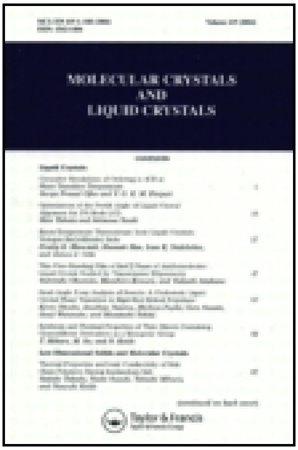

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SCANNING TUNNELING MICROSCOPY STUDY OF GRANULAR INTERCALATED FULLERENES

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Abstract We have studied by scanning tunneling microscopy (STM) the surface of polycrystalline powders of Rb_3C_{60}, $(KTl_{1.5})_3C_{60}$ and $(RbTl_{1.5})_3C_{60}$ (nominal compositions) in a high purity argon environment at 295 K. Large scale STM images reveal effective grain sizes of some hundred nanometers. This small grain size strongly reduces the superconductivity fraction of the diamagnetic shielding. On a molecular scale, the STM images show ball-shaped features which can be identified with individual fullerene molecules in case of Rb_3C_{60}(111) and (311) facets, but in case of $(KTl_{1.5})_3C_{60}$ and $(RbTl_{1.5})_3C_{60}$ their apparent diameter (1.7 nm) is significantly larger. Since AC-susceptibility and X-ray diffraction have traced metallic Tl in the $(KTl_{1.5})_3C_{60}$ and $(RbTl_{1.5})_3C_{60}$ samples, we interpret the larger apparent diameter of the ball-shaped units as a complex of Tl and Rb_3C_{60}.

INTRODUCTION

The discovery of superconductivity in alkali-metal doped C_{60} fullerites[1] at temperatures up to 33 K[2] has initiated widespread research activities. The search for new doped fullerene compounds is often stimulated by previous results obtained from other doped materials such as graphite intercalation compounds (GIC's). Among the GIC's with the highest critical temperatures to superconductivity T_c are $KTl_{1.5}C_4$ (2.7 K) and $KTl_{1.5}C_8$ (2.45 K)[3]. C_{60} fullerites doped with thallium-alkali metal alloys also show superconductivity[4,5]. Their T_c's, however, coincide in most cases with those of the non-thallium-containing K- and Rb-doped fullerites. Regarding the similar T_c's of the Tl-containing and non-Tl-containing K- and Rb-fullerites, it is rather straightforward to assume that the Tl-metal has little or no influence on superconductivity in these compounds. A recent report[6] has proved the presence of metallic Tl in $(RbTl_{1.5})_3C_{60}$. Within the scope of this paper, we present scanning tunneling microscopy (STM) images which support the presence of Tl-metal in doped fullerites with the nominal composition $(MTl_{1.5})_3C_{60}$ (M = K, Rb).

EXPERIMENTAL

Polycrystalline $C_{60/70}$ and the respective dopants (Rb, $KTl_{1.5}$ and $RbTl_{1.5}$) in the molar ratio 1:3 are heated in a pure argon atmosphere at 450 °C for 40 h (Rb_3C_{60}), 340 °C for 62 h ($(KTl_{1.5})_3C_{60}$) and 450 °C for 18 h ($(RbTl_{1.5})_3C_{60}$). The powders are sealed under vacuum and characterized within the sealed glass tubes by AC and DC susceptibility measurements[4,5].

Pellets are pressed at moderate pressure from the powders without exposure to air and moisture in a stainless-steel glove box filled with 1 bar of high-purity argon. A two-stage gas purification system keeps the O_2, N_2 and H_2O levels below our detection limit of 1 ppm. For the STM experiments in the argon-filled glove box[7], these pellets are mechanically cleaved to remove any contaminations introduced to the surface layers during compaction. Mechanically prepared $Pt_{90}Ir_{10}$ STM tips are used. The STM images show no significant dependence on the applied bias voltages (100-1000 mV) and tunneling currents (0.5-2 nA).

RESULTS AND DISCUSSION

Granular Rb_3C_{60}

Pressed pellets of Rb_3C_{60} (T_c = 27 K) exhibit by STM on a large scale a surface dominated by grains of a size of a few hundred nanometers (see fig. 1). This granularity might be responsible for the low diamagnetic shielding observed in that sample. J.R. Clem and V.G. Kogan[8] have calculated the effects of the finite grain size upon the temperature dependence of magnetization of a sample consisting of spherical grains. Grains with sizes R that are comparable to the magnetic field penetration depth $\lambda(T \rightarrow 0)$ give only small contributions (magnetic suppression factor P=0.2 for $R/\lambda(0) = 2$) to the signal observed in a magnetization experiment[8]. A typical value for the magnetic field penetration depth $\lambda(T \rightarrow 0)$ in Rb_3C_{60} is 247 nm[9]. This often leads to an underestimation of the superconducting volume fractions of doped fullerite superconductor powders if the fraction is determined from zero-field-cooling magnetization experiments without grain size corrections.

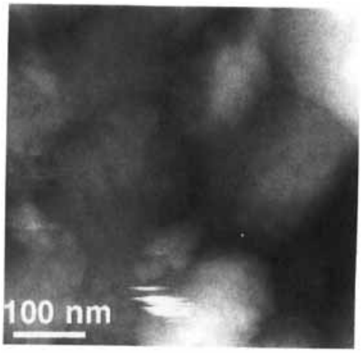

FIGURE 1. Large scale STM image of Rb_3C_{60} showing grains with typical sizes of a few hundred nanometers.

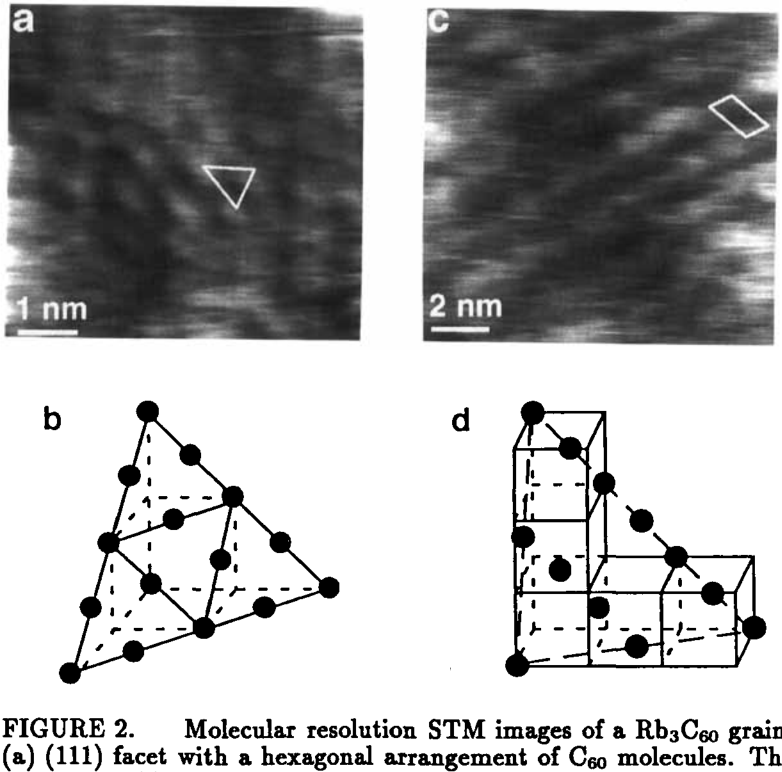

FIGURE 2. Molecular resolution STM images of a Rb_3C_{60} grain. (a) (111) facet with a hexagonal arrangement of C_{60} molecules. The nearest-neighbour-distance is about 1 nm, the apparent size of the molecules is 0.7 nm. The white triangle is the (111) mesh unit. (b) Schematic view of the fcc(111) plane. (c) (311) facet showing an oblique C_{60} lattice (a = 1 nm, b = 1.7 nm). (d) Schematic view of the fcc(311) plane. The white parallelogram is the (311) mesh unit.

Molecularly resolved STM images of Rb_3C_{60} grains show ball-shaped features with an apparent diameter of 0.7 nm. We assign these features to individual C_{60} molecules. Different crystallographic faces are observed (see fig. 2). Figure 2a shows the (111) face with a hexagonal arrangement of fullerene molecules with a nearest-neighbour-distance of 1 nm. A schematic view of the (111) plane in the fcc lattice is shown in fig. 2b. Figure 2c shows an oblique lattice ($a = 1$ nm, $b = 1.7$ nm), which is interpreted as the fcc(311) face (see for comparison the schematic view of the fcc(311) plane in fig. 2d).

Granular $(KTl_{1.5})_3C_{60}$ and $(RbTl_{1.5})_3C_{60}$

The $(MTl_{1.5})_3C_{60}$ (M=K,Rb) powders ($(KTl_{1.5})_3C_{60}$: $T_c = 17.6$ K, $(RbTl_{1.5})_3C_{60}$: $T_c = 27.5$ K) have been investigated by AC-susceptibility as a function of temperature [4,5]. Figure 3 shows the temperature dependence of the AC-susceptibility at $\nu =$ 107 Hz of $(RbTl_{1.5})_3C_{60}$ powder sample. The T_c (27.5 K) is very similar to that of Rb_3C_{60} ($T_c = 28$ K). A second transition is observed at 2.4 K which coincides with the T_c of metallic thallium. The shielding fraction of the Tl indicates that approximately 90 % of the Tl used for preparation of the $(RbTl_{1.5})_3C_{60}$ sample contributes to the diamagnetic signal.

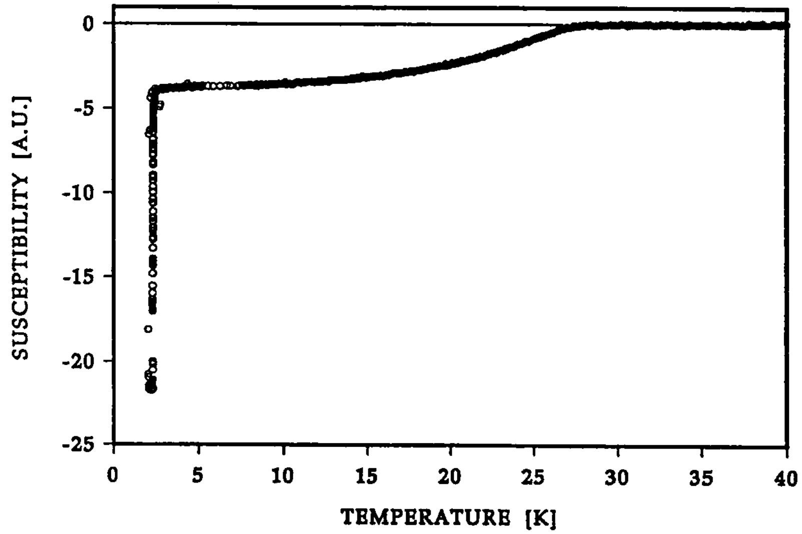

FIGURE 3. Temperature-dependent AC susceptibility data for a $(RbTl_{1.5})_3C_{60}$ powder sample. T_c (onset) is at 27.5 K. A second transition assigned to metallic thallium is observed at 2.4 K.

X-ray diffraction of RbTl-doped C_{60} samples shows, in addition to the Rb_3C_{60} reflections, peaks for both hexagonal and simple cubic thallium[6]. This implies that the initially homogeneous $RbTl_{1.5}$ alloy has separated into its components during the preparation of $(RbTl_{1.5})_3C_{60}$, and mainly Rb_3C_{60} is formed. Consequently, the Rb_3C_{60} powder contains metallic thallium.

A synthesis of Rb_3C_{60} using binary alloys can still be useful since the binary alloys are handled more easily (grinding, weighing) and processed at lower reaction temperatures. Zhang et al.[10] have used RbHg alloy to prepare Rb_3C_{60} at 200 °C.

STM images of the Tl-containing compounds show similar grain sizes as the non-Tl-containing compounds (see the large scale STM image of $(RbTl_{1.5})_3C_{60}$ in fig. 4a). However, a clear difference from the non-Tl-containing compounds is observed on a molecular scale. Figure 4b displays a STM image of $(KTl_{1.5})_3C_{60}$ showing ball-shaped features of an apparent diameter of 1.7 nm. This value is significantly larger than that of a single C_{60} molecule (0.7 nm).

We interpret these larger units as aggregates of C_{60} and the intercalant metals. Actually, a rough estimate of the diameter of a $(KTl_{1.5})_3C_{60}$ complex as composed of metal atoms and a C_{60} molecule in a close-packed-arrangement of hard spheres with the respective van-der-Waals radii gives a diameter of about 1.5 nm.

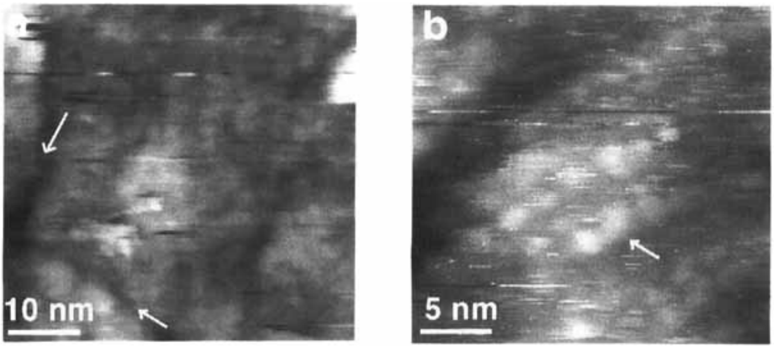

FIGURE 4. (a) STM image of $(RbTl_{1.5})_3C_{60}$ showing grain boundaries (marked by arrows). (b) Molecular resolution STM image of $(KTl_{1.5})_3C_{60}$. The apparent diameter of the ball-shaped features is significantly larger (1.7 nm) than that of a C_{60} molecule (0.7 nm). This might be explained by assigning the balls to a complex of C_{60} and the intercalant and/or electronic structure effects.

Since STM measures the local density of states at the Fermi level, the electronic structure of $(KTl_{1.5})_3C_{60}$ may also influence the size and shape of the spherical features in fig. 4b. No structure which could be assigned to metal intercalant atoms has been resolved within the ball-shaped units.

In summary, we have presented large scale STM images of alkali metal doped fullerite powder samples which show grain sizes of several hundred nanometers. This small size which is comparable to the magnetic field penetration depth may account for the observed small shielding fractions in magnetization experiments. Molecular scale STM images of Rb_3C_{60} reveal (111) and (311) arrangements of fullerene molecules, but no indications of the Rb intercalant are found. In $(KTl_{1.5})_3C_{60}$, however, the significantly larger molecular units can be explained by the AC susceptibility and X-ray diffraction evidence of metallic thallium in the thallium-alkali metal doped fullerites.

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