Vortex-glass behavior in superconducting K_3C_{60} and Rb_3C_{60}

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The temperature and field dependence of the magnetic susceptibility of well-characterized K_3C_{60} and Rb_3C_{60} show that the zero-field-cooled (ZFC) diamagnetism below T_c is irreversible for both systems, while the field-cooled (FC) curve is reversible, and that the ZFC diamagnetism is more than four times larger than the FC. This behavior is attributed to a vortex-glass state below T_c, similar to that observed in high-T_c cuprates as well as disordered conventional type-II superconductors. The field dependence of the vortex glass to vortex fluid transition temperature T^* is found to follow the de Almeida–Thouless relation $H = H_0[1-T^*(H)/T^*(0)]^\gamma$, where $\gamma = \frac{3}{2}$ for both compounds.

Phase transitions in the high-T_c cuprate superconductors, from vortex glass or vortex solid to vortex fluid, have attracted a great deal of attention.[1] The glasslike behavior of superconductors was in fact proposed by theorists before the discovery of high-T_c superconductors.[2–5] Muller *et al.* demonstrated the existence of superconducting glass behavior in the La-Ba-Cu-O system in 1987,[6] soon after Bednorz and Muller reported the existence of high-T_c superconductivity.[7] They found that the diamagnetism below T_c observed in the zero-field-cooled (ZFC) curves is much larger than that in the field-cooled (FC) curves. The field dependence of T^*, the temperature at which the ZFC and FC curves merge (essentially the glass transition temperature T_g), agreed with the form of the de Almeida–Thouless line,[8] i.e., $H = H_0[1-T^*(H)/T^*(0)]^{3/2}$. The remanent magnetization obtained on switching off the applied magnetic field was found to decay nonexponentially. Similar evidence for glasslike behavior has been observed in the La-Ba-Cu-O system,[9] $YBa_2Cu_3O_7$ (Refs. 10–12) and $Bi_2Sr_2CaCu_2O_8$.[13,14] These systems, all in the dirty limit, show a continuous transition. Recent work on clean untwinned single crystals of $YBa_2Cu_3O_7$ has been interpreted in terms of a first-order vortex melting transition.[15,16] The evolution from a first-order transition in the clean limit to a continuous transition in the dirty limit has not been investigated to date.

The discovery of superconductivity in the alkali-metal-doped fullerenes M_3C_{60} with M = K and Rb presents another challenge.[17] In particular, it is important to determine whether these are conventional type-II superconductors or in some way "exotic" like the high-T_c cuprates. Here we present measurements of the temperature and field dependence of the magnetic susceptibility for K_3C_{60} and Rb_3C_{60} which give evidence for vortex-glass behavior. We compare our results with those observed in the high-T_c cuprates and disordered conventional type-II superconductors, and with existing theories.

Samples were prepared by reacting weighed amounts of C_{60} and M in evacuated pyrex tubes. The C_{60} was first ground in an agate mortar in a glove box to enhance doping kinetics. Alkali metals were contained in 1-mm capillaries which were cut to length to give an approximate weight, which was then determined more accurately by subtracting the capillary weight using the known weight per unit length of an empty capillary. Batches of order 250 mg were prepared, resulting in an estimated error in M content x of ± 0.01. For both K and Rb, an initial heat treatment at 250 C for 2 days sufficed to ensure that all the M was taken up by the C_{60}, after which the product was reground to ensure homogeneity, resealed and annealed for 5 days at 400 C or 450 C for K and Rb, respectively. High-resolution, high-statistics synchrotron x-ray diffraction revealed single-phase behavior to much better than 1%. Rietveld refinements were consistent with a K/C_{60} ratio of 2.89 ± 0.03 and a Rb/C_{60} ratio in the range 2.90–3.00. Samples of order 2 mg were loaded into 1.1-mm-O.D pyrex tubes with 0.2-mm wall thickness. The powder was compressed into the tube bottom by applying hand force with a snug-fitting oxygen-free high-conductivity copper (OFHC) copper rod. Thus, as far as demagnetization factors are concerned, these samples are probably intermediate between loose powder and compacted pellets. The capillaries were sealed with low vapor pressure epoxy, removed from the glove box and torch-sealed at reduced glove box gas pressure (mostly argon with some helium for heat transfer) while chilling one end with liquid nitrogen.

Magnetic susceptibility was measured using a superconducting quantum interference device (SQUID) magnetometer. Samples were cooled in zero field to 2 K, a specific field value was applied, and the ZFC curve was taken as a function of increasing temperature up to $T > T_c$. The FC curve was then measured by decreasing the temperature to 2 K in the same field. The results for

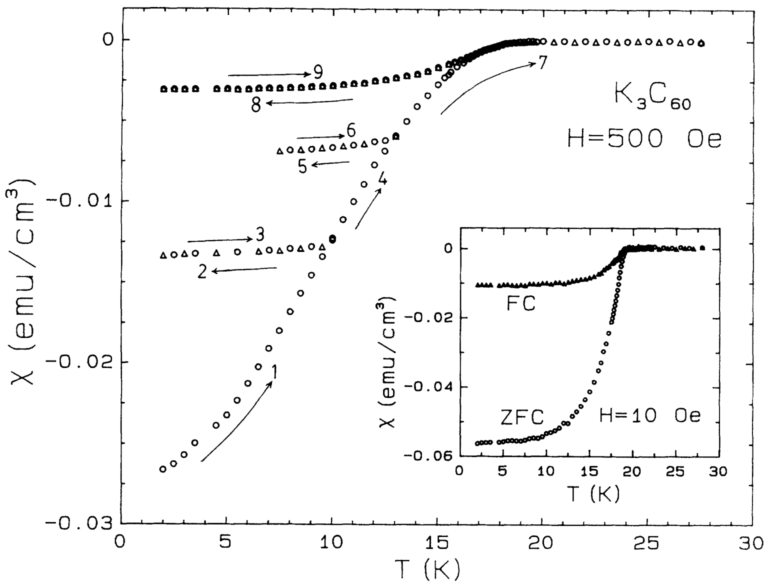

FIG. 1. Temperature dependence of the magnetic susceptibility of K_3C_{60} measured in $H=500$ Oe. Open circles for heating up (numbered arrows: 1, 3, 4, 6, 7, and 9); open triangles for cooling (numbered arrows: 2, 5, and 8). Inset: data for K_3C_{60} measured in $H=10$ Oe.

$H=10$ Oe are shown for K_3C_{60} in the inset to Fig. 1. Similar curves for Rb_3C_{60} are shown as the inset to Fig. 2, again for $H=10$ Oe. In both cases the ZFC and FC curves reach saturation at the lower temperatures, but the ZFC diamagnetism is more than a factor of 4 larger than the FC diamagnetism. T_c values determined from the onset of diamagnetism are 19.0 ± 0.1 K for K_3C_{60} and 29.0 ± 0.1 K for Rb_3C_{60}, and are the same for both the ZFC and FC curves. The shielding (ZFC) and Meissner (FC) diamagnetic fractions, determined by comparison to the ideal value of $-1/4\pi$ for a long cylinder, are 75% and 15%, respectively, for K_3C_{60} and 85% and 19% for Rb_3C_{60}.

The main portions of Figs. 1 and 2 reveal the irreversible behavior of K_3C_{60} and Rb_3C_{60} at a higher field, 500 Oe. For these cycles the samples were first cooled from $T \gg T_c$ to 2 K in zero field. Then the field was applied and held fixed for the remainder of the cycle. The sample was then heated to an intermediate temperature T_1 (2 K $< T_1 < T_c$) and a subcycle consisting of cooling the sample below T_1 and reheating it to T_1 was performed. This subcycle was followed by heating to a second intermediate temperature $T_2 > T_1$ and another cooling-reheating subcycle. This procedure was repeated for several higher intermediate temperatures. Finally the sample was heated well above T_c and then cooled to 2 K to obtain the FC curve and again reheated to $T \gg T_c$. The numbered arrows indicate the sequence of cooling and heating segments of the various subcycles. The reversible nature of those subcycles which consist of a cooling followed by a reheating (i.e., subcycle 2-3, 5-6, and 8-9) is in sharp contrast to the heating followed by cooling subcycles (i.e., subcycles 1-2, 4-5, and 7-8) which are clearly irreversible. This behavior is very similar to that reported by Muller *et al.*[6] for La-Ba-Cu-O, by Rossel *et al.*[18] for the superconducting $PbMo_6S_8$ system, and by

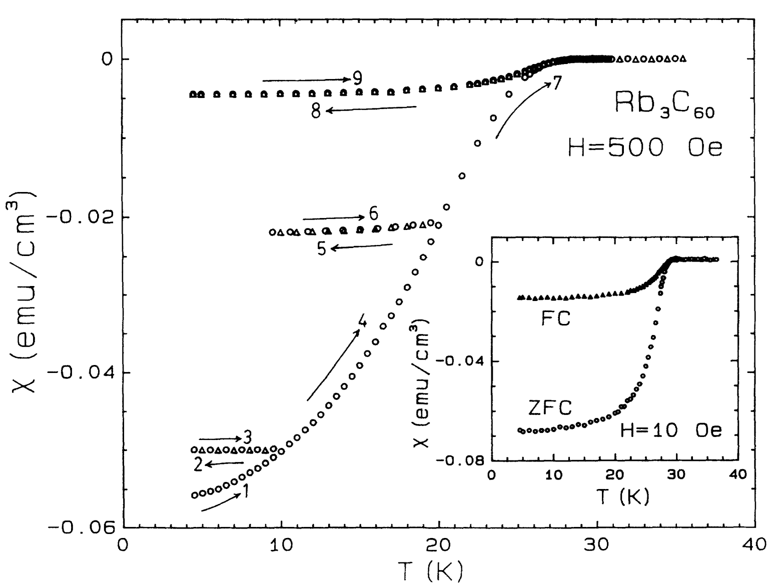

FIG. 2. Temperature dependence of the magnetic susceptibility of Rb_3C_{60} measured in $H=500$ Oe. Open circles for heating up (numbered arrows: 1, 3, 4, 6, 7, and 9); open triangles for cooling (numbered arrows: 2, 5, and 8). Inset: data of Rb_3C_{60} measured in $H=10$ Oe.

Schmidt *et al.*[19] for Nb films.

In the cooling and reheating subcycles (2-3, 5-6), the diamagnetic moment of the samples stays nearly constant, indicating that the vortices are frozen in, at least on the time scale of our measurements (approximately 10 min between data points). In the region of overlap of the FC and ZFC curves, flux lines enter and exit with equal ease, indicating a vortex fluid state. The demarcation between reversible and irreversible behavior, i.e., the "point" at which the FC and ZFC curves join together in Figs. 1 and 2, although difficult to determine precisely at high fields (see Fig. 3), represents the vortex-fluid to vortex-glass transition, and following Ref. 6, will be denoted by T^*.

The existence of irreversible behavior below T^*, together with the substantially different saturation values of the diamagnetism in the FC and ZFC states, are signatures of a superconducting glass state. Additional evidence was obtained as follows. After cooling to low temperature in zero field, then switching the field on and off, we observed a remanent moment (flux trapping) which decayed very slowly (on a time scale of days), as expected from the metastable vortex-glass state.[6] Furthermore, we have recently measured the time dependence of the magnetization for Rb_3C_{60} at different temperatures and fields. The results[20] show nonlinear logarithmic time decay behavior and thus support the existence of the vortex-glass state at low temperatures. This behavior is also typical of high-T_c cuprates in the dirty limit. Two other properties which are apparently common to both families are very low Fermi temperatures[21] and very short mean free paths.[22]

We measured T^* versus field for $H \leq 5$ kOe. For both compounds T^* decreases monotonically with increasing field. For $H > 5$ kOe the vortex fluid state dominates (see Fig. 3) in the region of temperatures accessible to us ($T \geq 2$ K). The resulting $T^*(H)$ are shown in the H-T diagrams of Fig. 4, which are very similar to those of high-T_c cuprates. Theoretical models developed for the cuprates might also explain our data. The ansatz $H \propto (1-T^*/T_c)^\gamma$ has been proposed to describe the vortex transition, with different values for γ in different approaches. We fit our low-field ($H \leq 5$ kOe) data to the relation $H = H_0[1-T^*(H)/T^*(0)]^\gamma$. The best fits gave $\gamma = 1.47 \pm 0.04$ and 1.59 ± 0.05 for K_3C_{60} and Rb_3C_{60}, respectively, where the uncertainties are determined by the fit quality without accounting for errors in the measured points. A more conservative approach which includes an estimate of these errors (shown as the error bars in Fig. 4) gives values of 1.41 ± 0.10 and 1.64 ± 0.14. Both approaches are consistent with an exponent of 1.5. Fixing γ at 1.5 yields $T^*(0) = 19.2 \pm 0.1$ K and the extrapolated zero-temperature transition field $H_0 = 12.2 \pm 0.07$ kOe for K_3C_{60}, and 29.1 ± 0.1 K and 27.2 ± 1.7 kOe for Rb_3C_{60}.

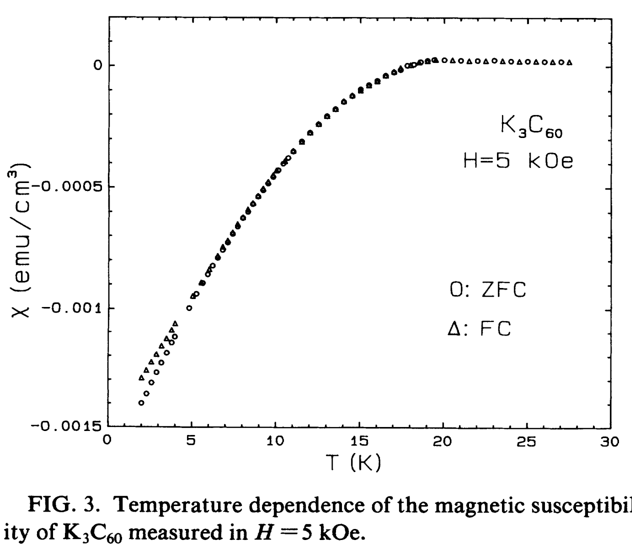

FIG. 3. Temperature dependence of the magnetic susceptibility of K_3C_{60} measured in $H = 5$ kOe.

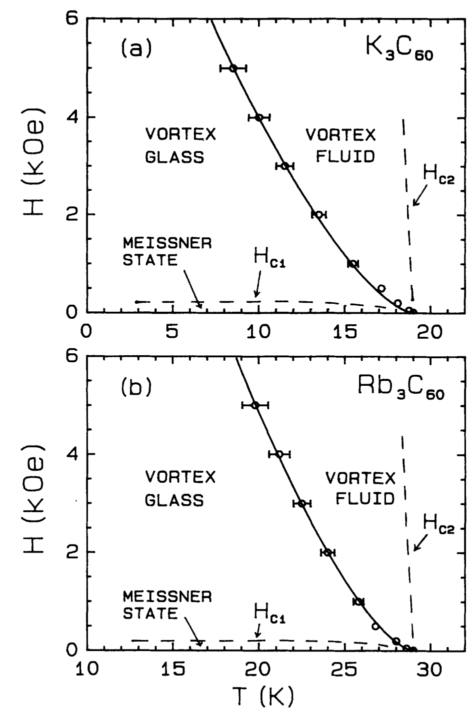

FIG. 4. Magnetic phase diagrams for K_3C_{60} (a) and Rb_3C_{60} (b). Solid lines are fits to the de Almeida–Thouless relation with $\gamma = \frac{3}{2}$, which represents the demarcation between vortex-glass and vortex-fluid phase. Dashed lines indicate schematically the critical fields $H_{c1}(T)$ and $H_{c2}(T)$.

Muller *et al.*[6] postulated that $T^*(H)$ would follow the de Almeida–Thouless prediction for the spin-glass state demarcation line[8] given by $H = H_0[1-T^*(H)/T^*(0)]^\gamma$ with $\gamma = 1.5$ and $H_0 = 1.17T$ for La-Ba-Cu-O. An exponent $\gamma = 1.5$ was predicted for the de Almeida–Thouless line separating ergodic and nonergodic regions for an infinite range interacting spin system and was found experimentally in the case of certain spin-glass systems.[23,24] A γ value of 2 was expected[25] for a lattice-melting phase boundary close to T_c. Thermally activated depinning, without invoking a phase transition of any sort[26] leads to the same result. A measurement on an untwinned single crystal of $YBa_2Cu_3O_7$ gave a value very close to 2, which was attributed to weakly coupled vortex lines between layers and a low defect concentration.[16] A plot of our data assuming $\gamma = 2$, in the form $H^{1/2}$ vs T^* shows visible curvature, clearly ruling out

$\gamma=2$. In the $YBa_2Cu_3O_7$ crystal, thermal energy which tends to depin the vortices could be dominant, and would lead to a vortex-lattice melting first-order transition with $\gamma=2$. On the other hand, K_3C_{60} and Rb_3C_{60} are three-dimensional (3D) superconductors and our polycrystalline samples certainly have a large density of grain boundaries. Thus the pinning energy that attracts the vortices to the defect sites could be dominant, giving rise to a second-order vortex-glass transition with $\gamma=1.5$. The latter value agrees not only with the de Almeida–Thouless line, but also with some of the measurements for dirty high-T_c cuprates.[6,15] A recent theory of quantum melting of the vortex lattice[27] also predicts γ close to 1.5, rather than the thermal depinning value of 2.0.

As mentioned earlier, the T^* value is difficult to determine in high fields. Some high-field measurements[11,28] on $YBa_2Cu_3O_7$ yield $\gamma=\frac{4}{3}$. In fact, if we fix the exponent to this value, we also obtain a reasonable fit, within the error bars of our T^* determinations.

We have demonstrated the existence of superconducting glass behavior and vortex phase transitions in the alkali-metal-doped fullerenes, similar to recent observations in the layer-structured oxide superconductors as well as disordered conventional type-II superconductors. It has recently been proposed that the ground state of the superconducting face-centered cubic fullerenes exhibits 2D antiferromagnetic ordering of the C_{60} molecules, and is disordered in the third direction,[29] analogous to the cuprates. Thus far there is no experimental evidence to support this. In fact, electrical conductivity measurements on single crystals point to the superconductivity being three dimensional.[30] The observation of vortex phases in the body-centered cubic superconducting Ba-doped fullerene[31] might serve to clarify these issues.

Note added in proof. We were recently made aware that recent work by Viktor Buntar on Rb_3C_{60} (using a somewhat different approach) also supports the vortex phase transitions.

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