

Three-dimensional electronic instabilities in polymerized solid AC_{60}

S.C. Erwin

Complex Systems Theory Branch, Naval Research Laboratory, Washington, D.C. 20375

G.V. Krishna and E.J. Mele

Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

(Received 28 December 1994)

The low-temperature structure of AC_{60} ($A=K,Rb$) is an ordered array of polymerized C_{60} chains, with magnetic properties that suggest a nonmetallic ground state. We study the paramagnetic state of this phase using first-principles electronic-structure methods, and examine the magnetic fluctuations around this state using a model Hamiltonian. The electronic and magnetic properties of even this polymerized phase remain strongly three dimensional, and the magnetic fluctuations favor an unusual three-dimensional antiferromagnetically ordered structure with a semimetallic electronic spectrum.

The family of alkali-metal-intercalated fullerenes, A_nC_{60} , has a remarkably rich phase diagram. For large alkali metals (K, Rb, Cs, and their binary mixtures) a variety of stable phases has been identified, the electronic and magnetic properties of which are still poorly understood. Conventional band theory appears to explain the insulating $n=0$ and 6 terminal phases, and suggests a conventional metallic normal state for the $n=3$ phase, but it incorrectly predicts that the intermediate $n=4$ phase is also metallic. Various scenarios have been advanced to explain this discrepancy, primarily by appealing either to very strong intramolecular electron correlations^{1,2} or to various possible spin- or charge-density-wave instabilities from the paramagnetic state. This latter point of view has received additional impetus from the recent discovery of a polymerized form of ($n=1$) RbC_{60} and KC_{60} .³ Electron spin resonance data for this phase show a phase transition at 50 K, below which the spin susceptibility decreases by an order of magnitude, suggesting an insulating ground state. Chauvet *et al.* have proposed that the single alkali electron results in a half-filled conduction band, and that the polymerlike crystal structure then promotes the formation of a spin-density wave that doubles the unit cell along the polymer chain direction and opens a gap at the Fermi level.³

In this paper, we use the results from density-functional electronic-structure methods to construct a physically realistic model Hamiltonian to describe the electronic states in the low-temperature phase of AC_{60} . Remarkably, we find that the electronic and magnetic properties of even this polymerized phase remain strongly three dimensional. Indeed, by studying the fluctuations around the paramagnetic reference state, we identify a broken-symmetry semimetallic ground state with a three-dimensional (3D) magnetically ordered structure quite different from the quasi-1D structure previously proposed for this phase. We note, however, that the quasi-1D electronic character hypothesized by Chauvet *et al.* might be achieved by dilation of the galleries between polymer chains, through the use of larger intercalants. The transition from the three-dimensional magnetic structure discussed here to a quasi-1D structure is quite interesting and is beginning to be explored.

AC_{60} ($A=K,Rb$) undergoes a first-order structural phase transition around 350 K, from a high-temperature fcc phase to a low-temperature orthorhombic phase.³ A striking feature of the orthorhombic phase is the unusually short nearest-neighbor fullerene distance of 9.12 Å (for both K and Rb intercalants).³ This intermolecular spacing implies a separation between interatomic carbon atoms on neighboring (icosahedral) fullerenes as small as 2.0 Å, leading to the suggestion that adjacent molecules are actually covalently bonded to form polymerlike chains $(C_{60})_n$ aligned along one crystallographic axis.³ This picture has been confirmed by Rietveld refinement of x-ray powder diffraction data.⁴

To study the electronic states in such a structure, we begin by performing electronic-structure calculations for the low-temperature orthorhombic phase of crystalline RbC_{60} , using the local-density approximation (LDA) to density-functional theory. For details regarding the computational methods, see Ref. 5, and references therein. We have made one structural simplification to the Rietveld model: by rotating every chain through 45° *in the same sense*, the Bravais lattice is changed from simple orthorhombic to body-centered orthorhombic (bco) and the number of formula units per unit cell is reduced from two to one. The resulting electronic conduction-band structure is shown in Fig. 1. Quite surprisingly, we find that in the occupied part of the spectrum, the dispersion perpendicular to the chains (Γ - M) is quite comparable to the dispersion along the chains (Γ - H). In other words, the amplitude for electron hopping is nearly isotropic, with the resulting Fermi surface exhibiting very strong three-dimensional character. Two other features of Fig. 1 deserve comment. First, the low symmetry of this structure admits only one-dimensional irreducible representations, so that the threefold degeneracy of the parent t_{1u} state (of the cubic phase) is lifted. The magnitude of this symmetry breaking is large on the scale of the conduction-band width, of order half a volt. Second, the lowest band, which is roughly half-filled, shows positive dispersion at Γ , so that the occupied sector of the Brillouin zone encloses the zone center. We find that this lower band transforms like z , that is, these wave functions have odd parity under reflection through the mirror plane normal to the chains.

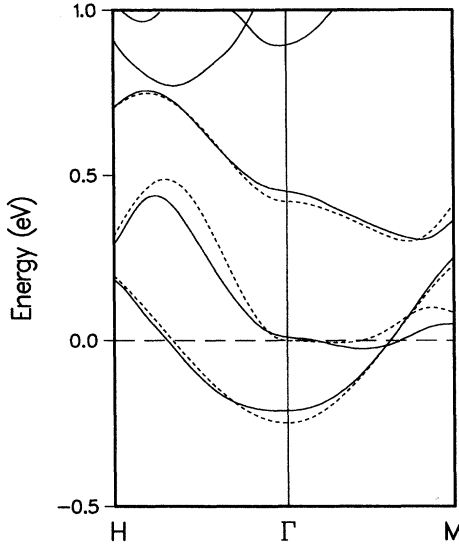


FIG. 1. Theoretical LDA conduction-band structure (solid curves) and tight-binding fit to the LDA spectrum (dotted curves) for polymerized Rb_1C_{60} , in the body-centered-orthorhombic structure described in the text. The labeling of symmetry points is taken from the more familiar body-centered tetragonal zone: H is the zone edge along the chain direction and M is the zone edge in the perpendicular direction. The Fermi level is the energy zero.

Qualitatively, the comparable longitudinal and transverse dispersion is a consequence of two distinct structural features.

(1) In order to covalently bond two adjacent C_{60} molecules, the valence orbitals on intermolecular nearest-neighbor carbon atoms rehybridize from threefold-coordinated (radial π) to fourfold-coordinated (approximately sp^3) orbitals. Consequently, the π -like conduction band in this polymerized phase contains only a very small admixture of orbitals on intermolecular nearest-neighbor atoms, so that dispersion in this direction is actually governed by the interaction of more distant neighbors.⁶

(2) Even with relatively weak interchain electron hopping, dispersion across the chains also benefits from high molecular coordination in the transverse directions. With a larger interchain separation, this benefit would be largely lost and intrachain hopping would predominate, leading to a regime whose consequences are briefly discussed below.

To study the stability of this paramagnetic reference state, we now focus our attention on the dynamics within the doped conduction band. We consider an effective Hamiltonian of the form

$$H = \sum_{i\mu, j\nu} (c_{i\mu}^\dagger T_{i\mu, j\nu} c_{j\nu} + \text{H.c.}) + U \sum_{i\mu} n_{i\mu\uparrow} n_{i\mu\downarrow} + V \sum_{i, \mu < \nu} n_{i\mu} n_{i\nu}, \quad (1)$$

where $c_{i\mu}^\dagger$ creates an electron on site i with orbital polarization $\mu = x, y, z$, and the $T_{i\mu, j\nu}$ are a set of 3×3 matrices giving the amplitudes for an electron hopping between dif-

ferent orbitals on different sites. The electron-electron interaction terms describe a residual short-range repulsive potential. For the kinetic-energy term, we retain terms coupling each molecule to its first 12 nearest neighbors; this closes the first coordination shell in the parent fcc structure (the orthorhombic distortion breaks this into five inequivalent shells). We also include a diagonal on-site term to correctly account for the orthorhombic crystal-field splitting of the threefold t_{1u} molecular state. The matrix elements $T_{i\mu, j\nu}$ are computed by direct Fourier inversion of the LDA eigenvalue spectrum; this generates the optimal tight-binding representation of the LDA bands, and closely reproduces the first-principles single-particle spectrum. (A detailed description of this parametrization procedure is given in Ref. 7.) The resulting tight-binding dispersion is shown in Fig. 1 as dotted curves; the quality of the fit to the LDA spectrum is clearly excellent.

For the case $V=0$, a mean-field decoupling of the interaction term in Eq. (1) yields an (inverse) generalized density-wave susceptibility

$$\chi_{i\mu\sigma, j\nu\sigma'}^{-1} = \partial^2 \Omega / \partial n_{i\mu\sigma} \partial n_{j\nu\sigma'} = -U (\delta_{ij} \delta_{\mu\nu} \delta_{\sigma, -\sigma'} + U \Pi_{i\mu\sigma, j\nu\sigma'}^0), \quad (2)$$

where Ω is the grand potential, and

$$\Pi_{i\mu\sigma, j\nu\sigma'}^0 = - \sum_{\alpha\beta} \langle \alpha | n_{i\mu\sigma} | \beta \rangle \langle \beta | n_{j\nu\sigma'} | \alpha \rangle \frac{f_\alpha - f_\beta}{E_\alpha - E_\beta}, \quad (3)$$

and α labels an eigenfunction of the single-particle piece of Eq. (1) with eigenvalue E_α and occupation number f_α . This interaction couples fluctuations in orbital μ on site i with those in orbital ν on site j . Diagonalization of the full susceptibility matrix then identifies both the wave-vector and orbital character of the dominant spin- and charge-density fluctuations in the model. We find that for a short-range repulsive potential $U > 0$, $V = 0$, the spin fluctuations within the z -polarized orbital are dominant. Interestingly, this situation survives in the presence of even a moderately large off-diagonal repulsive potential V satisfying $2.76U > V > 0$. This occurs because orbital ordering of the charge density is suppressed by the strong orthorhombic crystal-field potential in the single-particle part of Eq. (1), which has the effect of confining the charge and spin fluctuations to the z -polarized t_{1u} orbital. These fluctuations can be studied further by considering the matrix

$$K_{\mu\nu}^{zz}(q) = - \sum_{mnk} \langle m, k | P_\mu \sigma_z(-q) | n, k+q \rangle \times \langle n, k+q | \sigma_z(q) P_\nu | m, k \rangle \frac{f_{m,k} - f_{n,k+q}}{E_{m,k} - E_{n,k+q}}, \quad (4)$$

where P_μ projects the μ -orbital polarization. By examining the momentum dependence of the largest eigenvalue, $\kappa_z(q)$, of the matrix $K_{\mu\nu}^{zz}(q)$ we find that the dominant spin-density fluctuations are quite strongly peaked near the X point of the bco Brillouin zone. (Note that the Γ - X direction

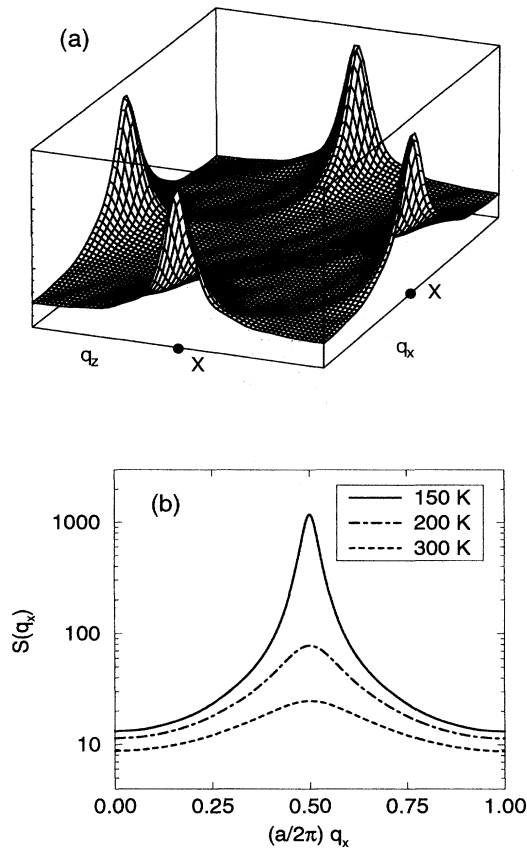


FIG. 2. (a) Surface plot of the static spin structure factor, $S_{zz}(q)$, for $T=0$ and $U=250$ meV, plotted in the q_x - q_z plane. The sharp peak at the X point of the bcc zone corresponds to the three-dimensional antiferromagnetic ordering described in the text. (b) $S_{zz}(q)$ plotted along Γ - X , for $U=280$ meV and shown for three temperatures approaching the ordering value, $T_c=130$ K.

is perpendicular to the chain direction and the X point is the center of the zone face.) To illustrate, Fig. 2(a) shows the static spin structure factor

$$S_{zz}(q) = \frac{\kappa_z(q)}{1 - (U/2)\kappa_z(q)}, \quad (5)$$

calculated at $T=0$ and $U=250$ meV. This interaction strength is less than the zero-temperature critical value $U_c=265$ meV so that here the paramagnetic phase is stable at low temperature. The data are plotted in the q_x - q_z plane, and the peaks of the correlation function are centered at the X point and its translates. Figure 2(b) shows the same data as a linear plot along the Γ - X direction, calculated at three temperatures approaching the mean-field ordering temperature T_c for $U=280$ meV. Within the mean-field theory, we find that a spin-density-wave transition at 100 K would require a repulsive potential $U \approx 270$ meV, a criterion easily satisfied by most theoretical estimates of the effective intramolecular repulsion.^{8,9}

A condensation at the X point for $T < T_c$ describes the ordering of a three-dimensional antiferromagnetic state with two sublattices, such that the spin polarization alternates between the corner and body-centered sites of the bcc structure.

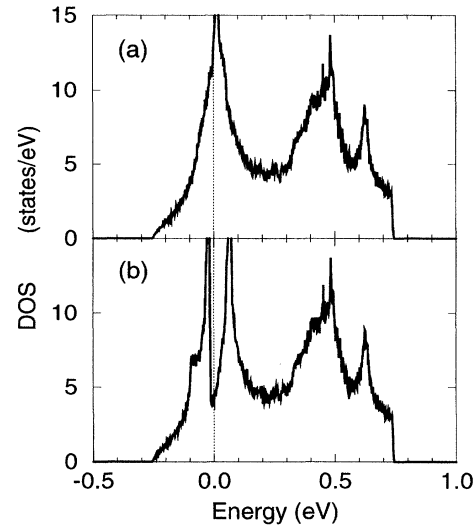


FIG. 3. Spectral density at $T=0$ for (a) the paramagnetic reference state and (b) the magnetically ordered ground state. The Fermi level is the energy zero.

This spin configuration can thus be described as ferromagnetic within each chain and antiferromagnetic between nearest-neighbor chains. We note that the three-dimensional character of this magnetic state might have been anticipated in view of the substantial three-dimensional character of the single-particle spectrum displayed in Fig. 1. If one views the unpaired spins on the fullerene molecules as localized and antiferromagnetically coupled via $J_1 > 0$ to nearest neighbors along a cell diagonal, and antiferromagnetically via $J_2 > 0$ along nearest neighbors within the chains, then the transition to one-dimensional behavior requires $J_2/J_1 > 2$. This limit is apparently well outside the regime that actually describes these materials. In fact, we find that the effective intersite interaction mediated by the polarization of the conduction electrons gives $J_2 < 0$; that is, the nearest-neighbor intrachain interaction is actually ferromagnetic for this structure.

Figure 3 shows the spectral density obtained at $T=0$ in the equilibrium phase of this model: panel (a) is the density of states calculated for the unbroken paramagnetic phase, while panel (b) is for the equilibrium magnetically ordered phase. We find that for $U=300$ meV the Fermi surface of the parent phase is partially gapped in the ground-state structure, and that a well-developed pseudogap is clearly evident in the density of states. Thus the system remains semimetallic at low temperatures. In the spectrum one can nevertheless clearly observe the signature of the ferromagnetic intrachain ordering, which essentially results in a rigid spin splitting of the lowest (z -polarized) conduction band, evident in the structure of the density of states around the Fermi level. The upper two unoccupied branches of the conduction manifold are relatively insensitive to this ordering transition. We find that the pseudogap is a robust feature of this ground state, and survives up to relatively large coupling strengths; a fully developed gap first opens in the single-particle spectrum for $U=470$ meV. We suggest that the decrease in the spin susceptibility measured by Chauvet *et al.*³ may be associated with the opening of the pseudogap at T_c . Further measure-

ments at temperatures much lower than T_c will be required to distinguish between insulating and semimetallic behavior in this phase.

Our density-functional calculations indicate that the transverse interchain hopping amplitudes in the Hamiltonian of Eq. (1) are very sensitive to the interchain separation. Indeed, we find that a 10% dilation of the interchain spacing leads to a regime where the electronic structure is dominated by one-dimensional dynamics along the chain direction. Here the spin fluctuations are again dominantly antiferromagnetic in character, but now with the ordering wave vector oriented along the chain. We emphasize that while this limit is apparently not realized in K- or Rb-doped samples, it might well be achieved by doping with substantially larger species. Experimentally, such a situation could conceivably be realized by alloying the alkali with "spacer molecules" such as NH_3 , as has been done for A_3C_{60} .¹⁰ If so, the resulting magnetic phase diagram as a function of alloying composition is expected to be quite complex.¹¹

The results reported above have been obtained for a model structure with a common orientation on each of the bco Bravais-lattice sites, and therefore it is natural to ask how sensitive the results are to this assumption about the orientational order. While detailed calculations are continuing, we should note that for the $Pmnn$ structure (determined by Rietveld refinement) with two inequivalent orientations per orthorhombic unit cell, our LDA calculations show that

the low-energy spectrum retains its strong three-dimensional character.¹¹ Since this feature controls the physics discussed above, we expect the scenario developed above for the single-orientation structure still to apply. Also, we should note that the possibility of a quenched orientationally disordered phase for AC_{60} has not yet been excluded experimentally.⁴

In summary, we have studied the paramagnetic phase of the polymerized fulleride AC_{60} and have examined magnetic fluctuations around this reference state. We find that repulsive interactions favor a two-sublattice three-dimensional magnetic structure for this system, which can be stabilized at relatively modest values of the repulsion strength. The three-dimensional character of this phase derives primarily from the rehybridization of the cubic t_{1u} conduction band in this polymerized phase, and from the large coordination transverse to the polymer chain axis. Finally, we observe that a physically plausible modification of the crystal structure, possibly by intercalation with larger species, may be sufficient to stabilize the quasi-1D magnetic state which had been earlier hypothesized for this phase.

This work was supported in part by the Laboratory for Research on the Structure of Matter (University of Pennsylvania), by the NSF under the MRL program (Grant No. 92 20668) and by the DOE (Grant No. 91ER 45118). Computations were carried out at the Cornell Theory Center, which receives major funding from NSF and New York State.

¹R. W. Lof, M. A. van Veenendaal, B. Koopmans, H. T. Jonkman, and G. A. Sawatzky, *Phys. Rev. Lett.* **68**, 3924 (1992).

²J. P. Lu, *Phys. Rev. B* **49**, 5687 (1994).

³O. Chauvet *et al.*, *Phys. Rev. Lett.* **72**, 2721 (1994).

⁴P. W. Stephens *et al.*, *Nature* **370**, 636 (1994).

⁵S. C. Erwin and M. R. Pederson, *Phys. Rev. Lett.* **67**, 1610 (1991).

⁶This possibility is considered in S. Pekker, L. Forró, L. Mihály, and A. Jánossy, *Solid State Commun.* **90**, 349 (1994).

⁷S. C. Erwin and E. J. Mele, *Phys. Rev. B* **50**, 5689 (1994).

⁸M. R. Pederson and A. A. Quong, *Phys. Rev. B* **46**, 13 584 (1993).

⁹S. Satpathy, V. P. Antropov, O. K. Andersen, O. Jepsen, O. Gunnarsson, and A. I. Liechtenstein, *Phys. Rev. B* **46**, 1773 (1992).

¹⁰M. Rosseinsky, D. W. Murphy, R. M. Fleming, and O. Zhou, *Nature* **364**, 425 (1993).

¹¹E. J. Mele, G. V. Krishna, and S. C. Erwin (unpublished).