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ESR and low-field microwave absorption study of sodium-doped C_{60}: pecularities of the doping using sodium azide

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We have studied ESR and low-magnetic field microwave absorption in new superconducting (SC) sodium-nitrogen-C_{60} ternary compound prepared utilizing the thermal decomposition of sodium azide (NaN_3). In dependence on the water content in preliminary NaN_3, final products of the doped C_{60} demonstrate two SC phases with T_{c1}=10-12 K and T_{c2}=14.7-17.3 K, and with different volume fractions.

1. INTRODUCTION

M_xC_{60} fullerides (M=K, Rb, Cs, or their mixture) have a face-centered cubic (f.c.c.) structure up to x=3, while for x≥4 they have a body centered tetragonal (b.c.t.) or a body centered cubic (b.c.c.) lattice. In contrast, Na_xC_{60} retains the f.c.c. structure in x up to 11 since Na atoms with a small ionic radius are intercalated at the octahedral vacant sites as Na clusters [1-3]. Na_3C_{60} does not exhibit superconductivity due to the phase separation at low temperature: Na_3C_{60} f.c.c. phase undergoes a disproportionation into Na_2C_{60} and Na_6C_{60} phases below 250 K [1]. A new superconducting (SC) phase in sodium-doped C_{60} might be created, if the phase separation is suppressed in some way.

Recently we have found superconductivity in sodium-doped C_{60}, in which nitrogen is incorporated as some Na-N cluster [4]. Here we report the study on ESR and low-field signal (LFS) of microwave absorption of the new SC sodium-nitrogen-C_{60} ternary compound.

2. EXPERIMENTAL

Experimental details of the synthesis of Na-doped C_{60} described in [4] presented also in this issue along with the characterization by X-ray, SQUID, and chemical analysis data [5]. We only point out here that three kinds of sodium azide with different water content has been used to prepare Na-doped C_{60}. The first one was NaN_3 of 90% purity from Wako Pure Chemical (named W-NaN_3); the second one was the ≥99.5% NaN_3 from Fluka (named F-NaN_3); then we have deliberately added a water into F-NaN_3 by dissolving it in distilled water. Vacuum dried product is named wet F-NaN_3. This treatment dramatically changed LFS properties, leading to the increase of T_c with the change of the LFS spectra shapes.

LFS spectra were measured on a X-band ESR spectrometer, Varian E112 (details of LFS method are reported in [6]). ESR measurements were carried out on a X-band spectrometer, Bruker ESP-300E. Integral intensity of the ESR signals was calculated by means of Bruker ESP-1600 Data system. To precisely measure g-values (with accuracy of Δg<0.00005) we have used both Takeda-Riken TR-5201M frequency counter with accuracy in control of microwave frequency of 10 kHz and NMR Gaussmeter Bruker ER035 with accuracy in control of magnetic field of 0.05 G.

3. RESULTS AND DISCUSSION

3.1. Low-field signal (LFS) of microwave absorption

We have measured a number of nominal composition Na_xC_{60} with x within the range of 1≤x≤12. Most intensive LFS was demonstrated by the samples either with x=3 (when we have used F-NaN_3) or with x=4 (for W-NaN_3 and wet F-NaN_3). The dependence of the LFS intensity on x for the samples prepared using W-NaN_3 is presented in Fig.1. Nevertheless, a weak LFS with measureable

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intensity and hysteresis has also appeared in the sample with x=9.

LFS showed a typical hysteretic behavior due to the flux pinning in granular superconductors [7] (Fig.2). Depending upon the kind of sodium azides, LFS either remains after long time annealing at 200°C for the samples prepared using W-NaN$_3$ and wet F-NaN$_3$, or disappears during first several hours of such annealing for the sample prepared using F-NaN$_3$. This result means that the water, penetrated into the lattice, possibly plays an important role to stabilize the SC phase. At the same time, water leads to another effect.

We observed two kinds of LFS spectra depending upon the temperature range. For example below 10-12 K, LFS has a small hysteresis and often shows an inverse sign in the usual experimental conditions (P$_{mw}$=2 mW and H$_{mod}$=10 G) as shown in Fig.2a. When we use the low microwave power (P$\leq$0.1 mW) in this temperature range, however, LFS changes the sign and thus shows ordinary shape opposite to an ESR signal. Above 12 K LFS increases the hysteresis and exhibits a normal "positive" sign as shown in Fig.2a. Moreover, as shown in Fig.3, the temperature dependence of the LFS intensities for the samples prepared with F-NaN$_3$ (curve a) and W-NaN$_3$ (curve b) shows a sharp drop around 10-12 K.

Another effect of water treatment is the increase of T$_c$. All Na$_x$C$_{60}$ samples, prepared using both W-NaN$_3$ and F-NaN$_3$, showed LFS at 14-15 K, while Na$_4$C$_{60}$ and N$_3$C$_{60}$, prepared from wet F-NaN$_3$ with the deliberately increased water content, exhibited LFS at 17.3 K. The icreasing T$_c$ may be caused by the lattice expansion due to the intercalation of water molecules. It seems to be similar to the result by Zhou et al who reported increase of T$_c$ up to 29.6 K in Na$_2$CsC$_{60}$ by intercalation of ammonia [8]. F. Bensebaa et al also found the increase in T$_c$ up to 38 K (LFS method) in Rb$_x$C$_{60}$ doped using RbN$_3$ [9]. Probably and in the last case water has played some role.

Earlier it has been shown that LFS is a fine method to search and study several SC phases in multiphase superconductors [10]. In turn, SQUID magnetometer can recognize only the bulk superconductivity, while LFS can detect the surface superconductivity as well as the bulk one. Let us discuss the relationship between LFS and SQUID results.
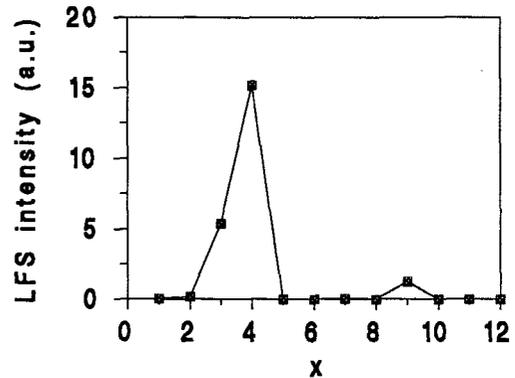
Figure 1. The LFS intensity in dependence on nominal x for samples prepared using W-NaN$_3$ and preheated C$_{60}$ (see [5]). Intensities were normalized to 10 mg for each sample.

(a)

(b)
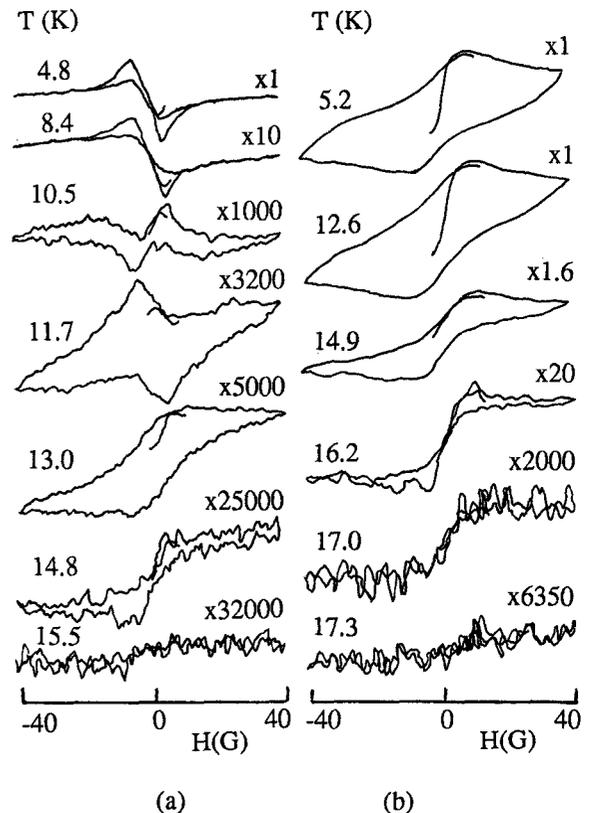
Figure 2. LFS at the different temperatures in x=4 samples, prepared using: a)W-NaN$_3$ and b) wet F-NaN$_3$.
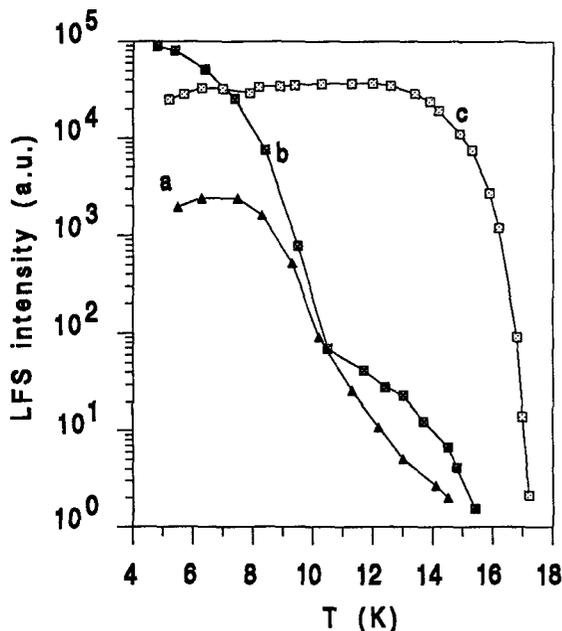
Figure 3. The temperature dependences of LFS for three samples with the same nominal composition Na_4C_{60}, prepared using: a) F-NaN$_3$; b) W-NaN$_3$; c) wet F-NaN$_3$.

1. The samples prepared using W-NaN$_3$ and wet F-NaN$_3$, showing LFS with a large hysteresis, exhibit also a strong magnetic flux explusion in the dc magnetization measurement. The volume fraction of the bulk SC phase was estimated to be about several percents: for example, Na_4C_{60} prepared from wet F-NaN$_3$, which showed one-component LFS with a large hysteresis (fig.2b) and smooth temperature dependence (Fig.3c), demonstrated about 9% of the bulk SC phase in SQUID. On the contrary, the samples with strong LFS, having a sharp inverse component, suppressed hysteresis, and the drop at 10-12 K in the temperature dependence (Fig.3a,b), show a weak Meissner effect. The highest volume fraction of the diamagnetic shielding estimated from the magnetic explusion in this goup was about 1%. And the sample of strongest LFS with spectra presented in Fig.2a and with temperature dependence presented in Fig.3b, shows only about 0.1% of the diamagnetic shielding. Furthermore, the samples which have a measurable LFS do not sometimes demonstrate any response in dc

magnetization. The example is Na_4C_{60} prapared using F-NaN$_3$, LFS of which is shown in Fig.3a. This sample does not show measureable signal in SQUID magnetometer down to 2 K.

2. We observed a difference in T_c between LFS and SQUID magnetometer. For instance Na_4C_{60} showed an onset at 15 K in dc magnetization method, while LFS was first detected at 17.3 K. Another sample of nominal composition Na_4C_{60} showed the onsets at 12 K (SQUID) and 14.7 K (LFS). Probably the apparent low critical temperature in SQUID measurement is attributable to the small volume fraction of the bulk SC phase, while LFS is affected also by surface.

Thus, keeping in mind the results of [10] and dc magnetization data, we came to the conclusion of the existence of two SC phases: with T_{c1}=10-12 K and with $T_{c2} \geq 14$ K. In accordance with the chemical analysis [4], and the results of SQUID and LFS, we conclude that the first SC phase with T_{c1}=12 K will be expressed by $Na_xN_yC_{60}$ where x is between 3 and 4 and y is unknown at the moment. Therefore, we may carefully suppose that the second SC phase with T_{c2}=14-17.3 K has $Na_xN_y(H_2O)_zC_{60}$ chemical formula.

3.2 Electron spin resonance

ESR spectra were measured in three groups of samples: 1) Na_xC_{60} ($1 \leq x \leq 12$) using W-NaN$_3$; 2) Na_xC_{60} ($2 \leq x \leq 5$) using F-NaN$_3$; 3) Na_xC_{60} (x=3, 4) using wet F-NaN$_3$.

The samples with x=6 and x$\geq$10 K demonstrated a Curie behavior from 10 K up to the room temperature in the T-dependence of the ESR integral intensity. All other samples showed a Curie dependence up to 150-210 K and a Pauli-like behavior above those temperatures up to 300 K. This observation coincides with the results of Glarum et al, who have reported the metallic features in Na_xC_{60} films above 150 K [12], and it confirms the existence of the metallic phase in our samples.

At the room temperature all samples gave the g-values within the range of 2.0010 $\leq g \leq$ 2.0015 (Table 1). This result confirms the creation of the C_{60}^{n-} anion radicals, which are characterized by a g-value less than the free-electron value, g_e=2.0023 [11-13].

Below the "Pauli-to-Curie" transition point, some

Table 1.
Parameters of room temperature ESR spectra in nominal composition Na_xC_{60} prepared using W-NaN_3.

	g-value	ΔH_{pp} (G)		g-value	ΔH_{pp} (G)
Na_1C_{60}	2.00102	10.52	Na_7C_{60}	2.00129	2.73
Na_2C_{60}	2.00127	11.66	Na_8C_{60}	2.00137	4.00
Na_3C_{60}	2.00140	9.39	Na_9C_{60}	2.00140	4.8
Na_4C_{60}	2.00132	9.53	$Na_{10}C_{60}$	2.00150	1.11
Na_5C_{60}	2.00133	5.26	$Na_{11}C_{60}$	2.00144	1.19
Na_6C_{60}	2.00133	2.05	$Na_{12}C_{60}$	2.00140	1.68
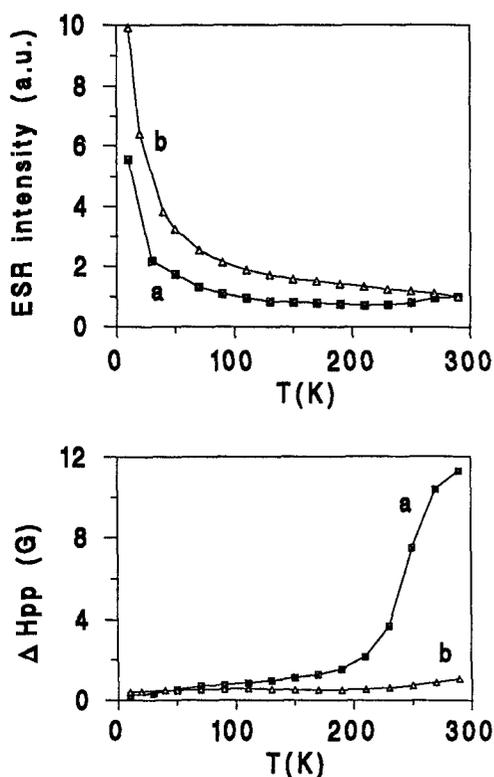
Figure 4. Temperature dependences of the ESR integral intensity (top plot) and line width (bottom plot) for two samples of the nominal compositions of Na_4C_{60} (a) and $Na_{10}C_{60}$ (b).

spectra consist of several lines with different g-values, still less than 2.0023. It is probably connected with the inhomogeneity of the sample. The deviation of the g-value from g_e has been already discussed in literatures. One of the origins of the anomalously low g comes from the partial quenches of the orbital angular momentum [14-15].

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