

Preparation, characterization and properties of C_{60} and C_{70} : Spectroscopy, structure, anions, interaction with electron donors and superconductivity

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Preparation and characterization of the fullerenes, C_{60} and C_{70} , are described in detail, including the design of the generators fabricated locally. The characterization techniques employed are UV-visible, IR, Raman and ^{13}C NMR spectroscopies, scanning as well as transmission electron microscopy and mass spectrometry. The electron energy level diagram of C_{60} as well as the one-electron reductions of C_{60} and C_{70} leading to various anions are discussed. Electronic absorption spectra of C_{60} and C_{60}^{2-} are reported. Phase transitions from the plastic to the crystalline states of C_{60} and C_{70} are examined. Based on a ^{13}C NMR study in a mixture of nematic liquid crystals, it has been demonstrated that C_{60} retains its extraordinary symmetry in solution phase as well. Interaction of C_{60} and C_{70} with strong electron-donor molecules has been investigated employing cyclic voltammetry. Superconductivity of K_xC_{60} has been studied by non-resonant microwave absorption; Na_xC_{60} as well as K_xC_{70} are shown to be non-superconducting. Doping C_{60} with iodine does not make it superconducting. Interaction of C_{60} with $SbCl_5$ and liquid Br_2 gives rise to halogenated products.

The closed-cage molecules of carbon, the fullerenes, and in particular buckminsterfullerene, C_{60} , first discovered by Kroto *et al.*¹ have become a topic of intense research after the preparative procedure involving vapourization of graphite in an arc, to prepare macroscopic quantities, became available². In our efforts³ to investigate the structure, properties and reactivity of C_{60} and C_{70} , we have designed generators which produce C_{60} and C_{70} in high yields at a fast rate. Besides producing C_{60} and C_{70} by contact-arc vapourization of graphite employing locally designed generators, we show that these fullerenes are formed in simple benzene-air flames in minute quantities. We describe here characterization of C_{60} and C_{70} by a variety of techniques including optical and NMR spectroscopy, mass spectrometry and electron microscopy. An electron energy level scheme of C_{60} consistent with the electronic absorption spectrum and the UV photoelectron spectrum is given. Also reported are four one-electron reversible reduction potentials of C_{60} giving rise to different anions, besides reliable electronic absorption spectra of the mono- and di-anions. The interaction of C_{60} and C_{70} with a few electron donor molecules has also been investigated employing cyclic voltammetry.

Since C_{60} is a highly symmetrical molecule with I_h

symmetry, we have investigated its ^{13}C NMR spectrum in a mixture of nematic crystals of opposite diamagnetic anisotropies to find out if any distortions are induced in the molecule in such an environment just as those found in the case of spherical molecules such as methane. Also examined are the phase transitions of C_{60} and C_{70} involving orientational disorder by means of differential scanning calorimetry. We have also studied the superconducting properties of doped fullerenes by employing non-resonant microwave absorption.

Materials and Methods

In order to prepare C_{60} and C_{70} , we have built two generators wherein contact-arc vapourization of graphite is carried out in a helium atmosphere. A schematic diagram of one of the generators fabricated by us³ is shown in Fig. 1. Two water-cooled copper electrodes and a water-cooled double-walled copper vessel form the essential parts of the generator. The graphite electrodes and the copper vessel are housed in a 30" long stainless steel vacuum vessel of 8" diameter mounted on a 4" diffusion pump through a liquid nitrogen trap. Graphite rods of 5 mm diameter (Johnson Matthey Chemicals Ltd., England) were used in the evaporation.

In order to facilitate the evaporation process,

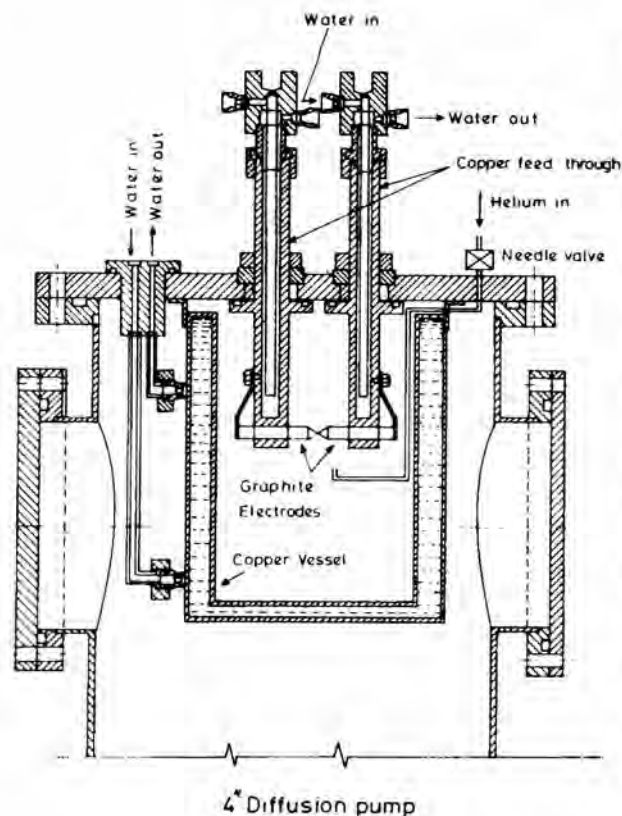


Fig. 1—Schematic diagram of a fullerene generator

both the graphite electrodes were sharpened to a conical shape and held in loose contact with each other with the help of two tungsten springs. The system was pumped to $\sim 10^{-6}$ torr and helium let into the copper vessel through a liquid nitrogen trap. The pressure of helium was maintained around 180 torr with slow pumping and by controlling the leak rate with the help of a variable leak valve. A current in the 100–180 amp range (5–8 volts AC, 60 Hz) was passed through the electrodes to initiate the arc. A gray plume was observed under these conditions. After three hours of evaporation, about 500 mg of soot could be collected from the copper vessel and the electrode surfaces. Still larger quantities of soot could be obtained after prolonged evaporation. The soot was extracted with toluene and filtered. The resulting red solution was evaporated to yield a solid which was characterised by mass spectrometry, ^{13}C NMR spectroscopy, etc. We have recently incorporated another set of electrodes in the system shown in Fig. 1 in a manner that enables us to move them from outside. This helps to sustain the arc for longer periods. With this design, larger quantities of C_{60} could be produced in a shorter period (50 mg in less than an hour). The yields of C_{60} – C_{70} mixtures ob-

tained by us were 10–30% of the soot and C_{70} content in the mixture was $\sim 10\%$ or less.

In Fig. 2 is shown the diagram of another generator fabricated by us. This consists of a water cooled stainless steel vessel of 8" dia. pumped to $\sim 10^{-6}$ torr by a 4" oil diffusion pump through a liquid N_2 trap. The graphite rods were connected to 1" copper feed-throughs and a current of 100–300 A (10V AC) was passed through the rods to obtain the arc. One of the electrodes is movable from outside so that a graphite rod of 4 cm could be evaporated completely in 10 min. Once the system is pumped to $\sim 10^{-6}$, the vacuum valve is closed and helium admitted to ~ 100 torr through a needle valve. The arc could be maintained continuously by keeping the distance between the electrodes constant. The design of this generator makes it possible to change the graphite rods and to remove the soot by opening just one flange. It is also possible to drive the copper feed-through by means of an electrical motor and automate soot generation.

In order to obtain pure C_{60} and C_{70} , the toluene extract was passed through alumina columns. After chromatographic separation, we could get pure C_{60} and C_{70} . The purity was ascertained by TLC, mass spectrometry, Raman spectroscopy and others techniques. One should note that C_{60} samples are often contaminated by C_{70} and vice-versa.

Mass spectrometry was carried out with a JEOL (direct inlet 70 eV EI source) instrument. UV-visible spectra were recorded with a Pye-Unicam instrument. Infrared spectra were recorded with a Brüker FT spectrometer and Raman spectra with a Spex Ramalog unit. ^{13}C NMR spectra were recorded with a 400 MHz Brüker spectrometer. High resolution electron micrographs were recorded with a JEOL 200CX instrument while scanning electron micrographs were obtained with a Cambridge microscope. Cyclic voltammograms were recorded with a PAR instrument. Differential scanning calorimetry was carried out with a Perkin-Elmer instrument at a cooling rate of $20^\circ/\text{min}$ under nitrogen flow.

We have prepared K_xC_{60} and K_xC_{70} by the solution route wherein ~ 75 mg of potassium metal was refluxed with ~ 15 mg of pure C_{60} or C_{70} in toluene for ~ 2 h under Ar flow. The black solid thus obtained was filtered under Ar flow and the powder was packed in a capillary tube of 0.1 mm diameter. Na_xC_{60} was prepared by reaction of Na with C_{60} in refluxing toluene. The samples were studied by non-resonant microwave absorption and ESR spectroscopy, using a Brüker ER-200D X-band spectrometer working at a nominal frequency of 9.4 GHz. Magnetic field modulation of 100 kHz with phase sensitive detection was employed to record the re-

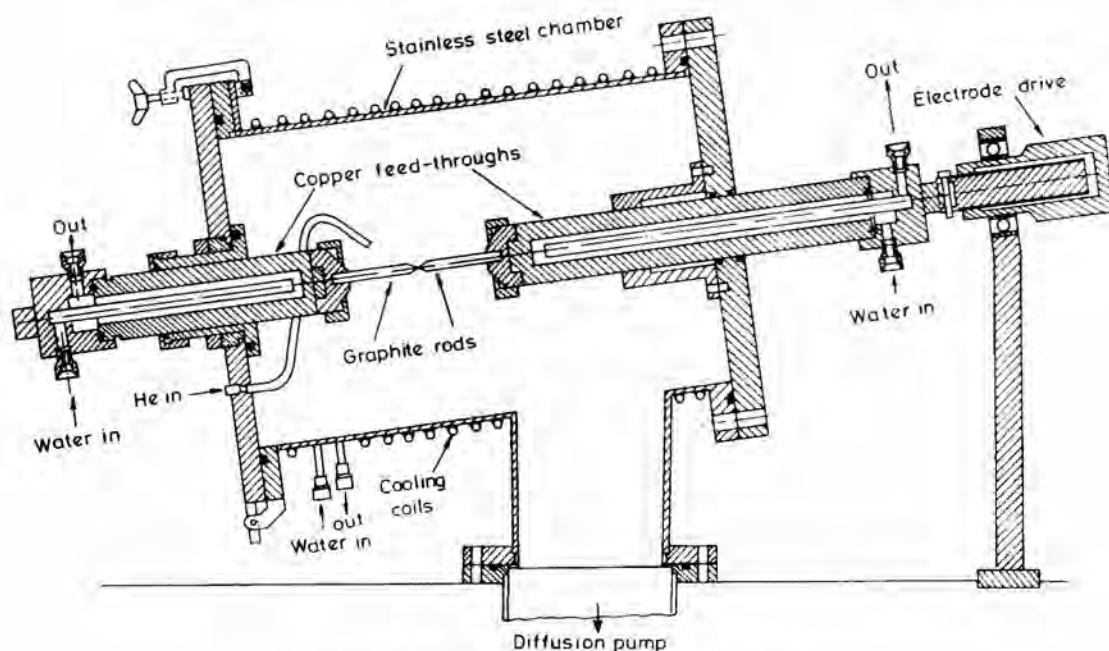
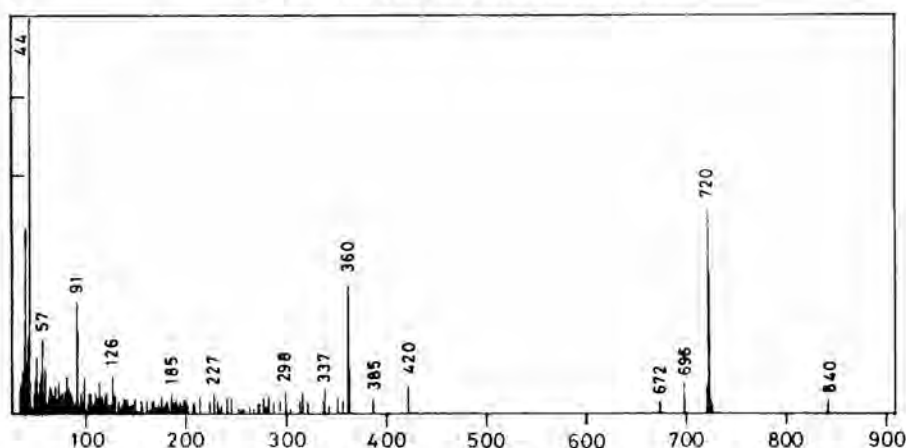


Fig. 2—Second design of a fullerene generator

Fig. 3—Mass spectrum of C_{60} + C_{70} mixture

sponse in the derivative form. A continuous flow He cryostat (Oxford Instruments) was used to vary the temperature down to 4.2 K with ± 0.1 K accuracy. The Na salt of C_{60} was prepared in a manner analogous to K_xC_{60} and it was also examined by non-resonant microwave absorption. C_{60} samples, subjected to interaction with iodine, were also similarly examined. Efforts to examine adducts of C_{60} with liquid Br_2 and $SbCl_5$ (in an organic solvent) failed since halogenated products were obtained. Rb and Rb-Cs derivatives of C_{60} were prepared by reaction in sealed tubes.

Results and Discussion

Characterization

Over the last few months we have been able to

generate C_{60} and C_{70} at fairly rapid rates. We have used mass spectrometry routinely to characterize C_{60} and C_{70} (Fig.3). ^{13}C NMR spectroscopy is also a good tool to distinguish C_{60} and C_{70} . While C_{60} shows a single line around 143 ppm, C_{70} shows five lines at 130.9, 145.2, 147.3, 148.6 and 150.5 ppm with intensity ratios of 10/20/10/20/10 as can be seen from Fig.4. C_{60} and C_{70} show characteristic infrared spectra (Fig.5), the remarkable simplicity of the spectrum of C_{60} due to its high symmetry being noteworthy. The Raman spectrum of C_{60} is shown in Fig.6.

Scanning electron micrographs of the C_{60} particles obtained after removal of the solvent show spherical aggregates of 1-5 microns (Fig.7a). High-resolution electron micrographs not only show lat-

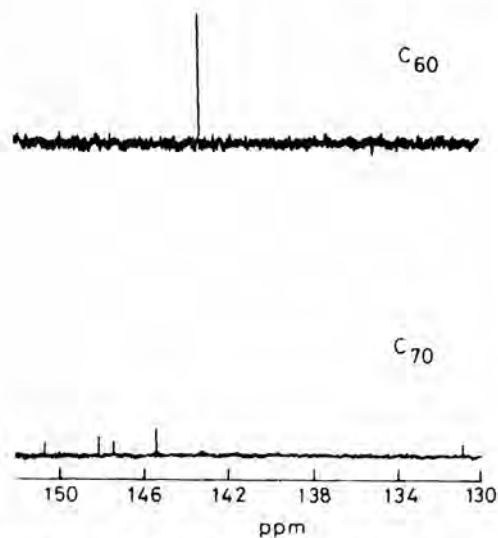


Fig. 4— ^{13}C NMR spectra of C_{60} and C_{70} in CCl_4 solution

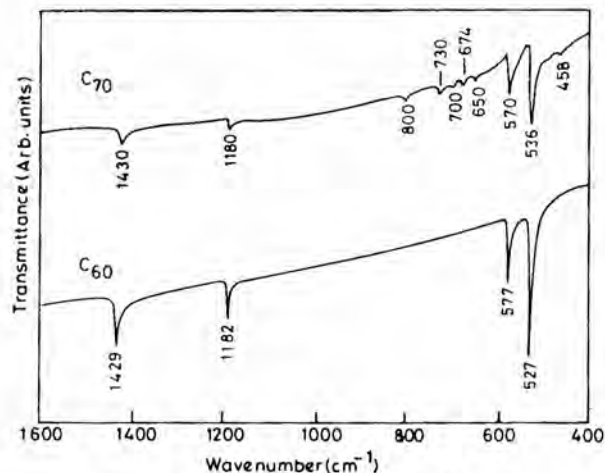


Fig. 5—Infrared spectra of C_{60} and C_{70}

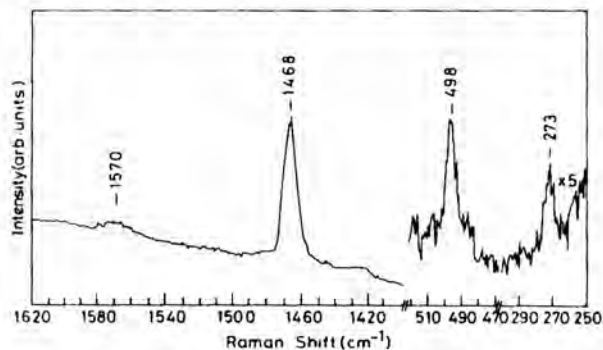


Fig. 6—Raman spectrum of C_{60}

tice fringes corresponding to $c/2$ ($\sim 8\text{\AA}$) as in Fig. 7b, but also the closed-packed arrangement of C_{60} molecules with a diameter of $\sim 7\text{\AA}$. In the inset of Fig. 7b, we show an image in which the nearly cir-

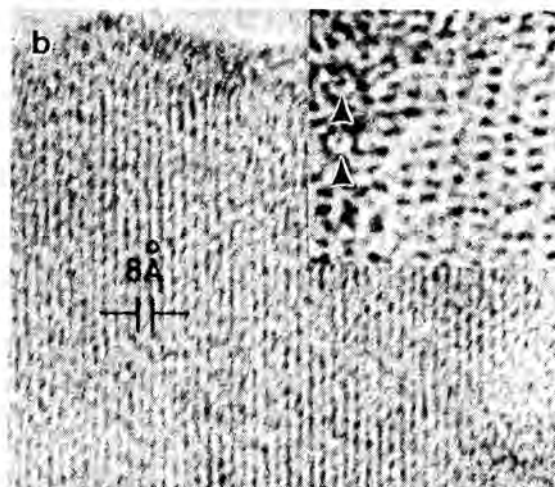


Fig. 7—(a) Scanning electron micrograph showing a spherical aggregate of C_{60} ; (b) Lattice fringes in the transmission electron micrograph; inset shows close-packed C_{60} molecules

cular white features with central black spots represent the projection of the hollow cage.

The electronic absorption spectrum of C_{60} in *n*-hexane solution (Fig. 8) recorded by us shows distinct maxima at 213, 257 and 328 nm ($\log \epsilon$, 5.1, 5.2 and 4.7 respectively) and a broad band centred around 555 nm; there is also a sharp feature at 404 nm in agreement with Hare *et al.*⁴. This spectrum can be understood by taking the first three π orbital energies to be approximately equal to the ionization energies from the UV photoelectron spectrum⁵. The ionization energies are at 7.6 (h_u), 8.9 ($g_g + h_g$) and 10.8 eV ($g_u + t_{2u}$). In Fig. 9 we show the energy level diagram³ of C_{60} which also indicates the various π - π^* transitions; in this diagram we have made use of the fact that the differences in some of the transition energies are close to the differences in the

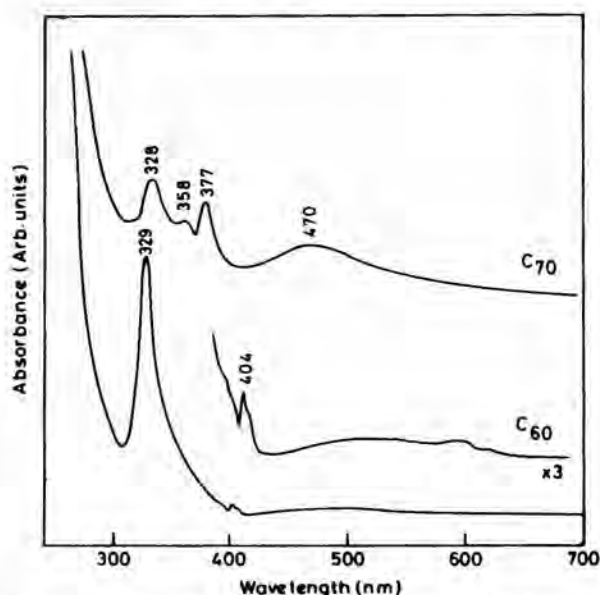


Fig. 8—Electronic absorption spectra of C₆₀ and C₇₀ in hexane solution

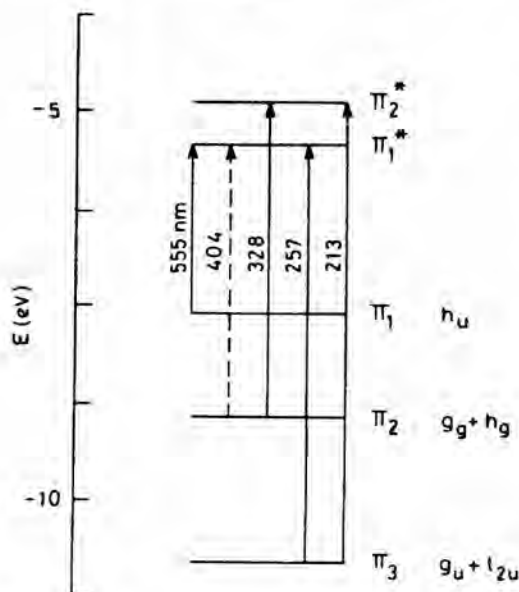


Fig. 9—Approximate electron energy level scheme of C₆₀

π orbital energies. The longest wavelength π - π^* transition around 550 nm corresponds to HOMO-LUMO separation of 2.2 eV, in agreement with theoretical expectations and the electron energy loss spectrum. The sharp 404 nm feature is likely to be due to the π_2 - π_2^* (rather than π_1 - π_2^*) transition as shown in Fig.9. Some of the structures in the 550 nm band seems to correspond to the known vibrational frequencies of the molecule. The UV absorption bands of C₆₀ show solvent red-shifts in polar solvents indicating an increase in the dipole moment

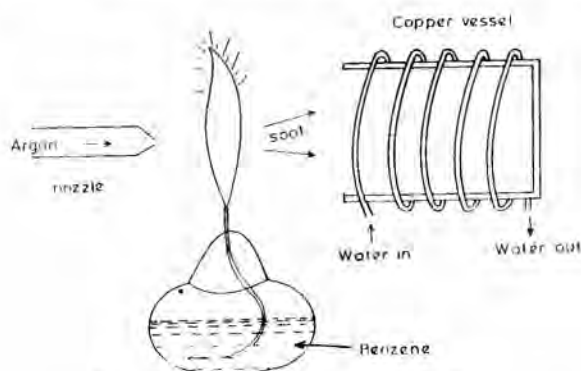


Fig. 10—Fullerenes from benzene-air flame

on excitation. The red-shifts of the 328 nm band in CH₃CN and DMSO solvents are 92 and 278 cm⁻¹ respectively with respect to *n*-hexane. In Fig.8 we have also shown the electronic absorption spectrum of C₇₀, but are unable to provide the energy level diagram due to the absence of information on orbital ordering.

Fullerenes from benzene flames

Recently, Howard *et al.*⁶ have found C₆₀ and C₇₀ in varying proportions in laminar flames of benzene and oxygen. These authors stabilized the flame in a partial helium atmosphere employing a specially designed low-pressure chamber and found the fullerenes to occur preferentially in non-sooty flames. We have been examining the nature of condensable compounds and soot in benzene-air flames for some time and have found fullerenes, C₆₀ and C₇₀, in sooty flames obtained from a simple laboratory spirit lamp using benzene as the fuel (Fig.10). We consider this to be of some general interest.

The technique employed by us involved quenching of a part of the sooting end of the flame by argon coming through a glass nozzle (1 mm dia) at a stagnation pressure of 1.5 atm and collecting the soot on a cooled copper surface positioned opposite to the nozzle (Fig.10). We could collect ~5 g of the soot after 3 hr of operation, expending 250 ml of benzene. The soot was washed with ether and the toluene extract of the residue dried and analysed by mass spectrometry. The mass spectrum showed the 720 and the 840 mass peaks (as well as the *m*/2 peaks). The proportion of C₆₀ was higher and the total yield of fullerenes was ~0.1% with respect to the soot. The yield can be improved by quenching a larger area of the flame. The observation of fullerenes in such simple benzene flames is not only of significance in understanding the origin of fullerenes as well as the formation of soot, but also suggests the possible occurrence of these species in the environment.

Phase transitions due to orientational disorder

Buckminsterfullerene, C_{60} , being a spherical molecule, would be expected to show a high degree of orientational disorder in the solid state. We were interested in examining whether C_{60} showed evidence for a transition from an orientationally disordered (plastic) state to an ordered state. We indeed found such a phase transition around 250 K. In the meantime, however, we noticed the paper of Heiney *et al.*⁷ who found the transition at 250 K to be accompanied by a change in crystal symmetry. We were equally interested to examine whether a plastic to crystalline phase transition is exhibited by C_{70} which has a near-spherical symmetry. For this purpose, we have carried out a study on C_{70} by differential scanning calorimetry. The sample of C_{70} was pure, although presence of minute quantities of C_{60} cannot entirely be ruled out.

In Fig. 11, we show the differential scanning calorimetric trace of C_{70} after subtracting the baseline. For purpose of comparison, we also show the DSC trace for C_{60} in this figure. The transition in C_{70} (218 K) occurs at a lower temperature than that in C_{60} . The transition takes place over a slightly wider temperature range than in the case of C_{60} . The enthalpy change of the transition in C_{70} from the area under the curves is around 5.4 kJ/mol, which is large showing that the transition is thermodynamically first-order. This can be compared with the enthalpy change of 4.8 kJ/mol of the corresponding transition in C_{60} . The presence of a single phase transition in C_{70} and C_{60} at 218 K and 250 K respectively leads us to believe that the two transitions found at 221 and 252 K in C_{60} by Tse *et al.*⁸ arise because of the presence of C_{70} impurity in C_{60} . We find no noticeable changes in the IR and Raman spectra of C_{70} across the phase transition.

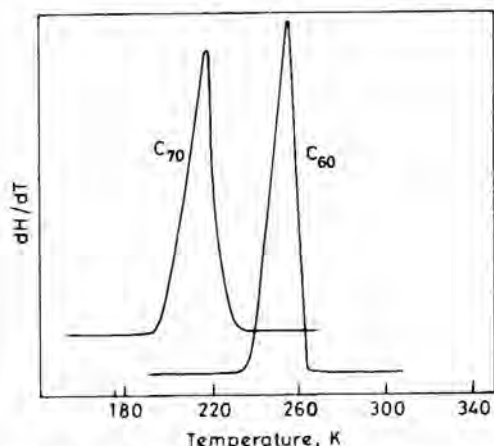


Fig. 11—Differential scanning calorimetric traces of powdered samples of C_{60} and C_{70}

¹³C NMR spectrum of C_{60} in nematic liquid crystal mixtures and the extraordinary symmetry of C_{60} in solution phase: Buckminsterfullerene, C_{60} , is a molecule with the highest finite point group symmetry, I_h , and the room-temperature crystalline phase is orientationally disordered ($Fm\bar{3}$ space group). In the low-temperature ordered phase ($Pa\bar{3}$ space group), weak bonding between C_{60} units appears to produce appreciable geometrical deviations from the $m\bar{5}m$ to the $\bar{3}$ point group⁹. Theoretical calculations show that in the free state, the C_{60} molecule prefers the I_h symmetry and does not have a more stable lower symmetry structure¹⁰. The ¹³C NMR spectrum of C_{60} in CCl_4 solution shows a single line with an isotropic chemical shift of 142.5 ppm establishing the exact equivalence of all the 60 atoms, consistent with the I_h symmetry. In order to determine whether slight distortions from the I_h symmetry occur in the solution phase, we have employed a novel method wherein the ¹³C NMR spectrum of C_{60} was recorded in a mixture of nematic liquid crystals of opposite diamagnetic anisotropies^{11,12}. This method is distinct from the well-known NMR technique¹³ wherein precise molecular geometries are obtained from the anisotropic NMR parameters of molecules dissolved in nematic liquid crystals.

In the method employed by us, we make use of the change in the anisotropic parameters resulting from the switching of the order parameters at the critical point of a nematic liquid crystal mixture; the change can be by a factor of -2 or $-1/2$ depending on the direction of approach of the critical point. By an adjustment of the concentration and temperature, it is possible to render both types of orientations to coexist, the shift between the two spectra providing the chemical-shift anisotropy. In tetrahedral molecules such as methane such a coexistence of spectra with shifts of ~ 0.5 ppm has indeed been observed. Observation of a single line spectrum near the critical point would, therefore, indicate the absence of any detectable distortions. In the present study, we have examined the ¹³C NMR spectra of C_{60} and tetramethylsilane in liquid-crystal mixtures in order to compare the behaviour of C_{60} with that of another nearly spherical molecule.

¹³C spectra were recorded with a temperature stability of better than ± 0.1 K. The proton decoupled ¹³C spectra were accumulated with the decoupler being "on" only during acquisition period. This prevents heating of the samples and eliminates the temperature inhomogeneities arising from the decoupling powers used while accumulating the spectra. A delay of 10s was introduced between the successive scans. Nearly 25,000 scans were accumulated and

Fourier transformed in each case. Spectra of the following systems were recorded: (i) pure S-1114 (*trans*-4-pentyl-4,4'-cyanophenylcyclohexane) with a positive diamagnetic anisotropy at 323.0 K in the nematic phase and 358.0 K in the isotropic phase; (ii) pure ZLI-1167 (a ternary eutectic mixture of propyl-, pentyl- and heptyl-bicyclohexyl carbonitriles) with a negative anisotropy at 323.0 K in the nematic phase and at 358.0 K in the isotropic phase; (iii) solution containing 0.2 wt% of C_{60} in S-1114 at 323.0 K in the nematic and at 358.0 K in the isotropic phases; and (iv) 0.2 wt% solution of C_{60} in ZLI-1167 at 323.0 and 358.0 K in the nematic and isotropic phases respectively. We then studied the spectra of a 1:1 mixture of (iii) and (iv) containing 4.2 wt% of tetramethylsilane (hereafter referred to as solution (v)) in both the nematic and the isotropic phases. The mixture showed spectra due to the coexistence of the two phases at 333.4 K.

Figure 12 shows intense, well-separated lines due to the ^{13}C resonances from the liquid crystal solvent carbons. The vertically expanded versions show the lines due to tetramethylsilane and fullerene C_{60} around 0.00 and 140.37 ppm respectively. Since the ^{13}C NMR signal of C_{60} was weak, in order to ensure that the assignment of the line at 140.37 ppm to C_{60} in the nematic phase was correct, experiments were performed with (i), (ii), (iii) and (iv) under identical conditions. Comparison of the various spectra with and without C_{60} unambiguously established that the

line at 140.37 ppm was due to C_{60} . Figure 13 shows the spectra due to the coexistence of the two types of orientations. Coexistence of the two ^{13}C lines separated by 0.54 ppm is clearly observed for tetramethylsilane. This was stable for over a week while the sample was in the magnet, indicating the stability of the temperature as well as the concentration homogeneity of the solution. The tetramethylsilane line in the isotropic phase is 0.18 ppm upfield with respect to the lower field tetramethylsilane line in Figure 13. The corresponding separation from the higher field line is 0.36 ppm downfield which is twice that for the lower field line. C_{60} gives only a single sharp line at -140.37 ppm with respect to tetramethylsilane. This is exactly at the same position as in the isotropic phase. This observation shows that the order parameter, S , rather than the chemical shift anisotropy, $\Delta\sigma$, is zero and conclusively establishes that there are no detectable distortions from the I_h symmetry in C_{60} in solution. C_{60} is the first molecule found to be undistorted in a nematic liquid-crystalline media. It should serve as a reference in the study of chemical shift anisotropies in nematic phases.

Anions of C_{60} .

C_{60} is clearly very electrophilic as evidenced by cyclic voltammetry. Cyclic voltammetry carried out by Haufler *et al.*¹⁴ in CH_2Cl_2 solution with a glassy carbon electrode showed two reversible anionic

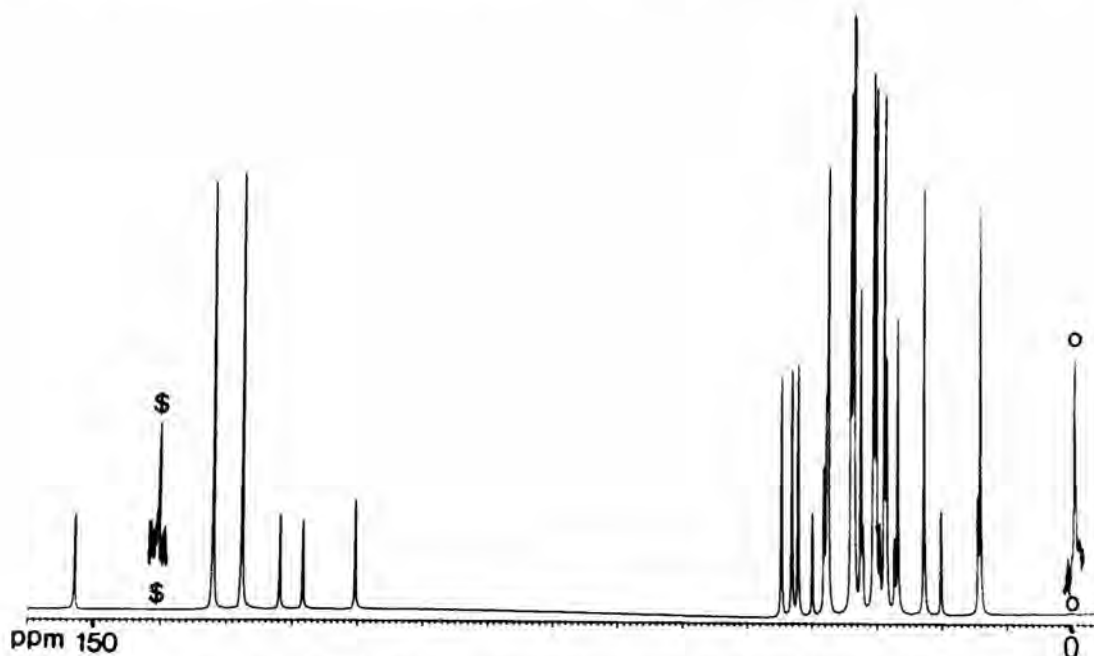


Fig. 12— ^{13}C NMR spectrum of solution (v) at 358.0 K (isotropic phase) showing the line of C_{60} (S) and tetramethylsilane (O). The lines due to C_{60} and tetramethylsilane are also shown with a magnified vertical scale

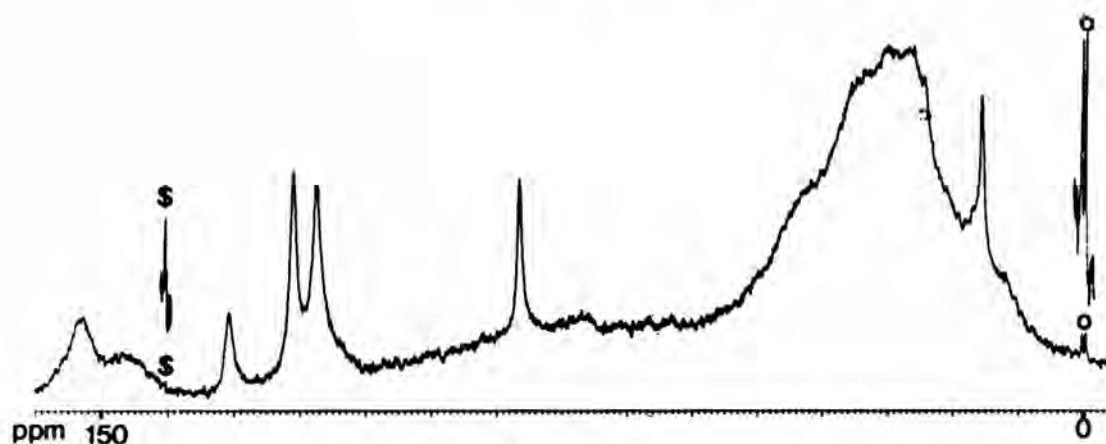


Fig. 13— ^{13}C NMR spectrum of solution (ν) at 332.4 K (nematic phase). The coexistence of two types of spectra is evident in the case of tetramethylsilane

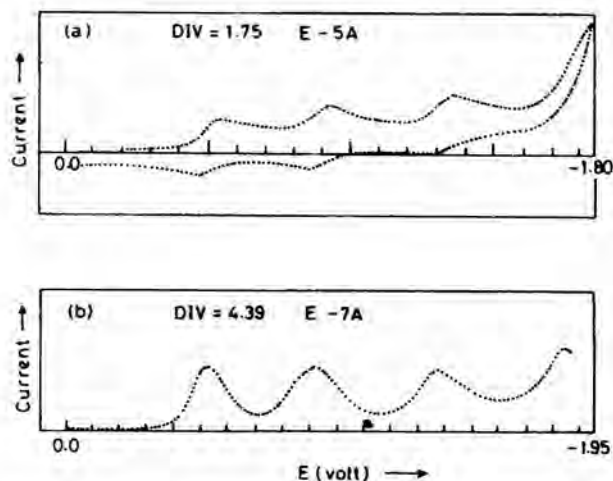


Fig. 14—(a) Cyclic voltammogram of C_{60} in CH_2Cl_2 solution (~ 1 mM). Au electrode with $0.05\text{ M}(\text{Bu})_4\text{NPF}_6$ as supporting electrolyte was used (scan rate 300 mV/s). (b) Differential pulse voltammogram of C_{60}

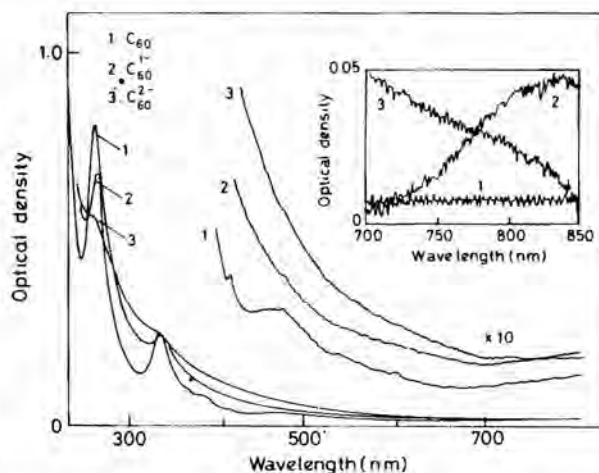


Fig. 15—Electronic absorption spectra of C_{60} , C_{60}^{1-} and C_{60}^{2-} obtained using a thin-layer spectroelectrochemical cell (electrolysis time 300 s). Inset shows the spectrum in the $700\text{--}850\text{ nm}$ region

forms. Dubois *et al.*¹⁵ found four reductions in the -0.4 to -1.7 eV range at a high scan rate of 20 V/s of which only the first two at 0.44 and 0.82 V were reversible. We have carried out cyclic voltammetry as well as differential pulse voltammetry in CH_2Cl_2 solution with Pt, glassy carbon and Au electrodes and found four one-electron reduction peaks in the range -0.4 to -1.9 V (Fig. 14). The reduction potentials are -0.464 , -0.856 , -1.292 and -1.661 V (vs Ag/AgCl), of which the first three are fully reversible while the fourth is quasi-reversible at a slow scan of $100\text{--}500\text{ mV/s}$. The four successive reduction potentials are independent of the electrodes and indicate the formation of C_{60}^{1-} , C_{60}^{2-} , C_{60}^{3-} and C_{60}^{4-} .

Thin-layer spectroelectrochemical measurements carried out with an optically transparent good mini-

grid electrode have enabled us to obtain good electronic absorption spectra of C_{60} and C_{60}^{2-} (Fig. 15). The UV absorption bands of C_{60} , besides showing red-shifts with respect to C_{60} , are less intense as expected. Also seen is a characteristic band at 830 nm due to C_{60} which disappears in the dianion. Our measurements also show that the two anions could be reversibly oxidized back to C_{60} .

Electron donor-acceptor interaction of fullerenes — a cyclic voltammetric study:

Recent studies have shown that C_{60} and C_{70} exhibit five one-electron reductions leading to the formation of mono, di, tri, tetra and penta anions and an irreversible oxidation at 1.76 V vs SCE. The last involves a four-electron oxidation process¹⁶. In our cyclic voltammetric (CV) studies, we observed the

formation of fullerene ion at 1.71 V (vs Ag/AgCl). The first reversible one-electron reduction of C₆₀ and C₇₀ occurs around -0.40 V (vs Ag/AgCl) in CH₂Cl₂ resulting in the formation of a mono-fulleride anion radical with a characteristic visible absorption band around 8.30 nm³. Pericaud *et al.*¹⁷ and Krusic *et al.*¹⁸ have shown that fulleride ion (C₆₀⁻) can function as a coordinating anion resulting in the formation of tetraphenylporphyrinatochromium (III) fulleride, [(CrTTP)⁺ C₆₀⁻]. Photolysis experiments involving C₆₀ with diverse donors result in formation of stable fulleride mono anion adducts. We have investigated the ground state electron donor-acceptor properties of fullerenes by cyclic voltammetry.

The donors chosen for the study are tetramethyl-para-phenylenediamine (TMPD), tetrakis-2,3,5,6-(N,N-dimethylamino)benzene (TDAB) and N,N,N',N'-tetramethylbenzidine (TMB) (Fig.16). Clearly, TDAB is a very powerful electron donor. It is recognized that CV studies of a mixture of an electron donor and an electron acceptor should re-

veal the existence and the strength of interaction in solution. In view of the fact that C₆₀ and C₇₀ are good electron acceptors, it is possible to observe the changes in their reduction potentials on interaction with the donors. Figure 17 displays the one-electron oxidation of the free donor TMPD in CH₂Cl₂. The voltammograms of solutions containing TMPD and the fullerenes reveal a marginal anodic shift of all the three reversible one-electron reduction peaks of C₆₀ and C₇₀. The fourth one-electron reduction of the fullerenes is irreversible and hence not reported. Interestingly, the oxidation peak of TMPD in the presence of the fullerenes is found to be split, suggesting interaction of TMPD with the fullerenes in the ground state. Tetramethylbenzidine in CH₂Cl₂ solution exhibits two reversible one-electron oxidations at +0.52 and +0.76 V (vs Ag/AgCl). These peak potentials remain unchanged on the addition of fullerenes; the one-electron reduction peaks of the fullerenes show no significant changes. These observations indicate that charge-transfer interaction of the fullerenes is minimal in these two donors.

We have obtained interesting results from our study of the interaction of C₆₀ with the powerful donor TDAB. TDAB in CH₂Cl₂ displays two oxidations at +0.22 and +0.30 V each corresponding to a two-electron process (Fig.18). On addition of C₆₀, each of the peaks is split into two peaks (with anodic and cathodic shift) exhibiting a four-step oxidation process. On the other hand, the first three reduction potentials of C₆₀ in the presence of TDAB are found to be shifted to the anodic side. The second reduction at -0.84 V becomes irreversible and possibly involves a two-electron process. These observations suggest that TDAB interacts fairly

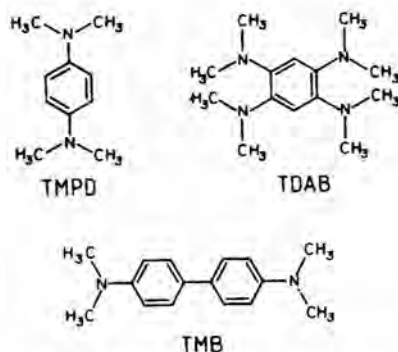


Fig. 16—Structures of the electron donors employed

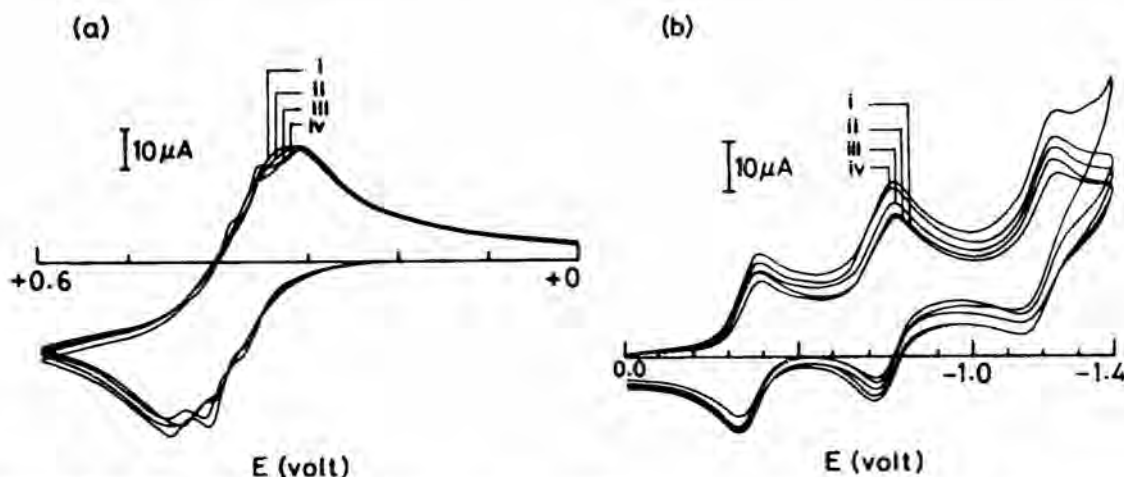


Fig. 17—(a) CV of (i) TMPD (0.5 mM) and (ii-iv) in the presence of different amounts of C₇₀ (1 mM – 5 mM) in CH₂Cl₂. (b) CV of (i) C₇₀ (0.5 mM) and (ii-iv) on successive addition of TMPD

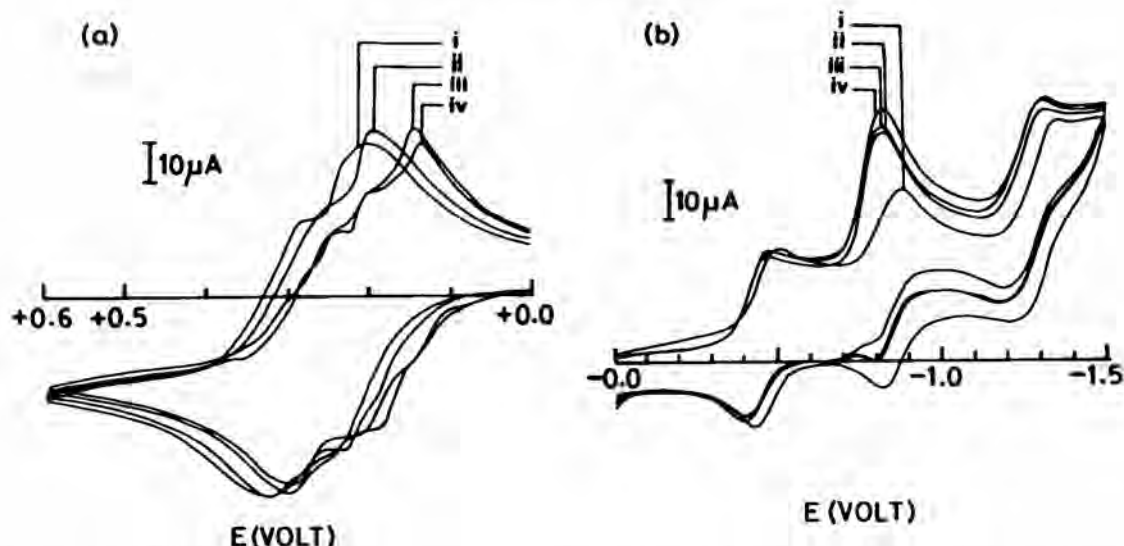


Fig. 18—(a) CV of (i) TDAB (0.5 mM) and (ii-iv) on successive addition of C_{60} (1 mM–10 mM) in CH_2Cl_2 . (b) CV of (i) C_{60} (0.5 mM) and (ii-iv) in presence of different amounts of TDAB (1 mM–10 mM) in CH_2Cl_2

strongly with C_{60} . The magnitudes of the shift is larger in case of the TDAB interaction relative to that obtained with the other two donors. These results agree with the recent finding¹⁹ that N,N-dimethylaniline forms a weak complex with C_{60} ($K_{ass} = 0.0047 \text{ dm}^3 \text{ mol}^{-1}$).

Preliminary CV studies on the interaction of fullerenes with tetraphenylporphyrato cobalt(II) in CH_2Cl_2 indicate that the oxidation of Co(II) (0.93V vs Ag/AgCl) in the porphyrin is shifted to lower potentials by about 80 mV. This indicates possible formation of fulleride anion coordinated Co(III) TPP species. However, use of ferrocene and ferricinium hexafluorophosphate does not seem to reveal any significant changes in their respective oxidation and reduction potentials on addition of C_{60} .

Superconducting properties of fullerene derivatives

Superconductivity around 20 K was first reported in potassium doped C_{60} by Hebard *et al.*²⁰. Since then, higher T_c 's upto 35 K have been achieved in Rb-Cs doped C_{60} ²¹. While C_{60} doped with rubidium alone shows a T_c of 28 K²², C_{60} doped with cesium is not superconducting. We have carried out several experiments on the superconducting properties of doped fullerenes and we present our results here.

In Fig.19 we show the appearance of non-resonant microwave absorption²³ by the controlled cooling of K_xC_{60} in zero-field signifying the presence of superconductivity below 21 K. We observe hysteresis on the forward and backward sweeps of the H-field confirming the granular nature of this superconductor. In Fig.20, we have plotted the intensity of the microwave signal against temperature to

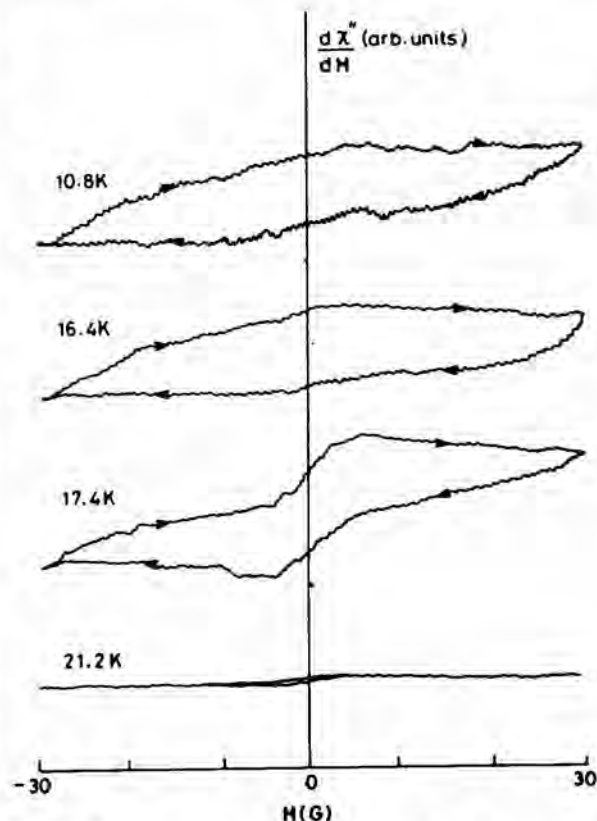


Fig. 19—Derivative microwave absorption by K_xC_{60} at various temperatures. Temperature dependence of the hysteresis is to be noted

demonstrate the sharp onset of superconductivity at 20 K. ESR studies of these samples showed the presence of a signal at room temperature as well as in the superconducting state which indicates the

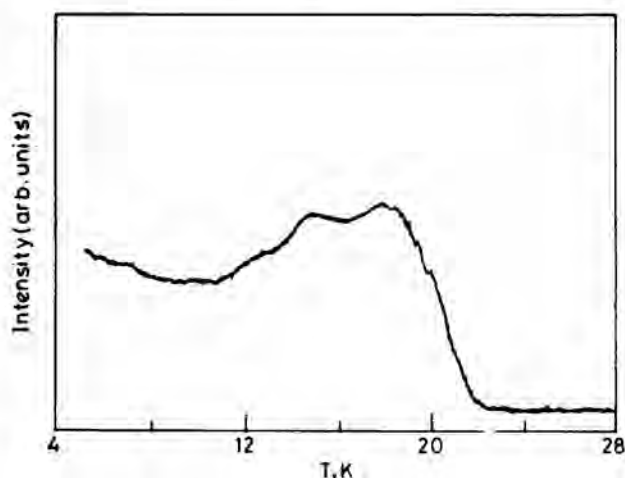


Fig. 20—Temperature dependence of the microwave absorption of K_xC_{60} .

presence of a non-superconducting impurity phase as reported previously²⁴. However, the nature of the ESR signal found by us is different in that at room temperature there is some structure in the signal whereas in the superconducting state there is only a single signal without structure. Although we do not have any control over the stoichiometry of the K_xC_{60} prepared by the solution route employed by us, the onset is sharp unlike in the case of the product obtained from solid state reaction.

We have carried out tests for superconductivity for the sodium salt of C_{60} which was synthesized by the reaction of a known excess of sodium metal with ~ 15 mg of C_{60} in toluene solution under conditions similar to those used for the preparation of K_xC_{60} sample. The black product of the reaction did not show any non-resonant microwave absorption above 4.5 K confirming the absence of superconductivity. We have also prepared potassium salt of C_{70} by the solution route. Although we got a black solid as the reaction product, there was no indication of superconductivity above 4.5 K.

Following a Japanese report²⁵ that C_{60} doped with iodine showed a superconducting transition around 60 K, we prepared several samples of C_{60} heated with iodine. Samples of nominal compositions I_2C_{60} and I_3C_{60} were prepared by the solid state reaction of pure C_{60} with iodine in a quartz tube of 5 mm diameter. The evacuated tubes were sealed under 10^{-2} torr of helium and heated first at 480 K for 50 h and later at 530 K for 25 h. Some of the samples of nominal composition I_2C_{60} were heated at 570 K for 50 h and for extended periods of time. The samples so obtained were examined by non-resonant microwave absorption. We found no evidence for superconductivity in any of the samples above 4.5 K. It

appears that the superconductivity in iodine-doped C_{60} reported in the literature is an artefact.

We tried to interact C_{60} with $SbCl_5$ to explore the possibility of superconductivity since $SbCl_5$ is a well-known electron acceptor. By refluxing a 1:1 mixture of $SbCl_5$ and C_{60} in CCl_4 solution, we got a brown product, due to the chlorination of C_{60} . Reacting C_{60} with liquid Br_2 gave a brominated product.

We have obtained results with Rb and Rb-Cs derivatives of C_{60} similar to those in the literature. We are now examining superconductivity in Pb_xC_{60} and other compounds.

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