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SUPERCONDUCTING PROPERTIES OF ALKALI DOPED C_{60} PREPARED BY PRECIPITATION FROM LIQUID METHYLAMINE OR AMMONIA

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Abstract An extremely convenient method of preparing alkali doped face-centered cubic phases of C_{60} consists of the partial solubilization of the constituent materials in liquid ammonia or monomethylamine followed by precipitation and annealing. The preparation and properties of Rb_3C_{60}, K_3C_{60} and Rb_2CsC_{60} prepared in this manner from monomethylamine are decribed. When attempting to prepare Rb_2NaC_{60} from liquid ammonia, one obtains a phase separated material, consisting of the energetically more stable superconducting Rb_3C_{60} and nonsuperconducting Na_xC_{60}. This sample exhibits a very sharp superconducting transition temperature at 26.3 K. The decrease in T_c with respect to that of pure-phase Rb_3C_{60} is explained as the result of the decrease in density of states in Josephson-like junctions formed between the two phases. This composition displays a large volume fraction of superconductivity, and all measurements of superconducting parameters are extremely well defined, implying high phase purity of the Rb_3C_{60}. The zero temperature values of the upper and lower critical magnetic fields are $H_{C2}(0)$=165 KOe and $H_{C1}(0)$=62 Oe, calculated from measurements of the field dependence of the magnetization as a function of temperature. The coherence length and penetration depth are 44 Å and 3400 Å, significantly higher than earlier literature estimates. The critical current density was found to be $J_c=7x10^6$ A/cm^2, larger by a factor of 5 than previously reported values.

INTRODUCTION

A substantial effort has been devoted to developing appropriate procedures for the intercalation of alkali, alkaline earth, and lanthanide metals into C_{60}, since the discovery that superconductivity occurs in M_3C_{60} (M=K and Rb) crystallizing in a face-centered cubic lattice. In this structure there are three sites associated with each C_{60} molecule: one is a relatively large octahedrally-coordinated position, while two smaller sites are tetrahedrally coordinated. In recent work from this laboratory[1], it has been shown that monomethylamine can be employed as a solvent for the preparation in addition to the use of liquid ammonia which had been previously reported.[2-5] Not only does the initial

solution partially dissolve the constituents, but also the extended temperature range of this solvent, as compared to ammonia, provides favorable conditions for the preparation of single phase, well-defined materials with high superconducting volume fractions. The materials were characterized by d.c. magnetization and x-ray diffraction measurements.

A brief summary of this published work[1] is as follows: The technique is particularly appropriate for more reactive alkali metals rubidium and cesium, whereas reactions with K and Na require extended reaction times. A high volume fraction of superconductivity was observed in Rb_3C_{60} reflecting the accuracy of the end-product stoichiometry. The shielding (ZFC) and Meissner (FC) diamagnetic fractions, estimated by comparison to the ideal value of $-1/4\pi$ for a long cylinder, are 90% and 8% respectively. Annealing the sample for two days at 375°C is required to produce the high diamagnetic fraction. T_c and lattice constants of the prepared materials agree quite closely with published values using solid state techniques.

A preparation with a Rb_2CsC_{60} stoichiometry produced a single phase with a lattice constant of ~14.45 Å comparable to the lattice parameter obtained from the solid state preparation (14.49 Å). Particle size is estimated to be about 205 Å for this sample. It is known that in Rb_2CsC_{60}, Rb ions mainly occupy the tetrahedral sites while the Cs ion occupies the octahedral interstitial site. Superconductivity occurs with an onset temperature of 30 to 31 K, similar to the T_c obtained from preparation via solid state reaction. The shielding and Meissner diamagnetic fractions were found to be 28% and 14% respectively.

In this report, data are presented on an attempt to prepare Rb_2NaC_{60} from liquid ammonia. One obtains a phase separated material, consisting of the energetically more stable superconducting Rb_3C_{60} and nonsuperconducting Na_xC_{60} which exhibits a very sharp superconducting transition temperature at 26.3 K. The decrease in T_c with respect to that of pure-phase Rb_3C_{60} is explained as the result of the decrease in density of states in Josephson-like junctions formed between the two phases. This composition displays a large volume fraction of superconductivity, and all measurements of superconducting parameters are extremely well defined, implying high phase purity of the Rb_3C_{60} moiety. The coherence length and the penetration depth are of great importance in characterizing the superconducting state of metal-doped C_{60}. The magnetic flux coherence length ξ is a

measure of the spatial extent of a superconducting pair. The penetration depth λ defines the distance over which a magnetic field is effective in a superconductor. The values of these two parameters, can be used to calculate several intrinsic properties of the materials in their normal and superconducting state.

In this mixed phase sample, superconductivity is found with an onset temperature of 26.3 K with a volume fraction of superconductivity of 88%. Investigations of d.c. magnetization indicate that both critical fields are significantly reduced. The resulting superconducting parameters, ξ=44 Å and λ=3400 Å, are considerably larger than those reported in "pure" Rb_3C_{60} which is consistent with the two phase samples being of high-quality. The critical current density (J_c=7x10^6 A/cm^2) is larger by a factor of 5 than the previously reported values for Rb_3C_{60}. The interesting question is why the two phase samples, which can be viewed as superconducting Rb_3C_{60} seperated by non-superconducting Na_xC_{60}, show such properties.

EXPERIMENTAL

The samples were prepared by dissolving the proper stoichiometric amounts of C_{60}, Rb and Na in liquid ammonia, following the published methodology which is aimed at obtaining homogeneous samples and high diamagnetic fractions.[4,5] Ten ml of liquid ammonia is condensed onto a dry ice/ acetone cold finger (-78^0 C) and dripped into the reactor containing the solids. The reaction continues for 1 hour under a N_2 atmosphere at -78^{0}C while the solution is stirred. The temperature is then raised to -55 ^{0}C (dry ice/ methanol) for another hour. The ammonia is evaporated and the powdery product is gently heated under dynamic vaccuum at 90 ^{0}C for 1 hour to remove any residual ammonia. Annealing the samples for 7 days at 150 ^{0}C results in the large superconducting fraction.

The temperature and field dependence of the magnetization was measured using a Quantum Design SQUID magnetometer in fields from 0 to 5 Tesla. In the temperature dependence of the magnetization the sample was first cooled to 5 K in the zero magnetic field from room temperature. The zero-field cooled curve (ZFC) was obtained by applying a magnetic field of 10 G to the sample and warming up slowly to 35 K. The field-cooled (FC) curve was obtained by again cooling the sample to 5 K in the same

magnetic field.

XRD measurements performed by a laboratory powder diffractometer indicated that Rb_2NaC_{60} is not a single fcc phase at room temperature. The x-ray profile revealed two fcc phases, Rb_3C_{60} and most probably Na_3C_{60} with lattice parameters of 14.433(2) Å and 14.180(3) Å respectively. The instability of an fcc crystal phase for Rb_2NaC_{60} is explained in terms of innappropriate ionic radii (0.98 Å for Na and 1.48 Å for Rb) which should occupy one octahedrally coordinated interstitial site whose radius is 2.06 Å and two tetrahedrally-coordinated sites (T-sites) whose radii are 1.12 Å. Phase instability occurs when alkali metals with large ionic radii force the T-site to expand and the lattice is reorganized to another lower energy structure. Thus, it is probably very difficult for Rb ions to locate in the T-sites in the case of Rb_2NaC_{60}, and it also appears difficult for both ions to co-exist in T-sites.

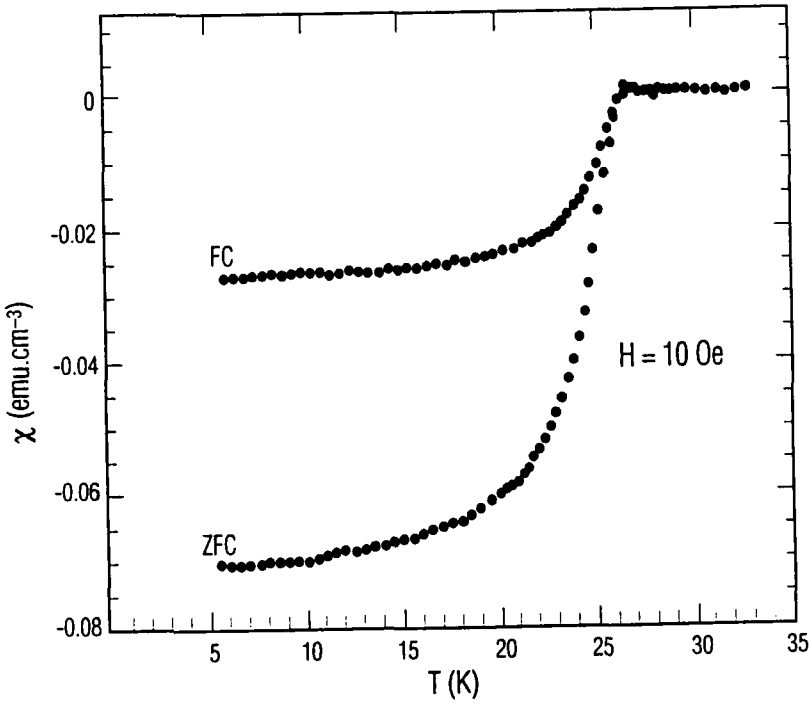

Fig. 1. Temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility of Rb_2NaC_{60} measured at an applied field of 10 Oe.

RESULTS

Figure 1 shows the temperature dependence of the dc magnetization of a Rb_2NaC_{60} sample. The superconducting transition temperature of both ZFC and FC curve is 26.3 K. The pure-phase Rb_3C_{60} displays superconducting onsets at 29 K. The 2.7 K decreases in T_c with respect to that for Rb_3C_{60} can be explained in terms of the formation of Josephson-like junctions between the two phases, the superconducting Rb_3C_{60} and nonsuperconducting Na_3C_{60}. The formation of such junctions decrease the density of states at the Fermi energy $N(E_F)$. A decrease in $N(E_F)$, in the BCS electron-phonon model, results in a decrease in T_c. The ZFC diamagnetism is a factor of 2.5 larger than the FC diamagnetism. The shielding (ZFC) and Meissner (FC) diamagnetic fractions,

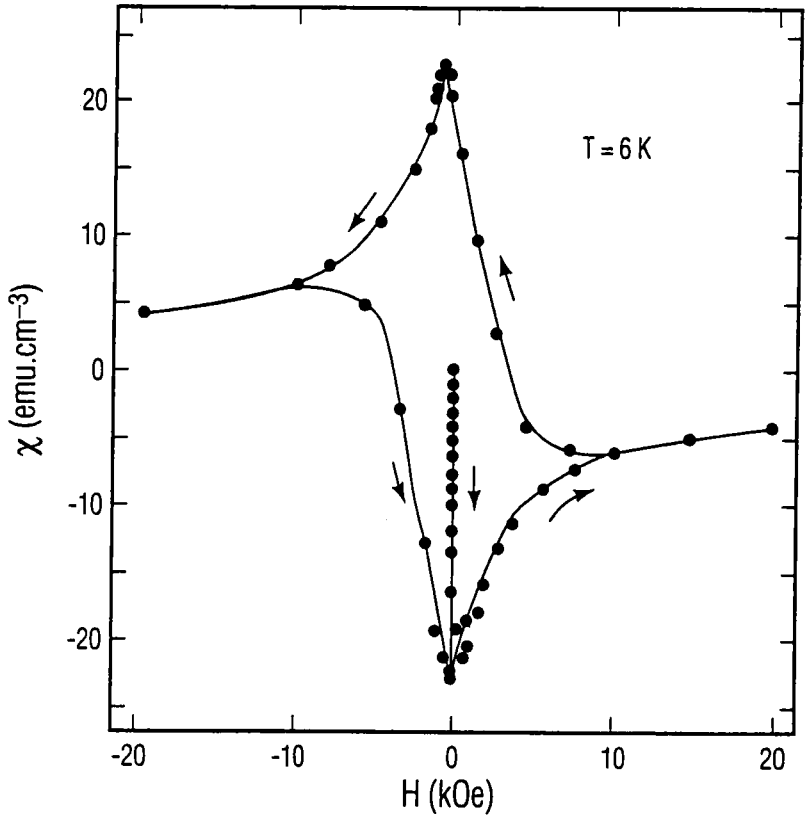

Fig. 2. Magnetic-field dependence of the magnetization recorded at T=6 K.

determined by comparison to the ideal value of $-1/4\pi$ for a long cylinder, are 88% and 35% respectively.

In superconductors, the critical current density J_c can be deduced from magnetization measurements, since $J_c(H,T)$ is proportional to the hysteresis in magnetization ($\Delta M=M_+-M_-$)[6], where M_+ and M_- are the magnetization of the decreasing and increasing field branches. If one assumes a cylindrical specimen of radius R, then J_c can be obtained, to a first approximation, from the following relation:[7] $J_c(H)(A/cm^2)=15[M_+-M_-(emu/cm^3)]/R(cm)$. Figure 2 displays the magnetic-field dependence of the dc magnetization at T=6 K. The sample was cooled to T=6 K in zero external field and the dc magnetization was measured with magnetic fields varying between +20 and -20 KOe. The observed magnetic hysteresis curve in Fig. 2 is typical of a type-II superconductor. If an average grain size of about 1 μm is used, then one

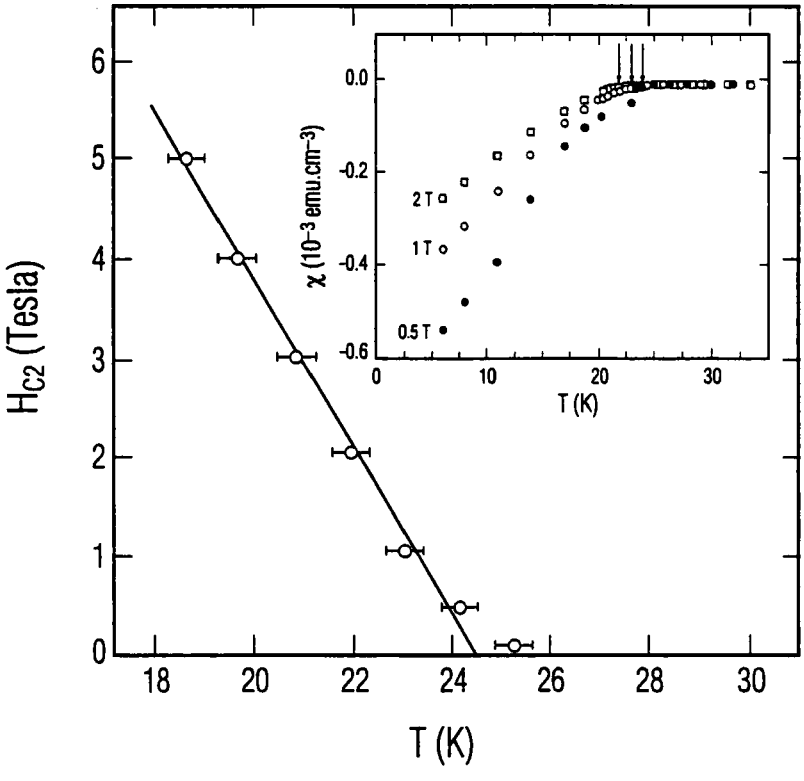

Fig. 3. Temperature dependence of the upper critical field H_{C2}. The insert shows the temperature dependence of the field-cooled magnetization in magnetic fields 0.5, 1, and 2 Tesla.

obtains a value of J_c of $7x10^6$ A/cm^2 for Rb_2NaC_{60}. This J_c value is 5 times larger than that observed for Rb_3C_{60}.[8] The large value of J_c indicate the existence of strong flux pinning in this superconductor,[9] and is consistent with the high diamagnetic fraction of this sample.

The upper critical field H_{C2} is determined from the temperature dependence of the FC magnetization near T_c. The insert in Figure 3 shows the variation of the magnetization for a Rb_2NaC_{60} sample at 0.5, 1 and 2 Tesla from which one deduces T_c of 24.2, 23 and 22, respectively. The suppression of T_c with increasing field is due to a pair breaking mechanism. The reversible behavior of the magnetization near T_c is indicative of a vortex fluid superconducting state where no pinning occurs. The broadened transitions, in the vicinity of T_c, observed in the larger applied fields are explained as the result of the increased flux motion in these fields. Figure 3 displays the temperature dependence of the upper critical field. Except for the region near T_c, a

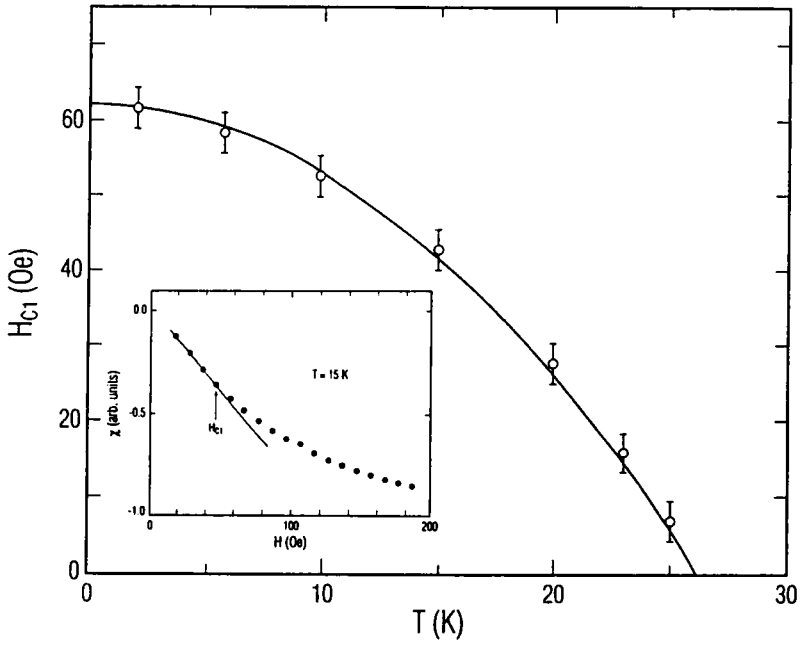

Fig. 4. Temperature dependence of the lower critical field H_{C1}. The insert shows the determination of H_{C1} at 15 K.

linear temperature dependence of H_{C2} is observed. The slope calculated from a linear fit is $\partial H_{C2}/\partial T$=-0.91 T/K. Using the Werthamer-Helfand-Hohenberg (WHH) formula,[10] $H_{C2}(0)=0.69T_c\partial H_{C2}/\partial T|_{T=Tc}$, one estimates the extrapolated zero temperature upper critical field to be $H_{C2}(0)$=16.5 T. We obtain the zero temperature superconducting coherence length ξ_0=44 Å using the relation[11] $H_{C2}(0)=\Phi_0/2\pi\xi_0^2$, where $\Phi_0=2.0678\times10^{-15}$ T·m^2 is the quantum of flux, hc/2e. This ξ_0 value is much larger than those reported for K_3C_{60} (26 Å)[12,13] and Rb_3C_{60} (20 Å).[8]

The lower critical magnetic field H_{C1} is determined from the field dependence of the magnetization. The insert in Figure 4 shows the magnetic field dependence of the magnetization at T=15 K, obtained by cooling the sample from the normal state to 15 K in zero magnetic field. The magnetization is then measured as a function of the increasing field. H_{C1} is the field at which a deviation from a linear M(H) dependence occurs. Figure 4 presents the temperature dependence of the lower critical field, which follows an empirical law $H_{C1}(T)=H_{C1}(0)[1-(T/T_c)^2]$. The lower critical field at zero temperature is obtained by extrapolation as $H_{C1}(0)$=62 Oe. Using the formula[11] $H_{C1}(0)=(\Phi_0/4\pi\lambda^2)\ln(\lambda/\xi)$, one estimates λ=3400 Å. This value is close to that obtained from μSR measurements[14] (4200 Å for Rb_3C_{60}) where λ is determined from the depolarization of the spin by an inhomogeneous magnetic field during the muon penetration of the sample.

CONCLUSIONS

Two phase Rb_2NaC_{60} samples prepared in liquid ammonia exhibit a superconducting volume fraction of 88% and show a well defined superconducting onset at 26.3 K. Since the Na_xC_{60} component of the sample does not superconduct, one can attribute the large fraction of superconductivity to Rb_3C_{60} being in particularly high purity in these samples. The decreases in T_c relative to Rb_3C_{60} is explained as the result of the decrease in density of states in Josephson-like junctions formed between the two phases. The temperature dependence of the lower critical field $H_{c1}(T)$ is determined by the field dependence of magnetization at several temperatures, and the zero temperature H_{C1} value is about 62 Oe. The penetration depth for this sample is calculated from $H_{C1}(0)$ and is about 3400 Å. The upper critical field $H_{c2}(T)$ is also determined from the temperature dependence of

magnetization at different fields, and the zero temperature $H_{C2}(0)$ value is estimated to be 16.5 T. The coherence length is calculated from $H_{C2}(0)$ and is much larger than those previously reported for K_3C_{60} and Rb_3C_{60}. The critical current density of the Rb_2NaC_{60} sample measured at 6 K is calculated to be $J_c=7x10^6$ A/cm^2. This large J_c value is related to the improved intrinsic properties of these samples.

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