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Superconducting properties of alkali-metal-doped C_{60} prepared by thermal decomposition of azides

Madoka Tokumoto, Yasumoto Tanaka, Nobumori Kinoshita, Tatsue Kinoshita, Shoji Ishibashi and Hideo Ihara

Electrotechnical Laboratory,
1-1-4 Umezono, Tsukuba, Ibaraki 305, Japan

An alkali metal doping process through the thermal decomposition of alkali azides was applied to the preparation of alkali metal binary alloy doped C_{60}. A systematic study on the superconducting properties of C_{60} doped with alkali-metal binary-alloys including Cs (Cs-Na, Cs-K, Cs-Rb) is presented. A substantial improvement in the superconducting volume fraction was achieved compared to the materials doped by the standard gas-phase reaction. For pure cesium and pure sodium, however, no indication of superconductivity has been detected.

1. INTRODUCTION

Most alkali-metal doped C_{60} compounds with a stoichiometric ratio of 3:1 (*i.e.*, A_3C_{60}, where A=K, Rb, or binary alloys of Na, K, Rb, Cs), and having an fcc structure were found to show superconductivity with various values of the transition temperature, T_c, up to 33 K [1-7]. In general, higher values of T_c have been obtained for larger ionic radii of alkali cations, or larger lattice parameter of the fcc crystal structure [8]. The cesium doped C_{60} is therefore expected to give the highest T_c among alkali doped C_{60}, if it forms a compound of Cs_3C_{60} with the fcc structure. Novikov *et al.* [9] calculated the electronic structure of A_3C_{60} (A=K, Rb, Cs) fcc crystals and gave estimated T_c values of 16 K for K_3C_{60}, 30 K for Rb_3C_{60} and 47 K for Cs_3C_{60}. These calculated T_c values for K and Rb doping are in good agreement with experiment and the predicted T_c value of Cs_3C_{60} are close to the value of 43 K obtained by a linear extrapolation based on the lattice constant [9]. In cesium-doped C_{60} both the presence [10, 11] and absence [3] of superconductivity have been claimed experimentally. However, in the former, the superconducting fraction was very small (1% or less).

Superconducting C_{60} compounds are usually prepared by direct reaction of pure alkali-metal vapor with C_{60} for typically 24 h or more. Several studies on binary-alloy-doped C_{60} have been reported [4-8]. Application of the thermal decomposition of alkali-metal azide to the doping of C_{60} was first reported by Bensebaa *et al.* [12] They used alkali-metal azides as the source of alkali-metal and prepared superconducting samples with nominal compositions of K_3C_{60} and Rb_3C_{60}.

In this paper, we report the application of the thermal decomposition of alkali azides to alkali-metal binary-alloy doping of C_{60}. Characterization of the superconducting properties of C_{60} doped with alkali metal binary alloys including Cs (Cs-Na, Cs-K, Cs-Rb), with the nominal compositions of 3:1, are presented.

2. EXPERIMENTAL

The pure C_{60} (>99.9%) used in this work was separated by flash chromatography, using activated charcoal (Norit-A), from the toluene extract of the carbon soot produced by DC arc discharge of graphite rods under a He atmosphere of around 100 Torr. For preparation of C_{60} doped with alkali-metal binary alloys including Cs (*i.e.* $Cs_{3-x}A_xC_{60}$ where A=Rb, K, Na), C_{60} powder (10 mg) and stoichiometric amounts of the azide of two alkali metals (a few mg in total) were weighed and loaded into a quartz tube (5 mm diameter) in air. While keeping the sample tube under dynamic vacuum, the sample was gradually heated until the decomposition takes place. Details of sample preparation by thermal decomposition of alkali azides are described separately [13]. The superconducting properties were measured, without further annealing, using a Quantum Design SQUID magnetometer. The sample was first cooled down to 5 K in zero field, and the magnetization was measured at 5 K in magnetic fields up to 10 Oe, and then the sample was gradually warmed in a magnetic field of 10 Oe up to 40 K to give ZFC (shielding) magnetization data.

3. RESULTS AND DISCUSSION

Figure 1(a) shows the temperature dependence of the ZFC magnetization of $Cs_{3-x}K_xC_{60}$. At 5 K, a diamagnetic shielding signal corresponding to a superconducting volume fraction of over 80% was obtained for x=2.0 and 2.5. These high superconducting fraction values suggest that the decomposition reaction of alkali azide is very efficient for achieving a uniform doping of alkali metals into C_{60}. Figure 1(b) shows the temperature dependence of the ZFC. magnetization of

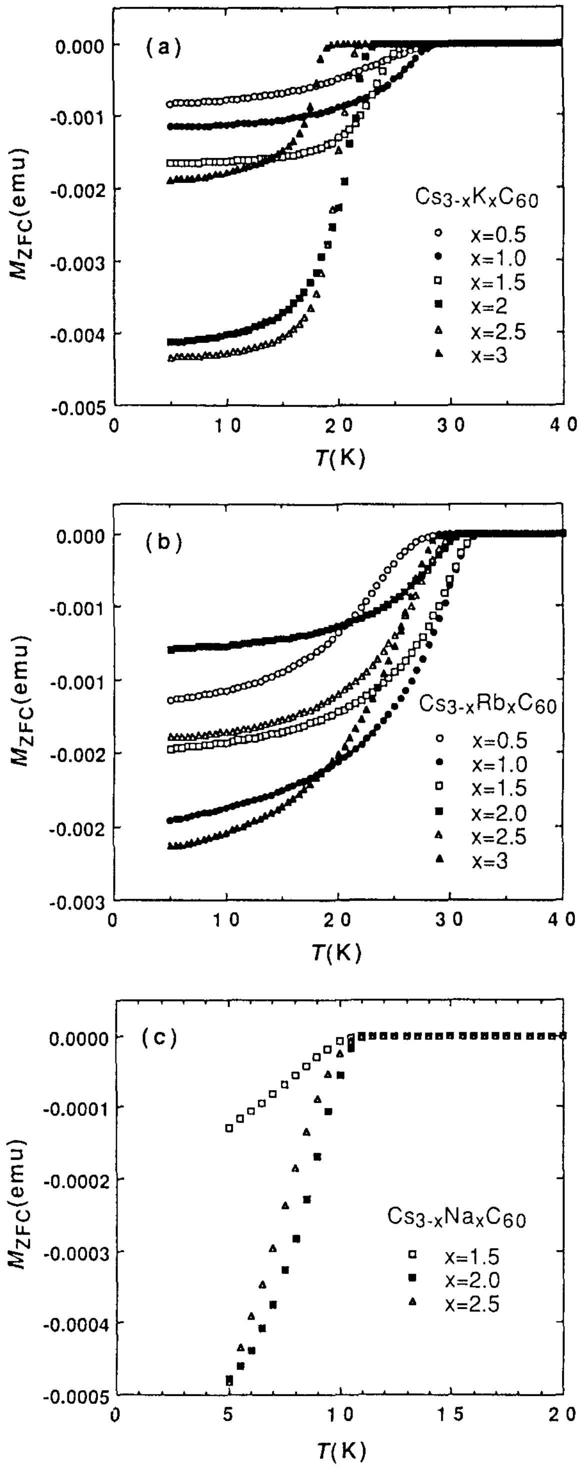

Fig. 1. Temperature dependence of the shielding magnetization of (a) $Cs_{3-x}K_xC_{60}$, (b) $Cs_{3-x}Rb_xC_{60}$, and (c) $Cs_{3-x}Na_xC_{60}$.

$Cs_{3-x}Rb_xC_{60}$. A diamagnetic shielding corresponding to a superconducting volume fraction of over 40% was measured for x=1.0 and 3.0. Figure 1(c) shows the temperature dependence of the ZFC magnetization of $Cs_{3-x}Na_xC_{60}$. A diamagnetic shielding of about 10% was obtained for x=2.0 and 2.5.

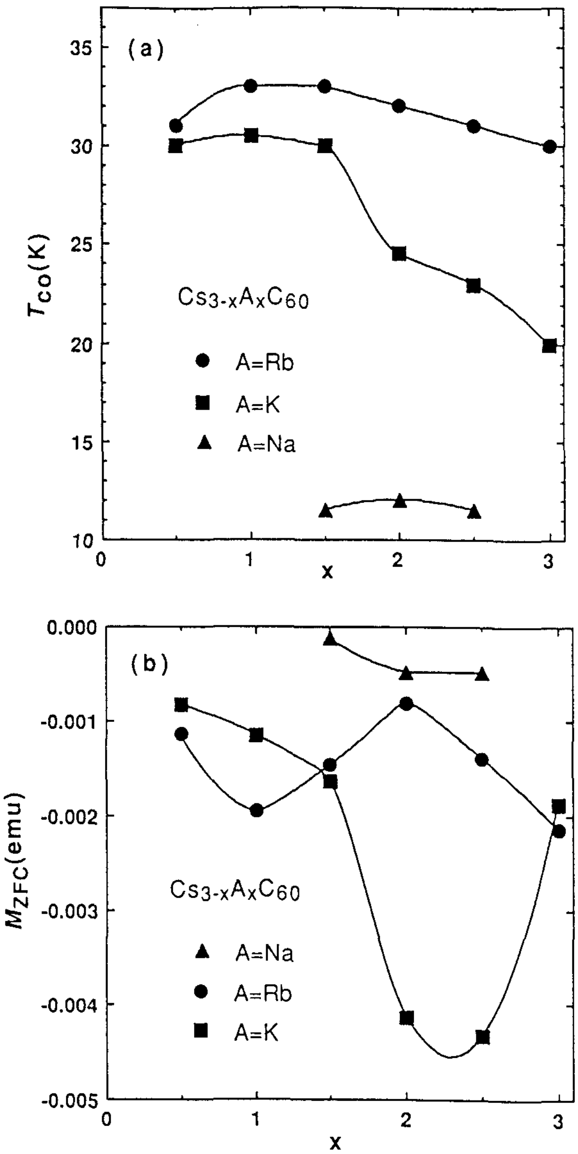

Fig. 2. (a) T_c onset (T_{co}) and (b) shielding magnetization (M_{ZFC}) at 5 K of $Cs_{3-x}A_xC_{60}$, for A=Rb, K and Na against composition x.

Figure 2 shows the (a) T_c onset and (b) superconducting shielding magnetization (ZFC) at 5 K of $Cs_{3-x}A_xC_{60}$ (A=K, Rb and Na) as a function of nominal composition x. For A=K, it is noted that neither the T_c onset nor the shielding signal are a smooth function of x, suggesting a phase separation in $Cs_{3-x}K_xC_{60}$. They can be classified into three groups as follows. (1)Samples with x=0.5, 1.0 and 1.5 correspond to $Cs_2K_1C_{60}$ with T_c onset=30-31 K and low superconducting fraction. (2)Those with x=2.0 and 2.5 corresponds to $Cs_1K_2C_{60}$ with T_c=23-25 K and high superconducting fraction. (3)x=3 or K_3C_{60} with T_c=20 K and relatively low superconducting fraction. The relatively small superconducting fraction in $Cs_2K_1C_{60}$ may suggest that this particular phase containing two cations with different size, a large Cs^+ and a small K^+, in two tetrahedral interstices is not stable thermodynamically. For $Cs_{3-x}Rb_xC_{60}$, T_c shows a very smooth and systematic change as a function of nominal composition x. The T_c onset is a linear function of x between x=3.0 to 1.5 and shows a downward deviation for x=1.0 and 0.5. The linear extrapolation to x=1 and x=0 gives T_c=34 K for $Cs_2Rb_1C_{60}$ and T_c=36 K for Cs_3C_{60}, respectively. Superconducting fractions for $Cs_{3-x}Rb_xC_{60}$ are relatively low but show high values for x=1 and 3. These observations suggest that (1) $Cs_{3-x}Rb_xC_{60}$ prepared by this method forms a uniform solid solution between x=0.5 and x=3, (2) T_c=33 K of $Cs_2Rb_1C_{60}$ is suppressed by some unknown reason and is lower than it should be and (3) fcc Cs_3C_{60} would be a superconductor with T_c=36 K or higher. For A=Na, superconductivity was observed for a limited composition range from x=1.5 to 2.5 with constant T_c=11-12 K, suggesting that $Cs_1Na_2C_{60}$ is the only superconducting phase in $Cs_{3-x}Na_xC_{60}$ [6, 7]. Recently, Imaeda *et al.* [14] reported a new superconducting sodium-nitrogen-C_{60} compound, prepared utilizing the thermal decomposition of sodium azide. However, we could not detect any indication of superconductivity for x=3, *i.e.* Na_3C_{60}, even when prepared under an appreciable amount of nitrogen atmosphere.

In the present study, we could not detect any indication of superconductivity for x=0, *i.e.* Cs_3C_{60}, prepared by this method. It is, however, consistent with the fact that the superconductivity observed in Cs_xC_{60} disappeared upon extended annealing [11].

4. SUMMARY

Doping by thermal decomposition of alkali-metal azide was applied to the preparation of superconducting C_{60} doped with alkali-metals and their binary alloys including Cs (Cs-Na, Cs-K, Cs-Rb). We achieved a substantial improvement in the superconducting volume fraction compared to alkali-metal doping by the standard gas-phase reaction, except for pure cesium and sodium, where no indication of superconductivity was observed. These results demonstrate that the thermal decomposition of alkali azides can be utilized for the preparation of high-quality superconducting C_{60} doped with alkali-metals and their binary or ternary alloys.

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