

MAGNETIC RESONANCE AND MAGNETIC SUSCEPTIBILITY STUDY OF ACCEPTOR DOPED FULLERENES $C_{60}(MF_6)_2$ (M=As, Sb, P)

A. M. Panich^a, I. Felner^b, A. I. Shames^a, S. Goren^a, P. K. Ummat^c, and W.R. Datars^c

^a Department of Physics, Ben-Gurion University of the Negev, P.O.Box 653, Beer Sheva 84105, Israel

^b Racah Institute of Physics, Hebrew University, Jerusalem 91904, Israel

^c Department of Physics and Astronomy, McMaster University, Hamilton, ON L8S 4M1, Canada

Corresponding author e-mail address: pan@bgumail.bgu.ac.il

Introduction

Intercalation of alkali metals into the interstitial sites of the C_{60} lattice produces A_3C_{60} (A=K, Rb, Cs, Tl) compounds showing superconductivity with transition temperatures up to 40 K. These doped fullerene solids exhibit essential *electron* charge transfer from metal (electron donor) to C_{60} (electron acceptor). In the acceptor-doped fullerene compounds with composition $C_{60}(MF_6)_2$ (M=As, P, Sb), electron is transferred from C_{60} to the intercalated molecules. These compounds show semiconducting behavior; the conductivity is of a *p*-type and is considered to be by *holes*. The objectives of the present investigation are to check whether superconductivity occurs in the aforementioned acceptor doped fullerenes and to study their magnetic properties, structural features and molecular dynamics by applying NMR, EPR and SQUID techniques.

Results

^{13}C NMR spectra show that C_{60} molecules in As and Sb compounds are not mobile up to 365 K. Reduction of the ^{13}C chemical shielding anisotropy of $(MF_6)_2C_{60}$ (in comparison to C_{60}) suggests charge transfer between C_{60} and intercalated species [1]. $C_{60}(PF_6)_2$ shows fullerene rotation at ambient temperature.

Room temperature ^{19}F spectra are characteristic for rotating (MF_6^-) complexes [2]. Temperature dependence of the second moment, S_2 , of $(AsF_6)_2C_{60}$ is typical for activation of molecular mobility on heating (Fig.1). Random reorientation of the (AsF_6^-) complex lasts at least down to 67 K, showing no sudden changes characteristic for phase transitions. The temperature dependence of S_2 for $(SbF_6)_2C_{60}$ (Fig.1) shows a strong change in the range of 200-270 K. At lower temperature, a plateau characteristic for freezing of the molecular reorientation occurs. Below ~ 100 K, another increase of S_2 starts to occur. This behavior indicates the existence of two fluorine species. The mobility of one of them is frozen around 200 K, while the second species is frozen below 100 K. Another explanation of the spectral transformation of $(SbF_6)_2C_{60}$ at 200-270 K is a phase transition in this temperature range.

Molecular dynamics is readily seen in ^{19}F spin-lattice relaxation measurements (Fig.1) that show relaxation minima characteristic for molecular rotation.

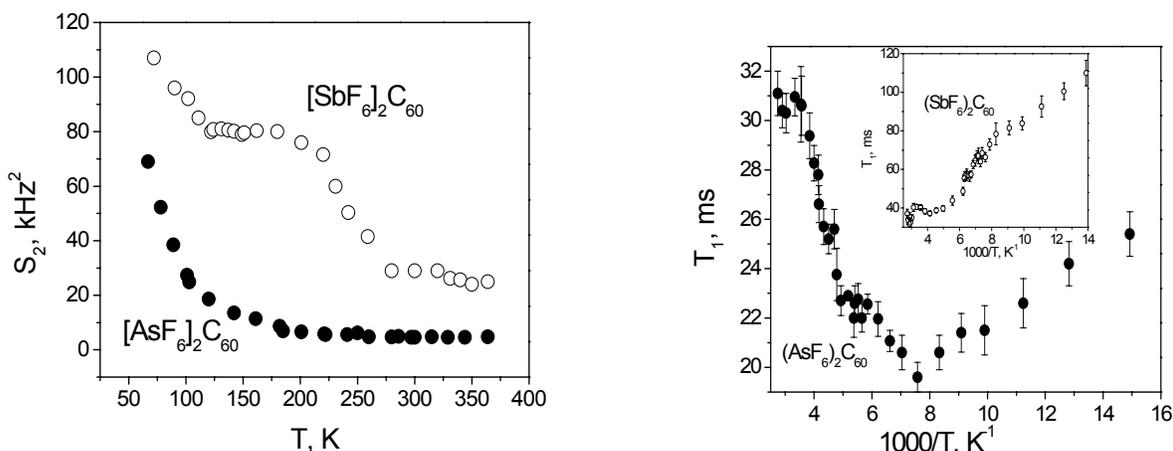


Fig. 1. ^{19}F NMR in $[\text{SbF}_6]_2\text{C}_{60}$ and $[\text{AsF}_6]_2\text{C}_{60}$: temperature dependence of the second moment S_2 and spin-lattice relaxation time T_1 .

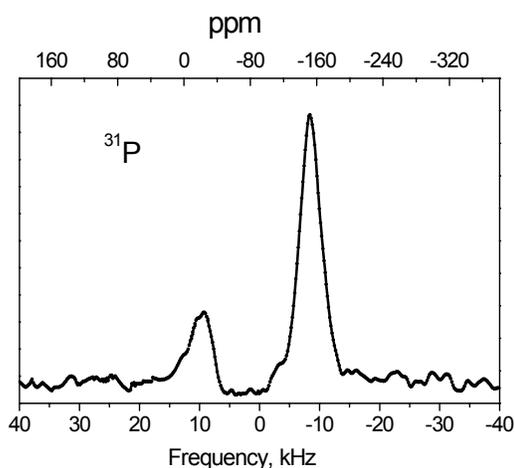


Fig. 2. ^{31}P NMR spectrum of $\text{C}_{60}(\text{PF}_6)_2$ at $T=295\text{ K}$.

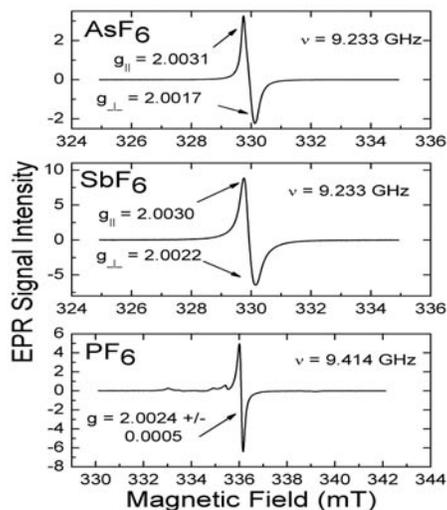


Fig. 3. EPR spectra of $\text{C}_{60}(\text{MF}_6)_2$ at $T=295\text{ K}$.

^{31}P spectrum of $\text{C}_{60}(\text{PF}_6)_2$ (Fig. 2) shows two resonances. According to the chemical shift, the intensive high field line is attributed to the $(\text{PF}_6)^-$ ion. The origin of the low field line is not clear. ^{19}F spectra of these compounds [2] are also superpositions of two lines corresponding to different fluorine species. According to the chemical shift, one of the lines in $\text{C}_{60}(\text{AsF}_6)_2$ and $\text{C}_{60}(\text{SbF}_6)_2$ is attributed to the $(\text{AsF}_6)^-$ and $(\text{SbF}_6)^-$ ions, respectively.

^{19}F spin-lattice relaxation measurements show that nuclear magnetization decay in all samples is well described by a stretched exponent. It means that the relaxation rate is strongly affected by paramagnetic centers, namely unpaired electrons that are located on broken dangling C-C bonds. Generation of such a bond having a localized spin might result from the reaction of C_{60} powder with AsF_5 , SbF_5 and NO_2PF_6 during intercalation and is typical for fluorine-graphite intercalation compounds, fluorinated graphite and fluorinated fullerenes [3,4]. The occurrence of the paramagnetic centers is confirmed by EPR measurements (Fig. 3). The observed lines, with g-factor varying from 2.002 to 2.003, are typical for free radicals and paramagnetic structural defects.

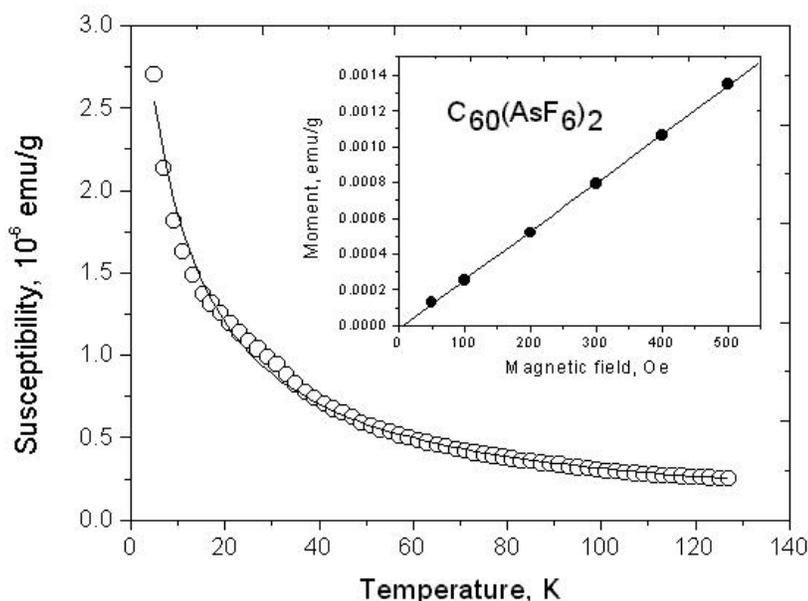


Fig. 4. Temperature dependence of magnetic susceptibility of $\text{C}_{60}(\text{AsF}_6)_2$. The solid line is the Curie-Weiss fit. In insert, field dependence of magnetic moment at 5 K is shown.

Temperature dependences of magnetic susceptibility (χ) of $\text{C}_{60}(\text{MF}_6)_2$ ($\text{M}=\text{As}$, P , Sb) samples (Fig. 4) show no sharp changes reflecting a phase transition into superconducting state [5]. Besides the diamagnetic contribution of C_{60} , a strong paramagnetic contribution into the total magnetic susceptibility occurs. The dependence $\chi(T)$ nearly follows Curie-Weiss law (Fig.4)

Measurements of the magnetic moment (M) of the $\text{C}_{60}(\text{MF}_6)_2$ samples at 5 K (Fig.4) show increase in M with increased magnetic field for all compounds under study [5]. Such behavior is characteristic for paramagnetics and is in contrast with the well-known behavior of superconductors that show a decrease of magnetic moment with the increased magnetic field. Thus one is led to a conclusion that no bulk superconductivity is observed in our compounds.

Discussion

C_{60} molecule is known to be a strong electron acceptor because of its rather high electronegativity [6]. For this reason, it is difficult to remove an electron from C_{60} . However, our studies, along with the literature data, show that the $(MF_6)^-$ ions are observed in $C_{60}(MF_6)_2$ compounds, corresponding to the electron removal from C_{60} and formation the composition of $C_{60}^{2+}(MF_6^-)_2$. Analogous to A_3C_{60} ($A=K, Rb, Cs, TI$), one could expect to obtain superconductivity in $C_{60}(MF_6)_2$ compounds. However, it was not observed in our experiments.

One of the possible reasons for such a result is that charge transfer in the compounds under study does not reach the value that is enough for the appearance of superconductivity. We note that the superconducting A_3C_{60} fullerides show the transfer of 3 electron charges per C_{60} molecule that corresponds to a half-filled conduction band [6]. In our compounds, the transfer is suggested to be of 2 holes per C_{60} molecule. It may not be enough for the occurrence of superconductivity. We note that recent calculations of superconductivity in hole-doped C_{60} predict that the value of T_c is maximized close to three doped holes [7].

Another reason for the absence of superconductivity may result from the partial disorder induced by the intercalation. As noted above, our experiments showed that at least two intercalate species exist in $C_{60}(MF_6)_2$. It is likely that these species randomly occupy several inequivalent cavities in the C_{60} lattice, resulting in a disordered crystal lattice. Such a disorder increases the residual resistivity. Moreover, since the overlap between the wave functions of neighboring buckyballs is rather small, the disorder might corrupt or partially break this overlap and eliminate bulk superconductivity. One can suggest that superconductivity could occur in homogeneous $C_{60}(MF_6)_2$ intercalation compounds. Moreover, taking into account the inhomogeneity of our compounds, one can speculate about a "local" superconductivity that may occur in the " $(MF_6)^-$ enriched" regions. The significant paramagnetic contribution, which appears in the compounds under study due to the unpaired electrons on broken bonds, may mask the changes in magnetic moment caused by "local" superconductivity if they are small. One can also suggest the occurrence of superconductivity at lower temperatures, below 5 K.

References

1. A. M. Panich, P. K. Ummat, and W. R. Datars, *Solid State Commun.* **121**, 367 (2002).
2. A. M. Panich, H.-M. Vieth, P. K. Ummat, and W.R. Datars, *Physica B*, **327**, 102 (2003).
3. A. M. Panich, A. I. Shames, and T. Nakajima, *J. Phys. Chem. Solids* **62**, 959 (2001).
4. A. M. Panich, A. I. Shames, and H. Selig, *J. Phys. Chem. Solids* **63**, 483 (2002).
5. A. M. Panich, I. Felner, A. I. Shames, S. Goren, P. K. Ummat, and W.R. Datars, *Solid State Commun.* **129** (2), 81 (2004).
6. M. S. Dresselhaus, G. Dresselhaus, and P.C. Eklund. *Science of fullerenes and carbon nanotubes*. Academic press, 1996.
7. M. Granath and S. Östlund, *Phys. Rev. B* **66**, 180501(R) (2002).