cmHg], where cm³ (STP) is the volume at standard temperature and pressure, cm is the membrane thickness, cm² is the exposed membrane area on the feed side, and cm Hg is the feed gas pressure.
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- films of poly(dimethoxyparaphenylenevinylene) and polythiophene derivatives, M. Colby for assistance with BET and density measurements, and R. Goethals for painting Fig. 3. Funded by the Air Force Office of Scientific Research under contract F4962-086-C-0060 (H.R.), the National Science Foundation [grant CHE-86-57822 (R.B.K.)], and the David and Lucille Packard Foundation (R.B.K.).

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A Room-Temperature Molecular/Organic–Based Magnet

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The reaction of bis(benzene)vanadium with tetracyanoethylene, TCNE, affords an insoluble amorphous black solid that exhibits field-dependent magnetization and hysteresis at room temperature. The critical temperature could not be estimated as it exceeds 350 kelvin, the thermal decomposition temperature of the sample. The empirical composition of the reported material is $V(TCNE)_x \gamma(CH_2Cl_2)$ with $x \sim 2$ and $y \sim 1/2$. On the basis of the available magnetic and infrared data, threedimensional antiferromagnetic exchange of the donor and acceptor spins resulting in ferrimagnetic behavior appears to be the mode of magnetic coupling.

ECENTLY THERE HAS BEEN GROWing interest in the preparation and characterization of molecular/organic polymer-based materials that exhibit cooperative magnetic interactions (that is, ferro- and ferrimagnetic behavior) (1-6). The electron-transfer salt [(FeCp*2]) [TCNE]⁻ (Cp^{*} = pentamethylcyclopen-tadienide; TCNE = tetracyanoethylene) is a bulk ferromagnet with a Curie temperature T_c of 4.8 K (5, 6). Subsequently, $[MnCp_2]^{+}[TCNQ]^{-}(TCNQ = 7,7,$ 8,8-tetracyano-*p*-quinodimethane) and $[MnCp*_2]^{+}$ [TCNE]⁻ were shown to have T_c 's of 6.2 (7) and 8.8 (8) K, respectively. These observed magnetic couplings and the trend in $T_{\rm c}$ are consistent, respectively, with the expectations of the extended-McConnell configurational admixture (9) and twospin-site mean-field Heisenberg models (10).

In addition to these electron-transfer ferromagnetic materials, the concept of having a large number of ferromagnetically coupled unpaired electrons in orthogonal orbitals was exploited by Day and co-workers in studies of (cation)₂CrCl₄. These compounds have extended network structures in two dimensions, T_c 's below 55 K, and are optically transparent (11). The ferrimagnetic coupling of differing spins sites has been promoted by Kahn's group, who used different metal ions (3) {for example, a Néel temperature, T_N , of 14 K for Cu^{II}Mn^{II}- $(obbz) \cdot H_2O$ [obbz = oxamidobis(benzoato)]} (12), and by the groups of Gatteschi and Rey, who used metal ions and nitroxide radicals in extended one-dimensional (1-D) network structures (4) [for example, 8.1 K T_N for Mn^{II}(hfac)₂NITEt (hfac = hexafluoroacetylacetonate; NITEt ethyl nitronyl nitroxide)] (13). Other research groups have demonstrated the ferromagnetic coupling of spins in organic systems (2, 5, 14); however, bulk cooperative magnetic behavior has not been achieved. Thus, to date magnetic ordering temperatures for molecular/organic polymer-based materials are all below that accessible by liquid nitrogen.

We have extended our research aimed at making high-T_c molecular-based magnets (5, 6, 9) to the reaction of V(C₆H₆)₂ (15) and TCNE (9). Like [Mn^{III}Cp^{*}₂]^{:+}, $[V^{I}(C_{6}H_{6})_{2}]^{:+}$ is an S = 1 cation with a ${}^{3}E_{2g}$ ground state $(a_{1g}{}^{1}e_{2g}{}^{3})$ (16, 17). The addition of $V(C_6H_6)_2$ to an excess of TCNE in dichloromethane at room temperature results in the precipitation of a black solid that is amorphous, as ascertained by powder x-ray diffraction. The empirical composition of this extremely air-sensitive material is $V(TCNE)_x \gamma CH_2 Cl_2$ (18), but because of the extreme insolubility of the precipitate and reactivity of the solvent, variations in composition as a function of preparation conditions have been observed. The first step in the reaction is electron transfer from $V(C_6H_6)_2$ to TCNE, which was followed unexpectedly by loss of the benzene ligands, as is evident from the infrared (IR) spectra, which lack ν_{C-H} absorptions in the 3060- to 3100-cm⁻¹ region (19). All of the materials exhibit strong, broad absorptions at 2099 \pm 5 and 2188 \pm 9 cm⁻¹, which are assigned to C=N ($\nu_{C=N}$) or perhaps $\nu_{N=C=C}$ (Fig. 1) (19). The breath of the $\nu_{C=N}$ absorptions and relatively low frequency are consistent with the presence of reduced TCNE, with some N atoms bound to V.

TCNE has been reported to be a σ -Nbound ligand for several V and Mn complexes. $V^{TV}X(C_5H_5)_2(TCNE)$ (X = Cl, Br, and I) (20) has $\nu_{C=N}$ absorptions at 2118, 2152, 2192, and 2211 cm⁻¹. Likewise $Mn^{II}(CO)_2(C_5H_5)(TCNE)$ (21, 22) exhibits $\nu_{C=N}$ absorptions at 2125m, 2205s, and 2230vw cm⁻¹(m, medium, s, strong, and vw, very weak). On the basis of the x-ray structures of these model compounds, the lower energy absorption is assigned to the M←NC interaction, whereas the higher energy absorption is attributed to the CN groups not bonded to M. With an increasing number of M NC interactions per TCNE, the $\nu_{C=N}$ absorptions shift to lower energy {that is, 2125m, 2160vw, and 2205vw cm⁻¹ for $[Mn(CO)_2(C_5H_5)]_2$ -(TCNE), 2105s and 2150m cm⁻¹ for $[Mn(CO)_2(C_5H_5)]_3(TCNE)$, and 2110s and 2160m cm⁻¹ for $[Mn(CO)_2(C_5H_5)]_4$ -(TCNE)} (22). Additional model V-TCNE

Fig. 1. Representative infrared absorptions in the 1900 to 2300 cm⁻¹ region that are assigned to $\nu_{C=N}$ for $V(TCNE)_x$. $\gamma(CH_2Cl_2).$



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complexes that would further aid in the interpretation of the IR spectra are not yet available. However, TCNE m-alkene bonding to V is an unlikely bonding mode, as $\nu_{C=N}$ would then occur above 2210 cm⁻¹ (23).

Thus, on the basis of IR, x-ray diffraction, and solubility data, the black precipitate is best described as a 3-D network of V cations linked together by N-bound, bridging [TCNE]⁻ ligands; the compound is not a simple electron-transfer salt. Attempts to discern the oxidation state of V by x-ray photoelectron spectroscopy were unsuccessful, however, the extreme oxygen sensitivity of the compound suggests V(0), V(I), or V(II).

The Faraday balance (24) magnetic susceptibility of $V(TCNE)_x \gamma(CH_2Cl_2)$ exhibits a field-dependent magnetic susceptibility and magnetization M between 1.4 and 350 K (Fig. 2) (25). The nearly linear increase of M with decreasing T is noted, but it is not understood at present. Hysteresis with a coercive field of 60 G is observed at room temperature (Fig. 3) and at 4.2 K. The strong magnetic behavior of the material is readily observed by its being attracted to a permanent magnet at room temperature. The critical temperature cannot be estimated as it exceeds 350 K, the thermal decomposition temperature of the sample. This mag-

netic behavior is in stark contrast to the antiferromagnetic behavior of V metal (T_N = 245 K), VO ($T_{\rm N}$ = 117 K), and V₂O₃ (which does not exhibit magnetic order above 4.2 K) (26). The amount of magnetism is equivalent to 1.5% by weight Fe at room temperature and 6.8% by weight Fe at 2 K. This amount is in excess of that determined by inductively coupled plasma (ICP) microanalysis (18). The sample exhibits a strong electron paramagnetic resonance signal at g = 1.96098 and 1.95648 with a peak-to-peak linewidth of 28.8 and 54.3 G at 298 and 96 K, respectively.

The magnetic material loses susceptibility with time with a half-life of ~50 days at 297 K and rapidly decomposes in air at the diffusion rate of oxygen and becomes nonmagnetic. The decomposed product has much weaker absorptions at 2225 cm⁻¹, which is in the region reported for neutral TCNE (27) as well as for TCNE π -bonded to metals (23). Thus, the only cyano-containing species is TCNE. Furthermore, upon treatment with air a broad (1200 to 1600 cm⁻¹) new IR feature appears.

Although the structure is as yet unknown, it is interesting to speculate as to the type of magnetic behavior present from this system. From the IR data and elemental analysis we can best formulate the precipitate as VII- $(\text{TCNE})_2 \cdot 1/2(\text{CH}_2\text{Cl}_2) \text{ with } S = 3/2 \text{ V}^{\text{II}}$ and two S = 1/2 [TCNE]⁻⁻ ligands (28). For ferromagnetic coupling, S_{total} is 5/2 and, assuming g is 2, the magnetization M is expected to be 28×10^3 emuG/mol. For antiferromagnetic coupling between the VII and the two [TCNE]'- ligands, and hence ferrimagnetic behavior, as observed for magnetite (Fe₃O₄), the S_{total} is 1/2 and M is expected to be 5.6×10^3 emuG/mol. The latter is in good agreement with the value of 6.0×10^3 emuG/mol observed at 2 K at 19.5 kG. The microscopic origin of the substantially increased exchange interactions that results in higher critical temperature with respect to Fe^{III} and Mn^{III} electrontransfer salts (10) is likely due to the direct bonding of the TCNE N atoms to V (that is, without the π -bound ligand spacer) and a 3-D network structure in the solid.

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- 18. For $V(TCNE)_x \gamma CH_2 Cl_2$ a range of x and y is observed for preparations differing in solvents and mole ratios of the starting materials; oxygen and perhaps benzene in small amounts are present in some cases. For the material discussed herein $x \sim 2$ and $\gamma \sim 1/2$. Magnetic materials with $1.5 \leq x \leq 2$ and $y \sim 1/2$. Magnetic materials with $1.5 \le x \le 2$ and $0 \le y \le 1$ have also been prepared. Elemental analysis: calculated (observed) for C_{12.5}HClN₈V: %C = 42.95 (42.81, 43.20, 43.00), %H = 0.29 (0.14, 0.68, 0.35), %N = 32.05 (30.63, 30.00, 31.04), and %V = 14.57 (15.31)⁻, % chlorine was not reproducible. Trace elements {Fe (41 ppm), Co [none detected (<25 ppm)], Ni [none detected (<50 ppm)], and Cr (34 ppm)] were determined by ICP microanalysis. Thermal decomposition in a mass spectrometer showed the loss of CH2Cl2 and TCNE
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- 25. In contrast, the reaction of V(C₆H₆)₂ with TCNQ, 2,3-dichloro-5,6-dicyanobenzoquinone, hexacyano butadiene, or 2,3,5,6-tetracyanobenzoquinone leads to precipitates that do not exhibit field-dependent magnetic susceptibilities χ and as evidenced from the fit of the susceptibility data to the Curie-Weiss expression $[\chi \propto (T - \theta)^{-1}]$, these materials exhibit antiferromagnetic behavior (that is, $\theta < 0$).
- 26. J. B. Goodenough, Magnetism and the Chemical Bond

Electronic States of $K_x C_{60}$: Insulating, Metallic, and Superconducting Character

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The recent report of electrical conductivity in the alkali metal fullerides and the discovery of superconductivity at 18 K for K_xC₆₀ has raised fundamental questions about the electronic states on either side of the Fermi level, their occupancy with K intercalation, and the mechanism of superconductivity. Direct photoemission evidence is presented of filling of bands derived from the lowest unoccupied molecular orbital as a function of K incorporation for the metallic and insulating phases. This filling is not rigid band-like, and it reflects disorder in the K sites. Theoretical analysis indicates that K_xC₆₀ is a strong coupling superconductor, and we suggest that the enhanced electron-phonon interaction is related to the unique hybridization of the C sp-derived states.

INCE THEIR DISCOVERY (1), THE fullerenes have revealed a succession of remarkable properties. These molecules represent the third form of pure C, joining sp^3 -bonded diamond and sp^2 -bonded graphite but exhibiting an intermediate form of hybridization of s- and p-states. For C_{60} , the molecular structure is especially symmetric with 60 equivalent atoms in a soccer ball-like configuration (2, 3). While these molecules are less stable by 0.4 eV per atom than diamond or graphite (4) and they can be burned (5), they are exceptionally stable against photofragmentation (6). Following the breakthrough in synthesis by Krätschmer et al. (7), studies of solid-state properties of single crystals of C₆₀ have shown that the molecules rotate (2) in fcc (face-centered-cubic) lattice sites (8) at temperátures well below 300 K. Photoemission and inverse photoemission studies (9, 10) have shown a richness in structure for the occupied and empty electronic states of condensed C_{60} and C_{70} as well as a novel molecular plasmon (9). First principles calculations have produced good agreement with experiment (9-12), and charge delocalization and dispersive band formation have been reported (10, 11). Alkali metal incorporation into the fullerite lattice has produced conducting fullerides (13). Finally, the discovery of superconductivity (14) in $K_{x}C_{60}$ at 18 K has generated intense interest in the conduction band states and the role of electron-phonon coupling.

This paper focuses on electronic structure changes due to K incorporation in solid C_{60} , starting with insulating C₆₀, progressing through the metallic state, and reaching the insulating K6C60 state. Photoemission spectra demonstrate the occupancy of ~1-eV wide bands derived from threefold degenerate lowest unoccupied molecular orbitals (LUMOs) of the molecule, but filling is not (Wiley-Interscience, New York, 1963), pp. 98, 100, and 104.

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- 28. Other less likely possibilities are $S = 1/2 V^{IV}$ and S = 0 $[\text{TCNE}]^{2^-}$. Mixed valent formulations, such as $S = 1 \text{ V}^{\text{III}}$ and $S = 1/2[\text{TCNE}]^-$ and S = 0[TCNE]²⁻, also cannot be ignored.
- 29. We acknowledge support from the U.S. Department of Energy Division of Materials Science grant DE-FG02-86ER45271.A000. We appreciate the EPR spectra provided by S. Hill and P. J. Krusic, XPS spectra provided by S. Thil and F. J. Kluste, ATS spectra determined by J. Wyre and G. Blackman, powder diffraction taken by G. Hyatt, C. M. Foris, and K. H. Gardner, IR spectra by A. P. Berry, synthetic assistance by C. Vazquez and S. Riggs, energy dispersive x-ray analysis by M. Harmer, hysteresis data taken by M. H. Reilly, P. F. Carcia, and K. S. Narayan, helpful discussions with D. A. Dixon, and ICP microanalysis by T. S. Connell and B. F. Burgess, Jr., Contribution no. 5228 of Central Research & Development, Du Pont.

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simply rigid band-like. Instead, the entire LUMO-derived band is evident after low doping, and emission from that band increases with K incorporation. We also observe band broadening associated with disorder in the K bonding sites. In addition, increases in spectral width for the valence band features reflect changes in the crystal field, reduced molecular symmetry, and modification of the band structure. Having identified the band responsible for superconductivity, we provide an estimate of the parameters relevant for superconductivity. From theoretical analysis, we find strong electron-phonon coupling and suggest that s-p hybridization in the conduction band is responsible for the increase in coupling compared to intercalated graphite (4)

Insight into the likely structure of K-incorporated C60 can be gained by analysis of results for K-intercalated graphite (15) where the structure can be explained in terms of packing of K ions (ionic radius 1.33 Å) between sheets of C (van der Waals radius 1.68 Å). With these atomic dimensions and the lattice constant of the fcc fullerene, 14.2 Å, it follows that K ions could occupy the interstitial tetrahedral (1.15 Å radius) and octahedral (2.1 Å radius) holes of the fcc lattice. The occupancy of each site by one ion would give a stoichiometry of K₃C₆₀. Our total-energy local-density calculations confirm that this is an energetically favored structure since the enthalpy of formation is ~ 1 eV per K atom (4). Fischer and co-workers (16) recently reported an x-ray diffraction study of K_xC₆₀ grown at 200°C. Their results for the fully reacted equilibrium phase showed a bcc (body-centered-cubic) lattice with K ions occupying tetrahedral sites. The occupancy of each such site would give K₆C₆₀ with each anion surrounded by 24 cations. For

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