Lower critical fields of alkali-metal-doped fullerene superconductors

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We report on the lower critical field of fullerene superconductors derived from a ''trapped magnetic moment'' method. Superconducting K_3C_{60}, Rb_3C_{60}, and $RbCs_2C_{60}$ crystals and powders with shielding fractions between 3 and 100 % were investigated. In contrast to all previous investigations made by other methods, the values of H_{c1} are much smaller and of the order of 1 mT at $T=0$. We show that the smallness of H_{c1} is not related to Josephson junctions and granularity, but is an intrinsic property of the fullerenes. [S0163-1829(96)50538-2]

Since the discovery of superconductivity in alkali-metal-doped fullerenes,[1] the lower critical field H_{c1} of these materials has been studied by various experimental techniques.[2–10] However, despite several years of research, the magnitude of H_{c1} is still controversial. The first values of H_{c1} for K_3C_{60} (Ref. 2), Rb_3C_{60} (Refs. 3 and 4), and $RbCs_2C_{60}$ (Ref. 9) and Ba_6C_{60} (Ref. 11) were obtained by a dc-magnetization technique. The lower critical field at zero temperature $\mu_0 H_{c1}(0)$ evaluated from these measurements was in the range from 11 to 16 mT.[2–6] The penetration depth λ, calculated from H_{c1} with the well-known equation

$$\mu_0 H_{c1} = \frac{\Phi_0}{4\pi\lambda^2} \ln(\kappa) \qquad (1)$$

(where Φ_0 is the magnetic flux quantum, $\kappa=\lambda/\xi$ is the Ginzburg-Landau parameter, and ξ is the coherence length) and from the coherence length known from independent measurements,[2,3,5,12–16] is of the order of 200–250 nm.[2,5,6,13,16] In these experiments the lower critical field was evaluated as the field, at which a deviation from a linear *M(H)* dependence first appeared. However, none of the magnetization data for fullerene materials showed good linearity or any cusps above H_{c1}. $M(H)$ usually has a smooth positive curvature, i.e., it is extremely difficult to obtain the point of the first deviation from linearity, since the deviations themselves are very small. Indeed, using the same method for determining H_{c1}, Irons *et al.*[17] showed recently, that deviations could be seen at much smaller applied fields, which were of the order of 3–4 mT in their experiments.

In addition, other methods often showed that the magnetic field penetrated the sample below 10 mT. For instance, a method based on measurements of the reversible magnetization at high external fields,[9] led to $\mu_0 H_{c1}(0)\sim 8$ mT for $RbCs_2C_{60}$. $\mu_0 H_{c1}(0)$ for Rb_3C_{60},[6] obtained from the Bean critical state model,[18] was of the order of 5 mT. Small values of the magnetic field, at which a trapped magnetization appeared, were observed on M(T) (Ref. 10) and M(H) (Ref. 8) curves. Moreover, in measurements of λ (Refs. 7 and 19) by μSR experiments, the penetration depth was found to be 480 nm for K_3C_{60} and 420 nm for Rb_3C_{60}. These results indicated that the lower critical field of fullerenes could be much smaller than obtained from magnetization measurements.

All these data compelled us to undertake more detailed and careful investigations of the lower critical field in fullerenes. In order to avoid the difficulties associated with the above methods, another way to estimate H_{c1} must be found. Hence, we employed a method[20] where H_{c1} is determined from a modified ''trapped magnetization'' technique.

We will show in this presentation that the lower critical magnetic field of the fullerene superconductors is of the order of 1–1.5 mT at zero temperature and that these small values of the lower critical field are not connected to a breaking of Josephson junctions in the sample, but are intrinsic features of these materials.

Samples of different compounds and quality were investigated in order to find influences of granularity and weak links, if any, on the lower critical field. In our experiments K_3C_{60} crystals with shielding fractions, x_{sh}, from 25 to 100 %, crystalline (x_{sh}=3%) and powdered Rb_3C_{60} and $RbCs_2C_{60}$ powder were measured. (Details of the sample preparation are given in Refs. 9, 21, and 22.) These samples show a large variation of granularity ranging from ''poor'' superconductivity (Rb_3C_{60} crystal and powders) to bulk crystals with a shielding fraction of 100%. One of the samples (with a weight of 2.1 mg and a size of approximately $2\times1\times1$ mm^3) was examined by ac-magnetization measurements and did not show granularity for current flow.[21]

Magnetic dc measurements were performed in a commercial superconducting quantum interference device magnetometer in the temperature range 5 K $\leqslant T \leqslant T_c$. This device has a very high sensitivity, which is mainly achieved by an environmental magnetic shield attenuating undesirable stray fields. Moreover, a special low-field option allows us to hold the residual field in the magnet at a very low level ($<5\times10^{-8}$ T). Due to these options very precise measurements of the trapped magnetization and very small increments of the external magnetic field can be achieved.

For the K_3C_{60} crystalline samples with 100% shielding fraction, the demagnetization factor was obtained from $M(H)$ and $M(T)$ zero-field-cooled (ZFC) measurements. We assume that complete flux expulsion prevails and fit both the magnitude of the ZFC magnetization at the lowest temperature and the slope of the straight $M(H)$ line to $M=-H$. Both methods give the same value of the demagnetization factor for each sample (n=0.4 and 0.14, respectively). For the K_3C_{60} sample with 25% shielding fraction,

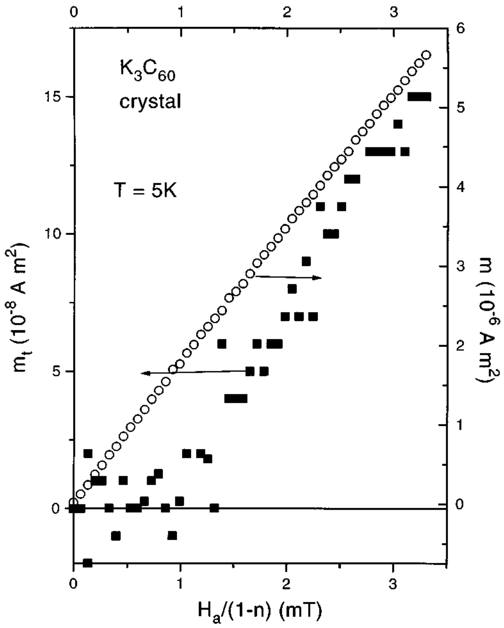

FIG. 1. Field dependence of the trapped magnetic moment (solid squares) and of the magnetic moment (open circles) of the K_3C_{60} single crystal taken at $T=5$ K.

which has the shape of a narrow plate parallel to the applied field, $n=0$. The demagnetization factor n is taken to be 1/3 for the Rb_3C_{60} sample, because the shape of the crystal is roughly spherical, and the same for the $RbCs_2C_{60}$ sample, because the powder can be approximated by a set of independent spheres.

The measurements of the trapped magnetization, m_t, were made according to the following scheme. The sample is cooled down from $T>T_c$ to the desired temperature in zero external magnetic field. After temperature stabilization, the magnetic moment m_1 is measured. After this first measurement, a certain magnetic field H_a is applied and kept fixed for some time (usually for 5 to 20 s). Then the magnetic field is reduced to zero and the magnetic moment, m_2, measured again. The trapped magnetic moment $m_{\mathrm{tr}}=m_2-m_1$. Afterwards, the sample is heated up to $T>T_c$. These cycles are repeated, the value of the applied field H_a being higher each time than during the previous cycle, with step increments of 10–50 μT. The principle of this experiment is based on the fact that magnetic fields do not penetrate the sample for $H_a/(1-n)<H_{c1}$ and that the magnetic moment measured before and after the application of H_a is the same. Though, as soon as $H_a/(1-n)$ exceeds H_{c1}, m_2 should be smaller than m_1 due to some trapped magnetic flux, which is pinned in the sample and $m_{tr}=m_2-m_1>0$.

This method is far more accurate than the measurement of δM because of the cancellation of a large linear contribution.[23] The advantage of this method for type-II superconductors with strong pinning was illustrated in Ref. 22, where the $m(H)$ behavior was shown to be quite linear in the vicinity of H_{c1}, whereas $m_t{}^{1/2}$ vs H showed a well-resolved kink at the field corresponding to H_{c1}.

The magnetic-field dependence of m_t at $T=5$ K is shown in Fig. 1 for a K_3C_{60} single crystal. As expected, there is no trapped magnetization at small fields, $H_a<(1-n)H_t$. m has some background value and is field independent. When the magnetic field exceeds some characteristic field H_t, a trapped magnetization appears and increases with increasing external field. It follows $m_t^{1/2}\sim H$ (Fig. 2), which occurs only[23] when the field penetrates the *bulk* of the superconductor. This means that the characteristic field H_t is equal to the lower critical field H_{c1}.

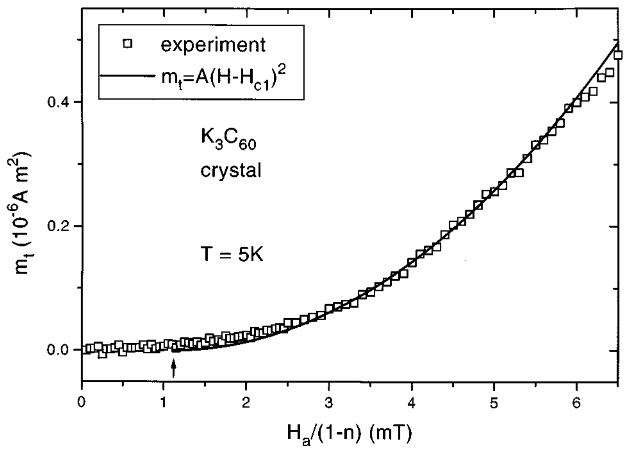

FIG. 2. Field dependence of the trapped magnetic moment of the K_3C_{60} single crystal at $T=5$ K. The solid line corresponds to the equation $m_t=A(H_a-H_{c1})^2$.

For comparison and to illustrate the advantage of the trapped magnetization measurements the m vs H_a curve is also shown in Fig. 1. As can be clearly seen, the $m(H)$ behavior looks quite linear at fields even far above H_{c1}, while the $m_t(H_a)$ curve demonstrates a well-resolved trapped magnetization in this field range.

The temperature dependence of the lower critical field, determined from trapped magnetization measurements, is shown in Fig. 3 for different fullerene superconductors. It roughly follows both the weak-coupling BCS theory (dashed lines in Fig. 3) and the parabolic law

$$H_{c1}(T)=H_{c1}(0)[1-(T/T_c)^2] \quad (2)$$

which is shown by the solid lines in Fig. 3. The error bars for th K_3C_{60} samples in Fig. 3 overlap and are shown as a common error bar for all samples.

The striking feature of the results is the smallness of H_{c1} compared with data obtained previously by other methods. However, the resolution of the δM measurements is very poor (Fig. 1) as mentioned above. Other techniques also led to smaller values of H_{c1} and the better the resolution of the method, the smaller is the magnitude of the first penetration field (see for instance Refs. 10 and 8). However, these smaller values of the first penetration field were usually attributed to the breaking of weak-coupling between grains. Since the same small values of H_t are observed in our experiments for powders and crystals of different quality, including crystals with $x_{\mathrm{sh}}=100\%$ and without granularity for current flow, it is very unlikely that the trapped magnetization appears at small fields because of granularity or imperfections of the samples. We can certainly state that the lower critical fields of these fullerenes are not higher than the values of H_t observed in our experiments, because magnetic field has clearly penetrated the sample (Figs. 1 and 2).

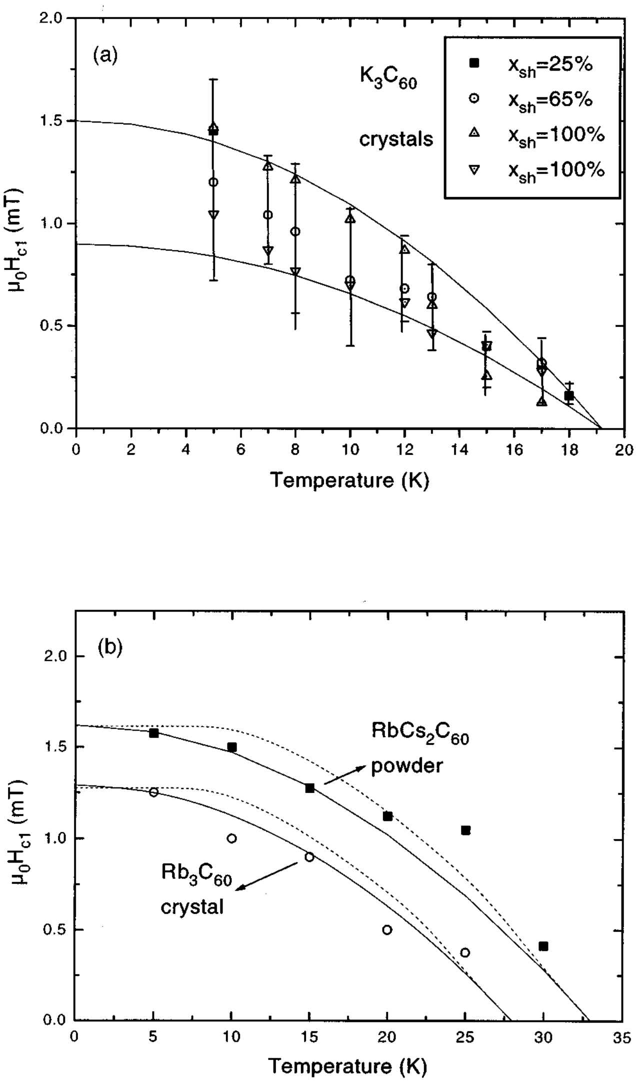

FIG. 3. Temperature dependence of the lower critical field of (a) K_3C_{60} crystals; (b) Rb_3C_{60} crystal (open circles) and $RbCs_2C_{60}$ powder (solid squares). Solid lines correspond to Eq. (2) and dashed lines correspond to the weak-coupling BCS theory.

Such small values of H_{c1} could be related to so-called molecular or zero-dimensional superconductivity in fullerenes, where the superconducting currents flow on the molecular surfaces. In this case we can hardly talk about a lower critical field and magnetic vortices penetrating the material, because any small magnetic field can easily penetrate the superconductor between the bucky balls. However, many experimental results (see, for instance, Ref. 24) show, that fullerenes are very strong (but usual) type-II superconductors and that the models of magnetic vortices describe many of the magnetic properties of these materials well. Moreover, as we can see from our $M(H)$ measurements, magnetic field completely penetrates the sample only at fields $\mu_0 H_p \sim 40$ mT. Such large H_p's would not occur in the case of molecular superconductivity, because the field would penetrate the sample to the center at arbitrarily small values. Therefore, we consider molecular superconductivity to be an unlikely explanation for the smallness of H_{c1}.

Small lower critical fields could also be explained by the fact, that the electron wave functions between adjacent C_{60}^{-3}ions overlap relatively weakly. This weak overlap can be easily destroyed and magnetic field starts to penetrate the sample between the C_{60} molecules.

From the lower critical fields at zero temperature we can estimate the penetration depths for these fullerenes using Eq. (1). According to Fig. 3 $\mu_0 H_{c1}(0)$ is 1.2, 1.3, and 1.6 mT for K_3C_{60}, Rb_3C_{60}, and $RbCs_2C_{60}$, respectively. Thus, we obtain the corresponding values of λ as 890 nm [ξ=2.6 nm (Ref. 2)], 850 nm [ξ=2.7 nm (Refs. 25 and 26)], and 720 nm [ξ=4.4 nm (Ref. 9)]. They are much larger than those obtained before for these compounds. However, they are close to the λ=800 nm obtained for Na_2CsC_{60} from muon-spin relaxation measurements.[19] The corresponding Ginzburg-Landau parameters for K_3C_{60}, Rb_3C_{60}, and $RbCs_2C_{60}$ obtained from our experimental data are κ=342, κ=315, and κ=163, respectively.

In summary, we have determined the lower critical field of fullerene superconductors from measurements of the trapped magnetization. We find that H_{c1} is of the order of 1.5 mT and show that these small values are not connected to breaking the Josephson junctions between superconducting grains, but represent the intrinsic values of fullerene superconductors. From our data, the penetration depth is estimated to be of the order of 800 nm, which leads to Ginzburg-Landau parameters $\kappa \sim 300$ for these superconductors.

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