

PRESSURE-INDUCED SHIFT OF THE PHOTOLUMINESCENCE BAND IN SINGLE CRYSTALS OF BUCKMINSTER FULLERENE C<sub>60</sub> AND ITS IMPLICATIONS FOR SUPERCONDUCTIVITY IN DOPED SAMPLES

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We report the first observation of a large pressure-induced red-shift of the photoluminescence band in single crystals of C<sub>60</sub> and the associated colour change of the sample from red to black at ~ 3.2 GPa. Interpreting the red shift of the luminescence band as a reduction of the bandgap E<sub>g</sub> of the crystal, we got the pressure derivative  $\partial E_g / \partial P = -0.138$  eV/GPa. This result taken in conjunction with the known compressibility, gives the deformation potential  $\partial E_g / \partial(\ln a) = 6.0$  eV, where 'a' is the lattice constant. Taking the same value for the alkali-doped fullerene, and combining it with the known pressure dependence of the transition temperature in the context of a simple BCS expression for T<sub>c</sub> we estimate the electron-phonon coupling parameter  $\lambda = 0.3$ .

The development of a simple technique for preparing the novel allotrope of carbon C<sub>60</sub> (Buckminster fullerene) routinely in copious quantities [1] has climaxed in the discovery of superconductivity in the alkali-metal doped samples A<sub>x</sub>C<sub>60</sub> (A = K, Cs, and Rb) with relatively high T<sub>c</sub> in the 18K - 40K range [2,3]. This has opened up new avenues both for materials science as well as theoretical aspects of superconductivity.

Though our present knowledge concerning the electronic structure of solid C<sub>60</sub> is far from being complete, we believe we have obtained an interesting result through a pressure experiment which has relevance to the electronic structure as well as the pressure dependence of the superconducting transition temperature T of doped C<sub>60</sub>.

Through a measurement of the shift in the photoluminescence peak with pressure we derive the pressure dependence of the bandwidths which combined with the known

pressure-[4] or lattice constant-[5] dependence of T<sub>c</sub> allows us to estimate the electron-phonon coupling constant. These results are relevant in the context of the recent debates on electronic [6] vis-à-vis phononic [7] mechanisms for superconductivity in doped fullerenes. These results will be presented and discussed in this paper.

C<sub>60</sub> was prepared by contact-arc vaporization of graphite in a Helium atmosphere by employing a locally fabricated generator [8]. The soot was initially washed with ether and the toluene extract of the residue was used for obtaining pure C<sub>60</sub>. The identity of C<sub>60</sub> was ensured by mass spectrometry and NMR spectroscopy. Single crystals of C<sub>60</sub> (size 80 x 80 x 25 μm) were grown by slow evaporation of the toluene solution. Our crystals were free from C<sub>70</sub>. This was confirmed by the absence

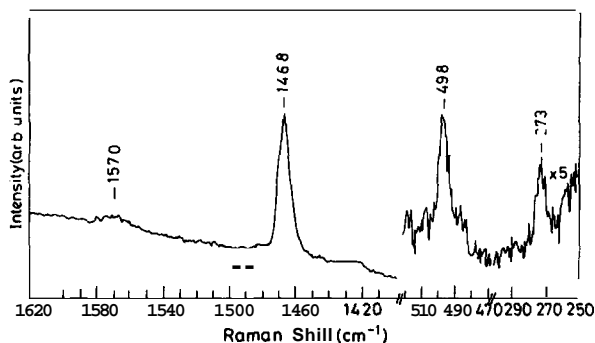


Fig. 1. Room temperature Raman spectrum of single crystal of  $C_{60}$ . Laser wavelength = 5145 Å, Laser power = 5 mW and spectral resolution =  $5\text{ cm}^{-1}$ .

of Raman lines at 260 and  $1570\text{ cm}^{-1}$  (strong phononic fingerprints of  $C_{70}$  [9]) in the recorded spectra of the crystals (see Fig. 1).

High pressure luminescence studies were carried out at room temperature in a gasketed Mao-Bell type diamond anvil cell with 4:1 methanol-ethanol mixture as pressure transmitting medium. Pressure was measured by the well known ruby fluorescence technique [10]. The ruby crystal (size  $\sim 20\ \mu\text{m}$ ) was kept as far away from the sample in the gasket hole (hole size  $\sim 250\ \mu\text{m}$ ) as possible so that the ruby fluorescence does not interfere significantly with the luminescence from the sample. The fluorescence from the ruby in the narrow range ( $\sim 14400$  to  $13500\text{ cm}^{-1}$  at ambient pressure) has been subtracted from the observed luminescence spectra. Photoluminescence (PL) spectra were recorded using a Spex double monochromator equipped with a conventional photon counting system. The 5145 Å laser line from an argon ion laser at a power level of  $\sim 30\text{ mW}$  was used for exciting the luminescence. The response of the spectrometer falls off after  $11500\text{ cm}^{-1}$  and hence the spectra are shown only up to this wavenumber.

Figure 2 shows the PL spectra recorded (after subtracting the ruby fluorescence) at four different pressures, 0.0, 0.23, 0.8 and 3.2 GPa. The inset shows the pressure dependence of the PL band maxima, marked as  $E_g$ , in the low pressure region. It is to be noted that the luminescence intensity decreases with increasing pressure and is not detectable beyond 3 GPa (see top curve in Fig. 2). This is accompanied by

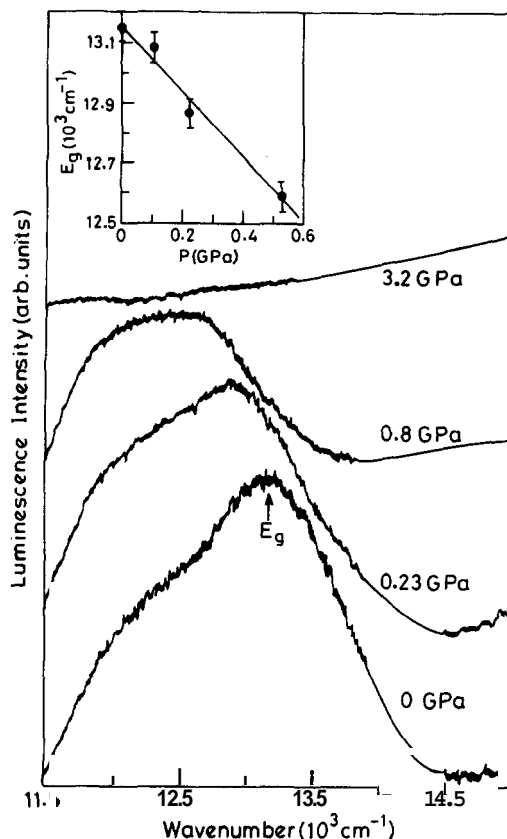


Fig. 2. The room temperature luminescence spectra of single crystal of  $C_{60}$  at four different pressures 0.0, 0.23, 0.8 and 3.2 GPa. The inset shows the variation of the peak positions, marked as  $E_g$ , for low pressures. The solid line in the inset is the linear least square fitted curve.

a striking colour change from red to black. The spectra at ambient pressure is similar to that reported earlier on solid  $C_{60}$  films at 20 Å by Reber et al [11] who have also reported the corresponding absorption spectrum.

In order to understand the observed PL spectra, we will discuss briefly the relevant electronic structure of  $C_{60}$  solid. Simple symmetry-based molecular orbital considerations suggest that the carbon atoms on the  $C_{60}$  ball are strongly  $\sigma$ -bonded by the tangential  $sp_2$  hybridized orbitals, while the radial p orbitals ( $\pi$  orbitals) combine linearly to give a five-fold degenerate highest occupied molecular orbital (HOMO) of h

symmetry and a three-fold degenerate lowest unoccupied molecular orbital (LUHO) of symmetry with the calculated HOMO-LUMO gap of -1.9 eV [12,13]. These molecular orbitals are, of course, broadened into the corresponding bands in the molecular solid. However, the  $C_{60}$ - $C_{60}$  interball overlaps are small (van der Waals), the bands are expected to be narrow. Experimentally [14] the conduction bandwidth is -0.6 eV which agrees well with the calculated one using the local density approximation (LDA) [13]. This bandwidth is, however, much larger than that of the conventional molecular solids like anthracene and naphthalene (bandwidth (W) - 10 to 20 meV) [15]. The latter is much less than the excitonic binding energy as well as  $k_B T$  in these systems. This makes it more appropriate to treat the optical properties of the conventional molecular solids in terms of localised states (e.g. singlet and triplet excitons) rather than in terms of band picture. On the other hand, in the present case of  $C_{60}$  solid W (- 0.6 eV, which is much larger than  $k_B T$ ) is expected to be larger than the excitonic binding energy. The latter can be roughly estimated to be - 27 meV with the calculated [13] dielectric constant (=18) and effective band masses of electrons and holes. Hence it is justifiable to use the band picture for  $C_{60}$ . Also, the state of the art LDA calculations of Saito and Oshiyama [13] show that the fcc  $C_{60}$  solid is a semiconductor with a direct band gap of - 1.5 eV at the X-point in the Brillouin zone. Although the LDA calculation may be underestimating the bandgap, the overall band structure features can be relied upon. We therefore identify the (pressure dependence of the) luminescence band maximum as (that of) the band gap  $E_g$  at the critical point. Since the observed luminescence maximum (- 1.63 eV) is close to the calculated direct band gap (1.5 eV) at the X-point [13], we believe that the electron-hole recombination responsible for luminescence takes place at the X-point. The interpretation of our data however, does not depend on the exact location of the bandgap in the electronic structure of solid  $C_{60}$ . Thus our picture of photoluminescence is that the electron-hole pairs created by the

exciting radiation of 2.41 eV or 2.56 eV itinerate non-radiatively to a critical point of the Brillouin zone where they recombine radiatively.

With the above interpretation in mind, the least-square fitted derivative (see the solid line in the inset in Fig.2.) gives  $\partial E_g / \partial P = -0.138 \text{ eV/GPa}$ . Using the known compressibility [16]  $\partial(\ln a)/\partial P = -2.3 \times 10^{-2} (\text{GPa})^{-1}$ , we get the "deformation potential"  $\partial E_g / \partial(\ln a) = 6 \text{ eV}$ . (The change in colour can also be understood as arising from the increase in the absorption coefficient of the visible light due to significant reduction in the band gap). We may add that irrespective of the details of the band picture for solid  $C_{60}$ , our measured pressure-induced large red shift of the luminescence unequivocally tells that the  $C_{60}$  -  $C_{60}$  interball hopping matrix element is a sensitive function of pressure [9]. The effect of pressure on the HOMO-LUMO bands of a single  $C_{60}$  ball can be neglected because of the high stiffness of the ball [16]. In band picture, therefore, our measured reduction of the band gap is directly related to the broadening of the valence and conduction bands due to increased interball resonance interaction. Assuming equal dispersion for the two bands (of width W),  $\partial E_g / \partial(\ln a) = -\partial W / \partial(\ln a)$ . This in turn gives the pressure dependence of the density of states N which scales as  $W^{-1}$ .

It is interesting to note that a combination of the above information with the known pressure- [4] or lattice constant- [5] dependence of the transition temperature  $T_c$  for doped  $C_{60}$  in the context of a BCS-electron-phonon mechanism formula for  $T_c$  allows one to estimate the dimensionless electron-phonon coupling constant  $\lambda$ . Ignoring coulomb pseudopotential effects, one has  $d(\ln T_c) / d(\ln a) = -\lambda^{-1} d(\ln W) / d(\ln a)$ , where  $\lambda = VN(E_f)$ . Here V is a measure of the electron-phonon coupling and is expected to be insensitive to pressure [5]. Thus the entire pressure dependence of  $T_c$  has been attributed to  $N(E_f)$ . Taking  $W=0.6 \text{ eV}$  [14], our data  $d(\ln W) / d(\ln a) = -10.1$  together with the measured [5]  $d(\ln T_c) / d(\ln a) = 40.2$  suggests  $\lambda=0.25$ . If the dispersion of the valence band were to be neglected,  $\lambda$

would be 0.5. These values of  $\lambda$  fall in the range reported recently ( $\lambda = 0.25$  to  $0.6$ ) (71 supporting a electron-phonon coupling mechanism for pairing).

In conclusion, we report here the pressure - induced changes in the band gap of single cryetale of C<sub>60</sub> for the first time and use the preeeure derivative of the band gap in conjunction with that of  $T_c$ , to make a simple estimate of the BCS based electron-phonon coupling constant. From the measured red shift, the band gap in crystalline C<sub>60</sub> will extrapolate (linearly) to zero at  $-13$  GPa, suggesting a ineulator-metal transition. If, however, there is a phase transition intruding, this event could well happen even at leeer preseuree. It would be interesting to investigate whether such a pressure induced metallization does occur, and if so, whether the resulting (undoped) metallic C<sub>60</sub> at high pressures is superconducting.

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