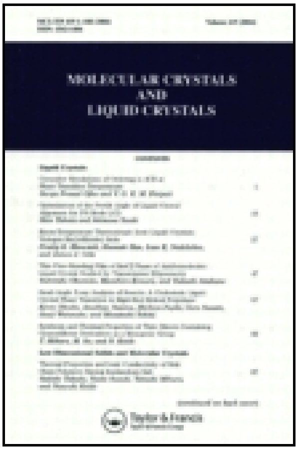

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SUPERCONDUCTING INTERCALATED FULLERENES – PREPARATION ROUTES AND PROPERTIES

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Abstract Superconducting C_{60} powder samples are investigated by means of dc magnetization and X-ray diffraction. We discuss effects on the superconducting behaviour arising from different sample preparation and grain sizes. We derive then the temperature dependence of the magnetic penetration depth which agrees best with theoretical expressions for weak-coupled BCS-type superconductors in the clean limit.

INTRODUCTION

The discovery that doped fullerenes are superconducting has stimulated a wide range of investigations. We report dc magnetization measurements on several samples with the intercalation of alkali metals done by different methods. The first doping routes were motivated by similarities to graphite intercalation compounds (GICs). Ternary GICs show superconductivity up to 2.7 K in $C_4KTl_{1.5}$[1] clearly exceeding the T_c values of the respective binary compounds.

SAMPLE PREPARATION AND CHARACTERIZATION

Fullerenes were sythesized from the soot of evaporated graphite according to Krätschmer et al [2]. For some samples we used commercially available C_{60} powder (MER) containing an amount of 10% C_{70}. The starting material of samples # 2, 5, and 6 (Table I) was purified to a purity of 99.99 % with respect to other fullerenes. We outgassed the pristine C_{60} carefully ($p = 10^{-6}$ mbar, $T = 300°C$, $t > 6$ h) in order to obtain well crystalline doped samples.

To intercalate samples # 3, 7, and 8 a preweighted amount of C_{60} was blanded with the respective amount of fine-ground Tl alloy and annealed at temperatures and for times given in Table I. So prepared samples yield a diamagnetic signal corresponding to a "superconducting volume fraction" of less or equal 10 %.

Table I Characteristics of preparation and onset temperatures to superconductivity

#	Nominal Sample Composition	Annealing time (h)	Annealing Temperature °C	T_c onset (K)	Preparation method
1	$K_3C_{60/70}$	3	300	19	direct contact
2	K_3C_{60}	5		19.5	Mc Cauley
3	$K_3C_{60/70}$	16 - 62	340 - 420	17 - 18	Tl alloy
4	$Rb_3C_{60/70}$	20	450	24	direct contact
5	Rb_3C_{60}	16 / 21	400 / 430	29.6	Mc Cauley
6	$Rb_3C_{60/70}$	16 / 21	400 / 430	23	Mc Cauley Tl alloy
7	$Rb_3C_{60/70}$	18	400	27.5	Tl alloy
8	$Rb_3C_{60/70}$	18 - 62	400 - 450	26 - 28	Tl alloy

Neither varying the annealing temperature, nor the total metal concentration or the ratio of alkali metal to thallium did result in a significant enhancement of the T_c values compared to that of binary compounds. We showed in previous work[3] through dc-magnetization (SHE SQUID), ac-susceptibility, NMR experiments and X-ray analysis (Figure 1) that a decomposition of the Tl alloy takes place during the annealing. The alkali metal is intercalated whereas metallic Tl is found outside the C_{60} structure.

Samples # 2, 5, and 6 were prepared in a way similar to that proposed by McCauley et al.[4]. Rb_6C_{60} (K_6C_{60}) was ground with an equivalent of C_{60}, pelletized in order to achieve a fast equilibration between rubidium-rich and rubidium-poor grains, and annealed at 350° C for 5 days. The intercalation process was controlled by X-ray diffraction. We determined the particle size of the intercalated material by SEM to be 10 ± 5 μm, whereas grain sizes of the Rb_3C_{60} sample # 7 were less than 2 μm, with only very few grains showing diameters up to 10 μm.

All samples, prepared by pressing the C_{60} and A_6C_{60} (A = K, Rb) powder before annealing it, showed a slight shoulder in the ZFC-curve and two pronounced absorption peaks in the imaginary part of the ac susceptibility[5]. This is significant for the electrical coupling between grains and the collective screening of several superconducting grains. Those specimen also showed a diamagnetic signal corresponding to a superconducting volume fraction of 109 ± 20 % for K_3C_{60} and 77 ±20 % for Rb_3C_{60}.

ANALYSIS OF THE TEMPERATURE DEPENDENCE OF THE MAGNETIZATION

In powder samples with small grain size the ratio of the (paramagnetic) surface near volume compared to the fully screened diamagnetic volume is by far greater than in large single crystals. Therefore one expects the temperature dependence of the total magnetic moment below T_c to be more pronounced. In the Meissner phase, the shape of the ZFC curve of powder samples with grain sizes of the order of the penetration depth is then governed by the temperature dependence of the magnetic penetration depth.

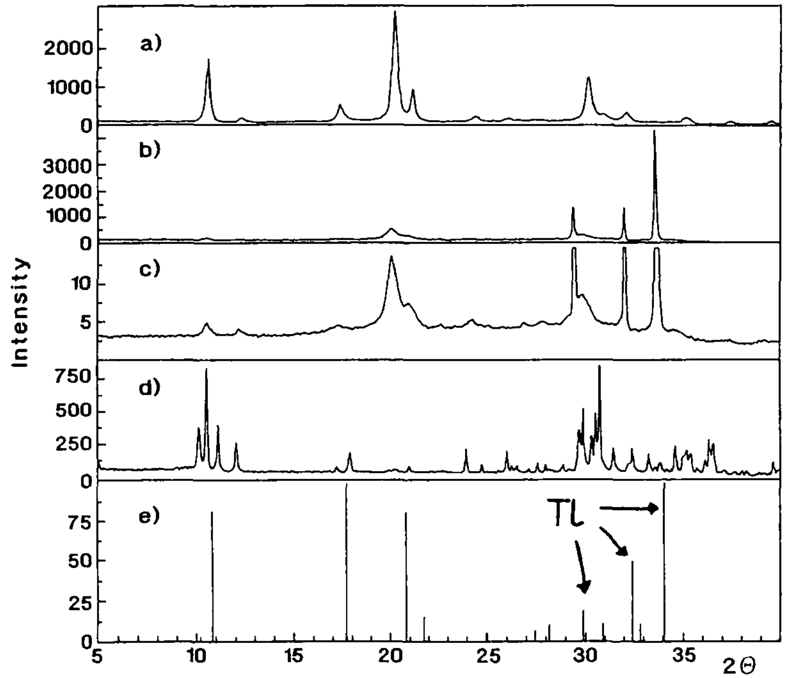

Figure 1 X-ray diffraction (Cu K_α) patterns of **a**) pure Rb_3C_{60}, **b**) and **c**) (extended scale) Rb_3C_{60} prepared using a RbTl alloy, in comparison with **d**) the spectra of the alloy used for preparation and **e**) of pristine C_{60} and metallic Tl.

Figure 3 plots susceptibility (dc SQUID) versus temperature for a $(RbTl_{1.5})_3C_{60}$ sample with grain diameters less than 2 μm. The temperature dependence of the magnetization is particularly affected by the finite grain size in this sample (λ (0) = 2470 Å for Rb_3C_{60}[6]). There should be no electrical coupling between the grains since no second absorption peak could be observed in the imaginary part of the ac susceptibility. If we thus assume that the overall magnetic moment μ may be written as the sum of the magnetic moments of the single grains and that the external magnetic field acting on each grain is equal to the applied magnetic field, the total magnetic moment $\mu\,(T)$

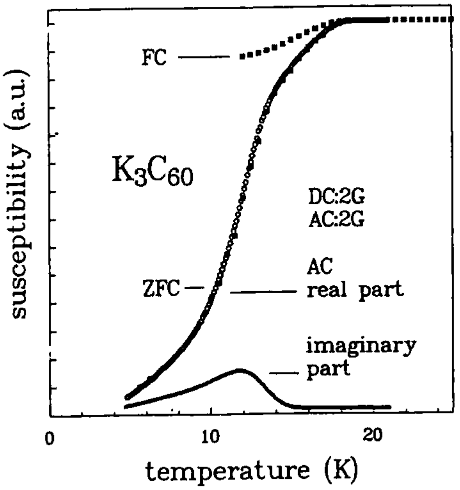

Figure 2 Comparison of dc (SQUID) and ac susceptibility of K_3C_{60}

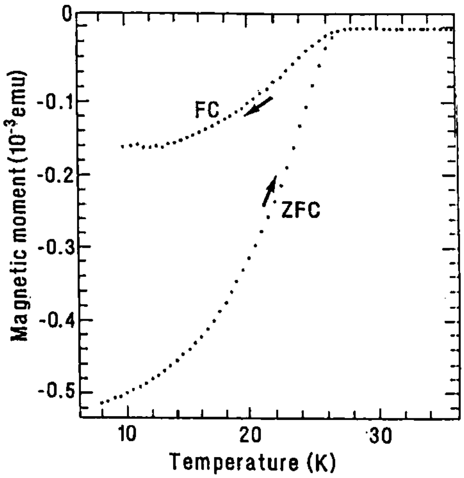

Figure 3 Dc susceptibility of $(RbTl_{1..5})_3C_{60}$ (H_{ext} = 8 G)

can be related to the magnetic penetration depth through [7,8]

$$\frac{\mu(T)}{\mu(0)}=\frac{1-N(0)}{1-N(T)}\;\frac{\left(1-\frac{3}{x}\right)\coth(x)+\frac{3}{x^2}}{\left(1-\frac{3}{x_o}\right)\coth(x_o)+\frac{3}{x_o^2}}. \tag{1}$$

Here $x=r/\lambda(T)$ $\left(x_o=r/\lambda(0)\right)$ with r being the mean radius of the single grain and $N(T)$ the demagnetization factor (in the following its temperature dependence will be neglected).

No universal temperature dependence exists for the magnetic penetration depth in BCS theory. It rather depends on the BCS coherence length ξ_0, the electronic mean free path l_0 and the gap function $\Delta(T)$ [9]. In this paper we consider three cases:

1) clean local limit $\lambda(0) >> \xi_0, l_0 \rightarrow \infty$

$$\frac{\lambda(T)}{\lambda(0)}=\left(1-\frac{1}{k_BT}\int_{-\hbar\omega}^{\hbar\omega} f(E)\big(1-f(E)\big)dE\right)^{-1/2} \tag{2}$$

While k_B is the Boltzmann's constant, ω an average lattice frequency and F(E) the Fermi function $E=\sqrt{\Delta^2+E^2}$. For the weak-coupling limit ($\Delta(0)$ = 1.76 k_BT_c) one can find the later by Mühlschlegel [10].

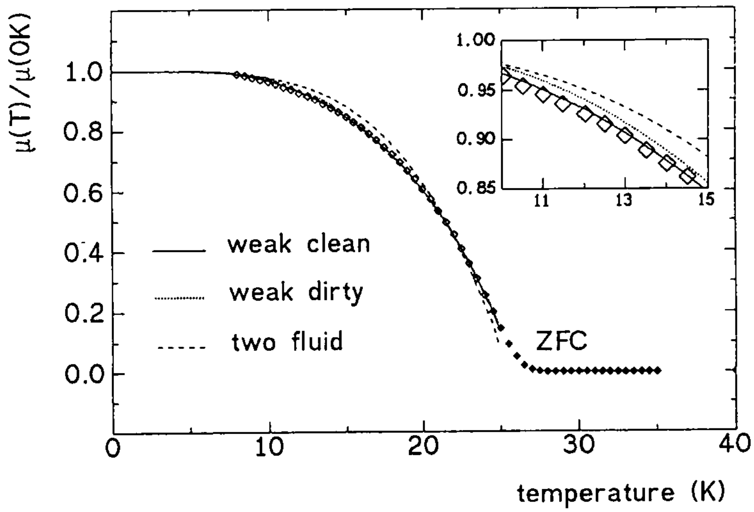

Figure 4 Fits to the experimental data of Figure 3 based on eqs. (1), (2), (4) and (5)

2) extreme anomalous limit $\xi_0 >> \lambda(0)$, $l_0 \rightarrow \infty$

$$\frac{\lambda(T)}{\lambda(0)} = \left(\frac{\Delta(T)}{\Delta(0)}\tanh\frac{\Delta(T)}{2k_BT}\right)^{-1/3}. \tag{3}$$

It can be shown[9] that for BCS superconductors in the weak coupling limit this equation with tabulated $\Delta(T)/\Delta(0)$ values[10] comes close to a curve obtained with the empirical "two-fluid" formula [11]

$$\frac{\lambda(T)}{\lambda(0)} = \left(1-\left(\frac{T}{T_c}\right)^4\right)^{-1/2}. \tag{4}$$

Eq.(3) however is expected to be inadequate for C_{60}-superconductors because the latter do not fulfill the condition $\xi_0 >> \lambda(0)$. The validity of Eq. (4), on the other hand, is not only restriced to the extreme anomalous and weak-coupling limit but also represents an appropriate approximation for $\lambda(T)$ in the strong-coupling local limit[12].

3) Dirty local limit, $\lambda(0) >> \xi_0 >> l_0$

$$\frac{\lambda(T)}{\lambda(0)} = \left(\frac{\Delta(T)}{\Delta(0)}\tanh\frac{\Delta(T)}{2k_BT}\right)^{-1/2} \tag{5}$$

Figure 4 shows a scaled plot of $\frac{\mu(T)}{\mu(0)}$ as measured for the Rb_3C_{60} sample # 7. The data are fitted on the basis of equation (1), (2), (4), and (5). Although the differences between clean and dirty local limit are not very pronounced the best agreement between calculated and experimental data is achieved if this sample is considered to be a BCS-type weak-coupling superconductor in the clean local limit (eq. 2). With this fit a value of $r/\lambda(0) = 3.34$ is obtained. Using a penetration depth $\lambda(0) = 2470$ Å[6] results in an average grain diameter of 1.65 μm which corresponds to what is observed by electron microscopy. An analysis of the ZFC-data of Rb_3C_{60} published by Politis et al.[13] also agrees best with the theoretical prediction if one assumes a BCS-type weak-coupling superconductor in the clean local limit.

In summary the preparation according to Mc Cauley et al.[4] leads to samples with higher crystallinity and a higher diamagnetic shielding signal. But it also seems to produce specimens that are agglomerates of particles with many voids inbetween and thus simulate a higher superconducting volume fraction. In powder samples with particle sizes comparable to the penetration depth the diamagnetic signal is reduced drastically by grain size effects. Here an analysis of the ZFC-curve in the Meissner state allows to study the temperature dependence of the magnetic penetration depth which is related to the electronic properties of the superconducting state. The best agreement is achieved if a weak coupled BCS-type superconductor in the clean local limit is assumed.

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REFERENCES

1. R.A.Wachnik, L.A.Pendrys, F.L.Vogel, and P.Lagrange, Solid State Commun. **43**, 5 (1982).
2. W.Krätschmer, L.D.Lamb, K.Fostiropoulos, D.Huffman, Nature **318**, 162 (1985).
3. M.Kraus, J.Freytag, S. Gärtner, H.M.Vieth, W.Krätschmer, and K.Lüders, Z.Phys.B - Condensed Matter **85**, (1991); M.Kraus, S.Gärtner, M.Baenitz, M.Kanowski, H.M.Vieth, C.T.Simmons, W.Krätschmer, V.Thommen, H.J.Güntherodt, and K.Lüders, Europhys. Lett. **17**, (5) 419 (1992); M.Baenitz, M.Kraus, S.Gärtner, H.M.Vieth, H.Werner, R.Schlögl, W.Krätschmer, M.Kanowski, and K.Lüders, in "Electronic Properties of High-T_c Superconductors", ed. by H.Kuzmany, Springer Series in Solid State Sciences, Springer, Heidelberg, 1992.
4. J.P.McCauley Jr., Q.Zhu, N.Coustel et al., J. Amer. Chem. Soc. **113**, 8537 (1991).
5. M.Baenitz, E.Straube, M.Kraus, H.Werner, R.Schlögl, and K.Lüders in this issue.
6. G.Sparn et al. Phys. Rev. Lett. **68**, 1228 (1992).
7. J.R.Clem and V.G.Kogan, Proc. 18th Int. Conf. Low Temp. Phys., Kyoto 1987, Jpn, J.Appl. Phys. 26 1161 (1987).
8. E.W.Scheidt, C.Hucho, K.Lüders, and V.Müller, Solid State Commun.**71**, 505 (1989).
9. M.Tinkham, "Introduction to Superconductivity" (McGraw-Hill, New York) 1975.
10. B.Mühlschlegel, Z. Phys. **155**, 313 (1959).
11. C.J.Gorter, H.D.G.Casimir, Z.Phys. **35**, 963 (1934).
12. J.Rammer, Europhys. Lett. **5**, 77 (1988).
13. C.Politis et al., Europhys. Lett. **17** 175 (1992); C.Politis et al., Modern Phys Lett.B **6**, 351 (1992).