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Superconductivity at 8 K in samarium-doped C_{60}

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We have synthesized the fulleride system Sm_xC_{60} $(x<3)$. It is found that Sm can be intercalated into interstitial sites of C_{60} to form a solid solution. For the nominal composition $x=3$, the sample shows superconductivity at $T_c=8$ K. X-ray diffraction reveals an orthorhombic structure with $a=28.17(5)$ Å, $b=28.07(3)$ Å, and $c=28.27(3)$ Å, derived from the face-centered cubic cell of A_3C_{60} by doubling in each direction and analogous to that of $Yb_{2.75}C_{60}$. The lattice parameters of Sm-doped C_{60} are significantly larger than those of Yb-doped C_{60} and the superconducting transition temperature of Sm_3C_{60} is 2 K higher than that of $Yb_{2.75}C_{60}$.

Since the discovery of C_{60} and higher fullerenes there has been considerable interest in the chemistry and physical properties of these molecular forms of carbon. Many fullerene-derived solid phases have been synthesized. Particularly, intercalation compounds of C_{60} have attracted a great deal of interest, due primarily to the existence of superconductivity in some members of the family but also to the richness of the binary phase equilibria vs metal concentration x, temperature T, and hydrostatic pressure p. Superconductivity in potassium-doped C_{60} was first reported by Hebard *et al.*[1] Following this observation, the structure and properties of several alkali-metal- (A) doped A_xC_{60} fullerides have been investigated.[2–4] It has been demonstrated that A_xC_{60} can give metallic or insulating compounds, depending on the dopant concentration. The A_3C_{60} fcc phases exhibit superconductivity with a transition temperature that increases with the cubic lattice parameter.[5] More recent success in making alkaline-earth metal doped C_{60} fullerides revealed that superconductivity can also occur in simple-cubic Ca_5C_{60} (Ref. 6) and bcc Ba_6C_{60}.[7] Ruoff and Tomanek *et al.* have carried out theoretical calculations for the formation enthalpy ΔH_f and studied the stability of lanthanide-doped C_{60}.[8,9] They found that the early lanthanides could form stable intercalation compounds. However, if Eu and Yb were considered as divalent, Eu- and Yb-intercalated compounds dramatically also became stable. Very recently superconductivity in Yb_xC_{60} has been reported by Özdas *et al.*[10] Its structure and stoichiometry were not clear until Özdas *et al.* recently reported that $Yb_{2.75}C_{60}$ is responsible for superconductivity and has an orthorhombic superstructure with space group *Pcab* due to cation-vacancy ordering.[11]

The synthesis and investigation of more such C_{60}-based superconducting materials are a key to a better understanding of the structures and properties of fullerides. In this context, we report that the lanthanide samarium can be intercalated into the interstices of the C_{60} structure to form a solid solution Sm_xC_{60} $(x<3)$. The magnetization measurement shows that samples of nominal composition Sm_3C_{60} are superconducting at $T_c=8$ K.

The pure C_{60} (99.9%) used in this work was purchased from Hoechst Company, Frankfurt. High-purity samarium metal was broken into powder, weighted, and mixed with C_{60}. The powder mixtures of C_{60} and samarium were pressed into pellets, which were placed in a high-purity tantalum holder to avoid contaminating the samples with unwanted reaction products. Samples of Sm_xC_{60} with $x=1$, 1.5, 2, 3, 4, and 5 were prepared and loaded into quartz glass tubes. All sample preparation was done in a controlled-atmosphere glove box where the oxygen and water vapor levels are maintained below a few parts per million. The quartz glass tubes were sealed under a vacuum of 10^{-5} Torr. Heat treatments were done between 550 and 600 °C with a duration of several hours. We have found that the optimum reaction temperatures are different for different concentrations of samarium. Higher concentrations of samarium require lower temperatures and shorter reaction time. Otherwise, there is a strong amorphous background in x-ray-diffraction patterns. Supposedly, the optimum preparation conditions represent a compromise between the formation of the desired phase and a competing gradual degradation of the fullerene molecule. For high temperatures and long durations, the products are almost completely amorphous. Following heat treatment, samples were removed from the tantalum holders inside the glove box and loaded into 0.5-mm quartz capillaries for x-ray-diffraction measurements. It was found that although samarium is fairly stable in air, the intercalation compounds Sm_xC_{60} are sensitive to air as is the case for alkali- and alkaline-earth metal doped C_{60}.

X-ray-diffraction measurements were carried out with Cu $K\alpha_1$ radiation. Figure 1 shows x-ray powder diffraction patterns for four different nominal compositions. Most of the strong peaks could be indexed by using a fcc structure with $a=14.08(1)$ Å, but some other peaks (especially in the 2Θ range 10°–20°) could not be indexed. The powder pattern of Sm_xC_{60} $(x=3)$ is, however, amazingly similar to that of the very recently published compound $Yb_{2.75}C_{60}$.[11] This suggests that Sm_xC_{60} has a structure very similar to that of $Yb_{2.75}C_{60}$ and that it shows the same cation vacancy ordering leading to a superstructure. Since one out of very eight T sites in the subcell is vacant, the Sm cations occupying the O sites and T sites also experience off-center displacements as the case of Yb-doped C_{60}.[11] The four Sm cations occupying the O sites move from the center of the O sites towards the neighboring vacancy, while the Sm cations occupying the T

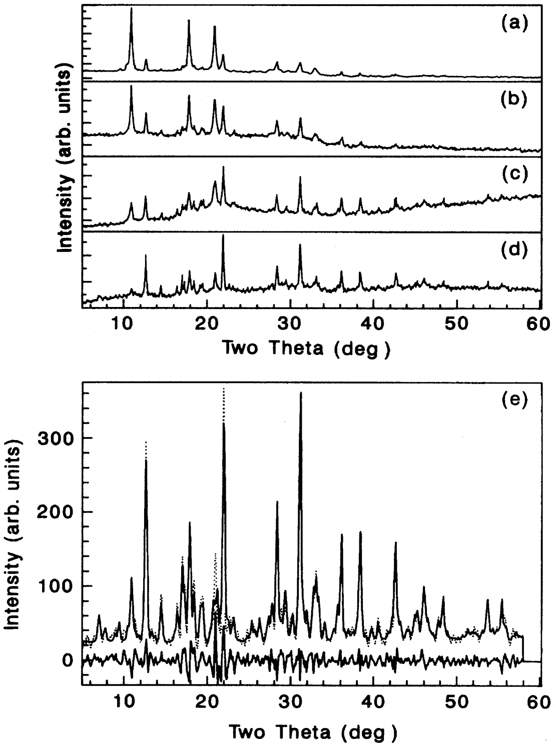

FIG. 1. X-ray powder diffraction patterns (Cu $K\alpha_1$ radiation) of nominal composition Sm_xC_{60}: (a) $x=1$, (b) $x=1.5$, (c) $x=2$, (d) $x=3$. (e) Powder x-ray diffraction pattern (dots) and least-squares fit (solid line) for the sample with nominal composition $x=3$. This refinement was only done on the lattice constants in the cubic unit cell with space group $Pa3$ and 38° rotation of C_{60}'s.

sites experience off-center displacements towards the middle of two neighboring C_{60} molecules. For the sample of nominal composition Sm_3C_{60}, the orthorhombic lattice parameters at ambient temperature are $a=28.17(5)$ Å, $b=28.07(3)$ Å, and $c=28.27(3)$ Å and the systematic extinctions are consistent with space group $Pcab$.[11] As an alternative, lattice parameter refinement with practically the same quality of the fit on sample Sm_3C_{60} with a primitive cubic cell (space group $Pa3$) yields $a=28.174(9)$ Å. The fit to x-ray-diffraction data of the sample Sm_3C_{60} is represented in Fig. 1(e). Dots are experimental data and the solid curve is a fit based on cubic symmetry $Pa3$ and 38° rotation of C_{60}'s as the case of Yb-doped C_{60}. We would like to state that the refinements were only done on the lattice constants. Due mainly to limited resolution and intense Sm fluorescence, the quality of the data is not sufficient to do a meaningful Rietveld refinement, in particular, the number of resolved x-ray lines is much smaller than the number of parameters which have to be refined for the structure proposed in Ref. 11. Due to these problems, we also have to leave the open question of the exact stoichiometry of the new phase. A detailed study of the Sm-C_{60} phase diagram would be beneficial in this context.

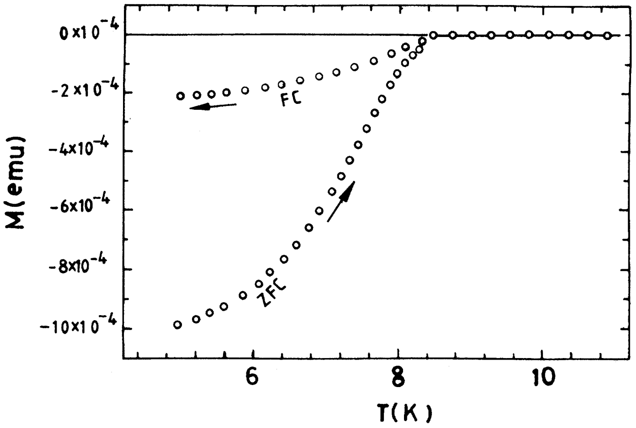

FIG. 2. Magnetic susceptibility measurements of the Sm_3C_{60} sample, FC, field cooled; ZFC, zero-field cooled.

From the series of diffractograms depicted in Fig. 1, it is obvious that in the dilute regime ($x=1.0$) a set of new peaks begins to develop mainly in the 2Θ between 10° and 20°. As the samarium content increases, the intensities of the new peaks continuously increase and characteristic intensity changes occur for pairs of neighboring peaks like (222)/(004) or (622)/(444). Calculation of simulated powder patterns shows that this is the joint effect of the lattice parameter change and a progressive occupation of the tetrahedral and octahedral voids. For $x<3$, the all peaks can be indexed by the orthorhombic structure with double lattice parameters in each direction with respect to the fcc A_3C_{60}, and no new peaks can be contributed to the samarium metal. This suggests that Sm-intercalated C_{60} is behaving like a solid solution in this range of Sm content, the Sm-vacancy ordering takes place as soon as Sm is intercalated into the interstitial sites of C_{60}. For $x>3$, weak peaks corresponding to Sm metal were also observed in the powder patterns, and for the samples with higher concentration, the peak intensities of Sm metal increase and no phase transition is observed.

It is well known that the ionic radius of the intercalants determines the lattice parameters in the intercalated C_{60} compounds. The lattice parameters for nominal composition Sm_3C_{60} are significantly larger than those of $Yb_{2.75}C_{60}$ ($a=27.874$ Å, $b=27.980$ Å, and $c=27.873$ Å).[11] In the paper of Özdas *et al.*, it is proposed that the oxidation state of Yb is +2, which is supported by near-edge and extended x-ray-absorption fine-structure measurements.[11] The ionic radius of Sm^{2+} is larger than that Yb^{2+}, while the ionic radius of Sm^{3+} is smaller with respect to ionic radius of Yb^{2+}. The large lattice parameter of Sm_3C_{60} therefore suggests Sm^{2+}. In addition, the theoretical calculation of Ruoff *et al.* indicates that the R_xC_{60} (R=rare-earth metals) with R^{2+} are more stable than with R^{3+}.[8] It is therefore quite probable that Sm is also divalent. Further research on the electronic structure of Sm-doped C_{60} is necessary to confirm this.

The temperature dependence of the dc magnetization of samples was measured by using a SQUID magnetometer. Figure 2 shows these measurements for the sample ($x=3$) (pattern *d*) shown in Fig. 1. The sample was first cooled to 5 K in zero field and then gradually warmed in a magnetic field of 100 G. The applied field was excluded to about 8 K. At $T=5$ K, a diamagnetic state with 10% shielding was measured. Magnetic flux expulsion in the superconducting state (Meissner effect) was observed when the sample was cooled in a field of 20 G. These measurements yield a Meissner fraction of 3%. This lower bound for the volume fraction of the superconducting phase is almost the same as that of alkaline earth metal doped C_{60}.[7] Although superconductivity was observed in the sample with nominal composition Sm_3C_{60}, the superconducting phase could well be $Sm_{2.75}C_{60}$. The superconducting transition temperature of the sample with nominal composition Sm_3C_{60} is about 2 K higher than that of $Yb_{2.75}C_{60}$ and the lattice parameters of Sm_3C_{60} are also larger than those of $Yb_{2.75}C_{60}$. This case is similar to that of A_3C_{60} (A=alkali metals), where T_c also increases as the lattice parameters increase.[3] It is believed that the increase in lattice parameter leads to an increase of the density of states at the Fermi level, $N(E_f)$. There is substantial evidence that the electron-phonon coupling plays an important role in C_{60} compounds.[1,12] Within the context of the BCS theory of superconductivity, T_c will depend exponentially on $N(E_f)$ and on the effective electron coupling, V_0. The fact that T_c of Sm-doped C_{60} with the larger lattice parameters is higher than that of Yb-doped C_{60} indicates that the increase in $N(E_f)$ is the dominant factor in Sm_xC_{60}.

In conclusion, we have synthesized new fullerides Sm_xC_{60} ($x<3$), whose structure is similar to that of $Yb_{27.5}$ C_{60}. The sample with the nominal composition Sm_3C_{60} shows a superconducting transition at 8 K, which is 2 K higher than that of $Yb_{2.75}C_{60}$. Very similar to alkali-metal doped A_3C_{60}, T_c of rare-earth metal doped C_{60} increases with increasing lattice parameter. Further work in this field would have to concentrate on the determination of the rare-earth C_{60} phase diagrams, the Sm valency, and on the determination of the electronic structure of the superconducting phase.

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