Superconductivity at 28 K in Rb_xC_{60}

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Meissner-effect and microwave-absorption measurements on bulk samples show that Rb_xC_{60} is superconducting with a maximum transition temperature of 28 K. This is a 10-K (60%) increase over the K-doped material. Only $Ba_{0.6}K_{0.4}BiO_3$ and the cuprate superconductors have higher transition temperatures.

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The observation of superconductivity at 18 K in K_xC_{60} (Ref. 1) demonstrated the possibility of obtaining high superconducting transition temperatures in the doped fullerenes. In this paper we report the observation of superconductivity at 28 K on doping of C_{60} with rubidium. This transition temperature is dramatically higher than previously observed in any molecular, elemental, or intermetallic superconductor, and is surpassed only by $Ba_{0.6}K_{0.4}BiO_3$ and the cuprate superconductors.

Previous work on K_xC_{60} showed the need for a variety of characterization techniques for these highly air sensitive materials.[1,2] These included *in situ* conductivity, Raman spectroscopy, microwave absorption, and dc susceptibility. In this study, as well, all doping reactions and measurements were carried out using sealed tubes. C_{60} was purified by chromatography of fullerite[3] on octadecylsilanised silica with toluene-isopropanol eluent, and dried at 160 °C under vacuum.

Room-temperature conductivities for alkali-metal-doped C_{60},[1] A_xC_{60}, ranged from 4 to 500 $\mathrm{S\,cm^{-1}}$, with the highest value for $A = \mathrm{K}$. These conductivities were dependent on doping level and a maximum conductivity was obtained for each alkali metal, beyond which the conductivity decreased. Our initial screening for superconductivity in A_xC_{60} ($A =$ alkali metal) by conductivity measurements in thin films (at the conductivity maximum) and by magnetic-field-dependent microwave absorption was positive only for potassium.[1] Subsequently, microwave absorption indicating superconductivity was observed with rubidium following appropriate heat treatments.

A bulk polycrystalline sample of nominal composition Rb_3C_{60} was prepared by reaction of 30 mg of C_{60} with 10.7 mg of Rb. The quantity of rubidium was controlled by cutting Rb-filled Pyrex capillary tubing to the required length in a dry box, to avoid overdoping the material.[1,2] The C_{60} was loaded into a 5-mm Pyrex tube sealed to a larger-diameter tube containing the Rb capillary, and the tube was sealed under 10^{-2} torr of helium. The tube was then heated for 24 h with the Rb end at 450 °C and the C_{60} end at 400 °C (corresponding to the natural gradient of our furnace). Some discoloration of the tube due to reaction with the glass was visible, but no unreacted rubidium was observed. Following this initial reaction, the tube was resealed close to the C_{60} end for final reaction (450 °C, 24 h) and characterization.

The dc magnetization $[M(T)]$ of the Rb_xC_{60} sample, shown in Fig. 1, was measured in a SQUID magnetometer in an applied field of 2 Oe. The sample was first cooled to 4.2 K in zero field and data were taken in a 2-Oe field on warming the sample to 40 K [zero-field-cooled (ZFC) data]. The sample was then cooled in the same field down to the base temperature [field-cooled (FC) data]. Data qualitatively similar to those in Fig. 1 were obtained at field values up to 50 Oe. The Pyrex sample container was paramagnetic and contributed less than 1% to the observed signal at 5 K. The overall behavior of $M(T)$ demonstrates superconductivity with an onset T_c of 28 K. In particular, the negative sign of the magnetization for $T \ll T_c$ and the Meissner-Ochsenfeld effect of flux expulsion, namely, the FC data of equal or

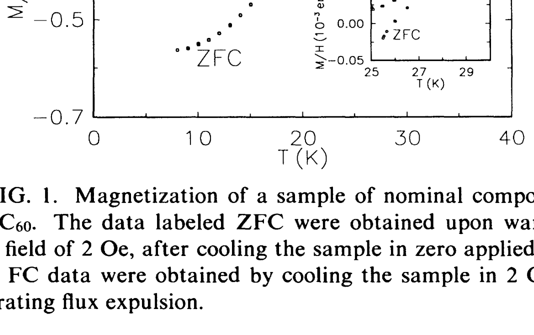

FIG. 1. Magnetization of a sample of nominal composition Rb_3C_{60}. The data labeled ZFC were obtained upon warming in a field of 2 Oe, after cooling the sample in zero applied field. The FC data were obtained by cooling the sample in 2 Oe, illustrating flux expulsion.

lower magnitude than the ZFC data, cannot be explained by any known phenomena other than superconductivity. The magnitude of the ZFC shielding signal is 1% of that expected for a homogeneous superconductor. This value is similar to that found in the K-doped samples, and is most likely due to sample inhomogeneity, a feature that is also reflected in the broad width of the superconducting transition.

Superconductivity was also demonstrated on the same sample by microwave-absorption measurements, shown in Fig. 2. These data, taken at a frequency of 9 GHz in an applied field of 100 Oe, show a dramatic rise in the absorption coincident with the onset of diamagnetism at 28 K. This absorption is attributed to motion of flux vortices and has become a well-documented test for superconductivity.[4] Absorption well below T_c is common in superconductors with weak links between superconducting regions.

Thin films of Rb_xC_{60} were prepared by a modification of the procedure reported previously.[2] Doping was achieved by heating Rb metal at the bottom of the ampoule or by using a commercial SAES Rb source in combination with a Zr getter. Both methods yielded room-temperature resistivities of about 10 mΩ cm. Cooling to liquid-nitrogen temperature increased the sheet resistance by more than 4 orders of magnitude. Some samples showed resistance drops at ≈ 5 K, but zero resistance was not observed. Examination of the various electrode configurations in the van der Pauw geometry indicated inhomogeneous doping. In addition, high contract resistances were noted. It should be noted that these preparative conditions are quite different from those used for the bulk sample, and, therefore, the observations are not inconsistent with the data on the bulk sample.

In the case of K_xC_{60}, superconductivity was readily obtained and resistivity, microwave absorption, and dc susceptibility all indicated a maximum T_c above 18 K.[1] With Rb, higher reaction temperatures appear to be required and the conditions are not readily duplicated for the thin films. For both K and Rb, optimization of synthetic conditions is still required to obtain homogeneous, single-phase samples.

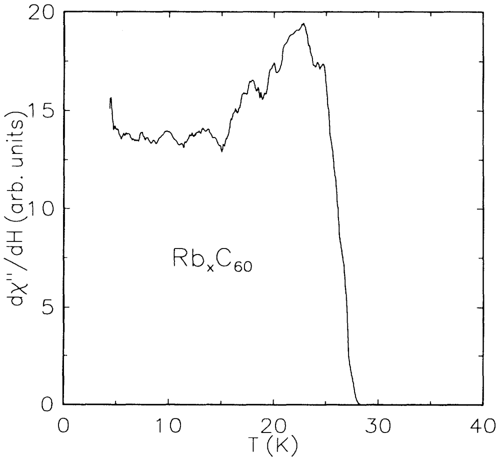

FIG. 2. Microwave loss vs temperature for a sample of nominal composition Rb_3C_{60} in a static field of 100 Oe.

Although the intercalated C_{60}'s are molecular systems, they have marked similarities to extended solids. The salient characteristics of molecular systems include (1) discrete molecular units and (2) formation of compounds with fixed stoichiometries. Extended solids in contrast (1) have no discrete molecular entities, but rather repeat units, and (2) form phases with either fixed or variable stoichiometry (solid solutions). The doped C_{60} may well have solid-solution regions, miscibility gaps, and phase diagrams more typical of extended solids. All of the classes of superconducting materials exhibit strong structure-bonding-property relationships, with T_c being optimized by control of both electron count and relevant interatomic distances. The fixed stoichiometries of other known molecular superconductors diminish the role of electron count as an experimentally variable parameter. However, a marked dependence of T_c on counterion size in molecular organic systems has been noted.[5] In extended systems, such as the copper oxides, the size and electron count are both variable and the range of properties is accordingly more extensive. In A_xC_{60}, several experiments sensitive to doping level suggest that variable stoichiometry is possible, e.g., the existence of a minimum in the resistivity, the shift in the 1467-cm^{-1} Raman mode,[2] and the continuous filling of the t_{1u} lowest-unoccupied-molecular-orbital-derived band seen in photoemission.[6] The possibility of varying the electron count in this case is unique for a molecular system.

Some comparisons with other systems are appropriate. The T_c's of graphite intercalation compounds of the same elements are 0.128–0.55 K for C_8K and 0.03 K for C_8Rb.[7,8] The ambient-pressure molecular organic superconductors, $(BEDT\text{-}TTF)_2X$, have fixed composition, with T_c varying with the size of the anion X.[5,9] However, the Chevrel phases[10] may provide the closest analogy with C_{60} superconductors. In these compounds, $Mo_6(S,Se)_8$ clusters condense to form an extended solid (the clusters are covalently linked and exist as molecules only as chemically modified derivatives). The parent compounds $Mo_6(S,Se)_8$ can be prepared, as well as ternary phases $MMo_6(S,Se)_8$. Several of the ternaries superconduct with T_c strongly influenced by the ternary atom [e.g., $BaMo_6Se_8$, $T_c=2.7$ K; $PbMo_6S_8$, $T_c=15$ K (Ref. 10)], similar to the large difference in T_c between K_xC_{60} and Rb_xC_{60}.

Several explanations are conceivable for the dramatic variation in T_c with alkali-metal dopant. Because of the small superconducting fraction, neither the composition nor structure of the superconducting phase has been identified for K or Rb. Assuming similar structure and composition of the superconducting phase in both cases, the changes in T_c may be discussed using a BCS-type relation,

$$T_c \propto E \exp[-1/VN(E_F)] = E \exp(-1/\lambda) . \quad (1)$$

Here E is the frequency of the pairing-mediating excitation, $N(E_F)$ the density of states at the Fermi level, and V the electron-excitation coupling strength. In view of the high transition temperature of 28 K and the polarizable π system of the C_{60} molecule, excitonic mechanisms of the type envisaged by Little,[11] where E is an electronic excitation energy, may be of relevance.

If we limit further discussion to phonon-mediated pairing, then $E = \omega_{ph}$, the average energy of the most strongly coupled phonon modes. In C_{60}, these modes possess characteristic energies of 1000–2000 K (intramolecular),[2] 80 K (intermolecular),[12] and ≤ 80 K (rotational). Doping will affect the modes in different ways. Population of the conduction band, derived from t_{1u} molecular orbitals (which are antibonding with respect to the C_{60} molecules), will decrease the *intramolecular* phonon frequencies.[2] The Raman frequencies for fully doped A_xC_{60} (A = Na, K, Rb, Cs) films are very similar, implying little change in intramolecular phonon modes between different alkali metals.[13] The *intermolecular* vibrations will harden on doping because the lower part of the conduction band is slightly bonding between C_{60} molecules. The rotational modes should also stiffen due to this increased intermolecular coupling.

In view of the high transition temperatures, we consider coupling to the highest-frequency phonons in these materials, i.e., the intramolecular vibrations. These frequencies are significantly larger than found in the intermetallic superconductors. Assuming a relevant phonon frequency of $\omega_{ph} = 2000$ K, the observed $T_c = 28$ K requires a coupling constant $\lambda = 0.35$, for which the BCS treatment is valid. The 10-K difference in T_c between K and Rb requires a change in λ of only 10%. In general, one expects that on expansion V will decrease due to the nonlinearity in the dependence of orbital overlap on ion separation, and $N(E_F)$ will increase due to band narrowing. If it is assumed that the C_{60} lattice responds elastically to the differing alkali-metal atom sizes ($r_K = 1.32$ Å, $r_{Rb} = 1.49$ Å), then one is led to the conclusion that T_c is primarily determined by modulation of $N(E_F)$. This shows that a variation in $N(E_F)$ is a physically reasonable explanation for the difference in T_c.

It is also conceivable that the high transition temperatures are related to the lower-frequency modes, i.e., the intermolecular and rotational phonons. A T_c of 28 K with a relevant phonon frequency of 80 K requires a coupling constant $\lambda = 5$ using strong-coupling theory.[14] However, in this case λ would have to change by as much as a factor of 2 to explain the different T_c's for Rb and K doping. If, however, weak coupling ($\lambda \leq 0.5$) is valid, then the phonons would have to stiffen by a factor of more than 2 to obtain a T_c of 28 K, with a smaller change in λ between K and Rb than in the strong-coupling limit.

In summary, superconductivity in intercalated C_{60} is shown to occur for Rb as well as K. The 28-K transition temperature observed by dc susceptibility is dramatically higher than observed in any molecular, elemental, or intermetallic superconductor, and is surpassed only by $Ba_{0.6}K_{0.4}BiO_3$ and the cuprate superconductors.

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