PHYSICAL REVIEW B VOLUME 50, NUMBER 18 1 NOVEMBER 1994-II

Critical magnetic fields of superconducting Ba_6C_{60}

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(Received 24 January 1994; revised manuscript received 5 April 1994)

We have measured the upper and lower critical fields of superconducting Ba_6C_{60}. Near T_c, from the slope of the measured upper critical field, $dH_{c2}/dT=0.45$ T/K, we obtain the zero-temperature Ginzburg-Landau coherence length as $\xi_{GL}=120$ Å. Using the lower critical-field data, the penetration depth at $T=0$ is estimated to be $\lambda(0)=1800$ Å. Combining $\lambda(0)$ with the value of ξ_{GL}, we estimate the Fermi energy E_F to be $\simeq 0.15$ eV. Thus, in comparison with the alkali-metal-doped fullerenes, the superconducting parameters H_{c2}, ξ_{GL}, and the resulting Ginzburg-Landau parameter κ, are significantly different in the case of the superconducting Ba-doped fullerene.

The discovery of superconductivity in metal-doped C_{60} compounds[1,2] has stimulated significant theoretical and experimental interest. For all alkali-metal-intercalated fullerides the superconducting phase has a face-centered cubic (fcc) structure[3] with a stoichiometry A_3C_{60} (where A is an alkali metal). Magnetic measurements on the two members of the family (Refs. 4–6), K_3C_{60} (with a transition temperature $T_c=19$ K) and Rb_3C_{60} ($T_c=29$ K), have shown that both these materials are extreme type-II superconductors with Ginzburg-Landau (GL) parameters $\kappa\approx 100$. It has been found[7] that fcc C_{60} can be intercalated with divalent group calcium intercalant, and that near Ca:C_{60} ratio of 5:1 a phase transformation occurs to a simple-cubic phase which becomes superconducting below 8.4 K. This result on calcium-C_{60} compound demonstrates that superconductivity in fullerene alloys is not limited to alkali-metal doping alone. Recently, superconductivity ($T_c=7$ K) has also been discovered in a barium intercalated fulleride[8] with a stoichiometry Ba_6C_{60}, in a pure body-centered phase. However, to the best of our knowledge no detailed study of the parameters for the Ca- or Ba-doped superconductors has been reported. In this paper we present our measurements of the upper and lower critical magnetic fields of the Ba_6C_{60} compound. Using the critical field data we evaluate the coherence length ξ, and penetration depth λ. We also discuss possible implications of the results obtained.

The Ba_6C_{60} samples were prepared via the metal azide route according to the procedure described by Iqbal *et al.*,[9] using C_{60} (99.9% pure) obtained from Texas Fullerenes and pure barium azide BaN_6. After each synthesis, the samples were transferred in a dry box to x-ray capillaries for diffraction measurements. The Ba_6C_{60} powder was then sealed in a Pyrex tube under 1 atm of helium as an exchange gas for Raman scattering and magnetization measurements. The diffraction data showed the presence of only the bcc Ba_6C_{60} phase. Raman measurements show absence of disordered carbon and C_{60} phases in the sample. Magnetization was measured with a Quantum Design-MPMS2 type superconducting quantum interference device (SQUID) magnetometer at temperatures down to 1.8 K. In the magnetic data corrections were made to account for demagnetization effects assuming a spherical shape for the particles with demagnetizing factor $n=\frac{1}{3}$. However, in determining the upper critical field, since $-4\pi M \ll H$, especially near T_c, no demagnetization corrections were made.

The low-field magnetization measurements showed a well-defined transition into a superconducting state with $T_c=7$ K. The data showed that even at 2 K the observed magnetization was far from saturation (about 12% shielding) and indicating partial field penetration into the sample which can be caused by the effects of the small particle size being comparable to the penetration depth of the material.[10]

The value of the upper critical field is an important quantity since it gives direct information about microscopic parameters among which is the superconducting coherence length. From the SQUID data for the magnetization we determine the coherence length at $T=0$ K, using a well-known approach,[11] as follows: A typical set of magnetic data obtained at two different applied fields, 0.1 and 0.4 T, respectively, are shown in Fig. 1(a). Along with the suppression of T_c at higher fields we observe a linear reversible regime in $M(T)$ close to and below T_c which is indicative of the absence of vortex pinning and expected from GL theory where the magnetization is linearly proportional to $|1-T/T_c|$ near the transition.[12] The field-dependent critical temperature $T_c(H)$ is thus determined as the intercept of a linear extrapolation of the magnetization in the superconducting state with the normal-state base line. We note that in the vicinity T_c the observed rounding in the $M(T)$ dependence might be caused by diamagnetic fluctuations. The suppression of $T_c(H)$ with the "critical field" H_{c2} at that temperature is shown in Fig. 1(b). A linear dependence adequately fits the temperature dependence of the so defined H_{c2} with a slope of 0.45 T/K. It may be useful to mention that the value of dH_{c2}/dT determined from an approach in which the temperature at which $M(T)$ starts to deviate from the normal state value is within 10% of the same range as obtained above. Using the Werthamer-Helfand-Hohenberg (WHH) expression[13] $H_{c2}(0)=0.7(\partial H_{c2}/\partial T)_{T_c}T_c$ we determine the extrapolated upper critical field at $T=0$ K to be $H_{c2}=2.2$ T. According to the relation[12] $H_{c2}=\Phi_0/2\pi\xi_{GL}^2$ we obtain the zero temperature coherence length to be $\xi_{GL}(0)=120$ Å.

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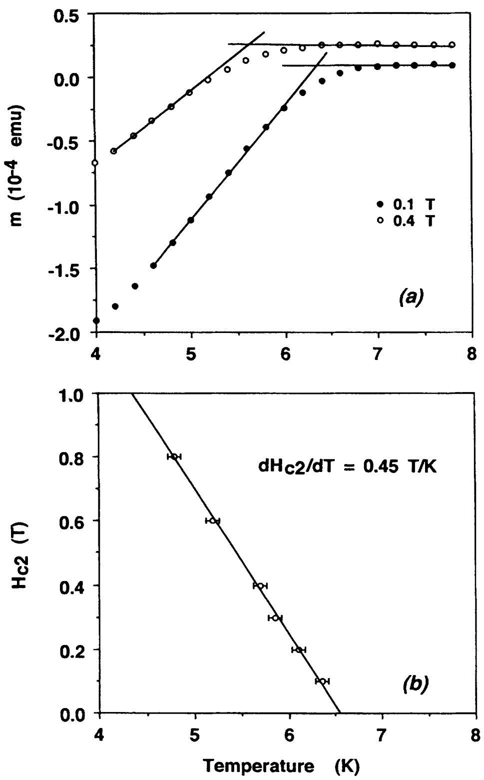

FIG. 1. (a) Temperature dependence of the field-cooled magnetization of Ba_6C_{60} in external magnetic fields of 0.1 and 0.4 T respectively. (b) The upper critical field as a function of temperature for Ba_6C_{60}.

The lower critical field was determined from the ZFC initial magnetization data. The sample was cooled from above T_c down to $T<T_c$ in zero field (remanent field of about 0.1 Oe). Once the temperature was stabilized the magnetic field was applied and the magnetization measured versus increasing field magnitude. We define the lower critical field $H_{c1}(T)$ as $1/(1-n)$ times the lowest applied field at

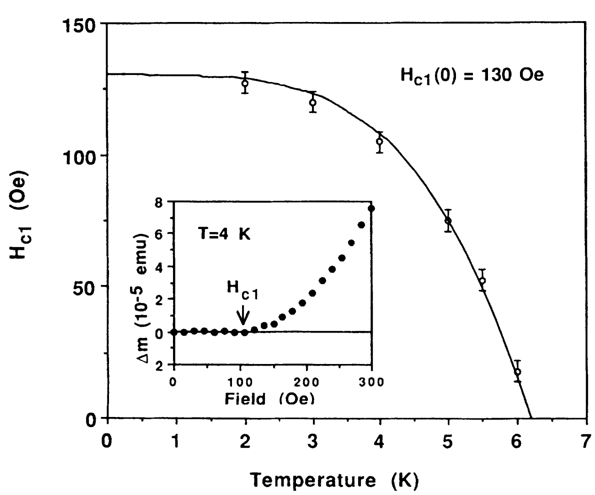

FIG. 2. Temperature dependence of the lower critical field of the Ba_6C_{60} superconductor. The inset shows a typical determination of H_{c1} from the deviation of the magnetization Δm, in the zero-field-cooled initial magnetization data at 4 K.

TABLE I. Superconducting parameters of Ba_6C_{60} (this work), K_3C_{60} (Ref. 4), and Rb_3C_{60} (Ref. 5).

Parameter	Rb_3C_{60}	K_3C_{60}	Ba_6C_{60}
T_c (K)	29.6	19.3	7
$-dH_{c2}/dT$ (T/K)	3.9	3.73	0.45
H_{c2} (T)	78	49	2.2
H_{c1} (Oe)	120	130	130
ξ (Å)	20	26	120
λ (Å)	2470	2400	1800
$k=\lambda/\xi$	124	92	15

which the magnetization deviates from the linear behavior, and the external field starts to penetrate the sample. The lower critical field obtained in this way is shown in Fig. 2 as a function of temperature. The data fit well to the two-fluid expression for the temperature dependence of H_{c1}: $H_{c1}(T)=H_{c1}(0)[1-(T/T_c)^4]$ (solid line in Fig. 2). From the fitting we extrapolate the lower critical field at zero temperature $H_{c1}(0)=130$ Oe. Using the relation:[12] $H_{c1}(0)=(\Phi_0/4\pi\lambda^2)\ln(\lambda/\xi_{GL})$, we estimate $\lambda(0)=1800$ Å and hence, the GL parameter $\kappa=\lambda/\xi_{GL}=15$.

The superconducting parameters determined for Ba_6C_{60} are compared in Table I with the values obtained for K_3C_{60} and Rb_3C_{60}. From this table it is obvious that the Ba_6C_{60} compound differs substantially from the alkali-metal-doped C_{60} systems in its superconducting properties. Besides the T_c, which is for example three times lower compared to that for K_3C_{60}, the upper critical field is extremely low, i.e., $H_{c2,Ba}(0)=2.2$ T which is $=0.045\times H_{c2,K}(0)$, resulting in a relatively long coherence length, $\xi_{Ba}(0)\approx 5\times\xi_K(0)$. The difference in H_{c2} cannot be accounted for just by the difference in T_c as may be done[4,5] for K_3C_{60} and Rb_3C_{60} systems where the upper critical field slopes are approximately equal and the extrapolated critical field values at $T=0$ are proportional to T_c. The hypothetical value of H_{c2} for Ba_6C_{60} estimated using the critical field slope of K_3C_{60} and $T_c=7$ K would be about 20 T which is an order of magnitude greater than the observed value. Obviously, we are dealing with a system having much weaker coupling strength, resulting in a much lower transition temperature and upper critical field, and as a result, much longer coherence length. An estimate of the coupling strength in Ba_6C_{60} based on the analyses in Ref. 20 assuming coupling to the same low-energy intramolecular phonons ($\Omega_{ph}=250$ cm^{-1}), $\mu^*\approx 0.2$ and the measured T_c gives $\lambda\approx 0.8$ which is to be compared with $\lambda\approx 1.5$ for K_3C_{60} and $\lambda\approx 2.1$ for Rb_3C_{60}. Thus, the coupling strength in Ba_3C_{60}, being in the intermediate range, is significantly weaker than that for the alkali-metal fullerides.

Several models have been proposed to explain superconductivity in the metal-doped fullerenes. Among them is the model based on phonon-mediated pairing employing either higher energy (0.12 eV) intramolecular modes[14,15] or low-energy (0.02 eV) metal-C_{60} intermolecular modes.[16] A model of a superconducting state in the fullerides with purely electronic pairing mechanism has also been proposed.[17] Recent isotope effect experiments on Rb_3C_{60} have yielded a sizable shift in T_c indicating that the lattice is involved in pair formation.[18,19] The analysis carried out in Ref. 20 (also dis-

TABLE II. Electronic parameters of superconducting fullerides, high-T_c oxides, and typical conventional superconducting metals.

Parameter	K_3C_{60}	Rb_3C_{60}	Ba_6C_{60} (this work)	La-Sr-Cu-O (Ref. 29)	Conv. Metals (Ref. 29)
k_F (10^7 cm^{-1})	6.8 [a]	6 [a]	7	3.5	10
	3.4 [b]				
m^*/m_e	22 [a]	16 [a]	13	5	1–15
	11 [b]				
v_F (10^6 cm/s)	3.6 [a]	4.3 [a]	6	8	100–200
E_F (eV)	0.08 [a]	0.085 [a]	0.15	0.1	5–10
	0.04 [b]	$\leqslant$0.1 [c]			
	0.16–0.3 [d]	0.14–0.18 [d]			
	0.325 [e]	0.2 [e]			
	0.1 (0.21) [f]	0.08 (0.16) [f]			
	0.09 (0.21) [g]	0.07 (0.18) [g]			

[a]Estimated from magnetic measurements of Refs. 4 and 5 for K_3 and Rb_3C_{60}, respectively.
[b]From μSR studies (Ref. 28).
[c]From IR reflectivity measurements (Ref. 22).
[d]From band structure calculations (Ref. 34).
[e]From thermopower studies (Ref. 35).
[f]Estimated from normal state magnetic susceptibility (Ref. 23). Values in parentheses are obtained assuming a factor of 2 enhancement in $N(E_F)$ due to spin fluctuation-induced effects (see Ref. 23).
[g]From NMR determined $N(E_F)$(Refs. 21 and 36). Values in parentheses are estimated from NMR data corrected as discussed by Antropov *et al.* (Ref. 34). E_F was estimated using $N(E_F)$ as described by Hebard (Ref. 37) (see also Ref. 34).

cussed above) supports a model of superconductivity with intermediate to strong coupling via low-energy intramolecular phonons. Within the phononic mechanism there have been indications of weak, intermediate, and strong coupling in A_3C_{60} systems (see, e.g., Refs. 18 and 21–24). Most of the experimental results and in particular variations of T_c can be explained on the basis of the weak-coupling BCS model with the density of states at the Fermi level varying with the structure (see, e.g., Refs. 5,14,15, and 25). However, in order to account for the measured T_c's within the weak-coupling BCS model high-energy ($\Omega_{ph}=0.1$ to 0.15 eV) intramolecular modes must be employed, and since the Fermi energy in the superconducting fullerides is low (see discussion below and Table II), $\Omega_{ph}\approx E_F$, which is outside the range of applicability ($\Omega_{ph}\ll E_F$) for the BCS as well as Eliashberg equations. This consideration gives further support to the strong-coupling model[20] described above. Nevertheless we assume the BCS expression for the superconducting energy gap $2\Delta/kT_c=3.5$ to be valid, although a larger value of this ratio corresponding to a stronger coupling would not affect the obtained qualitative results.[26] The clean limit expression for the penetration depth $\lambda(0)=(m^*c^2/4\pi n_s e^2)^{1/2}$ gives the ground-state value $n_s/(m^*/m_e)=8.75\times10^{20}$ cm^{-3}. Further, using the coherence length $\xi(0)=(\hbar v_F)/[\pi\Delta(0)]$ with $\Delta(0)=1.76kT_c=1$ meV, we obtain the Fermi velocity $v_F=6.1\times10^6$ cm/s. Combining these two results we find the Fermi energy $E_F=0.15$ eV and the effective electron mass $m^*=13m_e$ and $n_s=1.14\times10^{22}$ cm^{-3}. This value of the electron density implies[27] a charge transfer of 1.3 in order to be consistent with the theoretical value 1.72×10^{22} cm^{-3} obtained for a bcc structure with the lattice constant[7] of 11.171 Å assuming Ba-C_{60} charge transfer of 2. In Table II we compare the effective mass, m^*/m_e, Fermi momentum, k_F, Fermi velocity, ν_F, and Fermi energy, E_F, for different superconducting systems, including fullerides, high-T_c ceramics, and conventional metals.

A few comments on the assumptions regarding the "clean-limit" approximation which forms the basis of the discussions above would be informative. High resistivities of superconducting fullerenes result in extremely short mean free paths, if the Drude model is employed. For instance, the resistivity of the order of 1 mΩ cm in Ba_6C_{60} films[30] would imply an extreme dirty limit superconductor with a mean free path $l=1-2$ Å which is much shorter than the coherence length. This means that in order to use the clean limit analyses the coherence length and the penetration depth should be rescaled according to $\xi_{GL}=(\xi_0 l)^{1/2}$, $\lambda=\lambda_L(1+\xi_0/l)^{1/2}$, in order to obtain the values for ξ_0 the Pippard coherence length, and λ_L the London penetration depth which are the appropriate parameters in the "dirty-limit." Using our estimated values $\xi_{GL}=120$ Å, $\lambda=1800$ Å, and $l=2$ Å we thus obtain $\xi_0=7200$ Å and $\lambda_L=30$ Å. However, this value 30 Å for the London penetration depth would result in a ground-state value for the electron density n_s equal to 3.2×10^{24} cm^{-3} [obtained using the above relationship for the penetration depth and $n_s/(m^*/m_e)$], which is at least two orders of magnitude greater than the maximum possible value of 1.72×10^{22} cm^{-3}. There have been several studies addressing the issue of mean free path in superconducting fullerenes. Using specific heat and upper critical field data Ramirez *et al.*[23] estimated l to be ~10 Å for powder K_3C_{60}. About the same value (10–20 Å) was inferred from the magnetotransport studies of K_3C_{60} films by Wang *et al.*[31] Rotter *et al.*[22] obtained a mean free path of ~20 Å from their infrared reflectivity measurements of Rb_3C_{60} powder. Detailed longitudinal and Hall effect measurements of K_3C_{60} films led Palstra *et al.*[32] to conclude that the high resistivity does not arise from the microscopic disorder, but comes about from the granular nature of their films, with a grain size of ~70 Å. Fluctuation conductivity studies of K_3C_{60} and Rb_3C_{60} single crystals[33] showed no effects of granularity and gave a lower limit for the domain size of about 0.6 μm. If we assume the mean free path $l=10$ Å in our sample, the dirty limit corrections to the measured coherence length and penetration depth give $\xi_0=1440$ Å and $\lambda_L=150$ Å. As a result $n_s/(m^*m_e)=1.26\times10^{23}$ cm^{-3} which is more than one order of magnitude greater than the theoretical value (since $m^*/m_e>1$). The corresponding value for $l=20$ Å is $n_s/(m^*/m_e)=3.2\times10^{22}$ cm^{-3}, with $m^*/m_e\approx5$ yielding $n_s=1.7\times10^{23}$ which is still one order of magnitude too large. On the other hand, $l=70$ Å gives the electronic parameters to within a factor of 2 equal to the clean limit values: $\xi_0=206$Å, $\lambda_L=900m^*/m_e=12.5$, $k_F=1.1\times10^8$ cm^{-1}, $v_F=1\times10^7$ cm/s and $E_F=0.35$ eV. However, the electron density $n_s=4.4\times10^{22}$ cm^{-3} is still a little too high, implying that the mean free path should be even longer to account for the measured quantities and for the analysis to be self-consistent.

Interestingly, regardless of the substantial difference in superconducting properties, the superconducting fullerides have the same characteristics for the electronic system. For example, the Fermi energies found in K_3C_{60} and Rb_3C_{60} lie within the range 0.1 to 0.2 eV, which is exactly in the range at the value (0.15 eV) we have estimated for Ba_6C_{60}. A factor of 2 difference in the parameters is well within the uncertainties in the experimental data and due to assumptions made in the evaluations. In summary, enhanced effective mass and a Fermi momentum comparable to those of conventional superconducting metals, in addition to a small Fermi velocity and Fermi energy (about two orders of magnitude smaller than those in metals) appear to be the key features of superconducting fullerides. Table II also suggests that fullerene-based superconductors are similar to high-T_c superconductors as far as electronic properties are concerned. However, in contrast to the high-T_c cuprates with large anisotropy which has a strong impact on their physical properties, the fullerides have cubic lattice structures.

In conclusion, we have measured the magnetic properties of Ba_6C_{60} superconductor with $T_c=7$ K and a bcc lattice structure. The evaluated superconducting parameters, such as the upper critical field slope and the coherence length, differ substantially from those in K_3 and Rb_3C_{60} compounds possessing an fcc structure, indicating that Ba_6C_{60} is a weaker coupled superconducting system than the other members of the C_{60} family. Further studies are required to explain the interconnection between the structure and superconducting properties. What is remarkable, is that the parameters describing one-particle excitations are found to be roughly the same for alkali- and alkaline-earth-C_{60} systems, and very similar to those found in high-T_c cuprate superconductors.

We thank Dr. Hebard and Professor Kresin for many discussions and comments on this work. V. K. acknowledges research grants from the Swedish Institute and the Royal Institute of Technology under the Swedish-East European Program. This research was supported by the Swedish Material Science Consortium on "Clusters and Ultrafine Particles," the Swedish funding agencies NFR and NUTEK.

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