ \) the spiral phase smoothly connects to the ordered \( C_{3D} \) phase (this corresponds to the choice \( \theta = \pi/2 \) and \( \phi = \pi \)). A second critical point occurs at \( J_2/J_1 = 2 \). Here \( \phi = 2\pi/3 \) which describes the three-sublattice spiral phase. In fact, the geometric structure of the coplanar three-sublattice spin texture can already be deduced by a careful inspection of the sixth-order invariants in the Landau expansion of the free energy for a vector order parameter near the critical point connecting the three-sublattice phase to the paramagnetic phase.

Remarkably, the energy of Eq. (5) requires that for any finite \( J_2/J_1 \) (that is, for any nonzero \( J_1 \)) the ground state will always be a helical structure, albeit with a pitch which diverges as \( J_2/J_1 \to \infty \). This is confirmed by studying the spin-wave expansion for small fluctuations around a putatively ordered phase \( C_{1D} \) at \( T = 0 \) in the regime \( J_2/J_1 > 2 \). Here, global rotational invariance requires that the \( q = 0 \) mode occurs at precisely \( \omega = 0 \), but for \textit{nonzero} \( q \) near the zone center, we find that for all coupling strengths the transverse fluctuations around this phase are unstable. The width of this instability in momentum space collapses as \( J_2/J_1 \) diverges. Thus the commensurate structure \( C_{1D} \) is intrinsically unstable at \( T = 0 \) for all finite coupling ratios. In Fig. 4 one sees that the pitch asymptotically approaches the value \( \pi/2 \), which is its value for the \( C_{1D} \) phase, only in the limit of large \( J_2/J_1 \).

The phase diagram for the classical vector-spin model in the bco structure is shown in Fig. 3(c). The commensurate \( C_{3D} \) phase is stable for \( J_2/J_1 < 1 \), and the hatched regions to the right describe the continuum of coplanar spiral phases by which the \( C_{3D} \) phase winds out, asymptotically approaching the \( C_{1D} \) phase.

The energy density of Eq. (5) requires that the helical phases are all coplanar spiral textures; thus nowhere in the phase diagram do we obtain a phase in which the spin texture
orders in three dimensions. However, this can be the case if we treat the effects of a crystal-field anisotropy. Orthorhombic symmetry allows an on-site potential of the form \[ aS^4_x + bS^4_y + cS^4_z \]. Competition between this on-site potential and the planar spiral textures favored by the quadratic interactions can then “tip” the spins out of the plane, yielding a stable three dimensionally ordered conical spin configuration. Of course, in the presence of an external magnetic field, a weak external field acts as a director which orients the plane of the spiral modulation normal to the applied field, with the spins canted uniformly along the external field direction.

The analysis given above has been carried out for a model in which the spins are presumed to be localized on each lattice site of the structure. However, it is likely that the doped carriers of the polymerized solid are better described by the itinerant limit of this theory, along the lines of the theory discussed in Ref. [2]. In fact, we note the experimental transition temperature to a magnetically ordered phase occurs at 50 K, while the Fermi energy for the doped carriers is of order 3000 K, so that quantum fluctuations around the ordered classical phase can be quite significant for this system. Furthermore, we know that the intermolecular hopping amplitudes in the crystal are very sensitive to the interchain separation, and are somewhat sensitive the orientational state of the fullerene molecules. It would therefore be useful to carry out this analysis perturbing from the paramagnetic “metallic” phase of the doped system (containing both charge and spin fluctuations), as a function of varying the interchain separations. The structure of the resulting phase diagram as well as the character of the low lying quasiparticle excitations of the condensed phase in the presence of these ordered spiral spin textures would be particularly interesting to study. Even within the classical model, a distribution of \( J_2/J_1 \) ratios, such as might be introduced by orientational disorder on the fullerene sites, can be expected to couple strongly to the phase degree of freedom of the spiral phases and to lead to disordered phases with nontrivial magnetic properties which have yet to be studied.

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FIGURES

FIG. 1. (a) A portion of the pseudo-body-centered orthorhombic lattice for the polymerized phase. (b) The bco Brillouin zone and high-symmetry points in the $q_x - q_z$ plane.

FIG. 2. Spin structures on a cluster from the bco lattice. The axes of the polymer chains are indicated by the light lines.

FIG. 3. Phase diagrams for the frustrated spin model on the bco lattice: (a) phases considering only colinear structures; (b) phase diagram for the Ising model; (c) phase diagram for the classical Heisenberg model.

FIG. 4. Evolution of the pitch of the coplanar spiral phase as a function of the interaction ratio.
