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SUPERCONDUCTIVITY IN INTERHALOGEN-DOPED FULLERENES

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Interhalogen-doped fullerenes have been prepared by using iodine monochloride (ICl) as a dopant. SQUID magnetization measurements reveal signatures of superconductivity in these samples with a superconductive transition temperature above 60K. These new carbon-superconductors are stable in air.

Superconductivity in doped-fullerenes has recently become a subject of considerable interest[1]. However, most observations of these carbon-superconductors reported to date have been on alkali-metal-doped fullerenes. Although these electron-doped superconductors are known to exhibit some BCS-like behavior, there are still open questions about the mechanisms responsible for the high values of T_c in this class of molecular solids. In practice, due to the extreme sensitivity to oxidation, the alkali-metal-doped compounds are unstable in air, and most measurements of the superconducting properties were necessarily made with samples either prepared in-situ or encapsulated in an inert-gas environment. New approaches and a search for other types of doped-fullerene superconductors seem desirable.

In contrast to the case of electron-doping with alkali-metals, possible hole-doping in the fullerenes with halogen atoms appears to be an interesting possibility for searching new carbon-superconductors; but thus far no halogen-doped-fullerene superconductor has been reported from the previous attempts[2-5]. We have taken a different approach to halogen-doping in fullerenes by using the interhalogen compounds instead of pure halogens. This choice was based on the following considerations: (i) The interhalogen molecule has an electric dipole moment, and (ii) The interhalogens are very powerful oxidizing agents and more reactive than pure halogens, as indicated by the ready intercalation of interhalogens (ICl and IBr) in graphite[6]. After many trials, we first succeeded in doping a mixture of fullerenes with iodine monochloride (ICl) and discovered an unprecedented (albeit relatively weak) Meissner effect in a small volume fraction of this interhalogen-doped fullerenes. The superconductive transition temperature is above 60K.

The starting materials were fullerene powders containing a mixture of C_{60}, C_{70}, and a small fraction (about 1%) of higher fullerenes (possibly C_{76}, C_{78}, C_{84}, C_{92} etc.) purchased from Texas Fullerenes Corporation with a claimed content of C_{60} greater than 60%. In our earlier experiments, doping was achieved by placing a small quantity (approximately 20 mg) of this fullerene powder in a glass vial and exposed it to ICl vapor at room temperature for a few hours. The weight increase was monitored during this process, and a maximum diamagnetic signal in SQUID magnetization measurements was obtained with a weight-gain of about 50-60%. Overexposure caused condensation of liquid ICl on the powder sample. It was realized that this reaction process most likely did not reach the equilibrium condition, and there were mixed phases of both overexposed and underexposed fullerene powders. A more complete reaction would have to take a much longer time under a condition without condensation until the weight-gain levels off. The saturation level could be a complicated function of ICl vapor pressure and material purity. This method was later modified by setting up a temperature gradient between the fullerene powders and ICl in an enclosed flask with the liquid ICl at a temperature (e.g. 5-20°C) below that of the fullerenes. The fullerenes were heated to temperatures between 30 and 60°C and the reaction time varied from two to five days. A weight-gain of 60-80% was consistently found to yield reproducible magnetization results described below.

The ICl-doped fullerenes were placed in a gelatin capsule for magnetization measurements using a Quantum-Design MPMS SQUID magnetometer. The temperature-dependence of magnetization M for an ICl-doped fullerene sample cooled in zero magnetic field (ZFC) is shown in Fig. 1. For comparison, similar data obtained with an undoped fullerene sample are also shown in this figure. The results are summarized in the following:

(a) The undoped fullerene powders show weak paramagnetism, which might be related to some possible magnetic impurities in the material. The magnetization M (about 1×10^{-6} emu for a mass of 20mg in an applied magnetic field H of 100 Oe at 10K) follows the Curie law behavior ($M/H=C/T$) up to a temperature around 30K where the weak paramagnetic signal becomes indistinguishable from the background.

(b) The ICl-doped fullerenes exhibit a field-exclusion *diamagnetic* behavior at temperatures below a critical point which occurs at somewhere between 60 and 70K. Within experimental uncertainties, taking into account a small diamagnetic background arising from the gelatin capsule (about -0.5×10^{-6} emu, see below), the net *negative* (diamagnetic) magnetization signal is always 4-10 times larger than the background.

(c) To further ascertain that the signal for ICl-doped fullerenes is indeed negative, magnetization measurements were made in two different applied magnetic field values of 20 and 100 Oe, respectively, as shown in the two M-T curves labelled "doped fullerene" in Fig. 1. Except for a small temperature interval below 20K where a small paramagnetic tail is present, these two curves show a ratio of *negative* magnetization equal to 5 (which is the ratio of the two magnetic fields) within the experimental errors. The net negative magnetization is clearly *proportional* to the applied magnetic field. If the net magnetization is positive (for paramagnetic substances), an increase of H from 20 to 100 Oe would have moved the M-T curve upwards into the positive-M region above the M=0 base-line which could not satisfy the observed proportionality condition in the negative-M region below the base-line. This method provides an unequivocal test for distinguishing small diamagnetic signals from possible paramagnetic magnetization (e.g. due to magnetic impurities).

(d) The slight decrease of magnetization between 10 and 20K as shown in the bottom curve of Fig. 1 is believed to arise from the paramagnetic tail of residual undoped fullerene powders in the specimen. The net magnetization is therefore a superposition of the diamagnetic component from the ICl-doped fullerenes and paramagnetic contributions from the undoped material. The solid curve in Fig. 1 shows the difference in magnetization between the ICl-doped and undoped fullerenes. However, the net *negative* magnetization *increases* with increasing temperature above 20K, this shows a typical behavior of broad superconductive transition to normal state for granular superconductors. The transition temperature T_c lies somewhere above 60K.

Because of the small size of the diamagnetic signal, SQUID measurements must be made with extra caution and possible contributions from unwanted sources must be carefully evaluated: (i) The average SQUID output signal after every five length-scans as a function of sample position was monitored throughout the magnetization measurements. The scan length was 8cm while the sample was 3mm long, hence the sample could be viewed as a point dipole. Only those signals *symmetric* about the origin as the sample was moved through the pickup coils were used. (ii) The background magnetization due to the gelatin capsule without any sample in it was determined to be around $-(0.4 \pm 0.2) \times 10^{-6}$ emu in a field of 100 Oe for our system. This diamagnetic background is *temperature independent* for both ZFC and field-cooled (FC) measurements, as shown by the two bottom curves in Fig. 2. (iii) The total uncertainty in the determination of zero-magnetization base-line due to the remnant field of the magnet is always lower than $\pm 0.5 \times 10^{-6}$ emu.

For comparison, the ZFC magnetization of unreacted ICl is also shown in Fig. 2 along with that of the undoped fullerene powders. Both specimens show typical paramagnetic behavior as a function of temperature. The ICl molecule has an electric dipole moment of 1.24D (where D is the Debye unit 3.33564×10^{-30} C-m) which follows a Curie law behavior up to about 50K. Paramagnetic magnetization of the undoped fullerenes (up to about 30K) is about an order of magnitude weaker than ICl, possibly resulted from residual magnetic impurities. None of the M-T curves shown in Fig. 2 exhibits any *increase* of magnetization with temperature in the negative-M region, hence the possibility of contributions arising from any unreacted ICl

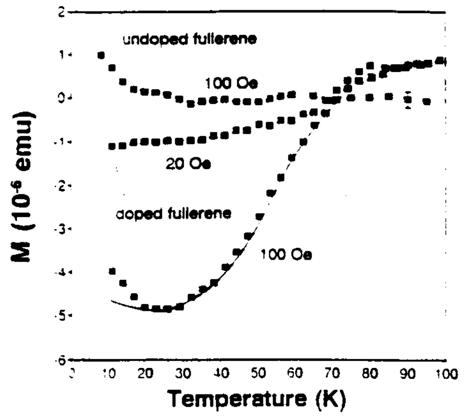

Fig. 1 -- Magnetization as a function of temperature obtained with zero-field-cooled samples of undoped fullerenes (top curve, H=100 Oe) and ICl-doped fullerenes (middle and bottom curves, at H=20 Oe and 100 Oe, respectively), the weight of each sample was approximately 20mg.

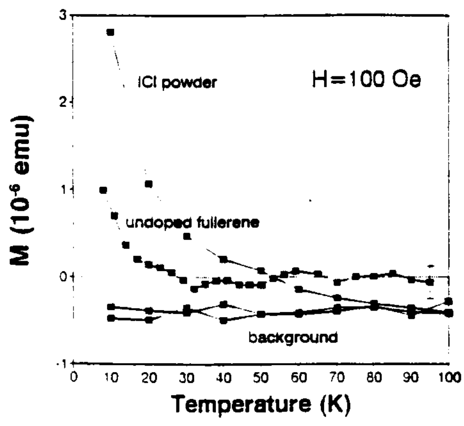

Fig. 2 -- Magnetization as a function of temperature obtained with zero-field-cooled samples of unreacted ICl (20mg), undoped fullerenes (20mg), and background (gelatin capsule) in a field of 100 Oe.

or undoped fullerenes to the temperature-dependent *negative* magnetization in ICl-doped fullerenes (which *increases* with T, as shown in Fig. 1) can be ruled out.

To further ascertain that the net diamagnetic signal is associated with the superconducting components in the ICl-doped fullerenes, ZFC and FC magnetization measurements were also carried out. A comparison of these results obtained by using a different sample is shown in Fig. 3 with a probing field of 100Oe. The initial drop in both ZFC and FC curves below 30K is most likely caused by paramagnetic contributions due to the residual undoped fullerene mixture or unreacted ICl. However, the ZFC and FC curves are parallel at low temperatures. This *constant* difference between the ZFC and FC curves is an indication of the effects of magnetic flux trapping due to superconducting components in the material. If the common paramagnetic part is properly subtracted out, there is a constant difference between the ZFC and FC curves of at least $2x10^{-6}$ emu below 40K (this signal is at least a factor of 2 above the noise level), and these curves again demonstrate the typical behavior of a superconductor with incomplete Meissner effect similar in shape to those found in oxide high-T_c superconductors. The width of superconducting transition is quite broad, ranging from around 40K to a higher temperature where these two curves merge, as a consequence of small granular superconducting components in the material. Note that in the *diamagnetic* region, the ZFC curve always lies below the FC curve, thus any unusual magnetic property such as a *paramagnetic* spin-glass-like behavior[7] can be safely ruled out.

The unreacted ICl and undoped fullerenes were also subjected to the same ZFC-FC tests in an applied field of 100 Oe. In both cases, the ZFC and FC curves coincide with each other, and no difference greater than the experimental error of $0.2x10^{-6}$ emu could be detected between these curves. The purely paramagnetic behavior was also reconfirmed by reversing the applied magnetic field (say from +100Oe to -100Oe) which

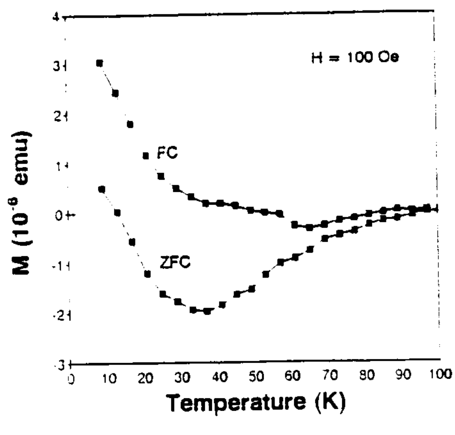

Fig. 3 -- Magnetization curves for zero-field-cooled and field-cooled (H=100 Oe) ICl-doped fullerenes, the weight of this sample was approximately 20mg.

showed the same effects except for a sign reversal of the magnetization and also provided a clear definition for the base-line of zero-magnetiztion. These results show that no flux trapping can occur in the unreacted ICl and undoped fullerenes, and further establish that our observed net negative magnetization and its temperature dependence (Figs. 1 and 3) are indeed arising from the ICl-doped fullerenes.

Using the present method of ICl-doping, the maximum diamagnetic susceptibility obtained so far was -$4.25x10^{-6}$ emu per c.c., which is only 0.005% of that expected for an ideal superconductor, or about a factor of hundred smaller than that found in alkali-metal-doped fullerenes. The small shielding fraction (incomplete Meissner effect) in our samples could result both from a small volume fraction of ICl-doped C_{60}/C_{70} (and/or higher fullerenes) and from small superconducting grain sizes being comparable to the penetration depth (estimated to be a few thousand angstroms). It seems probable that because of the large size of the ICl interhalogen, only a very small portion of the fullerene molecules is susceptible for ICl-doping. If the ICl-fullerene coupling is caused by dipole interactions, this effect should indeed be very small. Hence, the actual superconducting grain size could be much smaller than the particle size of the fullerenes (about a micron in the present case). This is also consistent with our x-ray diffraction data. Among over 80 samples prepared to date using various processing conditions, more than 30 specimens showed the typical behavior as displayed in Fig. 3. The sample purity cannot be precisely controlled at the present time, as it may depend on a number of factors such as the amount of unreacted ICl, and possible magnetic impurities or nonmagnetic defects contained in the raw materials. However, the effects shown in Figs. 1 and 3 are reasonably reproducible, the variations of measured magnetization values in repeated runs using different samples, as well as any hysteretic behavior observed in the normal state above 70K, are always within the range of $\pm 0.5x10^{-6}$ emu in an applied field of 100 Oe.

Results of x-ray powder diffraction measurements are shown in Fig. 4 for both undoped and ICl-doped fullerenes with 50% weight-gain. No apparent structural changes can be detected in this ICl-doped sample in comparison with that of the undoped fullerenes, as it was also found in the previous cases of alkali-metal-doped fullerenes. The solid structure remains as face-centered-cubic at this level of ICl-doping, with some changes in the diffraction peak intensity; but no shift in the peak position can be resolved with the present apparatus.

A useful feature of the ICl-doped fullerene superconductor is its stability in air. All the samples were processed in a fume hood, and handled in ambient atmosphere during various measurements, in contrast to the alkali-metal-doped fullerenes which are necessarily encapsuled to avoid exposure to air. After the initial tests, our samples are usually kept in a dry nitrogen atmosphere. One ICl-doped sample has been subjected to a stability test. SQUID measurements were made 4 days after the initial study; both the diamagnetic and flux trapping signals remained practically unchanged. Three

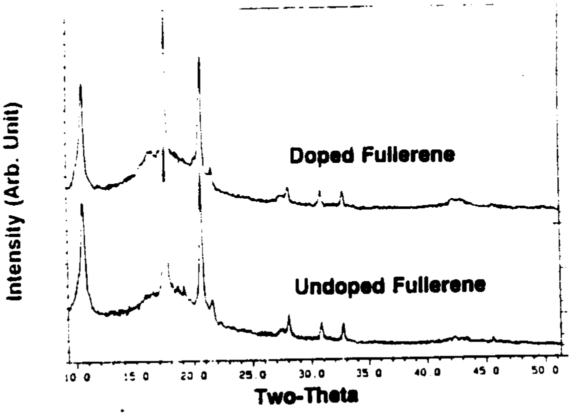

Fig. 4 -- XRD data for (a) undoped and (b) ICl-doped fullerenes.

weeks thereafter, the signals had deteriorated, and finally 45 days afterwards, these signals disappeared and the material turned weakly paramagnetic similar to the undoped fullerenes.

To provide an addition basis for comparison, IBr-doped fullerene samples were also prepared following a similar procedure as described for the case of ICl-doping, except only heating the fullerenes to temperatures between 22 and 28°C. Typical ZFC and FC M-T curves obtained with an IBr-doped fullerene sample are shown in Fig. 5. Although the basic features are similar to those found in ICl-doped fullerenes (see Fig. 3), the effects are relatively weak. The difference between ICl- and IBr-doped fullerenes may be related to the different electric dipole moments in ICl (1.24D) and IBr (0.73D). Since the negative magnetization observed in IBr-doped fullerenes was marginal and comparable to the noise limit, no superconducting behavior in these materials can be claimed at the present time.

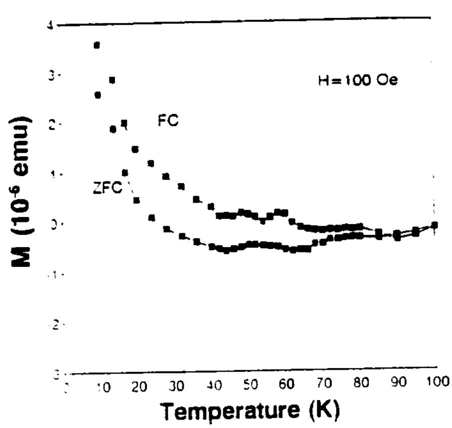

Fig. 5 -- Magnetization curves for zero-field-cooled and field-cooled (H=100 Oe) IBr-doped fullerenes, the weight of this sample was approximately 20mg.

As a note for comparison, magnetic behavior of halogen-doped C_{60} has recently been studied by Sekine *et al.*[5] Although they also started out by using solid IBr as a dopant, their material was heat treated at 250°C for 5 minutes and at 200°C for 20 hours. These temperatures were probably high enough to dissociate IBr, hence the final form of their dopants may be pure iodine or pure bromine. They observed a net *positive* magnetization about two orders of magnitude higher than our IBr-doped fullerenes. The paramagnetic behavior below 30K observed in their experiment was consistent with other previous studies of pure halogen-doped fullerenes[2-4] from which no trace of superconductivity was found. By contrast, although their paramagnetic M-T curves look somewhat similar to ours (Fig. 5), their ZFC and FC curves are not even nearly parallel to each other.

Further sample preparation and characterization measurements are in progress. The main efforts are to optimize the doping conditions and to perform resistivity measurements of ICl-doped fullerene films. Our most recent Raman spectroscopy studies have clearly confirmed that the ICl molecules are attached to C_{60} buckyballs. Onset of large Raman shifts in the $H_g(1)$ mode from 269 to 208 cm^{-1} were observed when the weight-gain reached 50-60%. This shift was not found in previous Raman studies of alkali-metal-doped fullerenes[8]. In the meantime, as a function of increased ICl-doping, the $A_g(1)$ mode at 490 cm^{-1} gradually disappears while the strength of the $A_g(2)$ mode at 1469 cm^{-1} and all other small features of C_{60} only show very slight shifts and broadening. These results, coupled with the XRD data showing no observable changes, indicate that at this level of 50-60% ICl-doping (so far the optimal condition for observing the Meissner effect), ICl is indeed attached to C_{60} while the fullerene structure still remain intact in our specimens. When the weight-gain is increased to 100%, most of the small features pertaining to C_{60} have disappeared except for the $A_g(2)$ (which suffers a very small down shift of about two wavenumbers) and $H_g(1)$ modes, and all the C_{60} lines in XRD have also disappeared. The failure of the charge-sensitive $A_g(2)$ mode to show a sizable shift with ICl-doping indicates that there is no significant charge-transfer taking place inside these doped fullerenes. This observation implies that (i) the superconducting phase is present in such a small amount that Raman scattering is unaffected (consistent with the small Meissner effect observed), or (ii) the molecular bands of fullerenes are practically unchanged such that no significant hole-doping is occurring, and there exists a different mechanism of compound formation (e.g. local complexes or clusters). The specific interaction between the ICl molecule with a large dipole and the highly-symmetric C_{60} buckyball structure may suggest a possibly new mechanism for excitation-mediated charge coupling which gives rise to superconductivity.

The temperature-dependence of diamagnetic behavior and the effect of magnetic flux trapping are earmark evidences (Meissner effect) commonly used to identify superconductivity. Possible spurious contributions from the instrument background and residual magnetic impurities in our ICl-doped fullerenes have been carefully ruled out. The volume fraction of superconducting component in our material is relatively small at the present time, being limited by the lack of detailed knowledge of the material structure and pairing mechanisms. However, the existence of high temperature superconductivity (T_c>60K) in these ICl-doped fullerenes (in contrast to pure halogen doping with F, Cl, Br, or I) as evidenced in Figs. 1-3 seems sufficiently clear and encouraging that the interhalogen-doped fullerenes can indeed reach a value of T_c comparable to that of the oxide superconductors. The main purpose of the present communication is to share this new information with other researchers in the field, and with a hope that more research on the ICl-doped fullerenes will be conducted in other laboratories. If the existence of superconductivity in the ICl-doped fullerenes can be further established by other experiments, the new record of high T_c found in these hole-doped carbon superconductors would indicate that the underlying mechanism is most likely more complicated than phonon-mediated pairing of charges and therefore poses further challenges for fundamental understanding of the fullerene-superconductors. The fact that the nonceramic ICl-doped carbon-superconductor is stable in air, and free from oxide or alkali-metals, will make this class of clean molecular solids very attractive for further fundamental studies as well as material applications.

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References

1. For a recent general review, see A.F. Hebard, Physics Today, November 1992, p.26; and references therein.
2. J.H. Holloway *et al.*, J. Chem. Soc., **Chem. Commun.** 966-969 (1991).
3. T.R. Ohno *et al.*, Nature **355**, 401 (1992).
4. Q. Zhu *et al.*, Nature **355**, 712 (1992).
5. H. Sekine *et al.*, J. Appl. Phys. **72**, 5448 (1992).
6. D. Ghosh, R. Gangwar, and D.D.L. Chung, Carbon **22(3)**, 225 (1984); and references therein.
7. Ch.D. Routsi, J.K. Yakinthos, and E. Gamari-Seale, J. Mag. Mag. Mat. **102**, 266 (1991).
8. K.A. Wang *et al.*, Phys. Rev. **B45**, 1955 (1992).