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13. Abbreviations used are as follows: Me = methyl; TCNE = tetracyanoethylenide; F_5benz = pentafluorobenzoate; nitMe = 2-methyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazoyl-1-oxy-3-oxide; pbaOH = 2-hydroxy-1,3-propanediylbis(oxamato).
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24. For a Prussian blue structure, magnetic orbitals on adjacent metal centers M and M′ will contribute to the superexchange as follows: e_g–e_g and t_{2g}–t_{2g} combinations (if present) have nonzero overlap and give rise to antiferromagnetic contributions; e_g–t_{2g} combinations (if present) have zero overlap and give rise to ferromagnetic contributions.
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26. We prepared $K_4[V(CN)_6]$ by adding a solution of KCN (2.56 g, 39.4 mmol) in water (60 ml) to a solution of $V(H_2O)_6(OSO_2CF_3)_2$ (*36*) (1.50 g, 3.28 mmol) in water (25 ml) under argon. The dark brown solution was brought to reflux for 30 min and then was taken to dryness under vacuum. The resulting yellow solid was washed with methanol (30 ml) and extracted into an aqueous 3.5 M KCN solution (70 ml). The orange-yellow extract was filtered, reduced in volume to saturation (~25 ml), and cooled to 5°C to afford orange needles of $K_4[V(CN)_6]$. The yield was 0.66 g (55%).
27. We prepared $(NEt_4)_4[V(CN)_6]$ by adding a solution of $(NEt_4)CN$ (1.37 g, 8.75 mmol) in acetonitrile (30 ml) to a solution of $V(H_2O)_6(OSO_2CF_3)_2$ (*36*) (0.50 g, 1.1 mmol) in acetonitrile (26 ml) under argon. The dark brown solution was brought to reflux for 30 min, filtered, reduced in volume to saturation (~20 ml), and cooled to −20°C to afford a brown solid. The crude product was collected by filtration and dissolved in a solution of $(NEt_4)CN$ (1.12 g, 72 mmol) in acetonitrile (60 ml). The resulting red-brown solution was brought to reflux for 5 min, filtered, concentrated to ~20 ml, and cooled to −20°C to afford $(NEt_4)_4[V(CN)_6]$ as a brown solid. The yield was 0.17 g (21%).
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29. Calculated composition for $C_6N_6Cs_2MnV$ (**1**): C, 13.6%; N, 15.9%; Mn, 10.4%; V, 9.65%. Found: C, 13.7%; N, 16.1%; Mn, 11.6%; V, 10.2%. Calculated composition for $C_9H_{13}Mn_{1.25}N_{5.5}O_2V$ (**2**): C, 30.8%; H, 4.02%; N, 21.9%; Mn, 19.6%; V, 14.5%. Found: C, 30.0%; H, 4.19%; N, 18.2%; Mn, 20.8%; V, 14.8%. Discussions of alternative formulations for **2** such as $(Et_4N)_{0.5}Mn_{1.25}[V(CN)_4(OH)]\cdot H_2O$ await additional data.
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32. The saturation magnetization was calculated from the formula $M = g\mu_B N_A S$, where μ_B is the Bohr magneton, N_A is Avogadro's number, and S is the net spin per formula unit. The Landé g factor was assumed to be equal to 2 for both metal centers.
33. Further support for a large local antiferromagnetic interaction between the V^{II} and Mn^{II} spin centers in **2** comes from the χT value of 6.1(2) cm^3 K mol^{-1} at 350 K, which is smaller than the value of 7.4 cm^3 K mol^{-1} calculated for a thermally random array of Mn^{II} (S = 5/2) and V^{II} (S = 3/2) spin centers in a 1.25 to 1 ratio.
34. In contrast, the ferrimagnetic Cr-based Prussian blue analogs $[Cr_5(CN)_{12}]\cdot 10H_2O$ and $Cs_{0.75}$ $[Cr_{2.125}(CN)_6]\cdot 5H_2O$, which have T_N of 240 and 190 K, respectively, exhibit minima in their curves of χT versus T below 300 K (*18*). The absence of such a minimum for **2** suggests that its exchange interactions are stronger than in these cyanochromates.
35. The remnant magnetizations for **1** and **2** are ~1.95 × 10^3 G cm^3 mol^{-1} at 10 K and ~1.39 × 10^3 G cm^3 mol^{-1} at 50 K, respectively.
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37. This work was supported by the Department of Energy. The work of W.R.E. was supported by a fellowship from the Department of Chemistry. We thank C. Treadway for valuable assistance. We thank M. Rosenblatt, D. White, and K. S. Suslick for assistance with Fig. 1.

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Orientational and Magnetic Ordering of Buckyballs in TDAE-C_{60}

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Spin ordering in the low-temperature magnetic phase is directly linked to the orientational ordering of C_{60} molecules in organically doped fullerene derivatives. Electron spin resonance and alternating current susceptometry measurements on tetrakis(dimethylamino)ethylene-C_{60} (TDAE-C_{60}) (Curie temperature T_c = 16 kelvin) show a direct coupling between spin and merohedral degrees of freedom. This coupling was experimentally demonstrated by showing that ordering the spins in the magnetic phase imprints a merohedral order on the solid or, conversely, that merohedrally ordering the C_{60} molecules influences the spin order at low temperature. The merohedral disorder gives rise to a distribution of π-electron exchange interactions between spins on neighboring C_{60} molecules, suggesting a microscopic origin for the observed spin-glass behavior of the magnetic state.

Soon after the discovery by Krätschmer *et al.* (*1*) of an efficient synthesis route for C_{60}, an organic magnetic material based on C_{60} was reported (*2*). The material, which is essentially C_{60} doped with the organic donor TDAE, showed a transition to a magnetic state at a temperature of 16.1 K. This discovery sparked a series of investigations, some aiming to find new organic magnetic materials based on fullerenes. As a result, systematic investigations provided a good phenomenological account of the magnetic properties of such materials. They appeared to be described well by a spin-glass model (*3*) with a nonzero local field (*4*), although alternative suggestions of superparamagnetism (*5*) and itinerant ferromagnetism (*2*) have also been proposed. In addition, two similar materials have now been synthesized with different donors and C_{60}-derived acceptor molecules exhibiting a cusp in the low-temperature static spin susceptibility similar to that of TDAE-C_{60}: cobaltocene-doped dinitro-spiromethano-fullerene ($T_c \approx$ 8 K) (*6*) and cobaltocene-doped 3-nitrophenyl C_{61} ($T_c \approx$ 30 K) (*7*). In spite of this, the microscopic origin of the glassy behavior remained a mystery until now.

Here we report the discovery of a direct link between the buckyball orientational (merohedral) order and the spin order. We suggest that the exchange interaction between π-electrons on neighboring C_{60} molecules is responsible for the spin-spin interaction and that the glassy behavior is a direct consequence of the inherent merohedral disorder. By externally manipulating the degree of fullerene molecular order, we are able to tune T_c, the temperature of the low-temperature magnetic transition, in effect changing the spin ordering through manipulation of the exchange interaction between spins on the fullerene molecules.

Our synthesis of the stoichiometric TDAE-C_{60} compound followed the standard route (*2*), resulting in a 1:1 ratio of TDAE and C_{60} in a solid with a monoclinic C2 structure, which is similar to the usual cubic symmetry of C_{60} but the unit cell has correspondingly smaller inter-

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buckyball distances (*8*) and β = 94.02°. The TDAE-C_{60} compound has already been investigated quite extensively, and numerous experiments have confirmed a charge transfer from TDAE to C_{60}. For example, (i) a strong electron spin resonance (ESR) signal implies one unpaired spin per molecule, (ii) the observation of a direct t_{1u}-t_{1g} optical transition in optical absorption spectra implies an occupied t_{1u} level in the lowest unoccupied molecular orbital of C_{60}, and (iii) a shift to lower frequency of the pentagonal pinch vibrational mode in Raman spectra is comparable to the shifts in KC_{60} and RbC_{60}. Similarly, (iv) the expected softening of the low-frequency infrared-active modes has been observed, along with (v) the ^{13}C nuclear magnetic resonance (NMR) frequency shift in TDAE-C_{60}, which is 188 parts per million (ppm) relative to tetramethylsilane and is very close to the shifts in CsC_{60} (177 ppm) and RbC_{60} (173 ppm) (*9*). The Raman, infrared, and NMR data show, at least in the case of the stoichiometric material, that one electron is transferred from TDAE to the C_{60} molecule. In spite of this, the material does not show metallic behavior, and instead, the dc conductivity shows activated behavior down to low temperatures ($T \approx 80$ K) (*10*), suggesting that electron localization leads to a hopping process for the electrical transport. In addition, no sign of low-frequency temperature-dependent Drude absorption in optical conductivity is seen, which would have been an indication of metallic conductivity (*11*, *12*). Because ferromagnetic coupling is, with few exceptions, a property of metals, TDAE-C_{60} appears to be unusual in this respect.

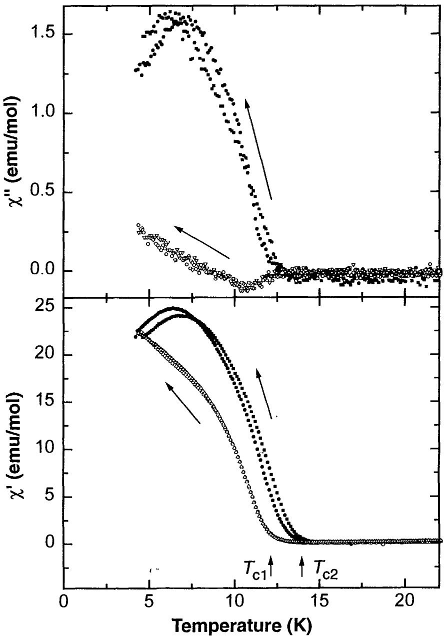

Fig. 1. The real (χ′) and imaginary (χ″) parts of the ac susceptibility of TDAE-C_{60} (H_{ac} < 10 G) are very different depending on whether the sample was quenched or slowly cooled through the ordering transition near 170 K. The filled symbols show χ for a sample cooled slowly (12 hours) from 300 to 30 K, and the open symbols are for the same sample quenched from 300 to 30 K. All the curves were obtained after cooling at a rate of 0.3 K/min starting at 30 K. Two repeated experiments done consecutively are shown to illustrate the reproducibility of the ordering procedure. Susceptibility is measured in electromagnetic units (emu) per mole (measured in magnetic field H_{pp}).

Here we show that the key to understanding the low-temperature magnetic properties in these fullerene materials lies in establishing a connection between the ordering of spins and the merohedral order of the C_{60} molecules. When incorporated in molecular solids, C_{60} molecules often display complex ordering behavior. In most fullerene solids studied so far, the molecules rotate at room temperature. Upon cooling, their rotation becomes preferential about their threefold molecular axes, which point along the body diagonals of the cubic or quasi-cubic crystal axes (*13*). The onset of ordering is usually around $T_0 \sim 250$ K. The molecules eventually freeze at low temperature in one of two preferred orientations relative to each other. The two merohedral energy minima correspond to the relative C_{60} orientations in which the hexagon-hexagon double bond (with the maximum charge density) on one molecule faces the local minimum charge density of the next molecule, which is at the center of either the pentagon or the hexagon. In pure solid C_{60}, the two minima are nearly degenerate (they differ by ~11 meV), with a barrier between them (corresponding to the two relative orientations) near $E_b = 250$ meV (~2900 K) (*14*). Similar behavior has been observed in other intercalated C_{60} solids (*14*, *15*) and appears to be relatively universal. In TDAE-C_{60}, ^{13}C NMR of the C_{60} carbon atoms shows an increase in line width below 170 K similar to that seen for pure C_{60}, which is indicative of rotational freezing (*16*). Also, the ESR data show an anomalous change in line width at 170 K, which is probably indicative of an ordering transition. Therefore, we conclude that, although the details of the ordering transition are yet to be determined, merohedral ordering takes place near this temperature in TDAE-C_{60}.

Given that the C_{60} merohedral molecular ordering occurs around T_0 ~170 K, we decided to study its effect on the low-temperature magnetic order. We first compared the low-temperature magnetic susceptibility $\chi(T)$ of a TDAE-C_{60} sample when quenched from 300 to 30 K (to just above T_c) with the behavior obtained when the same sample is slowly cooled over the same temperature range (Fig. 1). The susceptibility measurement is performed identically for the two cases, cooling from 30 to 4.2 K for both the quenched and slowly cooled case. The sus-

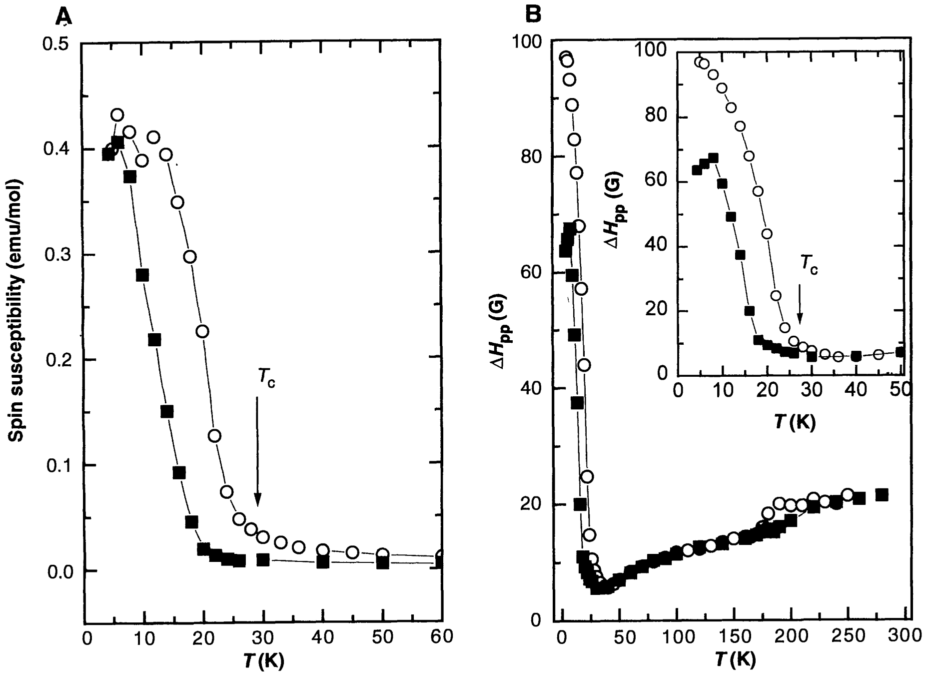

Fig. 2. Integrated ESR signal intensity (**A**) and ESR line widths (**B**) as a function of temperature for a zero-field cooled sample (full squares) and a sample oriented below 16 K in a 9-T magnetic field (open circles). A clear anomaly is observed near 170 K in (B). The inset in (B) shows the low-temperature range.

ceptibility measurements were performed in an ac susceptometer (AcSuS Systemprojekt) at very slow cooling rates (0.3 K/min) with the sample sealed in a quartz tube. There was a significant difference in the susceptibility in the two experiments. First, when the sample was cooled slowly, the onset of magnetic ordering was 2 K higher (14.0 versus 12.1 K) than when it was quenched. Second, the shape of $\chi'(T)$ was quite different for the two cases, and there was an even larger change in $\chi''(T)$. We have previously found a large glass-like dispersion in ac susceptibility in the low-frequency range of 75 to 1400 Hz (*17*).

The large effects seen upon quenching imply a significant change in the distribution of relaxation times, which is induced by the thermal merohedral ordering of buckyballs. Quenching from intermediate temperatures produces a systematic variation in χ' and χ'' from one extreme to the other (Fig. 1). The procedure is highly reproducible (Fig. 1). We observed no significant hysteresis in any kind of temperature cycling for $T < 30$ K, indicating that the ordering is fixed and cannot be significantly changed at these low temperatures in the absence of an applied external field. The experiment conclusively shows that ordering of C_{60} molecules by slow cooling through the merohedral ordering transition results in a significantly increased magnetic order with a sharper onset of magnetization, lower internal dissipation, and a higher T_c than for the quenched material.

Because there appears to be clear coupling between spin and merohedral degrees of freedom, it is reasonable to suppose that the converse also occurs: Merohedral order could be changed by externally manipulating the spin system with an external magnetic field. Spin susceptibility measurements of TDAE-C_{60} were performed using ESR for a sample cooled with and without external field B_{ext} (Fig. 2). The ESR measurements were performed on samples cooled with $B_{ext} = 0$ or cooled to 4 K with $B_{ext} = 9$ T and subsequently transferred to the ESR cryostat at 77 K. The increase in ESR intensity and the change in line width show, as expected, that the magnetic field significantly increased the magnetic order and increased T_c from 16 to 28 K. The spin order persisted to 28 K (open circles, Fig. 2), even when B_{ext} was no longer present. The fact that the sample was kept at 77 K for an extended period in between the magnetizing procedure and the ESR measurement shows that the system exhibits a memory of its low-temperature magnetization, even when heated well above T_c. When heated above 170 K, the sample lost memory of the molecular ordering; on subsequent measurements, we recovered the usual behavior in the susceptibility, and T_c was again near 16 K (squares, Fig. 2). Conversely to the thermal ordering experiment (Fig. 1), where we ordered the C_{60} first and then examined the magnetic order, with the external magnetic field B_{ext} we ordered the spins below T_c and found that this procedure imprinted a merohedral order on the C_{60} molecules that remained all the way up to T_0. The two experiments together prove the existence of a direct link between the spin and merohedral degrees of freedom in TDAE-C_{60}.

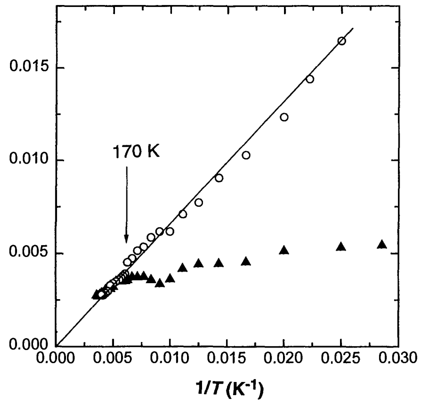

Fig. 3. A plot of ESR intensity versus 1/*T* (measured at 3000 G) shows a Curie-like susceptibility above 170 K for all samples obtained on heating from 4.2 K. Field-oriented samples (open circles) show Curie-like behavior from 4.2 to 300 K, whereas in the absence of orientation by external field, more complicated sample history–dependent behavior is observed for $T < 170$ K (triangles).

Ordering the buckyballs in the material with a magnetic field also has a profound effect on the susceptibility above T_c. Usually the material shows Curie-like behavior for $T > 170$ K, and for $T < 170$ K, it exhibits more complex, nonlinear behavior with a nonzero intercept (triangles, Fig. 3) (the shape of the curve depends somewhat on the thermal and magnetic history of the sample). In contrast, the field-oriented case is Curie-like over the whole temperature range of 28 to 300 K (circles, Fig. 3). To explain this behavior, we offer the following explanation. For $T > T_0$ the molecules are rotating, the spins on the individual molecules are equivalent, and the spin susceptibility is predominantly Curie-like. Below $T_0 \sim 170$ K, the molecular ordering starts to affect the spin system, giving rise to the complex non-Curie behavior usually seen in the spin susceptibility of TDAE-C_{60} between T_0 and T_c. The susceptibility could possibly be modeled as the sum of two contributions, their ratio depending on the degree of merohedral order. However, we also recover a Curie-like susceptibility between T_c and T_0 when the molecules are ordered by the application of a field B_{ext}. The field substantially orders the C_{60} molecules into one of the two minima of the double-well potential, and the susceptibility is then predominantly Curie-like, corresponding to that of a single paramagnetic center.

One of the puzzles so far has been the large pressure dependence of both the magnetization and T_c in TDAE-C_{60} (*18*). Because pressure has a large effect on molecular orientation, it immediately shifts the energy of the minima of the orientational double well. Thus, applying even slight pressure can destroy or significantly change the molecular order and consequently the magnetic order, which, as we have shown, is sensitive to the molecular orientations and overlap of the π-electron orbitals on neighboring C_{60} molecules. Measurements of the pressure dependence of molecular orientation in the magnetic phase could easily confirm this.

On the other hand, the spin-glass behavior arises as a result of the finite range of merohedral order that can be achieved in the solid, typically a few hundred spins ordered together (*5*) into glassy nanoclusters. Because the morphology cannot be reproducibly changed through thermal cycling or by a magnetic field, these spin structures are not related to the morphology of the material but are, according to our results, inherently determined by the merohedral ordering. The influence of the intracluster merohedral order on the distribution of exchange interactions and intercluster effects are important open questions.

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