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Brief Reports

Electron-spin-resonance study of the dimer state of KC_{60} and its transformations

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Recent x-ray results show that quenching the high-temperature fcc (rocksalt) phase of KC_{60} below 280 K produces a metastable orthorhombic structure in which the molecules exist as dimer pairs. Using electron-spin resonance, we find that this state is nonmagnetic and describe evidence for σ bonding. Upon heating, the dimer structure transforms first to the fcc phase at 280 K. The fcc phase is unstable at 300 K and transforms to the polymeric state at 340 K rather than undergoing equilibrium phase separation. We suggest that the transformation from dimer to fcc is driven by the onset of molecular orientational disorder.

The high-temperature ($T > 500$ K) equilibrium structure of MC_{60} is face-centered cubic (fcc), with M ions restricted to octahedral sites (rocksalt structure).[1] In this phase, unpaired electrons are localized on ${C_{60}}^{-1}$ anions and are in exchange interaction[2] leading to a Curie-type spin susceptibility.[2,3] With slow cooling (10 K/min), the fcc phase transforms into an orthorhombic structure with an unusually short intermolecular distance in one direction, 9.11 Å.[4,5] The metallic nature of these "orthopolymers" was inferred from nearly-temperature-independent spin susceptibilities determined by electron-spin resonance (M = Rb or Cs) Refs. (6,7) and from the Korringa law behavior of ^{133}Cs and ^{87}Rb NMR.[2,8] We have confirmed the metallic nature of RbC_{60} by pulsed ESR.[9] Recently, a second metastable form of KC_{60} has been obtained by quenching from 573 K to 273 K.[5] X-ray diffraction shows that this new state is nearly orthorhombic but with a cell roughly doubled along a and c, indicating the formation of C_{60} dimer pairs with greater interfullerene separation, 9.34 Å, which implies a different bonding than in the polymer state. In this work we first establish that this new dimer state of KC_{60} has no measurable Pauli spins, consistent with a nonmetallic system and in strong contrast to the polymer state. Then we use the ESR signatures of the various equilibrium and nonequilibrium states to study transformations between states, thereby obtaining more detail than was practical using high-resolution x-ray diffraction.

The KC_{60} sample came from the same batch studied in Refs. 2 and 5. ESR experiments were performed using a standard Bruker ESP 300 spectrometer equipped with nitrogen ($T > 150$ K) or helium gas flow ($T < 300$ K) systems. Spin susceptibilities were determined by double integration of the ESR line and by comparison with a coal reference sample. Quenching the sample in ice water was performed outside the ESR cavity, followed immediately by further cooling to lower temperature in the ESR apparatus.

Upon quenching from 590 K to 273 K and then immediately cooling to 4 K, we observe a small Curie-type spin susceptibility on heating from 50 K to 210 K (Fig. 1).

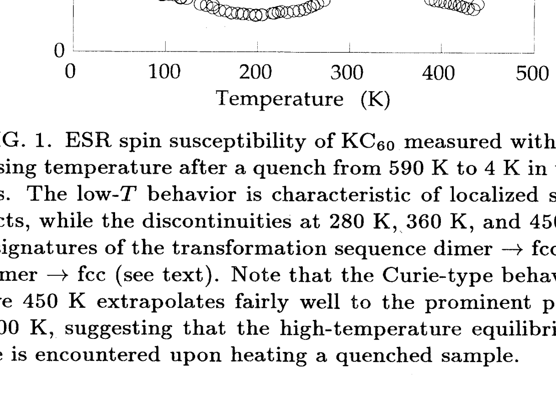

FIG. 1. ESR spin susceptibility of KC_{60} measured with increasing temperature after a quench from 590 K to 4 K in two steps. The low-T behavior is characteristic of localized spin defects, while the discontinuities at 280 K, 360 K, and 450 K are signatures of the transformation sequence dimer → fcc → polymer → fcc (see text). Note that the Curie-type behavior above 450 K extrapolates fairly well to the prominent peak at 300 K, suggesting that the high-temperature equilibrium state is encountered upon heating a quenched sample.

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$\chi(T)$ begins to increase slowly above this temperature, then increases dramatically at 280 K. This temperature dependence closely mimics that of the quenched dimer observed by Zhu *et al.*,[1] and so we conclude that the dimer is a diamagnetic insulator from 4 K to 210 K. The low-temperature Curie tail gives a spin impurity susceptibility of about 5% that observed at 300 K. The concentration of these spin defects depends strongly on the quenching conditions; the faster the quench, the lower the spin concentration. Previous ESR studies of RbC$_{60}$ showed a similar behavior of the spin susceptibility in the quenched state[6] (which, however, was interpreted as the ground state of the fcc structure). Optical measurements of RbC$_{60}$ also indicate that the quenched state is insulating.[10] Thus quenched KC$_{60}$ and Rb$_{60}$ are both insulators, and quenched RbC$_{60}$ is probably also dimeric.

Between 280 K and ~ 320 K the dimer is transforming to other states, and so $\chi(T)$ reflects a complex dynamical mixture (see below). This relaxation is quite irreversible; once the sample is heated above 320 K, the dimer cannot be recovered, either by slow cooling or by quenching, without first heating to 500 K and starting the whole process over.

From 320 K to 360 K, $\chi(T)$ is characteristic of essentially pure orthopolymer, as determined in separate experiments using different time-temperature conditions designed to optimize the metastability of the polymer state over a broader temperature range.[6] The ESR properties of ortho-KC$_{60}$ at 300 K are $\chi = 4.3 \times 10^{-4}$ emu/mol, peak-to-peak linewidth $\Delta H_{\rm p.p.} = 6.7$ G, and G=2.0004. The temperature independence of χ and the linear decrease of $\Delta H_{\rm p.p.}$ with decreasing T down to 70 K are consistent with a metallic state (Fig. 2); at lower temperatures the ESR signal is dominated by the impurity spins. Above 360 K, ortho-KC$_{60}$ separates into the thermodynamic equilibrium α-C$_{60}$ + K$_3$C$_{60}$ (α−C$_{60}$ = K$_x$C$_{60}$ with $x << 1$). Details about phase instabilities and their relaxations will be published separately.

The only thermodynamically stable pure phase of KC$_{60}$, namely, fcc, is finally reached at 450 K (Fig. 1). Its spin susceptibility decreases with increasing temperature, consistent with Curie behavior characteristic of isolated spins. The corresponding single ESR line is centered at g=1.9993. By slow cooling the high-temperature phase, only about half the sample transforms to ortho-KC$_{60}$ in agreement with the x-ray observations;[5] the orthopolymer fraction is optimized by heating the dimer rather than by quenching or slow cooling the fcc phase. (The same limitation is not true of RbC$_{60}$, in which the slower diffusion kinetics presumably favors the conversion from fcc to ortho-RbC$_{60}$.) The ESR signal obtained by quenching to 295 K has the same g, $\Delta H_{\rm p.p.}$ and amplitude as was observed after heating the dimer to 300 K (i.e, the peak in χ in Fig. 1). This result indicates that the strong peak in χ at 300 K corresponds to the fcc phase. In fact the measured $\chi(T)$ in the fcc phase above 450 K extrapolates quite well to the peak at 300 K [which probably underestimates χ(fcc) at 300 K since the system is not in steady state during the heating experiment]. It is interesting to note that the fcc state with localized spins has a higher value of χ (300 K) than the metallic polymer state.

The transformation sequence dimer → fcc → polymer → fcc with increasing T is confirmed by the temperature dependence of the g factor, Fig. 3. The dimer state has g = 1.9996 (T < 280 K), which drops to 1.9994 at 300 K (corresponding to the peak in χ, Fig. 1), the same as is observed in the high-temperature equilibrium fcc state above 450 K. Just above 300 K we find g = 2.0004 which is characteristic of an orthopolymer, while the jump to g = 2.0006 at 380 K is connected with the mixture of α-C$_{60}$+K$_3$C$_{60}$.

Figure 4 shows the thermal variation of $\Delta H_{\rm p.p.}$ through the fcc-dimer transformation. The cooling data were obtained first. To avoid rapid relaxation of the fcc phase into the polymer state, the linewidth values above

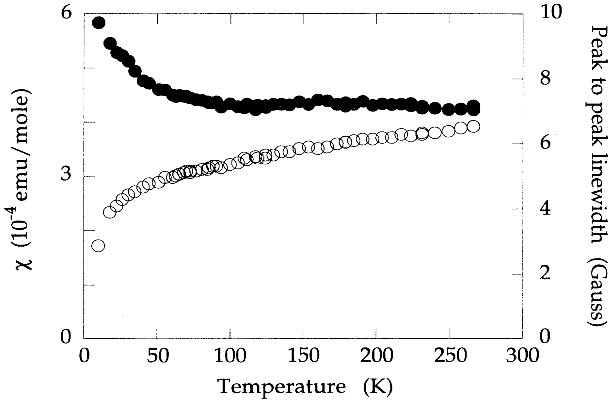

FIG. 2. Temperature dependence of the spin susceptibility (solid circles) and $\Delta H_{\rm p.p.}$ (open circles) of the polymeric state of KC$_{60}$, obtained by heating from the dimer state to 330 K and annealing for 90 min. The thermal variations of both quantities are consistent with a metallic state.

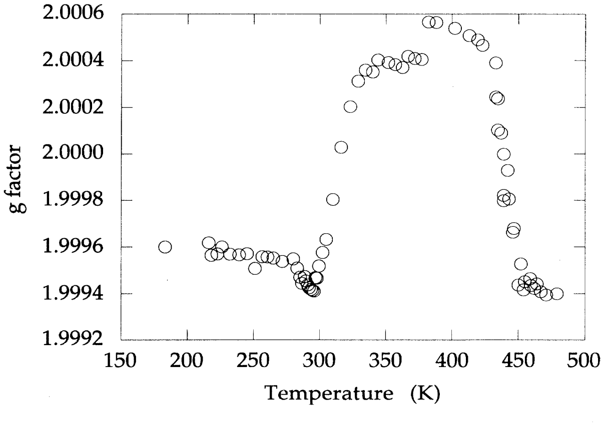

FIG. 3. Temperature dependence of the g factor of KC$_{60}$ measured with increasing T after a quench from 590 K to 180 K. The low-T value of 1.9996 is characteristic of the dimer state, while the discontinuities with increasing T are signatures of the same transition sequence observed in $\chi(T)$. Note in particular that the g factor drops to 1.9994 at 300 K, the same as the g factor in the high-T limit, confirming the conjecture described in Fig. 1.

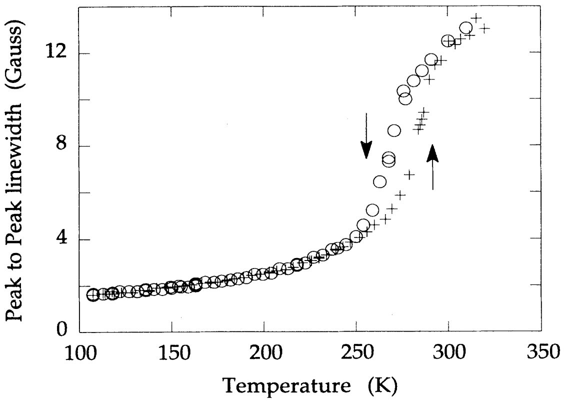

FIG. 4. Temperature variation of $\Delta H_{\rm p.p.}$ of quenched KC_{60} through the dimer → fcc transition (heating) and the reverse.

290 K measured on cooling were obtained after annealing the sample at 590 K and quenching to each desired temperature in the ESR apparatus and recording the spectra within 2 min after the quenches. For the heating runs the heating rate was increased to about 2 K/min. The data show a hysteresis of 20 K about a transformation temperature of 280 K. The same hysteresis is found in the susceptibility values and g factors. This transformation temperature is 20 K above the orientational ordering transition in pure C_{60}.[11] The lattice constant of quenched fcc KC_{60} is 13.98 Å at 300 K,[5] the C_{60} transition shifts to higher T with hydrostatic pressure at a rate of 10-12 K/kbar,[12] and the bulk modulus of C_{60} is 18 GPa.[13] Putting these together yields an estimate of 320 K for the ordering transition of hypothetical C_{60} compressed to the 300 K lattice constant of fcc KC_{60}. This is probably an overestimate since the octahedral K adds an interaction which competes weakly with the C_{60}-C_{60} interaction.[14] Note also that the ordering temperature in NaC_{60} is 330 K;[15] here the Na is tetrahedral and the Coulomb interaction does not compete with the C_{60}-C_{60} interaction.[14] At the very least, it seems plausible that the dimer → fcc transition in KC_{60} is connected to the onset of molecular orientational disorder. This could presumably be elucidated by detailed NMR and calorimetric measurements.

There are two possible explanations for the absence of magnetism in $(C_{60}^-)_2$ pairs: Either the electron spins on each molecule are antiferromagnetically coupled, or the molecules are bonded into diamagnetic dimer pairs. Antiferromagnetic coupling could explain the absence of an ESR signal at 10 GHz by either of two effects: a drastic broadening of the absorption line by strong dipolar interaction, or a shift of the resonance induced by a strong local magnetic field (greater than the Zeeman field). We find no evidence for either of these signatures of antiferromagnetic coupling, and so this hypothesis can be ruled out. The second hypothesis is appealing because the pairs are naturally diamagnetic when bonded, and the breaking of these bonds leads naturally to a paramagnetic (monomeric) state which explains the strong enhancement observed in $\chi(T)$ at 280 K. It has been proposed that the interfullerene bonding in the polymer state has at least partial π character and that π conjugation along the chain is responsible for the metallic behavior.[4] In the dimer state, the lower thermal stability (280 K vs 360 K) and the greater intermolecular distance suggest weaker σ bonding.

We have learned that, independent of our work, the dimer state of KC_{60} and Rb_{60} has been characterized by x-ray diffraction, conductivity, and ESR experiments.[16] These x-ray data confirm the results of Zhu *et al.*[1] as regards the dimer structure and the transformation sequence dimer → fcc → polymer. The low-T ESR results reproduce our Fig. 1 but do not address the issues of transformations, hysteresis, and phase instabilities.

In conclusion, we have shown using ESR that the dimer state of KC_{60} is spinless, suggesting an insulating state (consistent with electrical resistivity measurements[16]). The dimer → fcc transformation has been characterized in detail. It occurs at 280 K and is reversible (and hysteretic) as long as the temperature does not exceed 320 K, above which the fcc phase relaxes rapidly into the polymeric state. There is strong evidence that dimer pairs are σ bonded. There is circumstantial evidence pointing to a connection between the onset of molecular orientational disorder and the dimer → fcc transformation at 280 K; this should be easy to confirm or rule out. The only thermodynamically stable state of KC_{60} below 420 K is phase-separated α-C_{60} + K_3C_{60}.

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