

Solid state properties of C₆₀ and C₇₀

C.N.R. Rao, Ram Seshadri and A.K. Sood,

Solid State and Structural Chemistry Unit,
and Department of Physics,
Indian Institute of Science, Bangalore 560 012, India.

Properties of C₆₀ and C₇₀ in the solid state, in particular, the orientational phase transitions, pressure effects, ferromagnetism in C₆₀·TDAE and interaction with metal clusters are examined.

1. INTRODUCTION

Fullerenes exhibit novel molecular properties as well as chemical reactivity. In the solid state, they exhibit interesting properties and phenomena. In this presentation, we discuss few important aspects of solid C₆₀ and C₇₀. The topics covered include phase transitions associated with orientational order, effects of pressure on the structure and electronic properties, ferromagnetism in doped C₆₀ and interaction of C₆₀ and C₇₀ films with metal clusters.

2. PHASE TRANSITIONS OF C₆₀ AND C₇₀

Spherical molecules generally show orientational disorder in the solid state [1], and we would therefore expect that C₆₀ and C₇₀ show phase transitions associated with orientational order. Early structural studies on solid C₆₀ at room temperature showed that large thermal factors are necessary to obtain reasonable fits to X-ray data [2]. Based on the narrow NMR linewidths due to short orientational correlation times at room temper-

ature, solid C₆₀ was considered to be orientationally disordered [3,4]. X-ray diffraction and DSC measurements showed that C₆₀ undergoes a phase transition around 250 K on cooling from an orientationally disordered fcc phase to a sc phase where molecular rotation persists but only along preferred axes [5]. NMR studies show that below 250 K molecules jump between preferred orientations with a barrier of ~ 3000 K [6]. Molecular Dynamics simulation [7,8] reproduce experimental observations quite well. It seems necessary to add a Coulombic term to the L-J potential in order to reproduce the charge-transfer effects. Charge-transfer is also indicated by neutron diffraction measurements at 5 K [9], which show the proximity of electron-rich double bonds to adjacent electron-poor pentagonal faces.

Raman spectra of C₆₀ under pressure and related studies indicate the occurrence of an orientationally glassy state in C₆₀. Monte-Carlo studies [10] show that instantaneous cooling of the plastic-crystalline phase of C₆₀ leads to an orientational glassy

phase with $T_g \sim 80$ K (Figure 1). Neopentane which has a plastic phase, also shows a similar behavior. A glassy state in C_{60} has been experimentally observed using dilatometry [11].

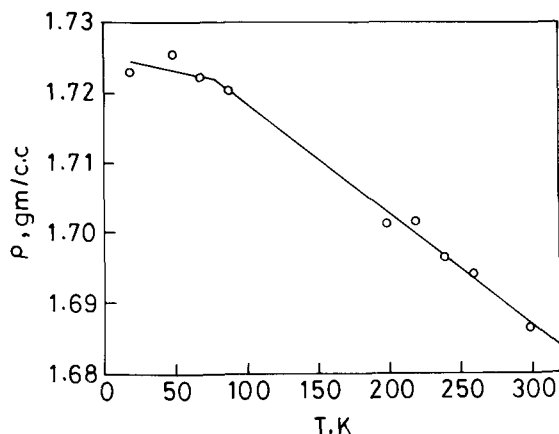


Figure 1. Density of C_{60} plotted as a function of temperature from isothermal, isobaric Monte Carlo simulations showing a transition ~ 80 K.

Ellipsoidal C_{70} shows a more complicated phase behavior than C_{60} . Vaughan et al. [12] reported two phase transitions of C_{70} at 337 K and 276 K. However, the structures of these three phases are yet to be established unequivocally. At room temperature and above, both fcc and hcp structures seem to coexist as they are energetically similar. Single crystals of as-grown C_{70} are usually twinned and unsuitable for X-ray studies. Based on X-ray studies, Verheijen et al. [13] reported the occurrence of fcc, rhombohedral, hcp2, hcp1 and distorted hcp phases on going from high to low temperatures. We have carried out powder X-ray diffraction studies on C_{70} as a function of temperature. The high-temperature phase is clearly

fcc and sluggishly transforms to a hcp phase. Thermal cycling increases the crystallinity of these materials as seen from X-ray line-widths. MD simulations [14] show that on cooling the high-temperature rotator phase, a transition to a phase with trigonal symmetry occurs followed by a transition to a mono-clinic phase.

Phase transitions of C_{70} have been investigated in this laboratory by both infrared [15] and Raman [16] spectroscopy. IR and Raman bands of sublimed C_{70} films show absorbance and linewidth changes across the orientational phase transitions around 340 K and 280 K (Figure 2). The phonon frequencies harden on cooling across these transitions possibly due to a combination of decreasing unit cell volume and increased intermolecular interactions. The linewidths decrease on cooling due to the hindering of the molecular motion resulting in a decrease in the rotational density of states. The changes in Raman frequency and linewidth across the phase transitions are continuous. This also appears to be true of C_{60} contrary to the earlier Raman work of van Loosdrecht et al. [17]. IR studies show evidence for the coexistence of phases in the 210-270 K region. Both IR and Raman spectra show that orientational disorder starts to freeze out below 150 K.

The effect of pressure on the phase transitions in C_{60} and C_{70} is interesting. In the case of C_{60} , the temperature of the transition at 250 K (at ambient pressure) increases at a rate of $10.3^\circ\text{C kbar}^{-1}$. The DSC curve of Samara et

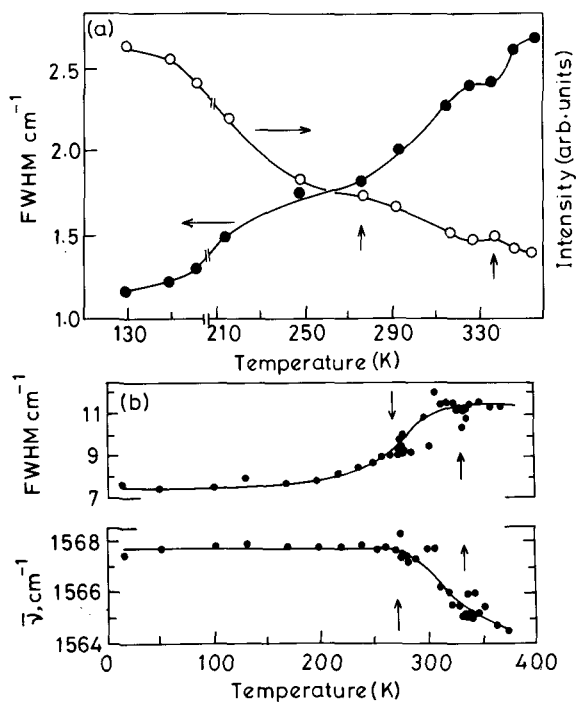


Figure 2 (a) Variation of the FWHM and intensity of the 643 cm^{-1} IR band of C_{70} with temperature. (b) Variation of the 1566 cm^{-1} Raman band FWHM and phonon frequency with temperature. Vertical arrows mark expected transition temperatures.

al. [18] shows a shoulder beyond 6 kbar indicating the presence of two nearly degenerate states near ambient pressure. Recent measurements (Ramasesha et al. to be published) show two distinct transitions. Raman investigations on C_{60} single crystals under pressure [19] show that the pentagonal pinch mode undergoes considerable softening around 3.5 kbar. The linewidth increases at higher pressures till around 130 kbar (Figure 3) when the lineshape has almost merged into the background indicating an orientationally glassy state as observed by others [11].

Under pressure, C_{70} shows three phase transitions, the highest transition temperature increasing

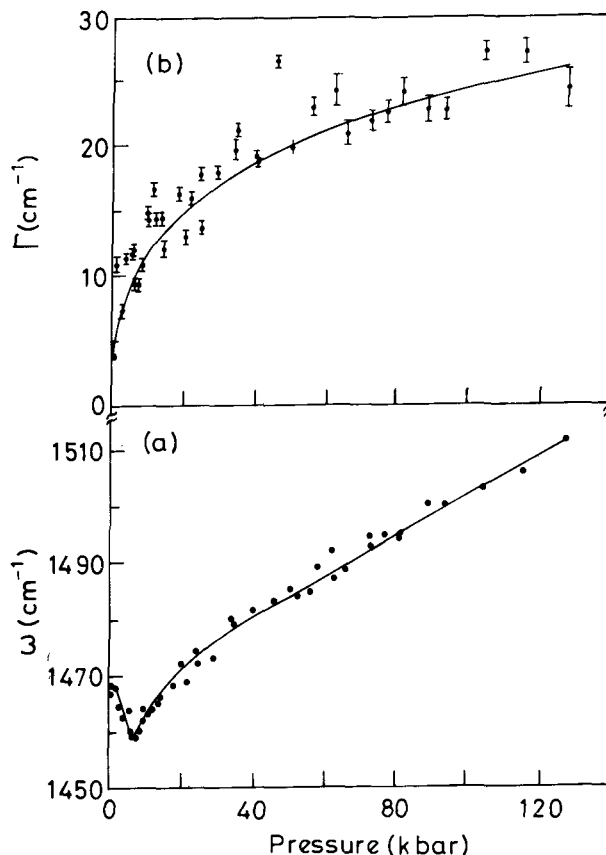


Figure 3 Variation of (a) the phonon frequency and (b) the linewidth of the C_{60} pentagonal pinch mode with pressure.

with pressure at a rate of $6.8^{\circ}\text{C kbar}^{-1}$, the lowest at $8.4^{\circ}\text{C kbar}^{-1}$ and the intermediate one at $5.3^{\circ}\text{C kbar}^{-1}$ (Ramasesha et al. to be published). At ambient pressure, two transitions are generally reported but the infrared studies of Varma et al. [15] indicate a plateau in FWHM and peak intensities around 330 K. A recent DSC study [20] shows however, three distinct transitions at 280, 330 and 337 K.

3. C_{60} LUMINESCENCE UNDER PRESSURE

Early high pressure studies on C_{60} crystals from this laboratory [21] showed that the photolumines-

cence band of C_{60} is red-shifted continuously with increasing pressure until at 3.2 GPa, the colour of the crystal changes from red to black, and the band disappears (Figure 4). Since the C_{60} ball itself is largely incompressible, this closing of the PL band is interpreted as being due to a broadening of the valence and conduction band arising from increasing inter-ball resonance. The near disappearance of the optical gap is consistent with decreasing activation energy for conduction with increasing pressure reported by a few

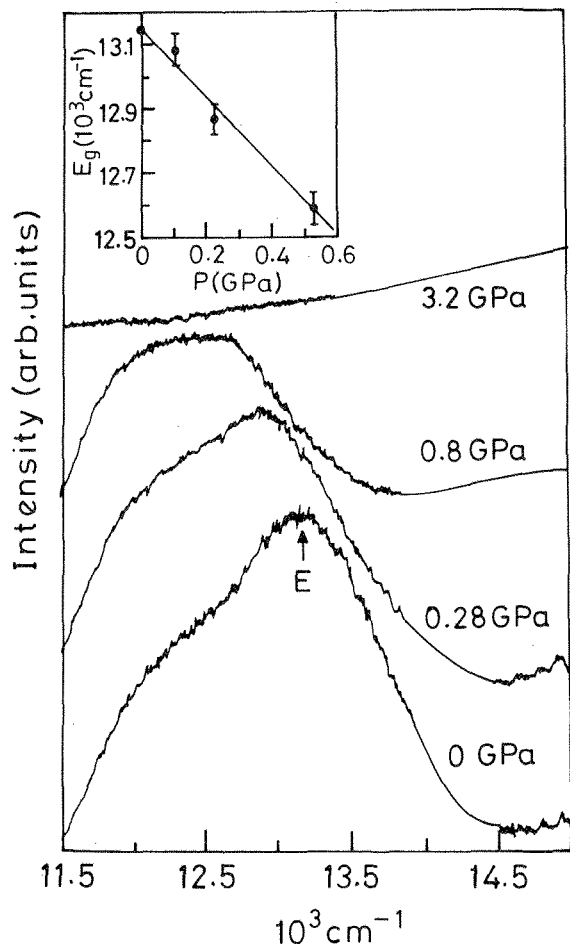


Figure 4 Photoluminescence band of C_{60} as a function of pressure. Inset shows variation of the optical gap with pressure.

workers. This study has certain implications for the strengths of electron-phonon coupling and therefore for superconductivity in alkali fullerenes.

4. FERROMAGNETISM IN C_{60} .TDAE

C_{60} is an excellent electron acceptor forming radical anions. With aromatic amines, it forms weak ground state complexes and exciplexes in solution [22]. A strong amine such as TDAE (tetrakis dimethylaminoethylene) forms a radical ion salt with C_{60} . C_{60} .TDAE is the best organic ferromagnet known to date with a T_c of 16 K [23]. The lattice structure has been established by X-ray studies [24]. The cell is monoclinic with a short C_{60} - C_{60} contact along the c-axis. ESR studies have shown that a single electron is doped from TDAE to C_{60} [25,26]. ESR linewidth decreases with decreasing temperature indicating that C_{60} .TDAE is metallic. Single-electron doping has been confirmed by our Raman studies, by titrating the observed phonon frequencies against n [27], using the data for C_{60}^{n-} from the $A_x C_{60}$ phases. As with $A_x C_{60}$, electron doping results in softening of the phonons. This phonon softening is consistent with theoretical calculations. Raman studies also show that the A_g modes of C_{60} in C_{60} .TDAE are split due to the lower symmetry of the system. By fitting the low-temperature susceptibility data to a series expansion for the spin-1/2, 1-D Heisenberg system [28], we have found evidence for quasi-ID behavior. The magnitude of the ferromagnetic coupling constant is 50 K. McConnell's model for ferromagnetic exchange has been used to understand this system [26,29] (Figure 5). Comparing C_{60} .TDAE with superconduct-

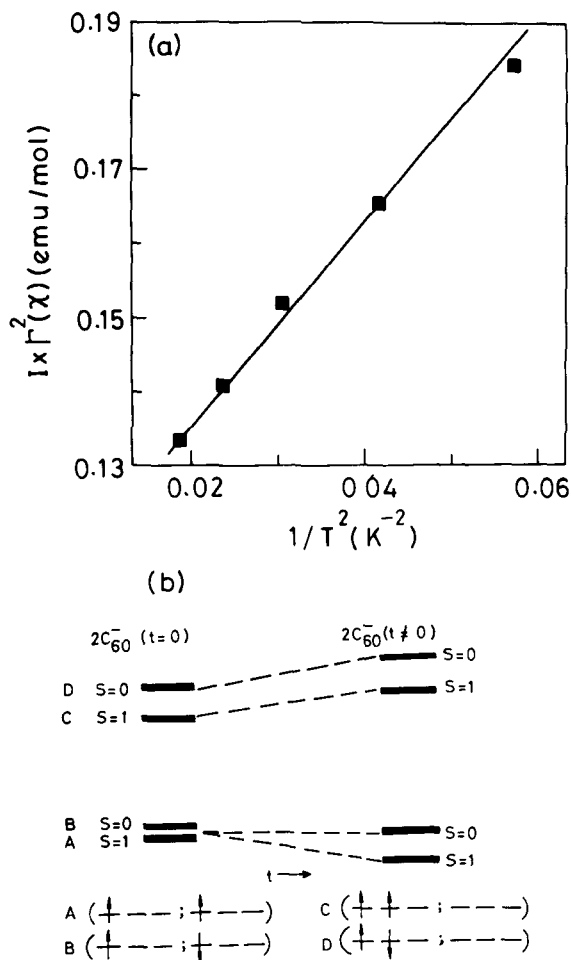


Figure 5 (a) Low temperature ESR susceptibility of C_{60} -TDAE plotted against $1/T^2$. (b) Configuration Interaction (CI) picture for a ferromagnetic ground state of singly occupied ground state of $2C_{60}^-$ species. t is the strength of the hopping integral.

ing A_3C_{60} , it would seem that the lower dimensionality and single electron doping are key features.

5. INTERACTION OF SOLID FILMS OF C_{60} AND C_{70} WITH TRANSITION METAL CLUSTERS

Interaction of varying coverages of transition metals such as Cu, Ni and Cr with C_{60} and C_{70} (depos-

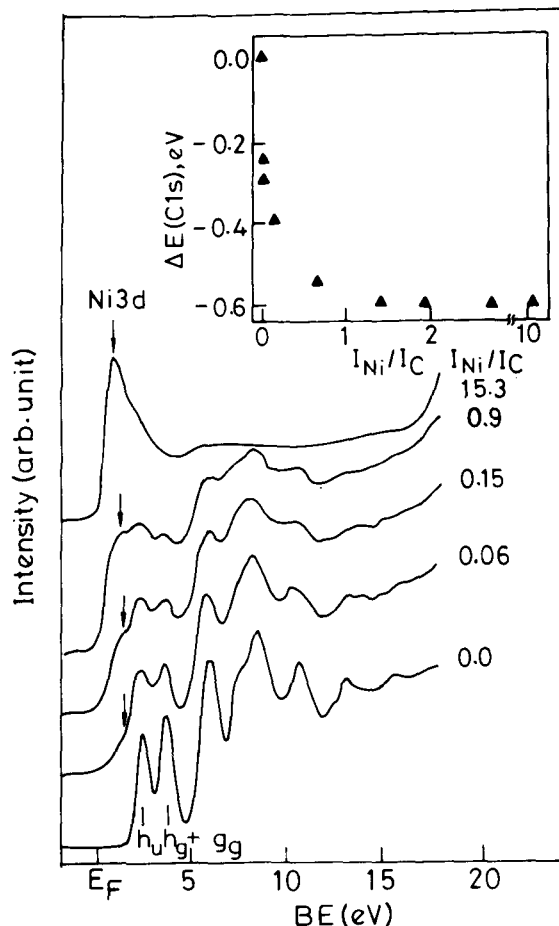


Figure 6 UPS valence band of C_{60} with increasing Ni coverage. Inset shows change in C1s binding energy as a function of Ni coverage.

ited under UHV) have been studied by UPS and XPS [30]. The observed shifts in the valence band of C_{60}/C_{70} with increasing Ni coverage is accompanied by a shift of the C1s level of the fullerene to a lower binding energy as depicted for C_{60} in Figure 6. This suggests charge transfer from metal to fullerene, an observation of possible implications in catalysis. The

fullerenes are known to act as electron deficient π systems in solution [31].

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