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Enhancement of Superconductive Shielding via Photoinduced Surface Modification

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The photoinduced modification of the near-surface region of K_3C_{60} samples generates very large enhancement of the diamagnetic shielding fraction (χ_{sf}) value. Before illumination, only ~10 vol % of the K_3C_{60} quenched sample exhibited diamagnetism. However, after illumination, values close to 100 vol % of χ_{sf} were obtained, however, Tc was not significantly changed. Furthermore, χ_{sf} was found to return to its original value upon heating, demonstrating that the transformation is reversible. The Raman measurements indicate that this reversible behavior is due to photopolymerization and thermal depolymerization of C_{60} molecules. These results indicate that the surface modification provides new ways to address important fundamental science and technological issues pertaining to this class of materials.

Introduction

The discovery of relatively high superconducting critical temperatures (T_c) for alkali metal-fullerides has generated great theoretical and experimental interest.[1-7] The main objective of such studies is to improve the superconducting properties, e.g., increasing T_c by altering the alkali metal[2,3] and enhancing the diamagnetic shielding fraction (χ_{sf}) by means of pressure[4-6,8] or thermal treatment.[3,9] Although high values of the diamagnetic shielding fraction (70~80%) can be achieved with fulleride superconductors,[7] it is difficult to obtain ~100% via conventional preparation techniques. Recently, light illumination has been used to generate new physical and chemical properties in a variety of materials, e.g., metal cyanide, C_{60}, and TiO_2 systems.[10-12] Photoinduced polymerization has been realized in pure C_{60};[13,14] however, no photoinduced effect on alkali metal fullerides has been reported. Here, we report a photoinduced enhancement of superconducting fullerides which allows the production of the superconductors with a large diamagnetic shielding fraction.

Experimental Section

K_3C_{60} powder samples were prepared by solid−gas reaction of stoichiometric quantities of high-purity polycrystalline C_{60} powders and potassium vapor.[2,3,15] A Pyrex tube containing C_{60} and K was degassed at 10^{-6} Torr and sealed under vacuum. The reactions were carried out at 200 °C for 48 h and followed by annealing at 250 °C for 12 h. The sample was quenched from 250 °C to liquid nitrogen temperature then warmed to room temperature. Finally, the Pyrex tube was resealed close to the C_{60} end for characterization and further treatments. Unquenched K_3C_{60} samples were also prepared by a similar method, except that a slow cooling procedure was applied for these samples. Light illumination of the quenched samples in the Pyrex tubes

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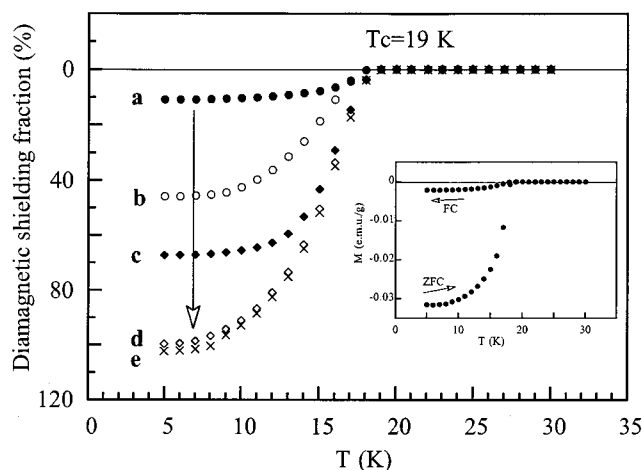‡ University of Tokyo, Hongo.
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Figure 1. Temperature dependence of the diamagnetic shielding fraction of K_3C_{60} as a function of illumination time: (a) before illumination; (b) 3 days; (c) 5 days; (d) 7 days; (e) 14 days. (inset) The zero-field cooled (ZFC) and field cooled (FC) curves at $H = 10$ Oe for the as-synthesized K_3C_{60} sample.
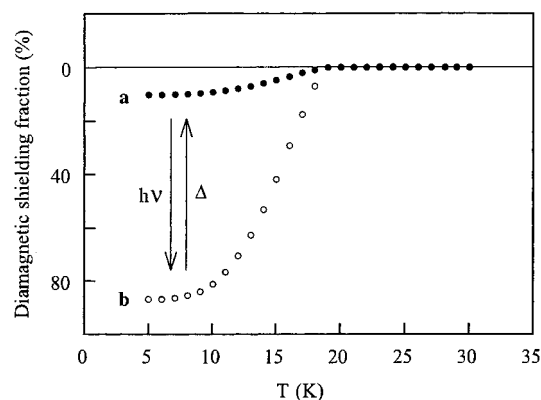

Figure 2. Typical reversible diamagnetic shielding fraction signal versus temperature for K_3C_{60} after light illumination and thermal treatment: (a) the sample after illumination heated at 250 °C for 10 h, then quenched rapidly; (b) the sample in (a) followed by light illumination again.

was performed by using a high-pressure Hg arc lamp (300W). The tube samples were slowly rotated in order to obtain effective light illumination of the samples. Optical microscopic observation indicates that the particle size is several micrometers and this size remains almost the same after illumination.

Results and Discussion

To demonstrate clearly the photopolymerization effect on χ_{sf}, we have selected the quenched samples with a low value of diamagnetic shielding fraction in this study. Figure 1 shows the diamagnetic shielding fraction (χ_{sf}) obtained from the zero-field cooled curves for the same K_3C_{60} quenched sample at various illumination times by using a SQUID magnetometer. The χ_{sf} value of the sample before illumination was estimated to be ~10% relative to a perfectly diamagnetic sample, using niobium as a standard. It is worth noting that the unquenched sample exhibited a value of 56% for χ_{sf} (not shown). Figure 2 (inset) also presents a typical temperature dependence of the dc magnetic susceptibility of the as-synthesized K_3C_{60} sample for both the field cooled (FC) and zero-field cooled (ZFC) modes at $H = 10$ Oe. The Meissner and shielding effects are clearly observed in both modes, with an onset temperature (T_c) of 19 K. These observations are consistent with the results reported for K_3C_{60},[2-4] indicative of a single superconducting phase.
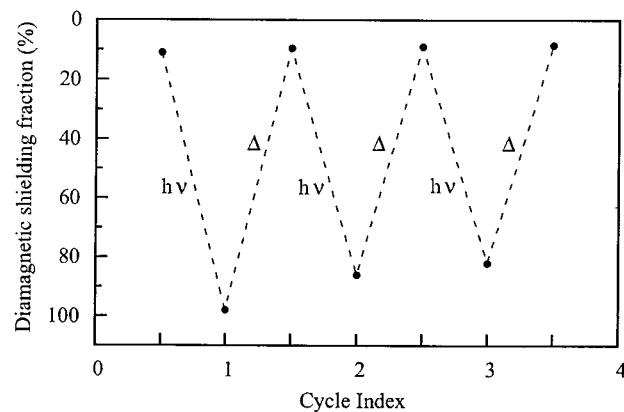

Figure 3. Reversible diamagnetic shielding fraction changes induced by alternating light illumination ($h\nu$) and thermal treatment (Δ).
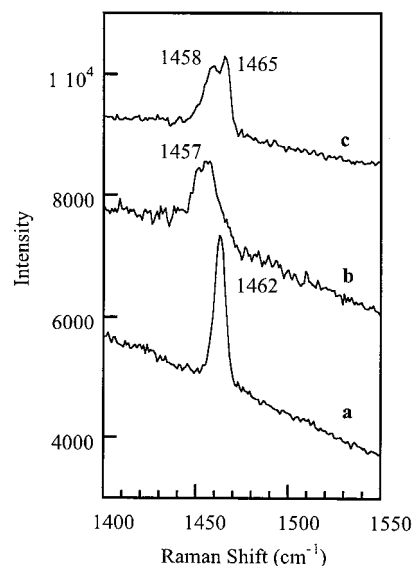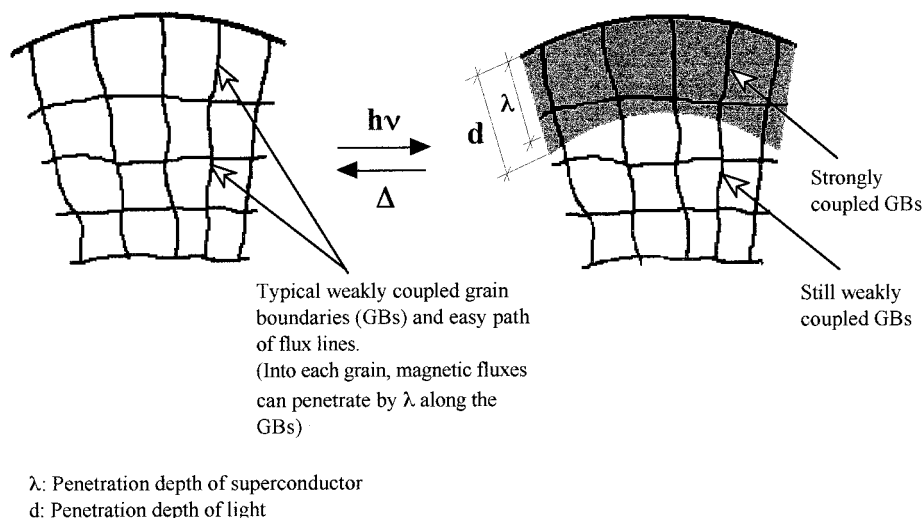

Figure 4. Raman spectra of the Ag symmetry pentagon pinch mode for K_3C_{60}: (a) before illumination; (b) after 7 days of illumination; (c) the sample in (b) heated in situ on the same spot size by high laser power (3000 mW/mm^2) for 1 h.

Measurement of the as-synthesized K_3C_{60} sample, curve a, was followed by light illumination. Surprisingly, χ_{sf} was substantially enhanced with increasing illumination time (Figure 1a−d). After 7 days of illumination, the diamagnetic shielding was about 10 times higher than that of the starting sample. This value did not change significantly upon further illumination, even after 14 days (curve e). Within our precision, an χ_{sf} value of ~100% has been reached after 7 days of illumination. The magnetic field was completely shielded from the sample at low temperature ($T < 7$ K). The material behaves as a perfect diamagnet. This phenomenon was replicated with three to four separately prepared K_3C_{60} samples. The largest shielding fraction obtained (~100%) after illumination indicates that the K_3C_{60} sample yields a perfect diamagnetic superconductor. The results also show that the photopolymerization of K_3C_{60} induced no significant change in T_c. Based on the fact that a monotonic relationship exists between T_c and lattice constant for alkali metal doped C_{60},[5-7] this suggests that the lattice constant should not essentially change as a result of photopolymerization. Although polymerization is always accompanied in the fulleride system by drastic changes in the lattice dimensions, for photopolymerized alkali-free C_{60}, only a slight contraction in the lattice constant has been reported.[13,14] This photoinduced

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SCHEME 1. Model of the Single Superconducting Particle Showing the Reversible Diamagnetic Shielding Fraction (χ_{sf}) Change Induced by Illumination ($h\nu$) and Thermal Treatment (Δ)

Typical weakly coupled grain boundaries (GBs) and easy path of flux lines.
(Into each grain, magnetic fluxes can penetrate by λ along the GBs)

Strongly coupled GBs

Still weakly coupled GBs

λ: Penetration depth of superconductor
d: Penetration depth of light

contraction is much less than one might expect for a simple polymerization of C_{60} units.

After illumination, the K_3C_{60} sample was heated at 250 °C for 10 h followed by rapid quenching. χ_{sf} decreased almost to its initial value; see curve a in Figure 2. However, after illumination again, χ_{sf} increased gradually and finally recovered to 86% after 7 days; see curve b. This cycle was repeated several times (Figure 3). Similar results were also obtained with Rb_3C_{60} ($T_c = 28.5$ K) under similar illumination conditions. However, the increase of χ_{sf} seems to be slower as compared to K_3C_{60}. This effect is probably due to the lattice constant of Rb_3C_{60} ($a_0 = 14.384$ Å) being larger than that for K_3C_{60} ($a_0 = 14.240$ Å). Also, photopolymerization is more difficult for Rb_3C_{60} as compared to K_3C_{60}.

To study the structural transformation, Raman measurements were carried out for K_3C_{60}. A Ti:sapphire laser (780 nm) was used as the excitation source,[16] with which no photochemical reaction is induced during the measurements.[17] Furthermore, the laser beam was operated at low power ($\sim$300 mW/mm^2) to obtain reproducible spectra. Figure 4 shows the Raman spectra for three states of the sample in the vicinity of the Ag(2) pentagonal pinch mode. The spectrum of K_3C_{60} before illumination, curve a, exhibited a sharp peak at 1462 cm^{-1}. After 7 days of illumination, however, the Ag(2) peak became broad and shifted to 1457 cm^{-1}; see curve b. Similar observations have also been reported for alkali metal free C_{60}; the frequency shifting from 1469 cm^{-1} (before illumination) to 1460 cm^{-1} (after illumination) was explained in terms of photoinduced polymerization.[13,18] The broad and shifted line (curve b) is therefore identified with a perturbed pentagonal pinch mode resulting from intermolecular covalent bonds,[13] indicating that the K_3C_{60} sample was also polymerized upon illumination. Furthermore, the same illuminated sample (see curve b in Figure 4) was heated in situ on the same spot size by increasing the laser power ($\sim$3000 mW/mm^2) for 1 h, and curve c was then obtained. Two pentagonal pinch peaks were observed at 1458 and 1465 cm^{-1}. The 1465 cm^{-1} peak appeared at the expense of the broad 1457 cm^{-1} peak, indicating that the covalent bonds cross-linking the C_{60} molecules were broken and the sample was partly driven back toward the initial state (Figure 4). On the other hand, the K_3C_{60} sample after 7 days of illumination was dissolved in toluene (the experiment was carried out in a nitrogen atmosphere drybox); a slurry due to a polymerized part

still remained after 48 h. This also indicates photopolymerization occurred at the surface of the sample.

For alkali metal doped C_{60} powders, the superconducting phase correlation between particles is negligible; that is, there are essentially no interparticle currents and no Josephson medium is formed.[19] Therefore, the magnetization is mainly representative of a single particle.[19] The reversible change of χ_{sf} in an individual particle upon illumination and heating can be explained in terms of Scheme 1. Before illumination, the particle exhibits a low diamagnetic shielding fraction ($\sim$10%). This suggests that there is a high concentration of defects, such as grain boundaries (GBs) inside the particles. In fact, the observation of the GBs in alkali metal−C_{60} superconductors has been reported by Weaver et al.[21,25] Although intergrain distances are very short, typically several nanometers,[21] they are comparable to the typical coherence length ($\xi \approx 2.6$ nm) reported for alkali metal−C_{60} superconductors.[4,20,23] The short coherence length induces considerable weakening of the pair potential at the GBs. This effect leads to the existence of internal Josephson junctions at GBs inside the particles.[24] Therefore, the particles are divided into a lot of superconducting grains. The GBs are weakly coupled, along which, the magnetic field can penetrate easily. It is important to note that diamagnetic shielding becomes imperfect unless the grain size in the particles is much greater than the penetration depth ($\lambda \approx 250$ nm).[3,15] The low diamagnetic shielding fraction of the sample before illumination suggests that most of the grain size in the particles are less than the value of λ. Thus, the magnetic field can partly penetrate through the particles along the GBs, and only a small χ_{sf} would be observed.

Upon illumination, a photopolymerization should occur on the surfaces of all of the particles and the extent of reaction should have a strong depth dependence within the particle (Scheme 1), according to the light penetration depth, d in the range 500−800 nm range.[22] Note that this light penetration depth value is greater than that of the penetration depth of K_3C_{60} superconductor ($\lambda \approx 250$ nm).[3,15] In fact, the requirement for the particle as a whole to be shielded is that it has a closed shell of superconducting material of thickness greater than λ between the surface and the particle center. As proposed by Rao et al.,[13] after photopolymerization, due to the C_{60} molecules being connected by chemical bonding bridges, superconducting couplings can be created at the GBs. We propose that weakly

superconducting GBs (before illumination) become strongly superconducting GBs (after illumination) within the surface shell, whose thickness corresponds to the light penetration depth, as shown in Scheme 1. Hence, the shielding currents can now flow within this intergrain shell, where the magnetic field can be expelled at low temperature ($T < 7$ K), and as a result, a 100% shielding diamagnetism can be reached. Upon heating, the intermolecular C_{60} covalent bonds are broken, resulting in a decrease of χ_{sf}. Moreover, the increase of the width of hysteresis curves ΔM (at 5 K) upon illumination can also be explained by this mechanism (not shown).[22] The critical current density J_c (average value) evaluated using the Bean model[20] was ~5 times higher compared to that of the starting sample. Therefore, it can be concluded that the enhancement of χ_{sf} is due to the creation of superconducting couplings at the GBs by covalent cross-linking of the C_{60} molecules. Moreover, the control of intraparticle junctions is of great practical importance, as these junctions considerably reduce the average current density in randomly oriented materials. Elimination of the weakly coupled GBs within particles by photopolymerization may represent a useful step toward the practical application of the alkali metal fulleride superconductor family.

The enhancement of χ_{sf} for pressed K_3C_{60} has also been reported and explained by an interparticle model.[4,6,15] At ~40 bar, weak electrical contacts between particles are formed and 100% of χ_{sf} can be reached. However, at high pressure (>2 kbar), T_c drastically decreases with pressure, accompanying a second, lower transition temperature.[4,6] Furthermore, the diamagnetic signal for this pressed sample was much more influenced by the AC field amplitude. Even at moderate fields, e.g., ~10 G, χ_{sf} is reduced to the value of the unpressed sample, indicating that the particles of the pressed sample are decoupled.[15] On the other hand, by thermal treatment, the increase of χ_{sf} was also observed, while the sample was slowly cooled from the doping temperature to room temperature.[3,9] However, there is an equilibrium of polymerization/depolymerization C_{60} reactions during the thermal treatment, giving the highest χ_{sf} of not more than ~80%.

Our results provide the first report of the photoinduced enhancement of χ_{sf} in K_3C_{60}. We propose that the enhancement is generated by transformation from weakly superconducting couplings to strongly superconducting couplings at the GBs within a shell on the surface of each particle; the thickness of the shell corresponds to the light penetration depth. This also suggests that the modification of superconducting properties in the near-surface region can also be important in comparison with that of bulk superconductors. Furthermore, the general concept of surface modification may be useful for this class of superconductors.

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