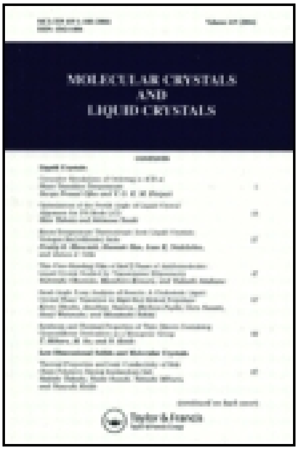

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Microwave Spectroscopy of Fullerene-Based Molecular Superconductors in Low Magnetic Filed: M_x C_{60} (MK, Rb, I_2, Ga, In), M_x C_n (n 70,76,78,84,90) and $M_x(C_{60})1$-$y(C_{70})_y$(MK, Rb)

A. A. Zakhidov [a] [c] , K. Yakushi [a] , K. Imaeda [a] , H. Inokuchi [a] , K. Kikuchi [b] , S. Suzuki [b] , I. Ikemoto [b] & Y. Achiba [b]

[a] Institute for Molecular Science, Okazaki, Aichi, 444, Japan

[b] Tokyo Metropolitan University, Tokyo, 192-03, Japan

[c] Dept. Thermophysics, Uzbek Acad. Sci., Katartal 28, Chilanzar C, 700135, Tashkent, USSR

Version of record first published: 04 Oct 2006.

To cite this article: A. A. Zakhidov , K. Yakushi , K. Imaeda , H. Inokuchi , K. Kikuchi , S. Suzuki , I. Ikemoto & Y. Achiba (1992): Microwave Spectroscopy of Fullerene-Based Molecular Superconductors in Low Magnetic Filed: M_x C_{60} (MK, Rb, I_2, Ga, In), M_x C_n (n 70,76,78,84,90) and $M_x(C_{60})1$-$y(C_{70})_y$(MK, Rb), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 218:1, 299-306

To link to this article: http://dx.doi.org/10.1080/10587259208047058

Mol. Cryst. Liq. Cryst. 1992, Vol. 218, pp. 299–306
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Printed in the United States of America

MICROWAVE SPECTROSCOPY OF FULLERENE-BASED MOLECULAR SUPERCONDUCTORS IN LOW MAGNETIC FILED: M_xC_{60} (M=K, Rb, I_2, Ga, In), M_xC_n (n=70, 76, 78, 84, 90) and $M_x(C_{60})_{1-y}(C_{70})_y$ (M=K, Rb)

A.A.ZAKHIDOV*, K.YAKUSHI, K.IMAEDA, and H.INOKUCHI
Institute for Molecular Science, Okazaki, Aichi, 444 Japan
K.KIKUCHI, S.SUZUKI, I.IKEMOTO, and Y.ACHIBA
Tokyo Metropolitan University, Tokyo 192-03, Japan

Abstract We have used the combined microwave spectroscopy: the nonresonant microwave absorption in low-magnetic field (so-called LFS) together with conventional ESR for the search and study of superconductivity (SC) in the new family of fullerene molecular solids: C_{60}, C_{70}, C_{76}, C_{78}, C_{84}, C_{90} and their alloys ($(C_{60})_{1-y}(C_{70})_y$), doped by different metals (K, Rb, In, and Ga) and iodine I_2. These experiments fall into two categories: 1) Search for SC in higher fullerenes and study of the evolution of SC properties upon doping of pure (one component) fullerenes including C_{60} thin films. 2) Investigation of the T_c change in molecular alloys of $M_x(C_{60})_{1-y}(C_{70})_y$ type. In the first category of experiments we discuss the evolution of LFS and ESR spectra upon variation of Rb-doping conditions: temperatures of doping: $T_d(C_{60})$, $T_d(M)$, and doping time t_d, and as a result we find the optimal conditions for vapour phase Rb-doping. Here we demonstrate that SC T_c appears and disappears with doping abruptly at a discrete value T_c=28K for Rb_xC_{60} similar to case of K_xC_{60} with a discrete T_c = 19K. It is shown that M_xC_n (n=70,76,78,84,90), In_xC_{60}, and Ga_xC_{60} do not show SC phase at least at T>5K, while ESR changes dramatically upon doping. I_xC_{60} doped in ESR tubes at T_d (C_{60},I_2)=210° and 260°C also do not show LFS meaning absence of SC transition. However intensive ESR-signal appears proving the occurrence of p-type charge transfer doping. In the second category we have found that T_c is strongly suppresed with increase of *y* in molecular alloys of $K_x(C_{60})_{1-y}(C_{70})_y$, and in $Rb_x(C_{60})_{1-y}(C_{70})_y$.

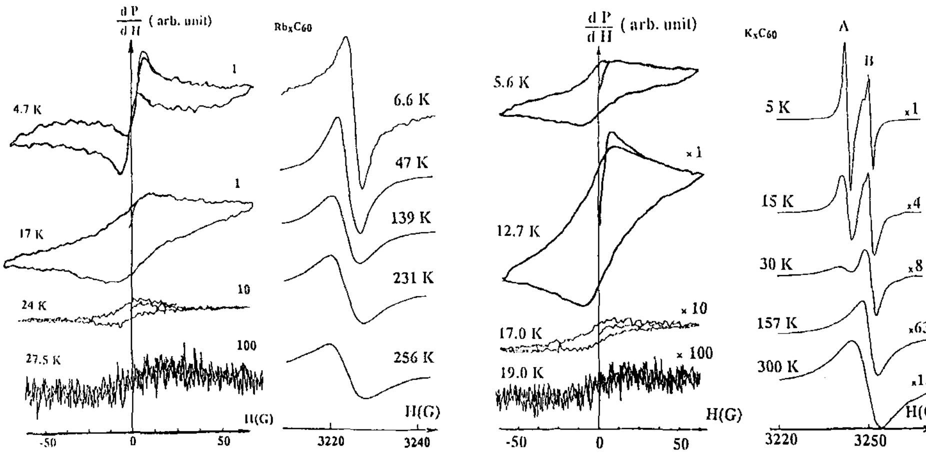
INTRODUCTION

The discovery of superconductivity (SC) in alkali-metal-doped C_{60} with unusually high[1,2] T_c compared to that of graphite intecalates[3], has spurred the search for new SC compositions of M_xC_{60}. The very recent increase of T_c to 33 K in Cs_2RbC_{60}[4] and to 45-48 K in a mixed dopant composition $Rb_{2.7}Tl_{2.2}C_{60}$ - $Rb_1Tl\ _2C_{60}$[5] shows that variation of dopant atoms still remains a promising way to obtain higher T_c.

Especially the recent report of T_c=57K in I_2C_{60}[6] though have been probably mistaken suggests that M may be a p-type dopant, similar to the case of conducting polymers.[7] Such p-doping apparently requires high temperature treatment[6] so the doping conditions and the very existence of charge transfer upon I-intercallation into C_{60} should be checked more carefully. On the other hand the recent separation of various stable higher fullerenes (C_{70}, C_{76}, C_{78}, C_{84}, C_{90})[8] suggests another possible way for SC search and varying T_c: by variation of the number of the carbons in fullerene, or by creation of molecular alloys such as $M_x(C_{60})_{1-y}(C_n)_y$[10]. Using this approach, the π-electron bands and electron-intramolecular phonon coupling can be directly influenced, which may be advantageous for the understanding of SC mechanism. We have recently shown that low-field nonresonant microwave absorption (LFS), combined with conventional ESR, provides a simple but highly sensitive way to study SC evolution in K-doped C_{60}[9-11]. In the present paper we extend this "LFS vs. ESR" method for the study of Rb_xC_{60} evolution and SC M_xC_{60} (M=K, Rb) thin films, for search of SC in M_xC_{70}, M_xC_{76}, M_xC_{78}, M_xC_{84}, M_xC_{90},In_xC_{60}, Ga_xC_{60} and I_xC_{60}, and for the study of SC properties in the molecular alloys of $M_x(C_{60})_{1-y}(C_{70})_y$, (M=K, Rb). The molecular alloys have been prepared by evaporation from the benzene solutions of pure C_{60} and C_{70} with the stoichiometric amounts. The details of K- and Rb-doping procedure and LFS vs. ESR measurements can be found in references 9, 10 and 11. Here we point that the LFS vs. ESR method has the following advantages as compared with the resistivity or magnetometry measurements of a SC state: 1) It can detect submicrogram quantities of SC phase, quickly determine T_c, and distinguish multiple T_c-phases without contacting the sample in a high vacuum. 2) It may check the relative change of the different SC fractions upon some treatments, say, annealing, aging or alloying as studied below. 3) It can provide the information about the quality of SC state (granular nature, glassy behavior, etc). 4) The ESR data of the same samples gives additional information about the nature (metallic, or localized) and the concentration of spins in doped M_xC_{60} compositions.

EVOLUTION OF SUPERCONDUCTING PHASE UPON Rb-DOPING of C_{60}

Earlier we have studied in detail the evolution of SC and other coexisting phases upon K-doping of C_{60}[9]. Here we present the new results of Rb-doping of C_{60} in similar vapor phase intercallation setup[9], and compare the behavior of LFS and ESR with those in K_xC_{60}. As already mentioned in literature the larger atomic radius of Rb (1.49 Å) compared to that of K (1.32 Å) requires the higher temperatures T_d=350°C when doped from stoichiometric mixtures.[2] We have found however that at $T_d(C_{60})$ =350 C and T_d(Rb) (temperature at Rb end of tube)~250-280°C the optimal doping time t_d becomes very short 1-2 hours, and overdoping is easily achieved at larger t_d, that is apparently connected with higher vapor pressure of Rb (compared to K) and higher diffusion rate of Rb in C_{60} matrix at T=350° C. So the optimal T_d (C_{60})=250°C, at T_d(Rb)=180-200°C has been found for C_{60} powder at which the doping process can be controlled and well doped region of t_d is extended to t_d = 5~10 hours (see Fig. 2). The typical LFS spectrum of the well doped Rb_xC_{60} is shown at Fig. 1a together with its conventional ESR spectrum. Below T_c<28 K LFS appears abruptly and shows the clear hysteresis.Moreover LFS demonstrates the reproducible periodic oscillations at T=7K, which is well known to be connected with the flux quantization in the SQUID-type weak-link loops.[9] In K-doped C_{60} such clear and highly reproducible periodic structures have not been found. Probably a better diffusion of Rb and thus the more homogeneous doping creates the better quality of the intergrain SQUIDS (in the case of K-doping the grain surfaces are easily overdoped[9])· In other aspects the evolution of LFS is quite similar to K_xC_{60}[9], with abrupt disappearance of SC-phase at the same discrete Tc=28K upon overdoping. However, the ESR spectrum of Rb_xC_{60} is found to be qualitatively different from that found in K_xC_{60} since only one single line with g=2.001 is found contrary to the two (or even three) lines in K_xC_{60} (see Fig. 1b) at



a) b)

FIGURE 1. LFS and ESR spectra at various T of optimaly doped: a) Rb_xC_{60} (t_d= 5h., $T_d(Rb/C_{60})$=190°/250°C) ; b) K_xC_{60} (t_d=13 h., $T_d(K/C_{60})$ = 160°/210°C)

different doping stages.[9] The T-dependence of ESR intensity of Rb_xC_{60} is of Curie-like (localized spins) and strongest in overdoped state, while in well doped (superconducting) composition it is Pauli-like (metallic behavior) at high T-region (see Fig. 3a) quite similar to K-case.[9]· However, the T-dependence of the ESR linewidth ΔH_{PP} in the overdoped (mainly Rb_6C_{60}) state is qualitatively different from that of K-doped case showing the narrowing of line (Fig. 3a), while in the well-doped region ESR line broadens similar to K_3C_{60} [9], while in the well-doped region ESR line broadens similar to K_3C_{60} [9].Summarizing the results of the SC-phase evolution in Rb_xC_{60}, the change of T_c with the doping time t_d (as plotted in Fig.2.) along with the similar $T_c(t_d)$ dependence of K_xC_{60}, we conclude that Tc appears and disappears abruptly at the discrete value $T_c = 27 \pm 1$ K, but the window of optimal doping time is much narrower for Rb-case as discussed above.

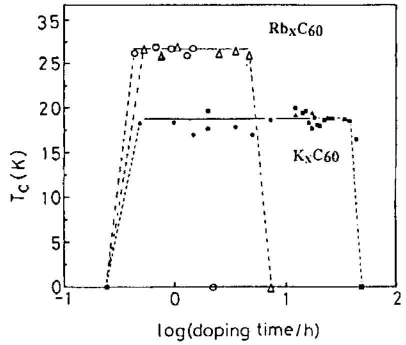


FIGURE 2. Dependence of T_c of Rb_xC_{60} on the doping time t_d compared to $T_c(t_d)$ of K_xC_{60} of Ref. 9,
O - $T_d(Rb/C_{60})$ = 280/350°C
Δ - $T_d(Rb/C_{60})$ = 190/250°C

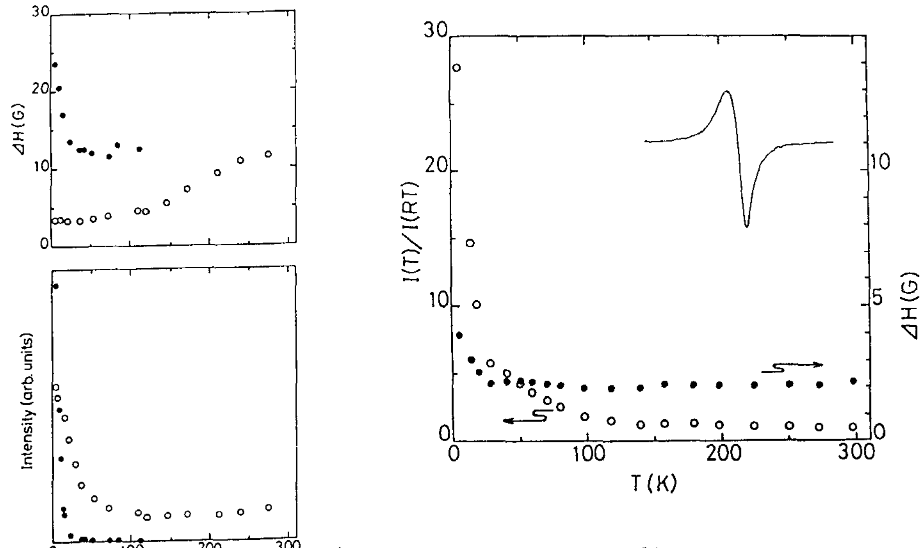
SUPERCONDUCTIVITY OF C_{60} THIN FILMS

In thin films (500~1000 Å) of C_{60} vacuum deposited on the narrow (3 - 4 mm) quartz substrates (5 - 8 mm long) we also have succeeded to observe the superconducting hysteretic LFS after both K- and Rb-doping. It should be emphasized that doping of thin films is rather delicate process since overdoping is easily achieved with the change of color from yellow to dark brown (K) or even black (Rb). We have found the optimal conditions of vapor phase doping: T_d (K and C_{60}) = 110°C, t_d = 4 ~ 5 hours, while for Rb case the temperature T_d(Rb and C_{60}) = 100°C and time t_d = 1.5 hour are even lower and can be controlled by color change. LFS in both K_xC_{60} and Rb_xC_{60} films is unusually intensive (by a factor of 10^2 compared to a lager (~1mg) amount of powdered sample) and shows clear angle dependence. The details and other interesting features of LFS in thin films will be discussed in separately published paper[12]. Here we only mention that SEM images of films revealed the highly granular morphology with the average diameter of grains 200 ~ 400 Å. So the dense network of intergrain weak links (Josephson junctions) is apparently responsible for the observed high intensity of LFS as well as for its unusual angle dependence.

SEARCH FOR SUPERCONDUCTIVITY IN M_xC_n (n =70,76,78,84,90) AND ALSO In_xC_{60}, Ga_xC_{60} .

We have used the highly sensitive LFS test to check the possible SC in higher fullerenes, and have found that M_xC_n (n=70, 76, 78, 84, 90; M=K, Rb), In_xC_{60}, and Ga_xC_{60} does not show any LFS above 5 K at the various doping conditions T_d (K) =180-250° C, T_d (Rb) = 250 - 350°C, which result means the absence of a SC phase. However, there is no doubt that the charge-transfer (CT) doping occurs in all cases since the ESR increases significantly upon doping. The Curie-type behavior of rather narrow ESR lines indicate the localized nature of the dopant-induced spins. K_xC_{70} and K_xC_{76} also showed an unusually intense ESR signal close to that of DPPH spin marker. In contrast to K_xC_{60} and Rb_xC_{60} it seems that the metallic phase cannot be formed by doping in all of these compounds. The details of ESR spectra (temperature dependences of intensities, linewidths, *etc.*) should be published separately. It should be pointed that in Ga_xC_{60} the LFS has been detected, but due to the presence of metallic Ga, with the onset at T_c=8 K that is close to known SC T_c of the thermodynamically nonequilibrium Ga thin film and γ phase of Ga.

IODINE (P-TYPE) DOPING OF C_{60}



a) b)

FIGURE 3. The temperature dependence of ESR intensity and linewidth for a) Rb_xC_{60} (○-well doped, ●-overdoped), b) I_xC_{60} (the inset shows the assymetric narrow ESR single line).

We have also investigated I_xC_{60} system[6] at various doping conditions, but no LFS can be found in the samples doped for t_d=25-50h at the reported[6] T_d of 210° and 260°C, which means the absence of the SC phase at least above $T \geq 5K$ and under these doping conditions. However ESR intensity gradually and significantly increases ($\times 10^2$) with the increase of T_d above 160°C, suggesting that the CT-doping occurs and charges with S=1/2 are introduced into C_{60}. The ESR spectrum of I_xC_{60} is shown in Fig.3 together with T-dependence of intensity and linewidth. The Curie type T-dependence indicates the localized nature of spins. However, the nearly twice decrease of the very narrow linewidth with temperature (see Fig. 3b) (qualitatively opposite to the behavior of K_xC_{60} and Rb_xC_{60}) is rather surprising and looks like the motional narrowing of solitonic ESR in conducting polymers[7]. At higher doping levels the line becomes broader but with the same T-dependence of ΔH_{pp}. The absence of SC in I_xC_{60} is possibly connected with the distortions of the cubic lattice structure of C_{60} by the introduction of the rod like I_3^- molecules that are probably the dopant species like in conducting polymers[7]. One may expect thus that p-type doping by smaller spherical dopants that do not destroy the symmetry of the cubic lattice may lead to the hole type SC state (which is theoretically predicted to have higher T_c due to interband pairing in higher five-fold degenerate vallence band[13]).

T_c DECREASE IN $M_x(C_{60})_{1-y}(C_{70})_y$ MOLECULAR ALLOYS

K- and Rb-doped $(C_{60})_{1-y}(C_{70})_y$ alloys show the typical hysteretic LFS spectrum appearing below $T_c(y)$. Similar to the case of K_xC_{60}[9] the intensity of LFS continuously increases and then decreases to zero upon overdoping while T_c appears and disappears abruptly at certain discrete values: $T_c(y=0.1)=16$ K, $T_c(y=0.25)=10$ K[10].(see Fig.4.) The near invariance of T_c during doping (about ±1 K) suggests the existence of a stoichiometric composition. The decrease of T_c from $T_c(y=0)=19$ K[9] plotted in Fig. 4 shows that alloying suppresses SC. The strong effect of $T_c(y)$ decrease at small y can be qualitatively discussed using the weak coupling BCS-type relation, $T_c = \omega_{ph}\exp(-1/\lambda)$. Assuming that the interaction with intramolecular phonons is important for pairing and estimating ω_{ph}=500 K (close to the Raman modes observed in doped C_{60}[14]) one arrives at $\lambda(y=0)= \lambda_o=0.3$. Then the observed changes of T_c can be fitted by $\lambda(y=0.1)=0.95\lambda_o$ and $\lambda(y=0.25)= 0.83\lambda_o$. Such small decreases of the coupling constant $\lambda(y)=V(y)N_y(E_F)$ may be caused by an effective decrease of the electron-intramolecular phonon coupling strength V(y) in substituted C_{70} molecules (*e.g.* roughly $V(y)=(1-y)V(0)$) and by the change of the density of states $N_y(E_F)$ at the Fermi level due to a band narrowing effect in the alloy. Note that for a strong coupling case λ should be decreased nearly 4-5 times to bring forth the observed decrease of T_c. To clarify the mechanism of SC suppression the y-dependent crystal structure is under investigation by the method of X-ray diffraction. The sensitivity of T_c on y indicates that C_{70} molecules are not segregated in $K_x(C_{60})_{1-y}(C_{70})_y$ but are instead more or less uniformly distributed in the host C_{60} matrix (otherwise T_c should not change since the SC correlation length is small[15] as ξ~26 Å). This view is consistent with the recent STM observation[16]. In the $Rb_x(C_{60})_{1-y}(C_{70})_y$ doped at high T_d=(200/350C), however, the dramatic decrease of T_c has not been observed: the T_c(y) dependence in this case is shown in Fig 4 as well. We attribute this result to the segregation of C_{60} and C_{70} under the high temperature (330-350°C) treatment of the initially prepared $(C_{60})_{1-y}(C_{70})_y$ alloy during the doping process. Since the sublimation temperature of C_{60} is close to 350°C, C_{60} and C_{70} may be separated into two phases, and the T_c of Rb_xC_{60} containing a small amount of C_{70} as an impurity is reflected into the small T_c change of Fig 4. However the careful measurements of $Rb_x(C_{60})_{1-y}(C_{70})_y$ obtained at lower T_d = 250°C have demonstrated the same significant decrease of T_c(y) similar to the case of $K_x(C_{60})_{1-y}(C_{70})_y$, suggesting that at this lower T_d=250C the alloy is not segregated, and thus SC is again suppresed. Further study of this phenomena is in progress now.

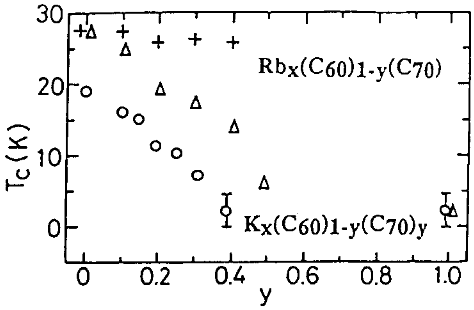


FIGURE 4
$T_{c(y)}$ dependence on
the concentration of C_{70}
o - $K_x(C_{60})_{1-y}(C_{70})_y$, T_d=160/210°C
+ - $Rb_x(C_{60})_{1-y}(C_{70})_y$ at Td=280/350°C
Δ - at T_d =190/250°C.

ACKNOWLEDGEMENTS

We are indebted to Prof. Y. Maruyama, Dr. H. Hoshi and Dr. D. M. Petty of IMS for the collaboration on the preparation and study of C_{60} thin films, which results will be published separately and to Dr.A.Ugawa for the previous help with K-doping. Thanks are also to Profs. R. H. Baughman and Z. Iqbal for fruitful collaboration[10] and useful comments on superconductivity and X-Ray study of $M_x(C_{60})_{1-y}(C_{70})_y$ alloys.

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* Permanent address: Dept. Thermophysics, Uzbek Acad. Sci., Katartal 28, Chilanzar C, 700135, Tashkent, USSR

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