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# The optical absorption and photoluminescence spectra of C<sub>60</sub> single crystals

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**Abstract.** A constant photocurrent method (CPM) was used to determine the relative optical absorption coefficient of the C<sub>60</sub> single crystal in the weak-absorption region. The result suggested the existence of extrinsic states in the C<sub>60</sub> single crystal. The photoluminescence (PL) peaks of the C<sub>60</sub> single crystal were observed at 1.48 eV and 1.65 eV these positions are different from those of C<sub>60</sub> thin films.

## 1. Introduction

Since the fullerenes became available in quantity [1] and crystalline C<sub>60</sub> turned out to have a face-centred cubic (FCC) structure, C<sub>60</sub> has attracted attention as a new functional material. In the FCC structure the C<sub>60</sub> molecules are brought together by weak Van der Waals forces. The (HOMO–LUMO) energy gap is estimated to be 1.5–2.0 eV by a UPS experiment [2] for C<sub>60</sub> clusters. Saito *et al* reported using a local density approximation that the energy gap between the h<sub>u</sub> (HOMO) state and T<sub>1u</sub> (LUMO) was calculated to be 1.9 eV for the C<sub>60</sub> cluster and that the band gap of solid C<sub>60</sub> with FCC structure was calculated to be about 1.5 eV, which is optically forbidden [3]. In the EELS study of solid fullerite the energy gap was estimated to be 1.8 eV [4]. These values are consistent with the optical spectrum reported to have an onset at about 1.5 eV for solid C<sub>60</sub> [5]. Recently Lof *et al* [6] concluded from photoelectron and inverse photoelectron spectra of solid C<sub>60</sub> that the band gap of solid C<sub>60</sub> is about 2.3 eV and that the 1.5 eV optical onset is of excitronic origin.

However, the C<sub>60</sub> single crystal is not easily prepared for measurements, which have mostly been carried out on C<sub>60</sub> thin films. Here we present the optical spectrum by a constant photocurrent method (CPM) and the photoluminescence (PL) spectra for C<sub>60</sub> single crystals, to make a comparison with those reported for C<sub>60</sub> thin films.

## 2. Experimental details

### 2.1. Sample preparation

A commercial pure C<sub>60</sub> (99.9%) was sealed in a quartz tube (1 cm ID, 12 cm in length) under 10<sup>-5</sup> Torr vacuum in a quantity of 20–50 mg. The quartz tube was kept at 560–600 °C at the end with the raw material and at 520–540 °C at the other end. The growth of C<sub>60</sub> crystals was continued for a few weeks. The largest size of crystal obtained by the sublimation process is about 3 mm×2 mm×0.8 mm. By x-ray diffraction measurement the

crystals were identified to be FCC. The single crystals were stored in vacuum immediately after preparation.

The  $C_{60}$  thin films were prepared by a vapour deposition method. The  $C_{60}$  powder was put into a W boat and heated to about  $500^{\circ}\text{C}$  to deposit on an Si single crystal which was kept at room temperature. The films did not show any crystalline peak in x-ray diffraction measurements.

## 2.2. Measurements

Sub-band-gap optical absorption spectra of the  $C_{60}$  single crystal were measured with the CPM, which was proposed by Vanecek *et al* [7] for observing the defect states in hydrogenated amorphous silicon (a-Si:H). In the CPM measurement, coplanar-type Au electrodes with a gap of 0.1 mm were evaporated on the  $C_{60}$  single crystal and a DC bias voltage of 9 V was applied between the electrodes at room temperature in air. A chopped low-frequency photocurrent (13 Hz) was kept constant by adjusting the number of photons when the photon energy  $h\nu$  of monochromatic incident light was varied. Figure 1 shows the experimental set-up for the CPM measurement.

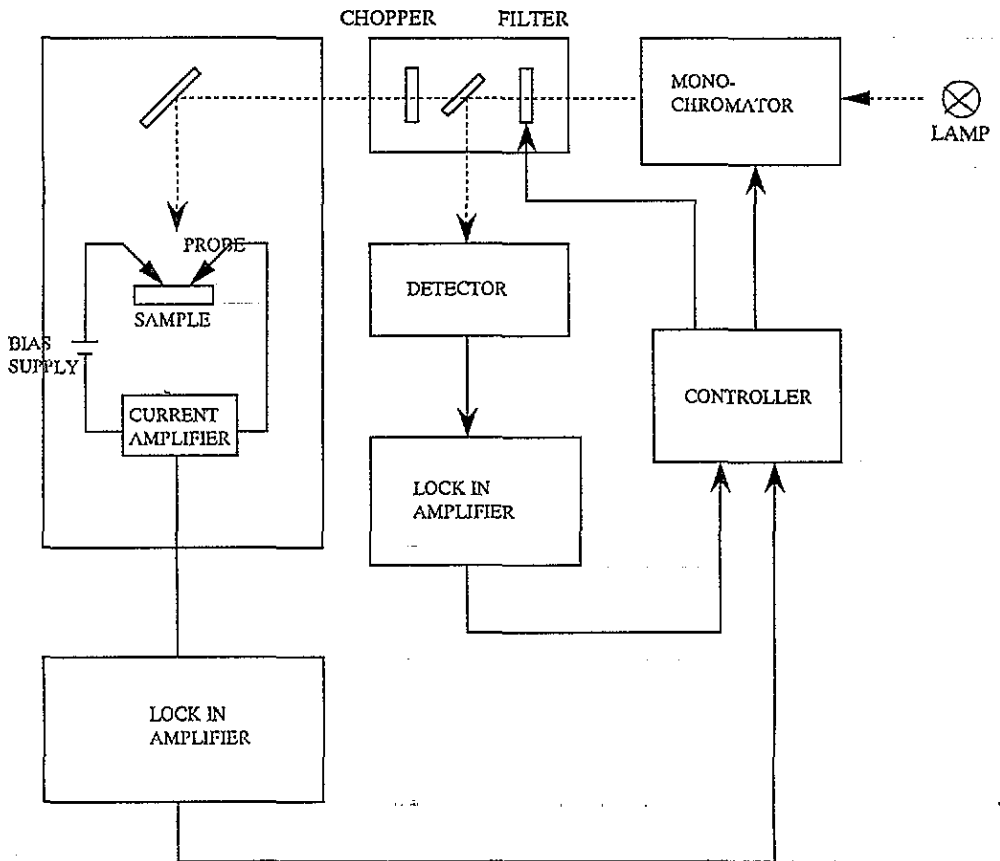


Figure 1. The experimental set-up for the CPM measurement.

An excitation source of the 514.8 nm line of an Ar laser, a Jobin-Yvon HR 640 monochromator and Hamamatsu Photonics R943-02 photon-counting electronics were used in the PL experiments. To ensure that the PL spectra were intrinsic to the samples, the wavelength-dependent response of the equipment was corrected by the spectral irradiance standard lamp against CIE. The measurements were carried out in the temperature range of 50–300 K.

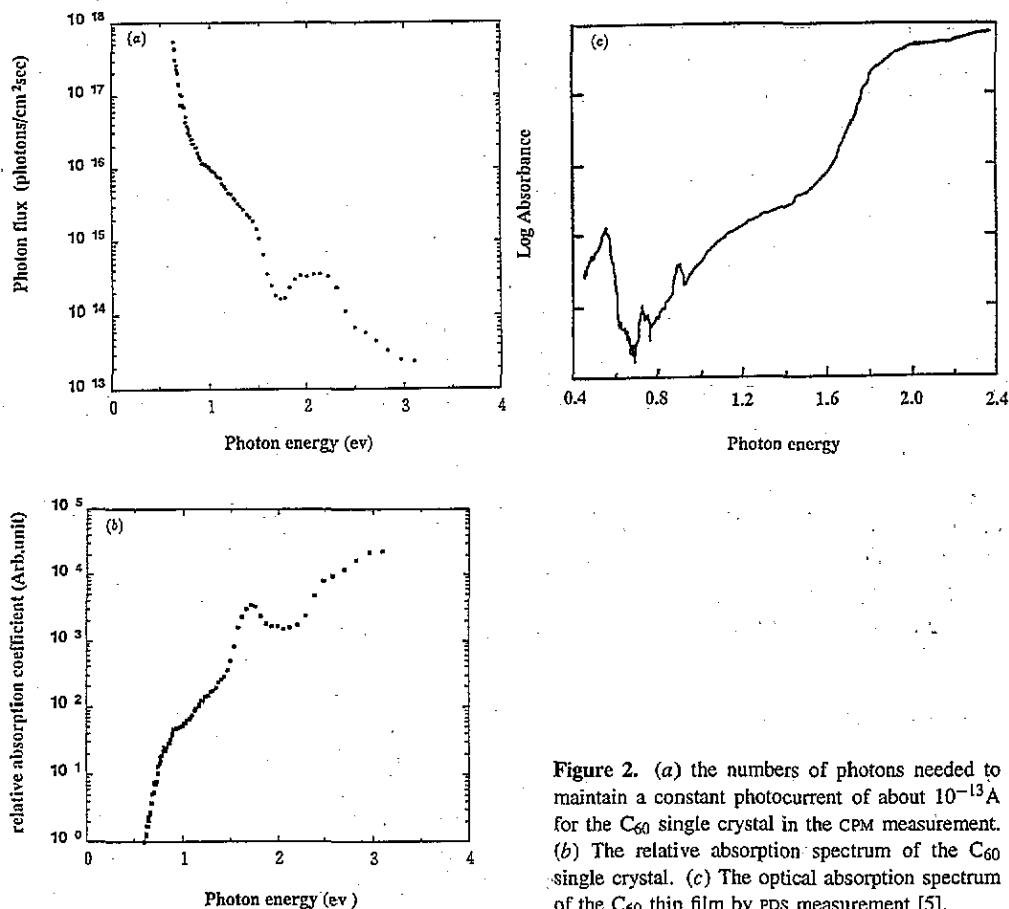


Figure 2. (a) the numbers of photons needed to maintain a constant photocurrent of about  $10^{-13}$  A for the C<sub>60</sub> single crystal in the CPM measurement. (b) The relative absorption spectrum of the C<sub>60</sub> single crystal. (c) The optical absorption spectrum of the C<sub>60</sub> thin film by PDS measurement [5].

### 3. Results

#### 3.1. CPM spectrum

Figure 2(a) shows the fluxes of photons required to excite the C<sub>60</sub> single crystal to keep a constant chopped photocurrent of about  $10^{-13}$  A for the photons in the range of  $\sim 0.6$ – $3.0$  eV. The relation between the photoconductivity  $\sigma$  and optical absorption coefficient  $\alpha$  can be given by

$$\sigma = qF(1 - R)\alpha\eta\mu\tau \quad (1)$$

where  $q$  is the electric quantum of an electron,  $F$  is the flux of photons,  $R$  is the reflectivity of the sample,  $\mu$  is the mobility of the electrons, and  $\tau$  is the lifetime of the electrons. When the photocurrent is kept constant, the product of  $F(1-R)\alpha$  must be constant. As the change of  $(1-R)$  is much smaller than that of  $\alpha$ , the absorption coefficient  $\alpha$  can be regarded as being inversely proportional to the photon flux  $F$ . Figure 2(b) shows the relative absorption spectrum of the  $C_{60}$  single crystal in the range of 0.6–3.0 eV. On the other hand, the ratio of the photoconductivity of the  $C_{60}$  thin films to its dark conductivity was too small to obtain steady and reproducible data by CPM measurement. However, the weak-absorption region of the  $C_{60}$  thin films has been reported by Skumanich using photothermal deflection spectroscopy (PDS) [5]. For comparison, the PDS spectrum for the  $C_{60}$  thin film is shown in figure 2(c). Both CPM and PDS measurements are used for measuring the weak-absorption region of samples. The CPM measurement is suitable for measuring the absorption of the bulk, but not suitable for measuring the absorption of samples with a high concentration of defects or impurities, while the PDS measurement is sensitive to the surface of samples and can be used for measuring samples with a high concentration of defects or impurities. The increase of the absorption coefficient near 0.6 eV as shown in figure 2(b) suggests that there are some sub-gap states which are 0.6 eV below the conduction band or above the valence band. In a-Si:H, the sub-gap states are formed by the existence of dangling bonds, which are characteristic of the amorphous structure. On the other hand, in crystalline  $C_{60}$ , the  $C_{60}$  clusters are brought together by Van der Waals forces without dangling bonds forming. It seems to be unlikely that these states are caused by defects in  $C_{60}$  itself. It is known that even in  $C_{60}$  crystals, there is O intercalating in the cells [8]. We assume that the states located in the forbidden gap of the  $C_{60}$  crystal result from impurities related to O intercalation.

As shown in figure 2(b), we observed a steep increase of the  $\alpha$  value from 1.5 eV to 1.7 eV and a decrease of absorption in the range of 1.7–2.0 eV. This decrease can be caused by the increase of recombination rate near the surface due to the increase of absorption.

### 3.2. Photoluminescence

The PL peaks were observed at 1.48 eV and 1.65 eV for the single crystal at 50 K as shown in figure 3. The intensity of the PL increases with decreasing of temperature, but the general appearance of the luminescence spectra was similar in the temperature range of 50–270 K. PL experiments on  $C_{60}$  have been performed on  $C_{60}$  or  $C_{60}/C_{70}$  thin films by many groups [9, 10], but our report is the first one on a  $C_{60}$  single crystal. There are discrepancies in the reported PL peaks of  $C_{60}$  thin films because of uncontrolled ambients. The origin of the luminescence was attributed to the decay of polarons–excitons which are known in conjugated polymers.

For comparison, the PL measurement was carried out for the  $C_{60}$  thin films prepared from the same raw material as the  $C_{60}$  single crystal. The result is shown in figure 4. The peaks (50 K) were observed at 1.51 eV and 1.69 eV, which had shoulders at 1.61 eV and 1.66 eV. The results are close to those of Sauvajol *et al* [11] for pure  $C_{60}$  thin film. The peaks at 1.66 eV, 1.61 eV and 1.51 eV can be assigned to  $250\text{ cm}^{-1}$ ,  $730\text{ cm}^{-1}$  and  $1468\text{ cm}^{-1}$  phonon replicas. On the other hand, for the  $C_{60}$  single crystal the peaks (50 K) shifted down to 1.65 eV and 1.48 eV and the phonon replicas of  $250\text{ cm}^{-1}$  and  $730\text{ cm}^{-1}$  were not found. The shift of the main peak to a low-energy region implies a smaller energy gap for the  $C_{60}$  single crystal than the  $C_{60}$  thin film.

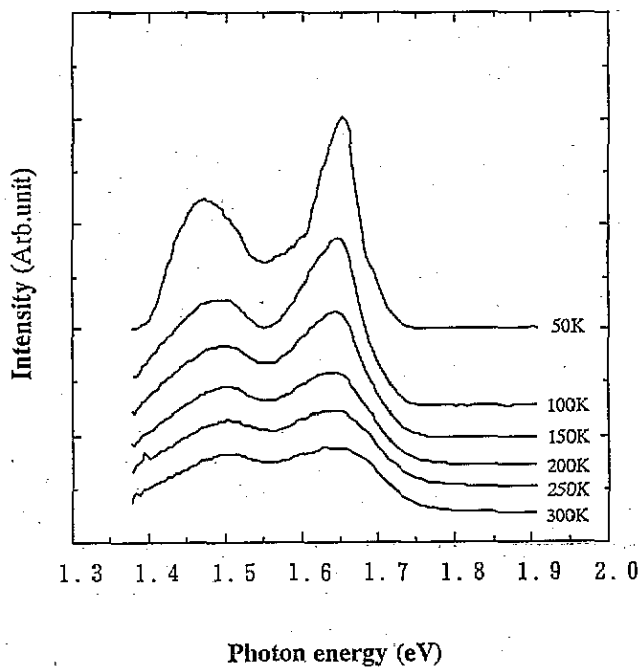


Figure 3. The PL spectra (50–300 K) of the  $C_{60}$  single crystal. Peaks were observed at 1.48 eV and 1.65 eV.

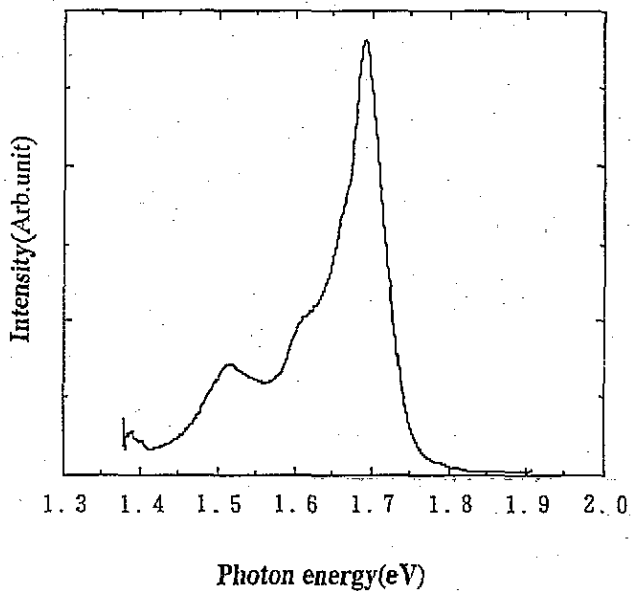


Figure 4. The PL spectrum (50 K) of the  $C_{60}$  thin film.

## 4. Discussion

### 4.1. The absorption spectra by CPM measurement for the $C_{60}$ single crystal

Generally, the optical absorption depends strongly on the structure of the semiconductors. However, the difference of the optical absorption for the  $C_{60}$  single crystal and the  $C_{60}$  thin films has not been clarified before this report. The sub-gap and above-gap absorption are related to the short-range order and long-range order of the phonons in the semiconductors, respectively. For solid  $C_{60}$ , the C atoms are ordered in the short range due to the stability of  $C_{60}$  clusters. Therefore the sub-gap features are not strongly dependent on the structure as in a-Si. The difference in the long-distance order cause the absorption edge shift to lower energy (about 0.1 eV) for the  $C_{60}$  single crystal, although the  $C_{60}$  clusters gather by Van der Waals forces, which are much weaker than the covalent bonds in semiconductors. Furthermore, the photoconductivity of the  $C_{60}$  single crystal is much larger than that of the  $C_{60}$  thin film in our measurement. This means that the absorption features are similar for the  $C_{60}$  single crystal and the  $C_{60}$  thin film, but the absolute values of the absorption coefficient are much larger for the  $C_{60}$  single crystal. It can be understood by that the band tailing of the  $C_{60}$  thin film decreases the density of states in the bottom of conduction band.

**4.1.1. The sub-gap feature.** The energy near 0.6 eV where the steep increase of the optical absorption occurs is much lower than the band gap of  $C_{60}$  obtained by theoretical calculation or experiments. The sub-gap features was also found for the  $C_{60}$  thin films (figure 2(c)). Skumanich [5] suggested that the most possible origin for the sub-gap absorption was that the films are bimodal in nature, comprised of both  $C_{60}$  molecules and an interstitial material. The peaks near 0.5 and 0.9 eV (figure 2(c)) were pointed out to be C-H and O-H overtones and attributed to the interstitial material, which has pregraphitic fragments with hydrocarbons incorporated. However, these peaks were not observed for the  $C_{60}$  single crystal by the CPM measurement. Arai *et al* [8] reported that the conductivity of the  $C_{60}$  single crystal free from O is three orders of magnitude larger than that of the  $C_{60}$  single crystal exposed to  $O_2$  gas, and the impurity-level energy of the  $C_{60}$  crystal free from O is 0.26 eV of donor type for the FCC structure phase. For the  $C_{60}$  single crystal exposed to the air, the impurity-level energy was obtained to be 0.58 eV in our previous work by measurement of the temperature dependence of the conductivity [12]. This activation energy corresponds to the absorption at 0.6 eV for the  $C_{60}$  single crystal. Thus, the carriers that originate from the impurities and were trapped by the O intercalated in the  $C_{60}$  single crystal can be the origin of the sub-gap absorption. The existence of impurities was attributed to the ease of contamination of  $C_{60}$  in the production and solidification processes, which occur for both single crystals and thin films. The discrepancy of the sub-gap feature for the  $C_{60}$  single crystal and the  $C_{60}$  thin film may be caused by the interstitial material, which is less likely to exist in the  $C_{60}$  single crystal than in the  $C_{60}$  thin film.

**4.1.2. The forbidden gap absorption.** The increase of the absorption near 1.5 eV could simply be explained by the weak absorption between the transition forbidden bands. This absorption can also be seen in figure 2(c) for the  $C_{60}$  thin film, for which seems to occur at a higher photon energy. The absorption edge from 1.5 eV to 1.8 eV is roughly exponential for the  $C_{60}$  single crystal as is that of the  $C_{60}$  thin film, for which the Urbach energy was calculated to be 61 meV. In amorphous semiconductors, this edge corresponds to the compositional, topological or structural disorder and can be characterized by the expression  $\alpha(h\nu) = \alpha_0 \exp(h\nu/U)$ , where  $U$  is the Urbach energy and a larger  $U$  implies less order of the semiconductor. However, this energy obtained for the  $C_{60}$  single crystal is 67.3 meV.

Therefore, it seems that it is not proper to attribute this edge to the disorder of the structure as for normal semiconductors. The decrease of  $\alpha$  value observed of  $\sim 1.7$ – $2$  eV for the single crystal might be caused by the absorption of excitons not attributed to the electrical conductivity in the CPM measurement. This seems to agree with the prediction that Frenkel-type molecular excitons locate at  $\sim 1.5$ – $2$  eV as reported by Lof *et al* [6]. However, the results of PL measurements carried out for the same crystal show the main peak at 1.65 eV (shown in the next section) which is close to but not coincident with the decreasing region of absorption at 1.7–2.0 eV observed by the CPM measurement. The possible reason for this decrease is the increase of recombination rate near the surface due to the increase of absorption.

#### 4.2. Photoluminescence for the $C_{60}$ single crystal and the $C_{60}$ thin film

4.2.1. *The main peak of the PL spectra.* The main peak at 1.69 eV for the  $C_{60}$  thin film shifts down to 1.65 eV for the  $C_{60}$  single crystal. In solid  $C_{60}$  the covalent binding within  $C_{60}$  molecules is strong in comparison with the Van der Waals binding between molecules, so the excitons are localized on the  $C_{60}$  molecules (Frenkel-type excitons). The translation states of these excitons have the form of a propagating wave in a periodic structure and form exciton bands. Thus the excitation energy of the crystalline solid is lower than that of an individual molecule. Sinha *et al* [13] reported that the main peak of the PL of the  $C_{60}$  thin film shifts to the lower-energy side of 0.2 eV relative to that of the  $C_{60}$  molecules in  $CS_2$  solution. The  $C_{60}$  molecules locate less periodically in the  $C_{60}$  thin film than in the  $C_{60}$  single crystal. This could cause the discrepancy in PL peak locations for the thin film and single crystal at 1.69 and 1.65 eV respectively.

4.2.2. *The phonon replicas.* An enhancement of the peak at 1.48 eV, which corresponds to the peak at 1.51 eV for the  $C_{60}$  thin film, was found for the  $C_{60}$  single crystal. The origin of the peak near 1.5 eV was assigned to  $1468\text{ cm}^{-1}$  phonon replicas by Sauvajol *et al* [11]. The energy differences between the main peak and the peak at about 1.51 eV are found to be 0.18 eV ( $1452\text{ cm}^{-1}$ ) and 0.17 eV ( $1371\text{ cm}^{-1}$ ) for the  $C_{60}$  thin film and  $C_{60}$  single crystal respectively. These differences are close, but not coincident, due to the solid state effect. The enhancement of this peak for the  $C_{60}$  single crystal can be understood by the fact that the possibility of energy transfer to the phonons is larger because of the high periodicity of the phonons in the single crystal. In our experiments, the intensity of this peak was weakened after being exposed to air. The O intercalated seems to disturb the interaction between the excitons and phonons.

The peaks at 1.61 and 1.66 eV found for the  $C_{60}$  thin film, which can be assigned to phonon replicas of  $250\text{ cm}^{-1}$  and  $730\text{ cm}^{-1}$ , respectively, were not observed for the  $C_{60}$  single crystal. Because the signal of the PL for the  $C_{60}$  single crystal is much stronger than that for the  $C_{60}$  thin film, it is difficult to identify whether there are weak signals of luminescence for these energies.

## 5. Conclusion

CPM and PL measurements have been performed on  $C_{60}$  single crystals. There are sub-gap states located in the  $C_{60}$  single crystal that are also found in  $C_{60}$  thin films. The carriers that originate from the impurities and were trapped by the O intercalated in the  $C_{60}$  single crystal could be the origin of the sub-gap absorption. The forbidden band absorption can be seen at about 1.5 eV. The PL peaks of the  $C_{60}$  single crystal were found at 1.65 and 1.48 eV, at lower energy than those for the  $C_{60}$  thin film (1.69 and 1.51 eV), and the peak at 1.48 eV is enhanced for the  $C_{60}$  single crystal.



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