Magnetic properties of TDAE-C_{60} and TDAE-C_{70}, where TDAE is tetrakis(dimethylamino)ethylene

Kazuyoshi Tanaka, Anvar A. Zakhidov,[*] Kazunari Yoshizawa, Kenji Okahara,[†] and Tokio Yamabe[†]

Department of Hydrocarbon Chemistry and Division of Molecular Engineering, Faculty of Engineering,
Kyoto University, Kyoto, 606-01 Japan

Kyuya Yakushi

Institute for Molecular Science, Myodaiji, Okazaki, 444 Japan

Koichi Kikuchi, Shinzo Suzuki, Isao Ikemoto, and Yohji Achiba

Department of Chemistry, Tokyo Metropolitan University, Hachi-oji, Tokyo, 192-03 Japan

(Received 8 June 1992; revised manuscript received 1 October 1992)

Magnetic properties of C_{60} and C_{70} complexes with tetrakis(dimethylamino)ethylene (TDAE) have been studied based on the measurements of the Faraday-balance magnetization and the electron-spin resonance (ESR). It has been found that both TDAE-C_{60} and TDAE-C_{70} possess about one radical spin per fullerene molecule. TDAE-C_{60} has been confirmed to show a ferromagnetic-type transition at $T_c = 16.7$–17.5 K. Appearance of a broad and intense ESR signal below T_c for TDAE-C_{60} suggests that the radical spins in the magnetically ordered state are rather localized on each C_{60} molecule and are ferromagnetically correlated. On the other hand, TDAE-C_{70} does not show ferromagnetism at temperatures above 4.5 K.

I. INTRODUCTION

A recent report of the observation of "soft" ferromagnetism below 16.1 K in the 1:1 complex of C_{60} with one of the strongest organic donors tetrakis-(dimethylamino)ethylene (TDAE) (Ref. 1) leads to the suggestion that C_{60} may possess other unexpected interesting properties besides superconductivity at high T_c as found in M_3C_{60} ($M =$ K, Rb, RbCs, or RbTl).[2–5] This unusual ferromagnetism observed by a SQUID magnetometer does not show hysteresis in the magnetization curve and exhibits a complicated temperature dependence for the magnetic susceptibility. This gives rise to a simple question of its origin and requires a more careful study of its magnetic properties with other methods more direct and simpler than the SQUID measurement (see, e.g., Ref. 6).

On the other hand, the absence of superconductivity in M_xC_n ($n =$ 70, 76, 78, 84, and 90) (Ref. 7) and a strong decrease in T_c in the molecular alloys of $M_x(C_{60})_{1-y}(C_{70})_y$ ($M =$ K, Rb) (Refs. 7 and 8) indicates that there could be some definite discrimination of C_{60} from C_{70} and higher fullerenes. In this sense, it also seems to be of interest to compare the magnetic properties of TDAE-C_n ($n \geq 70$) with those of TDAE-C_{60} and to check whether the exceptional properties of C_{60} are reflected in its magnetic behavior.

We have briefly reported[9] the early results of a comparative study of magnetic properties of TDAE-C_{60} and TDAE-C_{70}, where the former shows a ferromagnetic-type transition at $T_c = 16.7$–17.5 K and the latter demonstrates the usual Curie-type narrow electron-spin resonance (ESR) peak for the entire temperature range suggesting an absence of the ferromagnetic transition at least

down to 4.5 K. In the present paper, we report results of a more detailed study of magnetic properties of TDAE-C_{60} and TDAE-C_{70}. For the magnetization measurement the Faraday-balance method that is more direct and conventional than the SQUID method was employed at about 4.5 and 20 K and the ESR measurement was performed in the temperature range 4.5–290 K. It is demonstrated that TDAE-C_{60} shows significantly distinct behavior at low temperatures both in terms of its magnetization and its ESR spectrum, suggesting that C_{60} is again exceptional. A preliminary check of TDAE-C_{60} and TDAE-C_{70} with the use of the low-field-signal (LFS) microwave absorption has proved the absence of a superconducting state down to 4.5 K in these two materials.

II. EXPERIMENT

The sootlike material containing C_{60}, C_{70}, and higher fullerenes was prepared by arc heating of graphite (99.997%) in He at about 100 Torr.[10] Crude products were Soxhlet extracted from the carbon soot using carbon disulfide. A preparative high-performance liquid chromatography (HPLC, model LC-908 with JAIGEL 2H, 2H, Japan Analytical Industry Co.) employing toluene as an elution was used to separate several kinds of fullerenes from very concentrated extract and to further purify C_{60} and C_{70}.

TDAE fullerides were prepared by a recipe similar to that reported in Ref. 1. That is, 0.60 mg of C_{60} (or 0.39 mg of C_{70}) was dissolved in 1 ml of a benzene-toluene mixed (1:1) solvent and then a large excess amount of TDAE was added under a nitrogen flow. Care was taken to purge the oxygen in the solvent before the reaction. Black precipitate of TDAE-C_{60} or TDAE-C_{70} was ob-

tained and the solvent and unreacted TDAE were removed. Elemental analyses gave the molecular ratio of the samples to be $(TDAE)_{1.35}(C_{60})_1$ and $(TDAE)_{1.30}(C_{70})_1$.

For the magnetization and the magnetic-susceptibility measurements, 36.8 mg of TDAE-C_{60} and 34.4 mg of TDAE-C_{70} were thus prepared in separate Pyrex NMR tubes under nitrogen flow and sealed after evacuation down to less than 10^{-4} Torr for 2 h. For the ESR measurement, all of these processes were performed directly in the quartz-ESR tube with a 5-mm outer diameter to keep the sample away from the atmosphere in the same manner as that for the magnetization and the magnetic-susceptibility measurements.

The magnetization and the magnetic-susceptibility measurements were carried out with an Oxford Instruments Faraday-type balance. The sample holder (sealed Pyrex NMR tube) was hung in the magnetic field using a very thin quartz fiber. Magnetic susceptibility of this holder was eliminated from the raw data. The magnetization curves were recorded at 4.5 and 20 K for each sample under magnetic fields up to 50 kG (see Sec. III A). The temperature dependence of the magnetic susceptibility was examined in the range 1.8–260 K at the constant magnetic field of 5 kG.

The ESR spectra were recorded at 9.1 GHz with a field modulation of 100 kHz in the temperature range 4.5–290 K on a Varian E-112 spectrometer equipped with an Oxford liquid-helium-flow cryostat. The modulation width was kept at 0.5 G for most of the measurements. During single ESR measurements taking ~3 min each, the temperature was maintained within ±2 K of its set value. Peak-to-peak linewidth (ΔH_{pp}) (Ref. 11) and g values were determined using a Mn^{2+}-MgO solid solution as a standard. For the LFS measurements, Helmholtz coils were used in the usual ESR procedure.[12]

III. RESULTS

A. Magnetization and magnetic susceptibility

The magnetization (M-H) curves of the TDAE fullerides measured under the magnetic field change $0 \rightarrow 50$ kG$\rightarrow 0 \rightarrow -50$ kG$\rightarrow 0 \rightarrow 50$ kG$\rightarrow 0$ at about 4.5 and 20 K are shown in Figs. 1(a) and 1(b). The shape of the magnetization curve of TDAE-C_{60} at 19.5 K shows a typical paramagnetic behavior, whereas at 4.6 K a saturation of the magnetization occurs indicating the existence of ferromagnetic correlation of spins due to superparamagnetism of the TDAE-C_{60} sample as described below. Hence, a magnetic transition between these two temperatures definitely occurs in accordance with the report in Ref. 1. At 4.6 K the saturation is achieved approximately at the magnetic field 45 kG and the saturation magnetization is 0.84 emu G g^{-1}.[13] We have also found that there is no hysteresis in the magnetization curve in correspondence with the data reported in Ref. 1. For TDAE-C_{60} the effective Bohr magneton number n_{eff} and the spin quantum number S at 4.6 K were estimated from the initial M-H curve based on the expressions at $S \gg 1$,[14]
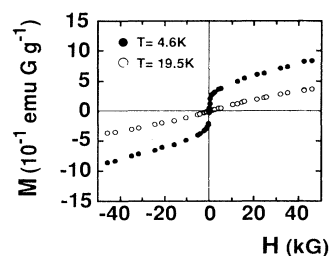
(a)
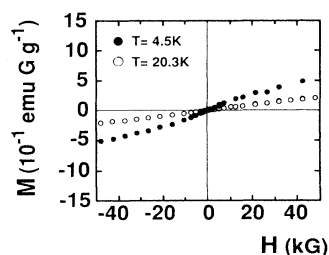
(b)

FIG. 1. Magnetization curves of (a) TDAE-C_{60} and (b) TDAE-C_{70} at 4.5 and 20 K (see text).

$$n_{eff} \equiv \frac{\mu_{eff}}{\mu_B} = \frac{3k_B}{\mu_B M_S} \left[\frac{\partial M}{\partial (H/T)} \right]_{H=0} \quad (1)$$

and

$$g\sqrt{S(S+1)} = n_{eff}, \quad (2)$$

where μ_{eff} stands for the effective magnetic moment, μ_B is the Bohr magneton, k_B is the Boltzmann constant, and g is the Landé g factor. Here g was assumed to be 2 for simplicity and the total orbital angular momentum quantum number (L) to be zero as for usual organic radical spins. The S value thus estimated is listed in Table I, which suggests that in the present TDAE-C_{60} sample at 4.6 K about 170 spins are ferromagnetically correlated. This value is supposed to give an average of the spin alignments in the "spin clusters," which is acceptable since morphology of the present sample is not crystalline but probably polycrystalline, and hence the saturation magnetization observed here should be attributed to superparamagnetism. If there is an appropriate distribution of spin clusters with large n_{eff}, the system can accidentally show a ferromagnetism of bulk scale characterized by a hysteresis loop of the magnetization curve at

TABLE I. Saturation magnetization (M_S in emu G g^{-1}), effective Bohr magneton number (n_{eff}), spin quantum number (S), and spin-cluster concentration [N_S in (mol-TDAE-C_{60})$^{-1}$] of TDAE-C_{60} at 4.6 K.

M_S	n_{eff}	S	N_S[a]
0.84(±0.1)	170.8(±0.5)	84.9(±0.5)	4.9(±0.1)×10^{20}

[a]This value corresponds to the spin concentration of 8.3×10^{23} spins (mol-TDAE-C_{60})$^{-1}$.

low temperatures. This has been actually demonstrated in a certain sample of pyrolytic carbon prepared from adamantane.[15]

When the magnetization curve is saturated, the "spin-cluster" concentration N_S is expressed by

$$M_S = N_S g \mu_B S \ , \qquad (3)$$

where M_S is the saturation magnetization. Employing $S = 84.9$ obtained above, the spin-cluster concentration at 4.6 K is calculated to be 4.9×10^{20} $(\text{mol-TDAE-C}_{60})^{-1}$ as listed in Table I. On the other hand, TDAE-C$_{70}$ showed no existence of ferromagnetic correlation but typical paramagnetic behavior in the M-H curve at both 4.5 and 20.3 K as shown in Fig. 1(b).

In general, if the observed total magnetic susceptibility χ follows the Curie-Weiss behavior, it can be decomposed as in the following formula,

$$\chi = \chi_0 + C/(T - \Theta) \ , \qquad (4)$$

where χ_0 is the temperature-independent magnetic susceptibility, T is the temperature, C is the Curie constant, and Θ is the Weiss constant. Such behavior was observed at temperatures above 100 K for TDAE-C$_{60}$, and above 4.5 K for TDAE-C$_{70}$ as shown in Fig. 2(a). The Curie-type spin concentration N_C was determined from the following formula,

$$C = N_C g^2 \mu_B^2 S(S+1)/3 k_B \ , \qquad (5)$$

where, in this case, S was set at $\frac{1}{2}$.

An analysis of the Curie-type susceptibility data measured at 5 kG is listed in Table II. The quantity χ_0 of TDAE-C$_{60}$ is very small suggesting almost complete cancellation of diamagnetic and Pauli-paramagnetic susceptibilities, if any, whereas that of TDAE-C$_{70}$ signifies a dominant diamagnetic term over a very small Pauli-paramagnetic term as is expected from small electrical conductivity of K$_x$C$_{70}$.[8] Employing the value 1:1 for the molecular ratio of fullerenes and TDAE, the Curie-type spin concentrations (N_C) per mol of TDAE fullerides were estimated to be on the order of 10^{23} spins, being very close to the Avogadro number. The N_C value of TDAE-C$_{60}$ reasonably agrees with the reduced spin concentration of TDAE-C$_{60}$ with ferromagnetic spin alignment at 4.5 K as shown in the footnote of Table I.

The χ^{-1} plots in Fig. 2 again confirm that TDAE-C$_{70}$ has a simple Curie-type dependence in the whole temperature range and that TDAE-C$_{60}$ definitely shows an obvious magnetic transition at 17.5 K, the Curie temperature in this case. This value is in good agreement with the
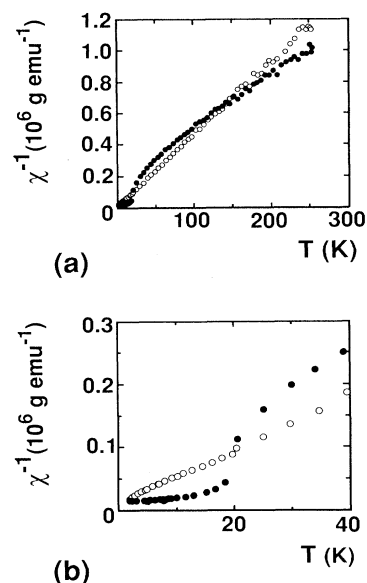

(a)

(b)

FIG. 2. χ^{-1}-T plot for TDAE-C$_{60}$ (filled circles) and TDAE-C$_{70}$ (open circles) below (a) room temperature and (b) 40 K.

value 17.2 K reported in Ref. 1 for $H = 1$ kG. It is striking that the Weiss constant Θ of TDAE-C$_{60}$ obtained by the extrapolation of the curve for above 100 K shows a negative value (-58 K) as is seen in Fig. 2(a), indicative of antiferromagnetic behavior, which will be discussed in Sec. IV. In contrast, Θ of TDAE-C$_{70}$ is zero within experimental error so that it follows the Curie law without any evidence of an appreciable cooperative phenomenon.

B. ESR analysis

The ESR spectral shapes are of simple Lorentzian type at room temperature for both TDAE-C$_{60}$ (see Fig. 3) and TDAE-C$_{70}$, with $\Delta H_{1/2}/\Delta H_{pp}$ being equal to 2.336 and 2.615, respectively, where ΔH_{pp} and $\Delta H_{1/2}$ indicate the peak-to-peak linewidth and the outside half-height linewidth, respectively, of the ESR peak.[11] Purely Gaussian and Lorentzian line shapes give the values 1.92 and 2.40, respectively, for this ratio. The TDAE-C$_{60}$ line shape becomes asymmetric under 40 K, which will be discussed later.

The relative errors of the observed ΔH_{pp} and g values are less than 4% and 0.03%, respectively. The temperature dependence of ΔH_{pp} of the two samples is shown in

TABLE II. Temperature-independent magnetic susceptibility (χ_0 in emu g^{-1}), Curie constant (C in emu K g^{-1}), Weiss constant (Θ in K), and Curie-type spin concentration [N_C in spins (mol-TDAE-fulleride)$^{-1}$] of the present samples.

	χ_0	C	Θ	N_C
TDAE-C$_{60}$[a]	$3.6(\pm 0.1) \times 10^{-7}$	$3.1(\pm 0.1) \times 10^{-4}$	$-58(\pm 1)$	$4.6(\pm 0.1) \times 10^{23}$
TDAE-C$_{70}$	$-4.0(\pm 0.1) \times 10^{-6}$	$2.1(\pm 0.1) \times 10^{-4}$	$0(\pm 1)$	$3.5(\pm 0.1) \times 10^{23}$

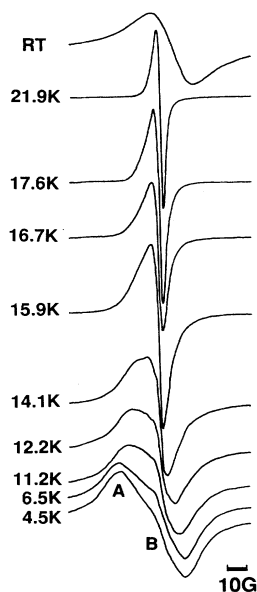[a]Data in the temperature range from 100 K to room temperature where the Curie-Weiss law holds.

FIG. 3. Selected ESR spectral shapes of TDAE-C_{60} in the low-temperature region. Mark A signifies the broad peak appearing under 16.7 K, whereas mark B signifies the narrow peak with the Curie-Weiss-type behavior (see text).

the inset of Fig. 4. ΔH_{pp} decreases more abruptly in TDAE-C_{60} than in TDAE-C_{70} with the decrease in the temperature. This narrowing, probably attributed to the increase in exchange interaction among electronic spins, continues down to 20 K in both the samples. Under 16.7 K, however, another broad ESR peak grows in TDAE-C_{60}, eventually causing the two phases A and B as seen in the spectrum of Fig. 3. This broad ESR peak A appears independently from the narrow one B in TDAE-C_{60}. The peak B could not be decoupled from the big peak A, since the intensity of the former is much smaller at lower temperatures in particular. Hence the ΔH_{pp} of the peak B was immeasurable and the g value of the peak A was
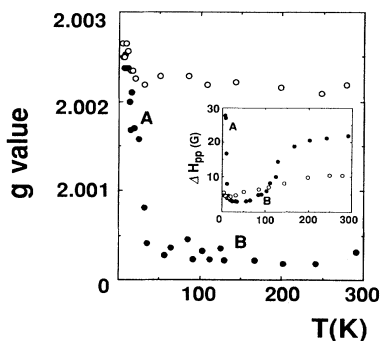

FIG. 4. The g values of the ESR spectra of TDAE-C_{60} (filled circles) and TDAE-C_{70} (open circles). The inset shows the peak-to-peak linewidths (ΔH_{pp}) of the ESR spectra. See the caption of Fig. 3 with regard to the marks A and B.

measured from the zero crossing of the total ESR curve.

It is thus considered that 16.7 K corresponds to T_c for the magnetic transition of TDAE-C_{60} by the ESR measurement at $H \approx 3$ kG. On the other hand, ΔH_{pp} of TDAE-C_{70} monotonically decreases at low temperatures until a slight drawback occurs under 10 K. Such a clear difference of the ESR spectra between TDAE-C_{60} and TDAE-C_{70} offers strong evidence that the radical spins mostly reside on the fullerenes. The signal of TDAE$^+$, the reported g value which at room temperature is 2.0036,[16] does not appear in the present ESR charts of TDAE-C_{60} and TDAE-C_{70}. This observation result is guaranteed from the relative error range in the present measurement mentioned above and signifies that the concentration of detectable radical spins of TDAE$^+$, if any, should be $\sim 10^{-3}$ times as low as that of C_{60}^- or C_{70}^-. Hence, interpretation of the lack of observation of the counter spins that should exist on the donor side (TDAE$^+$) would require some spin-cancellation mechanism such as spin-flipping processes, the details of which are currently not clear.

The temperature dependence of the g value shown in Fig. 4 is of similar nature to that of ΔH_{pp}; that is, the g value of TDAE-C_{60} becomes large below 20 K. This increased g value is due to the appearance of the broader peak A, so the higher g value (2.0017–2.0025) can be assigned to the ferromagnetically ordered phase of TDAE-C_{60}. The g value of TDAE-C_{60} is 2.0003 at room temperature in good agreement with 2.0008 for TDAE-C_{60} (Ref. 17) and 1.9991 and 1.998 for electrochemically prepared C_{60}^-.[18,19] On the other hand, TDAE-C_{70} shows no drastic change in the g value which is 2.0022 at room temperature, and which is also similar to the value reported for the central ESR peak (2.003) of electrochemically prepared C_{70}^-.[19] Note that this value resembles that found in polyacenic materials consisting of condensed aromatic rings.[20]

IV. DISCUSSION

Although the origin of the ferromagnetic spin alignment and the species of the spin carriers in TDAE-C_{60} in Fig. 2(b) are as yet unclear, the comparison and differentiation of the magnetic properties of TDAE-C_{60} and TDAE-C_{70} would be useful at the present stage. The χ^{-1}-T behavior of TDAE-C_{60} indicates the sudden change from the Curie-Weiss dependence with an antiferromagnetic interaction ($\Theta = -58$ K; see Table II) to superparamagnetism with a temperature-independent ferromagnetic spin state at less than 20 K. The latter temperature-independent state suggests the possible presence of Pauli-paramagnetic behavior in that temperature range. On the other hand, TDAE-C_{70} shows a simple Curie-type dependence with the Weiss constant of nearly zero. Moreover, a complicated ESR behavior of TDAE-C_{60} was observed at 40 K in which the peak becomes asymmetric and twice as broad as that at room temperature, showing a deviation from a simple Curie-Weiss dependence. Finally, a broader ESR peak A (see Fig. 3) with a larger g value appeared at 16.7 K in correspon-

dence with the ferromagnetic transition. The appearance of the broader peak suggests the correlation of spins as has been found in the superparamagnetism of pyrolytic carbon prepared from adamantane.[15] On the other hand, the ESR peak of TDAE-C_{70} is narrow and always symmetric, indicative of the ordinary Curie-type spins although the charts are omitted here.

The present ESR signals of the high-temperature phase of TDAE-C_{60} as well as of TDAE-C_{70} in the entire temperature range indicate that the spins are largely on the fullerides to a very small extent on the TDAE side. This situation is in contrast to, for instance, the tetrathiafulvalene (TTF) -tetracyanoquinodimethane (TCNQ) charge-transfer salt, in which the spins reside on both TTF and TCNQ.[21] We currently consider that the magnetic property of the low-temperature phase of TDAE-C_{60} showing the ESR spectrum with a larger g value is determined by polaronic spins on C_{60}^- as described in what follows.

Assuming a 1:1 composition in TDAE-C_{60}, one transferred electron should occupy the lowest unoccupied molecular orbital of the neutral fullerene, causing a split of the orbital level known as the Jahn-Teller distortion[22] or, in other words, the polaronic effect in C_{60}.[23,24] In a TDAE-C_{60} crystal the shortest C_{60}-C_{60} distance of 9.98 Å along the c direction and a much larger lattice constant of 10.25 Å within the a-b plane[17] must provide highly anisotropic polaronic bands in which electrons should be delocalized, contributing to Pauli-type temperature dependence. On the other hand, internal orientational disorder such as that found in K-doped C_{60} (Ref. 25) could always cause a certain number of localized states and contribute to Curie-type spin behavior. Such interplay of the Pauli- and the Curie-type spins can cause a complicated temperature dependence especially in the present noncrystalline samples.

As has already been pointed out in Ref. 17, the electrons in highly anisotropic (quasi-one-dimensional) bands of TDAE-C_{60} are generally known to be unstable and tend to exhibit various electronic and/or magnetic phase transitions, i.e., with the formation of charge-density

wave, spin-density wave, or other ordered states. Then the localization of spins in polaronic bands after any of these phase transitions (e.g., Wigner-type crystallization of a dilute polaron gas) should create different types of localized spins such as observed here in the phase A in the ESR spectra below T_c shown in Fig. 3. It may be of interest to point out that a prototype for a polaronic ferromagnet has actually been devised by employing a modified skeleton of polyacetylene with regularly separated π conjugation.[26] Further studies of the low-temperature phase of TDAE-C_{60} by NMR and inelastic neutron scattering analyses should give additional information on the type of phase transition responsible for ferromagnetic alignment of TDAE-C_{60}.

In conclusion, the occurrence of ferromagnetic correlation in superparamagnetic domains of TDAE-C_{60} with $T_c = 16.7$–17.5 K has been confirmed by Faraday-balance magnetization and ESR measurements. No appreciable concentration of radical spins on TDAE$^+$ was detected by the ESR measurements for both TDAE-C_{60} and TDAE-C_{70}. The unusual appearance of a broad ESR signal below T_c of TDAE-C_{60} suggests that the spin correlation of the radical spins resides on each C_{60} molecule. On the contrary in TDAE-C_{70}, the lack of such a magnetic transition signifies that ferromagnetic correlation does not occur at least down to 4.5 K. Studies of TDAE complexes with higher fullerenes C_n ($n \geq 84$) are also now in progress to further clarify the special role of C_{60} compared with other members of the fullerene family.

ACKNOWLEDGMENTS

*Permanent address: Department of Thermophysics, Uzbek Academy of Science, Katartal 28, Chilanzar, Tashkent, 700135 Uzbekistan, Commonwealth of Independent States (CIS).

†Also at Institute for Fundamental Chemistry, 34-4 Nishihiraki-cho, Takano, Sakyo-ku, Kyoto, 606 Japan.

[1] P.-M. Allemand, K. C. Khemani, A. Koch, F. Wudl, K. Holczer, S. Donovan, G. Grüner, and J. D. Thompson, Science 253, 301 (1991).

[2] A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Kortan, Nature (London) 350, 600 (1991).

[3] K. Tanigaki, T. W. Ebbesen, S. Saito, J. Mizuki, J. S. Tsai, Y. Kubo, and S. Kuroshima, Nature (London) 352, 222 (1991).

[4] Z. Iqbal, R. H. Baughman, B. L. Ramakrishna, S. Khare, N. S. Murthy, H. J. Bornemann, and D. E. Morris, Science 254, 826 (1991).

[5] A. A. Zakhidov, A. Ugawa, K. Imaeda, K. Yakushi, H. Inokuchi, K. Kikuchi, S. Suzuki, I. Ikemoto, and Y. Achiba, Solid State Commun. 79, 939 (1991).

[6] K. Tanaka, K. Yoshizawa, A. Takata, T. Yamabe, and J. Yamauchi, J. Chem. Phys. 94, 6868 (1991).

[7] A. A. Zakhidov, K. Yakushi, K. Imaeda, H. Inokuchi, K. Kikuchi, S. Suzuki, I. Ikemoto, and Y. Achiba, Mol. Cryst. Liq. Cryst. 218, 299 (1992).

[8] A. A. Zakhidov, K. Imaeda, A. Ugawa, K. Yakushi, H. Inokuchi, Z. Iqbal, R. H. Baughman, B. L. Ramakrishna, and Y. Achiba, Physica C 185-189, 411 (1991).

[9] K. Tanaka, A. A. Zakhidov, K. Yoshizawa, K. Okahara, T. Yamabe, K. Yakushi, K. Kikuchi, S. Suzuki, I. Ikemoto, and Y. Achiba, Phys. Lett. A 164, 221 (1992).

[10] K. Kikuchi, N. Nakayama, M. Honda, S. Suzuki, K. Saito, H. Shiromaru, K. Yamauchi, I. Ikemoto, T. Kuramochi, S. Hino, and Y. Achiba, Chem. Lett. 1991, 1607.

[11]See, for instance, Ref. 20 with respect to the nomenclature.

[12]A. A. Zakhidov, I. I. Khairullin, V. Y. Sokolov, R. H. Baughman, Z. Iqbal, M. Maxfield, and B. L. Ramakrishna, Synth. Met. **41-43**, 3717 (1991).

[13]There are slight changes in the data values from those in Ref. 9 due to the refinement of the adjustment of the holder in the magnetization and magnetic-susceptibility measurements.

[14]See, for instance, A. Weiss and H. Witte, *Magnetochemie* (Chemie GmbH, Weinheim, 1973), Chap. 5.

[15]K. Tanaka, M. Kobashi, H. Sanekata, A. Takata, T. Yamabe, S. Mizogami, K. Kawabata, and J. Yamauchi, J. Appl. Phys. **71**, 836 (1992).

[16]K. Kuwata and D. H. Geske, J. Am. Chem. Soc. **86**, 2101 (1964).

[17]P. W. Stephens, D. Cox, J. W. Lauher, L. Mihaly, J. B. Wiley, P.-M. Allemand, A. Hirsch, K. Holczer, Q. Li, J. D. Thompson, and F. Wudl, Nature (London) **355**, 331 (1992).

[18]P.-M. Allemand, G. Srdanov, A. Koch, K. Khemani, F. Wudl, Y. Rubin, F. Diedrich, M. M. Alvarez, S. J. Anz, and R. L. Whetten, J. Am. Chem. Soc. **113**, 2780 (1991).

[19]D. Dubois, M. T. Jones, and K. M. Kadish, J. Am. Chem. Soc. **114**, 6946 (1992).

[20]K. Tanaka, T. Koike, T. Yamabe, J. Yamauchi, Y. Deguchi, and S. Yata, Phys. Rev. B **35**, 8368 (1987).

[21]Y. Tomkiewicz, A. R. Taranko, and J. B. Torrance, Phys. Rev. Lett. **36**, 751 (1976).

[22]K. Tanaka, M. Okada, K. Okahara, and T. Yamabe, Chem. Phys. Lett. **193**, 101 (1992).

[23]K. Harigaya, J. Phys. Soc. Jpn. **60**, 4001 (1991).

[24]B. Friedman, Phys. Rev. B **45**, 1454 (1992).

[25]R. Tycko, G. Dabbagh, M. J. Rosseinsky, D. W. Murphy, R. M. Fleming, A. P. Ramirez, and J. C. Tully, Science **253**, 884 (1991).

[26]D. A. Kaisaki, W. Chang, and D. A. Dougherty, J. Am. Chem. Soc. **113**, 2764 (1991).