Magnetic interactions in TDAE-C_{60}

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(Received 11 July 1995)

We have introduced the two-channel Sherrington-Kirkpatrick (SK) model to account for the temperature dependency of the magnetization of TDAE-C_{60} measured under very small magnetic field of order of 0.1 Oe. The two-channel SK model includes another glassy degree of freedom than spins. The second glassy degree of freedom couples to spins and hence has influence on the magnetic properties. This model is successful in explaining the rapid increase of the field cooling (FC) magnetization in the low-temperature region below the freezing temperature as well as the onset of the remanence, the difference between the FC and zero-field cooling magnetization, found in the experiment, both of which are difficult to explain simultaneously by the standard spin-glass models or ferromagnetic domains. While the phase in the two-channel SK model we found relevant for the experiment is quite different from the standard spin-glass models in the meaning described above, it has a similarity with the mixed phase of the SK model, in the meaning that both the Edward-Anderson order parameter and the spontaneous magnetization have nonzero values. This does not contradict the muon-spin-relaxation experiment, which shows the existence of the spontaneous magnetization in TDAE-C_{60}. We have also discussed the possible microscopic origin of the second glassy degree of freedom.

Magnetism observed in TDAE-C_{60} is one of the most interesting physical properties in the series of the fullerite.[1–3] While the mechanism of superconductivity in $A_3\,C_{60}$ is almost resolved with the electron-intramolecular-vibration (e-MV) coupling model,[4–7] which is quite different from that of cuprates where short-ranged strong electronic correlation effect is essential,[8,9] the mechanism of the magnetic phenomena in TDAE-C_{60} has not yet been explored well.[10,11] Possible transition or freezing temperature of the ferromagnetic or the spin-glass state is thought to be about 10–15 K by experiments, which is quite larger than the ferromagnetic transition temperature of other existing organic compounds.[12,13] Alloy complexes TDAE-$(C_{60})_{1-x}(C_{70})_x$ were studied. It was found that the suppression of the magnetic transition temperature is weakly dependent on x.[14] The authors of Ref. 14 concluded on the basis of their experimental result that TDAE-C_{60} is a three-dimensional magnetic system, in spite of the fact that its c-centered monoclinic structure is suggestive of one dimensionality.

Some recent experimental results obtained with pulsed electron-spin resonance and ac magnetization depict the spin-glass picture.[15,16] It has recently been found that the annealing temperature in the sample preparation process may correspond to the composition parameter x in the metallic alloy compounds that exhibit spin-glass phenomena.[17]

This suggests that the mean value and the standard deviation of the Gaussian distribution of the exchange interactions and their ratio are related implicitly with the rotational degree of freedom of each C_{60} molecule in the bulk TDAE-C_{60}. Indeed, merohedral disorders and even the rotational glass transition are found in the simple cubic (sc) phase of neutral C_{60} solid.[18] The possible relation of such rotational disorders whose energy scale may be of order 100 K with spin-glass-like behavior in TDAE-C_{60} is one of the greatest concerns in this field. We need more convincing evidence to conclude if TDAE-C_{60} is a spin-glass system or not. Whether TDAE-C_{60} can be explained with the standard spin-glass models or not should be investigated in much more detail.

Recently, Tokumoto *et al.* have observed the remanence, the difference between the field-cooled (FC) and the zero-field-cooled (ZFC) magnetization in TDAE-C_{60} under the very small magnetic field of order of 0.1 Oe.[19] In Fig. 1, we summarize the experimental result[19] of the temperature dependence of the FC and the ZFC magnetization. Below the onset temperature of the remanence, after making a broad

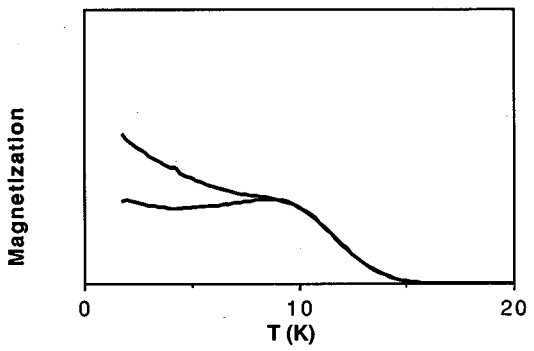

FIG. 1. The experimental FC (upper curve) and ZFC (lower curve) magnetizations. The magnetization is given in arbitrary units. $H=1.0$ Oe. The temperature T is in Kelvin. The onset temperature of the remanence is about 10 K. Below the onset temperature, after making a broad peak at the onset temperature, the FC magnetization gets larger as we go down to the low temperature. More details should be found in Ref. 19.

peak at the onset temperature, the FC curve increases as we go down to low temperature. The FC magnetization does not saturate below the freezing temperature, in sharp contrast to the standard spin-glass models such as the Sherrington-Kirkpatrick (SK) model.[20] The FC magnetization measured by Tokumoto *et al.* is consistent with that obtained by Allemand *et al.*[1] There may be something missing in the standard spin-glass models to account for the glassy magnetism found in TDAE-C_{60}. It should also be pointed out that the FC magnetization does not show a step-function-like increase at the onset temperature of the remanence, which is often found experimentally in ferromagnets (possibly due to the ferromagnetic domain).[21] We are not able to exclude the possibility of either the superparamagnetism or the ferromagnetic domain walls to explain the behavior of the magnetization in the most rigorous sense. The possibility should be examined by various experiments.

To explain the experimental results of the temperature dependence of the magnetization, we have introduced the two-channel SK model defined as follows:

$$H=-\sum_{i\neq j} J_{ij}S_iS_j-h\sum_i S_i-\sum_{i\neq j} O_{ij}R_iR_j-\sum_{i\neq j} KS_iS_jR_iR_j, \tag{1}$$

where the first two terms are just the SK Hamiltonian for spins and the third term is the SK Hamiltonian for the second degree of freedom, whose origin is not known, and the fourth term is the Hamiltonian to represent coupling between these two degrees of freedom. h is external magnetic field. The exchange interactions J_{ij} and interactions O_{ij} have independent Gaussian distributions of the mean values $J_m/(N-1)$, $O_m/(N-1)$ and the standard deviations $J_v/(N-1)^{1/2}$, $O_v/(N-1)^{1/2}$:

$$P(J_{ij})=\left(\frac{N-1}{2\pi J_v^2}\right)^{1/2}\exp\left[-\frac{[J_{ij}-J_m/(N-1)]^2}{2J_v^2/(N-1)}\right], \tag{2}$$

and

$$P(O_{ij})=\left(\frac{N-1}{2\pi O_v^2}\right)^{1/2}\exp\left[-\frac{[O_{ij}-O_m/(N-1)]^2}{2O_v^2/(N-1)}\right], \tag{3}$$

respectively.

We have adopted the Thouless-Anderson-Palmer method[22] to solve the two-channel SK model. The mean-field (MF) free energy for each configuration J_{ij} and O_{ij} is[23]

$$F=-\sum_{i\neq j} J_{ij}m_im_j-H\sum_i m_i-\sum_{i\neq j} O_{ij}r_ir_j-K\sum_{i\neq j} m_im_jr_ir_j+1/2k_BT\sum_i\left[(1+m_i)\ln\frac{1+m_i}{2}+(1-m_i)\ln\frac{1-m_i}{2}\right]$$
$$+1/2k_BT\sum_i\left[(1+r_i)\ln\frac{1+r_i}{2}+(1-r_i)\ln\frac{1-r_i}{2}\right], \tag{4}$$

where $m_i=\langle S_i\rangle$ and $r_i=\langle R_i\rangle$. We have neglected the Onsager terms such as: $-\beta\Sigma_{i\neq j}J_{ij}^2(1-m_i^2)(1-m_j^2)$, etc. for the free energy just for simplicity to handle the two coupled MF equations:

$$m_i=\tanh\left\{\beta\sum_{i\neq j}(J_{ij}+Kr_ir_j)m_j+\beta H\right\}, \tag{5}$$

$$r_i=\tanh\left\{\beta\sum_{i\neq j}(O_{ij}+Km_im_j)r_j\right\}. \tag{6}$$

One should also keep in mind that the MF equation is just to ensure a stationary state rather than a minimum state. It is known that such simplifications do not incur qualitative differences from results obtained with more elaborate calculations.[24] We adopted the Box-Müllar algorithm to generate the Gaussian distribution of $\{J_{ij}\}$ from the uniform random number produced in the computer. The following convergence criterion was adopted in the two coupled MF equations for both m_i and r_i:

$$\frac{\Sigma_i[(x_i)_n-(x_i)_{n-1}]^2}{\Sigma_i[(x_i)_n]^2}\leqslant 10^{-6}, \tag{7}$$

where $(x_i)_n$ is m_i or r_i in the nth iteration of the MF equation. Hereafter, we take J_v as the unit of energy and temperature, and hence $J_v=1$. Because the photoelectron spectroscopy measurement resulted in one-electron transfer from TDAE to C_{60},[25] the spin quantum number S should have been 1/2, but we substitute it with $S=1$. We have also used the quantum number 1 for the pseudo Ising spin describing the second glassy degree of freedom. These are just for simplification of the numerical calculations.

The temperature dependencies of the FC and the ZFC magnetizations of the two-channel SK model were calculated and are shown in Fig. 2. The ZFC state at $T=0.1$ was generated by cooling the system with $H=0$ from $T=4.0$. Care should be taken if the unique ZFC state could be generated, while avoiding the numerical accuracy problem in the convergence check. The ZFC magnetization was calculated by warming from $T=0.1$ by using the ZFC state generated, described above as an initial guess for the self-consistent-field (SCF) iteration. The SCF solution was used as an initial guess for the next calculation at the subsequent temperature.

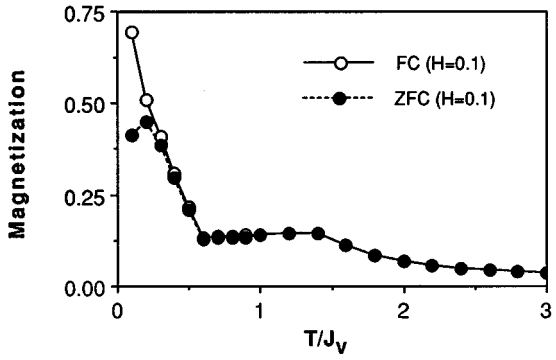

FIG. 2. Calculated temperature dependencies of the FC (open circles connected by the solid line) and the ZFC (closed circles connected by the dotted line) magnetizations of the two-channel SK model. The ratio $J_m/J_v=0.0$. $O_m=0.4$, $O_v=0.3$, $H=0.1$, and $K=1.1$, respectively. The unit of energy is J_v and hence $J_v=1.0$. The unit of temperature T is also J_v. After making a broad peak at $T=1.5$, the FC magnetization increases rapidly as we go down to low temperature. The onset temperature of the remanence is about $T=0.5$, but the difference is not so large before the ZFC magnetization makes a sharp peak at $T=0.2$. Below $T=0.2$, the remanence becomes rather large.

The FC magnetization was calculated by cooling from $T=4.0$. The temperature interval ΔT between $T=4.0$ and $T=1.0$ is 0.2 but it is 0.1 between $T=1.0$ and $T=0.1$. We used the parameter values $J_m=0.0$, $J_v=1.0$, $O_m=0.4$, $O_v=0.3$, $H=0.1$, and $K=1.1$. The number of sites we used was 200. 500 independent configurations for each J_{ij} and O_{ij} were generated. The FC and ZFC magnetizations were plotted by closed and open circles, respectively. The unit of temperature T is J_v. The magnetization starts to increase slowly at about $T=2.0$. The magnetization has a broad peak at $T=1.5$, but it is flat between $T=0.5$ and $T=1.5$. Below $T=0.5$, the FC magnetization increases very rapidly. This is in sharp contrast to the saturated magnetization below the freezing temperature, which should be found in the standard spin-glass models such as the SK model. The onset temperature of the remanence is about $T=0.5$, but the difference between the FC and the ZFC magnetizations is not so large before the ZFC magnetization makes a sharp peak at $T=0.2$. Below the temperature, the difference between the FC and the ZFC magnetizations becomes rather large.

The overall feature of the magnetization is quite similar with that obtained by the experiment done by Tokumoto *et al.* It should be noted that O_v for the second glassy degree of freedom is 0.3 and is 3 times smaller than J_v for the spin glass. Rapid increase of the FC magnetization in the low-temperature region found in the experiments[1,19] may be originated from the interaction between the spins and the second glassy degree of freedom whose energy is much smaller than that of spins. On the other hand, we get clear remanence, which does not contradict the experiment. We also obtained nonzero spontaneous magnetization as well as the nonzero Edward-Anderson order parameter. With this meaning, the phase we found relevant for TDAE-C_{60} has a similarity with the mixed phase of the standard spin-glass models. This is also consistent with muon-spin-relaxation observation of the spontaneous magnetization in this system.

The microscopic origin of the second glassy degree of freedom other than spins is beyond the scope of our phenomenological theory. Taking into account the small magnitude of interaction strength imposed on the second glassy degree of freedom, we may, however, suppose that the pseudorotation degree of freedom due to the Jahn-Teller effect on each C_{60} molecule might be one of the possibilities. C_{60}^{n-} has the Jahn-Teller instability. In the monoanion C_{60}^{-1}, there are three local minima with D_{3d}, D_{5d}, and D_{2h} symmetries.[26] The transition between these minima may be called a pseudorotation. Each minimum corresponds to different orientations of the wrinkle nearly on the equatorial line of the C_{60} ball with the north pole defined by each symmetry axis.[26,27] In the TDAE-C_{60} solid, different orientations of the wrinkle may bring small energy differences into the intermolecular interaction of order of 1 K. The Jahn-Teller contribution to the intermolecular interaction energy may also depend on the orientational configuration of each C_{60} ball in solids. Randomness of the orientational conformation of each C_{60} molecule may bring about the Gaussian distribution $P(J_{ij})$ for exchange interactions between spins as well as the Gaussian distribution $P(O_{ij})$ for the Jahn-Teller contribution of the intermolecular interaction energy. As each interacting spin is almost on the wrinkle on each C_{60} ball, we expect that there are some contributions to the exchange interaction that depend on the orientation of the wrinkle.

To summarize, we have succeeded in explaining the temperature dependence and the remanence of the magnetization of TDAE-C_{60} by introducing the two-channel SK model. The rapid increase of the FC magnetization in the low-temperature region rather than the saturated magnetization just below the freezing temperature characteristic of the standard spin-glass models may be interpreted as a consequence of the interaction between spins and the second glassy degree of freedom. The interaction energy of the second glassy degree of freedom should be much smaller than that of the spin-glass degree of freedom to conform with the experiment. Though we found a difference in the temperature dependence of the magnetization between our two-channel SK model and the SK model, the phase in the two-channel SK model we found relevant for the experiment has a similarity with the mixed phase in the SK model in the regard that it has the nonzero Edward-Anderson order parameter as well as the nonzero spontaneous magnetization. It is also consistent with the μSR experiment. Taking into account the small energy scale imposed on the second glassy degree of freedom, we have suggested that the pseudorotation degree of freedom is that of the candidates. Such a possibility will be studied both quantum chemically and experimentally in the future.

ACKNOWLEDGMENTS

Calculations were made on some workstations in the research information processing system (RIPS) of the Agency of Industrial Science and Technology (AIST) in Japan and the Computer Center of the Institute of Molecular Science (IMS) in Japan. One of the authors (Y.A.) would like to thank the RIPS and IMS for admitting him to use their facilities.

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