PRESSURE-INDUCED SHIFT OF THE PHOTOLUMINESCENCE BAND IN SINGLE CRYSTALS
OF BUCKMINSTER FULLERENE C₆₀ 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 C₆₀ and the associated color 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 Δ₀ of the crystal, we get the pressure derivative ΔE₁ΔP = -0.138 eV/GPa. This result, taken in conjunction with the known compressibility, gives the deformation potential ΔE₁ΔP(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 Tc, we estimate the electron-phonon coupling parameter λ = 0.3.

The development of a simple technique for preparing the novel allotrope of carbon C₆₀ (Buckminster fullerene) routinely in copious quantities [1] has climaxed in the discovery of superconductivity in the alkali-metal doped samples A₅C₆₀ (A = K, Cs, and Rb) with relatively high Tc 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 C₆₀ 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 C₆₀.

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 Tc allows us to estimate the electron-phonon coupling constant. These results are relevant in the context of the recent debates on electronic [6] vs-α-phononic [7] mechanisms for superconductivity in doped fullerenes. These results will be presented and discussed in this paper.

C₆₀ 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 C₆₀. The identity of C₆₀ was ensured by mass spectrometry and NMR spectroscopy. Single crystals of C₆₀ (size 80 x 80 x 25 μm) were grown by slow evaporation of the toluene solution. Our crystals were free from C₇₀. This was confirmed by the absence
Fig. 1. Room temperature Raman spectrum of single crystal of C₆₀. Laser wavelength = 5145 Å, Laser power = 5 mW and spectral resolution = 5 cm⁻¹.

of Raman lines at 260 and 1570 cm⁻¹ (strong phononic fingerprints of C₇₀ [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 20 μm) was kept as far away from the sample in the gasket hole (hole size 250 μm) 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 (-14400 to 13500 cm 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 ~30 mW was used for exciting the luminescence. The response of the spectrometer falls off after 11500 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 variation of the peak positions, marked as E₁g, 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 C₆₀ 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 C₆₀ solid. Simple symmetry-based molecular orbital considerations suggest that the carbon atoms on the C₆₀ ball are strongly σ-bonded by the tangential sp² hybridized orbitals, while the radial p orbitals (π 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 (LUMO) 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 kT 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 solid W (-0.6 eV, which is much larger than kT) 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, doesnot 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 \( \partial E/\partial P = -0.138 \text{ eV/GPa} \). Using the known compressibility [16] \( \delta(\ln a)/\delta P = -2.3 \times 10^{-6} \text{ eV} \), we get the "deformation potential" \( \delta E/\delta(\ln a) = 6 \text{ eV} \). (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), \( \delta W/\delta(\ln a) = - \delta W/\delta(\ln a) \). This in turn gives the pressure dependence of the density of states N which scales as W. 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 \( d(\ln T_c)/d(\ln a) = -\lambda^2 d(\ln W)/d(\ln a) \), 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 eV [14], our data d(\ln W)/d(\ln a) = -10.1 together with the measured [5] d(\ln T)/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 ($A - 0.25$ 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 C60 for the first time and use the pressure 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 C60 will extrapolate (linearly) to zero at -13 GPa, suggesting a insulator-metal transition. If, however, there is a phase transition intruding, this event could well happen even at lower pressures. It would be interesting to investigate whether such a pressure induced metallization does occur, and if so, whether the resulting (undoped) metallic C60 at high pressures is superconducting.

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REFERENCES