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Growth and characterization of potassium-doped superfulleride thin films

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Growth conditions for the formation of thin films (100–300 Å) of potassium-doped superfullerides (K_xC_{60} , $x > 6$) are examined. Thin films of these compounds are formed by depositing C_{60} onto a potassium precovered single crystal quartz substrate maintained at 200 K or lower, in a proportion of K: $C_{60} > 12:1$, followed by annealing the surface to the K-sublimation temperature (300 K). *In situ* measurements of electrical and optical properties are used to identify the compounds. The formation of superfullerides is confirmed by C_{60} doping of these phases to check for the formation of insulating K_6C_{60} with a characteristic absorption spectrum. The absorption spectrum of the superfullerides shows distinct features corresponding to the filling of the t_{1g} band. The presence of two superfulleride phases is suggested, a near-metallic superfulleride K_xC_{60} ($x \approx 11.2$) and a more insulating K_xC_{60} ($x \approx 8-9$). © 1998 American Vacuum Society. [S0734-2101(98)01104-X]

I. INTRODUCTION

Alkali-metal-doped fulleride compounds have generated great interest in the past^{1,2} due to the discovery of superconductivity in K_3C_{60} ($T_c = 18$ K),³ Cs_3C_{60} ($T_c = 40$ K),⁴ and mixed fulleride phases.⁵ These compounds were formed by half filling of the t_{1u} (LUMO derived) band of C_{60} . Despite of the high electron affinity of C_{60} , it was contended that charge transfer saturation apparently occurred at six electrons per C_{60} molecule for the alkali metal-doped compounds,⁶ and early attempts were unsuccessful^{7,8} in filling the t_{1g} (LUMO+1 derived) band and forming superfullerides (K_xC_{60} , $x > 6$). The deposition in these experiments was carried out by evaporating potassium on C_{60} films at room temperature. The occupation of the t_{1g} band was, however, obtained for alkaline earth metal-doped fullerides.^{9,10} More recently, Benning *et al.*¹¹ and Jiang *et al.*¹² altered the growth conditions by depositing potassium first on a liquid nitrogen-cooled substrate, followed by C_{60} deposition. The occupation of the t_{1g} band was then observed for the K-doped superfullerides in photoemission spectroscopy.¹²⁻¹⁴ Herein we draw on these earlier studies that concerned the growth of few monolayers thick superfulleride films and demonstrate the growth of 100–300 Å superfulleride films by correlating the electrical and optical properties of these compounds with their electronic structure.¹¹⁻¹⁴

Optical absorption is an important *in-situ* tool for characterizing these thin films. Bulk C_{60} is a molecular solid,¹⁵ and hence the bands in the absorption spectra of C_{60} thin films can be correlated to electronic bands derived directly from the molecular states of the C_{60} molecule. Further, due to the similarity in the absorption spectra of various alkali-metal-doped C_{60} compounds, the peaks of the spectra may be assigned to electronic transitions in the host fullerene molecule, rather than those of the dopant.¹⁶ Thus, the peaks in the absorption spectra of C_{60} , K_3C_{60} , and K_6C_{60} have been assigned in previous publications,¹⁵⁻¹⁷ and the extent of elec-

tron transfer from alkali metal to C_{60} and the related changes in film stoichiometry and conductivity have been explained.^{18,19} Our work presented here uses the growth techniques described by Jiang *et al.*¹³ in a high vacuum chamber with instrumentation similar to that employed by Wilson *et al.*¹⁶ to report the first determinations of electrical resistivity and optical absorption spectra of these superfulleride compounds. The compounds are identified by correlating resistivity measurements with distinct features in the absorption spectrum corresponding to the filling of the t_{1u} and t_{1g} bands of C_{60} . We suggest the growth of two superfulleride phases occurs, a near metallic K_xC_{60} ($x \approx 11.2$) phase and a more insulating K_xC_{60} ($x \approx 8-9$) phase.

II. EXPERIMENTAL METHODS

The deposition and growth of potassium-doped fulleride compounds was carried out in a high vacuum chamber, as shown schematically in Fig. 1, with a base pressure of 5×10^{-7} Torr. C_{60} of 99.5% purity was vacuum sublimed from a tantalum crucible at a rate of 15–25 Å/min onto single-crystal quartz substrates polished on both sides. The substrate was mounted onto a sample holder made of oxygen-free copper of dimensions $5 \times 6 \times 0.3$ in³, which could be cooled using liquid nitrogen to 200 K and radiatively heated to 400 K. Potassium doping was carried out using 40 mm SAES K getters at a rate of 6–10 Å/min. The distance between the substrate and the evaporating source was 12 in. Deposition rates were determined using a water-cooled quartz microbalance (Inficon XTM/2) positioned close to the substrate. About 100–300 Å of the phases of interest were grown, where the thickness of the films was determined primarily by the quartz microbalance, but this was confirmed by *ex situ* ellipsometry (Rudolph Technology Auto EL). *Ex situ* x-ray diffraction was performed on the C_{60} films using Cu K_α radiation from a rotating anode source and a highly oriented pyrolytic graphite (HOPG) monochromator and analyzer.

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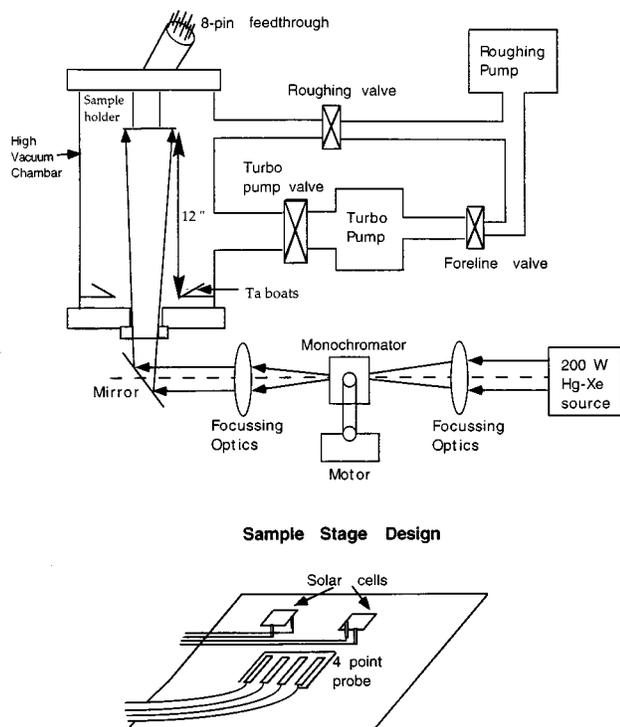


FIG. 1. Schematic of the vacuum deposition system used for synthesis and characterization of superfulleride thin films.

Due to the air sensitivity of the K-doped fullerenes, *in situ* optical and electrical measurements were used to identify the phases. The thin films were grown on substrates that contained four 1000 Å thick silver pads (evaporated on the quartz substrate prior to film deposition) that can be used as electrodes in four-point resistivity measurements of the films. For optical measurements, the chamber was equipped with a sapphire window (transparent from 250 to 1500 nm). The absorption measurements utilized a 200 W Hg-Xe lamp as a source and the optics (scanning monochromator, focusing lenses, and mirrors) produced a 2×1 in² beam of 300–700 nm light onto the quartz substrate. Two solar cells, mounted on the sample holder, were used as detectors. UV-visible absorption spectra of the phases of interest were determined in the 300–700 nm wavelength range by depositing the thin films on a portion of the substrate such that one cell detected light passing only through the substrate, while the other cell detected light passing through the phase of interest and the substrate. The absorbance was determined from the currents of the two solar cells. The instrumentation was set up such that resistivity and optical measurements could be obtained simultaneously as a function of doping.

III. RESULTS AND DISCUSSION

Powder x-ray diffraction (XRD) was used to determine the quality of C₆₀ films grown in our chamber. The XRD in Fig. 2 establishes that the 300 Å C₆₀ films are fcc and polycrystalline with a lattice parameter of 14.2 Å and grain size of approximately 100 Å. We then grew thin films of K-doped fullerenes (K₃C₆₀ and K₆C₆₀) by dosing potassium on the C₆₀

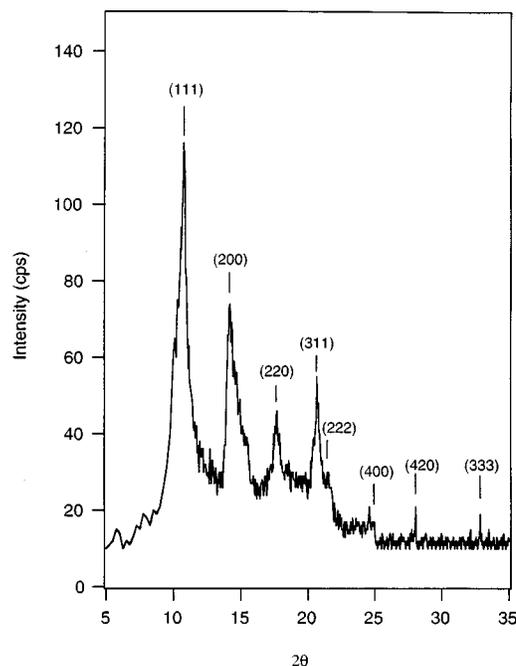


FIG. 2. X-ray scan of a 300 Å C₆₀ film on single-crystal quartz showing the major fcc peaks.

films as has been done earlier.⁷ No charge transfer occurred beyond the formation of K₆C₆₀ under these conditions. The resistivity decrease at longer K deposition times has been attributed to unreacted metallic potassium depositing on the surface and contributing to a resistance decrease.⁷ Working on the premise that formation of higher fullerenes is limited by the relatively low potassium concentrations that can be achieved at room temperature prior to compound formation, potassium was deposited on the quartz surface cooled to 200 K, followed by C₆₀ deposition in a proportion such that K:C₆₀ > 12:1. The surface was then annealed to 300 K for about two hours, yielding a phase labeled as K_xC₆₀ which has a near metallic resistivity, as shown in Fig. 3. Metallic potassium conductivity could not be detected until the deposition of some C₆₀ on the surface, which suggests that potassium grows on the quartz surface as islands rather than as a uniform layer. A possible growth model for the fulleride films is that C₆₀ and K interdiffuse to form fulleride compounds that grow as polycrystalline films atop the quartz substrate. Annealing to 300 K promotes interdiffusion and brings about desorption of excess potassium from the surface. The latter is evident from the observation that for annealing temperatures lower than the K-sublimation temperature (300–325 K), the low resistivity of metallic potassium dominates the resistivity of the thin film. The presence of metallic potassium under the above conditions is also supported by the UV-visible absorption spectra. We assume that our fulleride thin films are polycrystalline since we have obtained resistivity values that match data for K₃C₆₀ and K₆C₆₀ grown from polycrystalline C₆₀ films by the room temperature deposition of K on C₆₀.

The K_xC₆₀ phase formed as in Fig. 3 has a resistivity of about 9.5×10^{-3} Ω cm, which is lower than that of insulat-

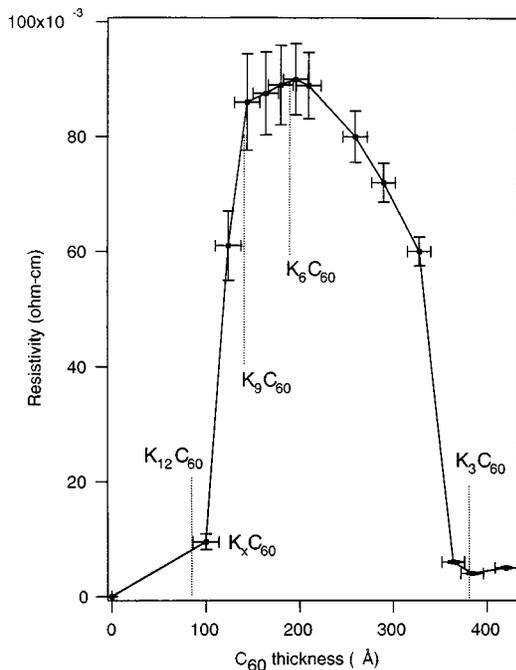


FIG. 3. Resistivity of the K-doped fulleride and superfulleride phases. The K_xC_{60} phase was formed by C_{60} deposition on K multilayers (approximately 170 Å) at 200 K, followed by annealing to 300 K until the resistance stabilised. All other points were generated by C_{60} deposition on this K_xC_{60} phase at 200 K followed by annealing to 300 K for points between the K_xC_{60} and K_6C_{60} phases, and annealing to 400 K for points after the K_6C_{60} phase. Expected relative positions of $K_{12}C_{60}$, K_9C_{60} , and K_6C_{60} phases are marked based on the minimum resistivity denoting K_3C_{60} and the assumptions stated in the text.

ing K_6C_{60} but higher than that of metallic K_3C_{60} ($\rho = 4.2 \times 10^{-3} \Omega \text{ cm}$). In order to ascertain if the K_xC_{60} phase is a superfulleride ($x > 6$), C_{60} was doped at a constant rate and the resistivity was monitored, as shown in Fig. 3, to detect the formation of lower fulleride compounds. The points in this figure were generated by C_{60} deposition on the existing K_xC_{60} phase at 200 K followed by annealing to 300 K for points between the K_xC_{60} and K_6C_{60} phases, and annealing to 400 K for points after the K_6C_{60} phase. It has been shown by photoemission¹³ that the superfullerides may not decompose until 325 K, while photoemission¹³ and resistivity measurements¹⁸ demonstrate that the fulleride compounds are stable until at least 500 K. Figure 3 shows that the resistivity rises rapidly and then begins to plateau, culminating in the characteristic cusp upon the formation of the K_6C_{60} phase.¹⁸ This demonstrates that the K_xC_{60} phase is indeed a superfulleride. All of our resistivity measurements were at 290 K, and the resistivity calculations are based on the total deposited C_{60} thickness, rather than that of the corresponding superfulleride/fulleride phases, since the crystal structure and the lattice parameter of these are not known. Since the differences in the unit cell volume of these phases is expected to be small, the error in the reported resistivities is not expected to be large. The phase transformation of $C_{60} \rightarrow K_3C_{60} \rightarrow K_6C_{60}$ does not involve the large scale rearrangement of C_{60} molecules and results in a volume increase

of only 2.3%.²⁰ Similarly, it is expected that the phase transformation to form superfullerides should involve only a small volume change. This also concurs with the sodium superfulleride ($Na_{11}C_{60}$) structure proposed by Yildirim *et al.*²¹ It should be noted, however, that the resistivity of thin films of doped fullerides is dependent on grain size of the phase being grown.¹⁹ While the grain size of the C_{60} film in these experiments is known from x-ray diffraction (100 Å), that of the fulleride and superfulleride phases is not known. Hence variations from the resistivity values reported here may be found due to the dependence of the grain size on the technique used for the preparation and growth of the superfulleride phases. The resistivity error bars in Fig. 3 include an accounting for thickness errors and electrical measurements errors. The horizontal error bars are based on comparison of the measured C_{60} thicknesses using the quartz microbalance with measurements from ellipsometry. In all cases the error bars represent the maximum possible error in the data and include estimates of systematic errors derived from independent measurement techniques.

In addition, Fig. 3 shows the expected relative positions (dashed lines) of $K_{12}C_{60}$, K_9C_{60} , and K_6C_{60} phases based on the minimum resistivity in the curve assigned to K_3C_{60} . The stoichiometry is determined by assuming that the change in lattice parameter on formation of the various phases is negligible and that no K desorption occurs during annealing. If the thin films contain only a single phase of doped fulleride/superfulleride, then the indicated phases would be formed as shown. This prediction of the conditions for forming the K_6C_{60} phase agrees very well with the cusp characteristic of the K_6C_{60} phase.

The UV-visible absorption spectrum of this K_xC_{60} phase is shown in Fig. 4 and compared with that of thin films of other fulleride compounds. The peaks may be assigned using the schematic of induced electronic transitions shown in Fig. 5, indicating the expected absorptions (solid arrows) and bleaches (dashed arrows) upon occupation of the t_{1u} and t_{1g} levels. The spectra for K_3C_{60} and K_6C_{60} show bleaching of the band corresponding to the $g_g + h_g \rightarrow t_{1u}$ transition seen for C_{60} at 360–370 nm. It has been demonstrated by Wilson *et al.*¹⁶ that this bleaching is related to the filling of the t_{1u} band. Based on this, it may be argued that filling of the t_{1g} band to form the superfulleride phase should be accompanied by bleaching of the band corresponding to the $h_u \rightarrow t_{1g}$ transition, which occurs for K_6C_{60} in the broad region between 500 and 550 nm.^{15–17} For K_6C_{60} the band centered at 460 nm has been assigned¹⁷ to three distinct transitions. These are the $t_{1u} \rightarrow h_g$ transition, which has been moved down in energy from its expected molecular value, and the $h_u \rightarrow t_{1g}$ and the $t_{1u} \rightarrow t_{2u}^*$ transitions that give rise to the broad shoulder toward higher wavelengths. Comparing the spectra of K_xC_{60} and K_6C_{60} in Fig. 4, the notable features of the former are the narrowing of the peak at 460 nm ($t_{1u} \rightarrow h_g$ transition) and the continued bleaching of the $g_g + h_g \rightarrow t_{1u}$ transition. The bleaching of the $h_u \rightarrow t_{1g}$ transition is seen in the difference spectrum of Fig. 6 as a negative peak at about 530 nm (2.35 eV), consistent with the energy band

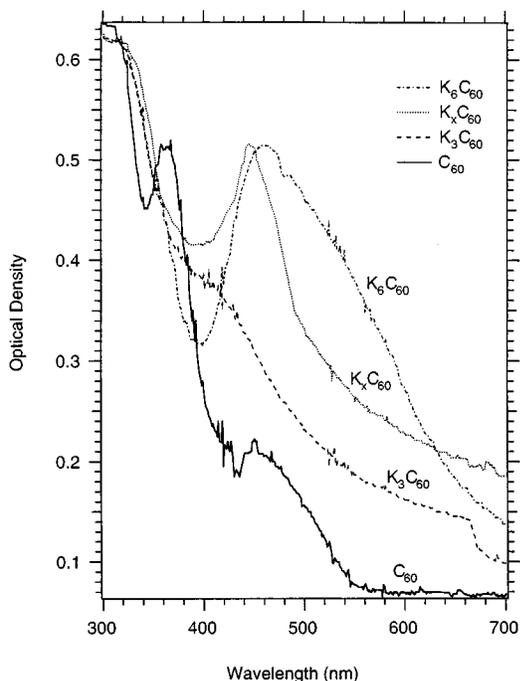


FIG. 4. UV-visible absorption spectra of the superfulleride phase ($K_x C_{60}$ with resistivity of $9.5 \times 10^{-3} \Omega \text{ cm}$) and the other K-doped fulleride and fullerene phases. The thickness of the films in all cases is approximately 300 Å.

assignment for this transition from photoemission data for the superfullerides.¹⁴ These results, taken along with the doping resistivity data of Fig. 3, confirm the growth of a superfulleride phase ($K_x C_{60}$, $x > 6$).

We can provide some justification for labeling several of these films to be comprised of single homogenous phases. As

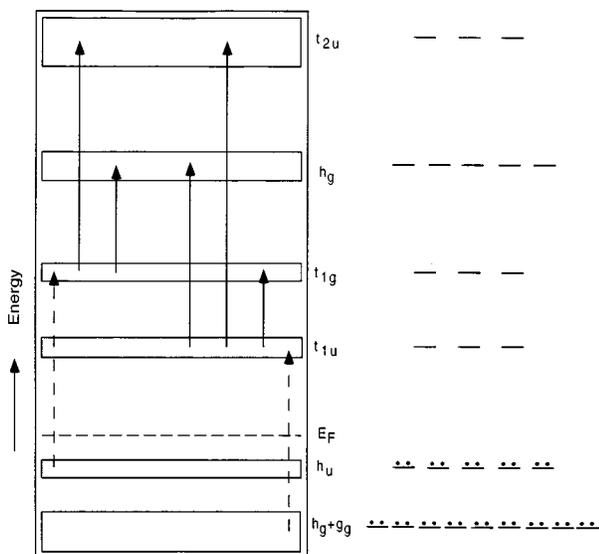


FIG. 5. Schematic one electron diagram of the electronic transitions in superfullerides and the energy levels of the C_{60} molecule. The absorptions (solid arrows) and bleaches (broken arrows) are shown that are expected upon formation of superfulleride phases [modified from Wilson *et al.* (see Ref. 16)].

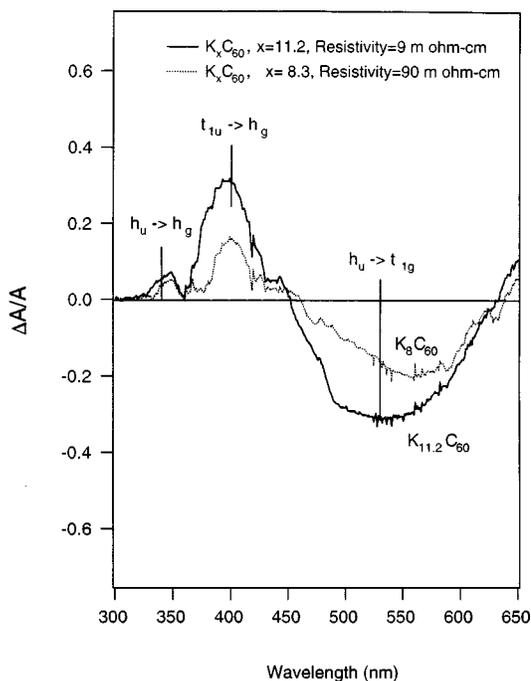


FIG. 6. Difference spectra of the superfulleride phases. The ordinate is the difference in the optical densities of the respective superfulleride phases and $K_6 C_{60}$, normalized to the optical density of $K_6 C_{60}$. The positions marked for the $h_u \rightarrow h_g$ and $t_{1u} \rightarrow h_g$ transitions are based on $K_6 C_{60}$ assignments (see Ref. 17), while that for the $h_u \rightarrow t_{1g}$ transition is from photoemission data for the superfullerides (see Ref. 14).

discussed earlier, the overall stoichiometry of these phases was indicated in Fig. 3. The resistivity was attributed to a single phase of fulleride/superfulleride, but in reality it could result from a mixture of fulleride/superfulleride phases and even some retained excess potassium that is not metallic but partially oxidised. However, in studies comparing bulk and thin film potassium fullerenes ($K_x C_{60}$), Murphy *et al.*²⁰ determined that a continuous variation of x was obtained for the latter as opposed to discrete x values of 0, 3, 4, and 6 for the former. Further, they conclude that low temperature film doping can produce “metastable” homogenous compositions. Also, Jiang and Koel¹³ have demonstrated that K and C_{60} deposition at substrate temperatures as low as 100 K is sufficient to form the superfulleride phase, suggesting that interdiffusion of K and C_{60} is high at low temperatures. Hence, we believe that a more or less homogeneous superfulleride phase that may be continuously doped with C_{60} to form the subsequent lower fulleride phases are obtained for all the low-temperature film doping experiments reported herein.

Based on the above arguments and the stoichiometries shown in Fig. 3, we propose formation of the superfulleride phase $K_x C_{60}$ with $x \approx 11.2$. A phase with a similar stoichiometry and with fewer than 12 electrons accepted per C_{60} molecule was observed by Maxwell *et al.*¹⁴ and predicted to have metallic behavior based on emission at the Fermi energy in photoemission spectra. We carried out a number of experiments searching for a more insulating phase with a higher K stoichiometry, and we have no evidence for the

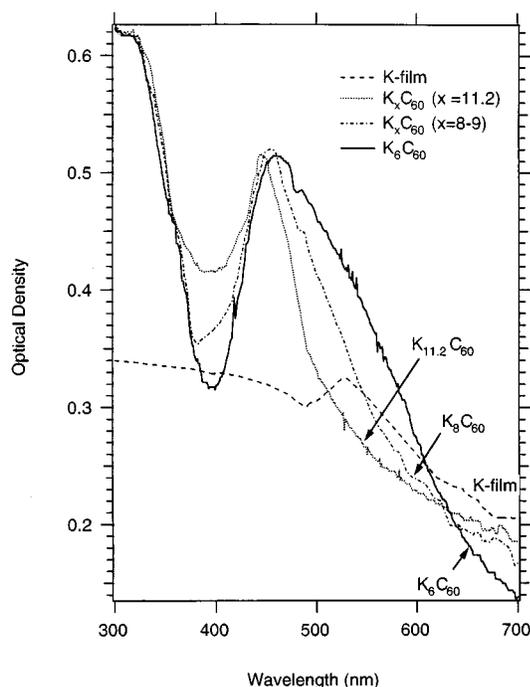


FIG. 7. UV-visible absorption spectra of the superfullerides K_xC_{60} , $x = 11.2$ and K_xC_{60} , $x = 8-9$, along with that for K_6C_{60} and a K film for comparison. These phases were obtained by depositing C_{60} on K multilayers as described in Fig. 3.

existence of such a phase, however there are substantial experimental difficulties with isolation and characterization of such a phase due to the presence of excess metallic potassium. It could also be that charge transfer saturation occurs resulting in incomplete filling of the t_{1g} band, and possible reasons for this have been discussed in the literature.^{14,22}

Another feature apparent from Fig. 3 is that upon C_{60} doping, the rapidly increasing resistivity values beyond K_xC_{60} ($x \approx 11.2$) plateau much before the formation of the characteristic cusp for K_6C_{60} . The UV-vis spectrum of a phase where the plateauing begins ($x \approx 8.3$) is shown in Fig. 7, and this spectrum is quite different from that of K_6C_{60} or K_xC_{60} . The main peak at 450 nm appears to have a shoulder corresponding to the $h_u \rightarrow t_{1g}$ transition, suggesting only partial filling of the t_{1g} band and the possible presence of another phase of K_xC_{60} with $x \approx 8-9$. Benning *et al.*¹¹ have identified a C_{60}^{8-} state based on photoemission results which may correspond to this phase, especially because it is also expected to be insulating. Hence, based on the above discussion, we contend that two superfulleride phases, a near-metallic K_xC_{60} ($x \approx 11.2$) phase and a more insulating K_xC_{60} ($x \approx 8-9$) may be formed.

IV. CONCLUSIONS

The growth of thin films (100–300 Å) of potassium doped superfullerides has been demonstrated. The first determinations of the electrical resistivity and optical absorption spectra of these compounds have been presented. Growth conditions for formation of these compounds have been derived by correlating electrical resistivity with distinct features in the

absorption spectrum corresponding to the filling of t_{1u} and t_{1g} bands of C_{60} . Based on electrical and optical properties of the superfulleride phases, the presence of two distinct phases, K_xC_{60} with $x \approx 11.2$ and K_xC_{60} with $x \approx 8-9$, is suggested.

ACKNOWLEDGMENT

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