

# Disorder/order phase transition in C<sub>60</sub> thin films studied by surface photovoltage spectroscopy

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The electronic properties of C<sub>60</sub> thin films have been studied using surface photovoltage (SPV) spectroscopy at 120–300 K. Temperature variations of the SPV spectra are correlated with temperature-dependent x-ray diffraction patterns of the same samples, which indicate the first-order phase transition at  $T_c = 250$  K. Absolute values of both the band-to-band and band (or band tail) -to-band tail SPV signals are shown to exhibit a clear minimum at  $T_c = 250$  K in contrast with the well-known increasing background of the SPV intensity with decreasing temperature. The energy positions of the thresholds of the band-to-band and band (or band tail) -to-band tail regions in the SPV spectra also exhibit nonmonotonic behavior with a mirror symmetry and distinct extrema near  $T_c$ . On the basis of the presented results, we discuss possible reasons behind the effect of rotational and orientational states of C<sub>60</sub> molecules on the electronic structure of the C<sub>60</sub> fullerite and charge carrier transport in C<sub>60</sub> thin films. © 2003 American Institute of Physics.  
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## I. INTRODUCTION

Solid C<sub>60</sub> is a molecular crystal with C<sub>60</sub> molecules occupying the lattice sites of a face-centered-cubic (fcc) structure<sup>1</sup> with the basic central intermolecular forces being of predominantly van der Waals nature.<sup>2</sup> Near the critical temperature  $T_c = 250$ –260 K, the C<sub>60</sub> crystal is known to undergo a first-order phase transition associated with changes in molecular rotations. Above  $T_c$ , C<sub>60</sub> molecules rotate almost freely and therefore are equivalent, thus resulting in a fcc structure. Below  $T_c$ , the molecular rotations are partially locked with the fivefold symmetry axes having specific orientations. As a result, the molecules stay in their positions but acquire four different orientations, and the fcc structure transforms into a Pa3 structure with four interpenetrating simple cubic (sc) sublattices.<sup>3</sup> Now, the average anisotropic forces are nonzero and negative, which corresponds to an extra constricting force and which thus results in a negative (upon cooling) jump in the lattice parameter.<sup>1,3</sup> Free rotations above  $T_c$  provide a dynamic disorder but ensure the least possible orientation-related static disorder. On the contrary, below  $T_c$  the orientations are (at least partially) ordered, however, the presence of nonequivalent mutual orientations of adjacent C<sub>60</sub> molecules entails an extra static disorder.

The relation between the rotational state of the molecules and electronic transport in solid C<sub>60</sub>, and in particular its conductivity and photoconductivity near  $T_c$ , have recently become of great interest. The published data on C<sub>60</sub> single crystals<sup>4–6</sup> consistently report a sharp increase in conductivity, over a narrow range of about 0.4 K, when the temperature is lowered through  $T_c$ . These results were explained by the corresponding jumps ( $\sim 1.5$  times) in the charge carrier mobility at  $T_c$ .<sup>7</sup> However, very recently, sharp changes in conductivity, near  $T_c$ , by an order of magnitude<sup>8</sup> or even 4–5 orders of magnitude<sup>9</sup> have been reported for highly crystalline C<sub>60</sub> films. These results have been interpreted in terms of trap-controlled mobility of the dominant charge carriers so that the temperature-related changes in the conductivity are attributed to variations in the concentration, energy distribution, and population of the carrier traps around the phase transition.<sup>8</sup> Further insight into this phenomenon requires detailed study of the relationship between crystalline structure, orientational state and electronic structure of C<sub>60</sub> films near  $T_c$ . In this article, we report results of joint analysis of the variation of x-ray diffraction (XRD) patterns and surface photovoltage (SPV) spectra of C<sub>60</sub> thin films with temperature.

SPV spectroscopy,<sup>10,11</sup> which provides information on the electronic structure of semiconductors, has already proved to be efficient in studying C<sub>60</sub> thin films.<sup>12,13</sup> In particular, the SPV spectrum contains information on the band gap and the energy positions of the defect states in the gap.

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Formation of a SPV signal requires both photogeneration and transport of charge carriers. Therefore, SPV signals also reflect changes in mobility and lifetime of charge carriers.

## II. EXPERIMENTAL DETAILS

$C_{60}$  thin films were deposited on a substrate of optical glass predeposited with an Ag layer using a vacuum deposition technique. The starting  $C_{60}$  powder (Super Gold Grade, >99.9%) was commercially obtained from Hoechst AG. The substrate temperature, the  $C_{60}$  deposition rate, and the thickness of the  $C_{60}$  films were of about 200 °C, 20 Å/s and 1000 Å, respectively. A detailed description of the deposition conditions was given elsewhere.<sup>14</sup>

The crystalline structure of the  $C_{60}$  films was characterized first at room temperature by powder XRD in  $Cu K\alpha$  and  $Fe K\alpha$  radiation, and subsequently by temperature-resolved XRD over the temperature range from 300 to 15 K. In the latter case, the XRD patterns also included reflections from a reference substance (high-purity copper). These reflections were utilized as a reference to reduce the error in the lattice parameter. The error in the lattice parameters thus did not exceed  $\pm 0.02\%$ . The sample temperature was measured with a platinum resistance thermometer, keeping the temperature stable at every measurement within  $\pm 0.05$  K. Morphology of the front surface of the films was studied by atomic force microscopy (AFM).

The SPV spectra were measured over the temperature range of 300–120 K, using a commercial Kelvin probe (Besocke Delta Phi, Jülich, Germany) with a sensitivity of  $\sim 1$  mV, and a gas flow helium cryostat. Carrier generation was provided by light source and 0.25 m single monochromator (Oriel). Light intensity was adjusted using neutral density filters. Prior to the SPV measurements, the samples were kept in the dark, in air, and at room temperature. After being mounted in the cryostat they were annealed *in situ* in a vacuum of  $10^{-3}$  Torr at 150 °C for 2 h. This treatment ensured the removal of most of oxygen from the sample.<sup>4</sup>

## III. RESULTS AND DISCUSSION

Room-temperature XRD revealed that the  $C_{60}$  films have fcc polycrystalline structure with a strong  $\langle 111 \rangle$  texture. Their room-temperature XRD patterns are the same as that shown in Fig. 2(a) in Ref. 14 and consist only of a very narrow and intensive (111) peak and its higher harmonics (222) and (333).

Figure 1 shows results of two sets of the temperature-resolved XRD measurements of the lattice parameter,  $a$ , in a typical  $C_{60}$  sample. The second set of measurements was performed two days after the first one. We observed a well-defined discontinuity in the lattice parameter,  $\Delta a/a = 0.06\%$ , near the temperature  $T_c = 250$  K, which corresponds to the known disorder/order phase transition from the fcc to sc structure.<sup>3</sup> The results of both sets of measurements almost coincide, except the very narrow vicinity of  $T_c$ . Note that in our films the critical temperature is lower and the change in the lattice parameter is smaller than in bulk  $C_{60}$  samples, for which  $T_c \approx 260$  K and  $\Delta a/a = 0.32\%$ .<sup>3,15,16</sup> We have presented elsewhere<sup>17</sup> XRD results on  $C_{60}$  films of vari-

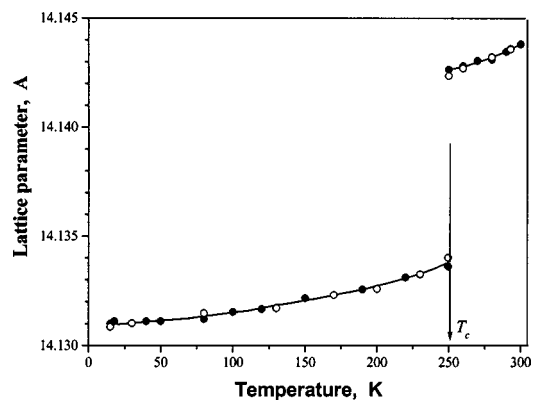


FIG. 1. Temperature dependence of the lattice parameter in a polycrystalline  $\langle 111 \rangle$ -textured  $C_{60}$  film determined by two sets of the temperature-resolved powder XRD data. The second XRD experiment was run two days after the first one. The solid line is a guide for the eye.

ous crystalline structure. A gradual reduction in  $\Delta a/a$  and  $T_c$  with decreasing grain size in those samples has been demonstrated. This behavior, in comparison with single crystals, may originate from the relatively high density of structural defects (including grain boundaries), strain and impurities in thin films. In fact, it was previously shown that structural defects,<sup>18</sup> impurities,<sup>18–21</sup> strain,<sup>22</sup> or an increased surface/volume ratio<sup>23–25</sup> can reduce the  $T_c$  value of solid  $C_{60}$  by up to 30 K. The contribution of all these defects could suppress the discontinuity in  $a$  at the phase transition.<sup>19,21,24</sup> It should be noted, however, that the changes in the orientational state of  $C_{60}$  molecules occurring at the phase transition have a much stronger effect on the material's electronic properties than the discontinuity in the lattice parameter. In particular, we have demonstrated recently<sup>8</sup> a strong effect of the phase transition on the conductivity and photoconductivity of a  $C_{60}$  film with coexisting amorphous and nanocrystalline phases for which no discontinuity in  $a$  was observed.

Figure 2 shows the SPV spectra measured at various temperatures for the same  $C_{60}$  film as in Fig. 1. In the SPV spectroscopy, information on the band gap and the energy

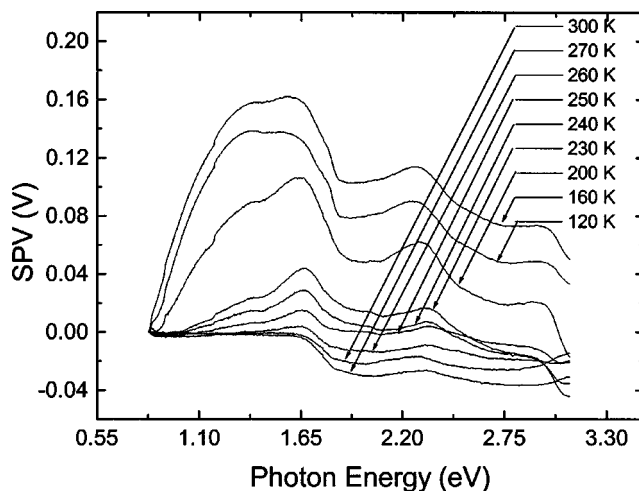


FIG. 2. SPV spectra for the polycrystalline  $\langle 111 \rangle$ -textured  $C_{60}$  film on an Ag predeposited glass substrate as measured at different temperatures in the range of 300–120 K.

positions of the defect states inside the gap is determined from changes in the spectral line slope that are caused by the photon assisted population or depopulation of electronic states.<sup>10,11</sup> Accordingly, it is useful to distinguish three particular regions in measured spectra. To start with, we will determine these regions for the room-temperature spectrum. Excitation by photons with an energy of 0.8–1.6 eV defines region I. The sharp SPV signal with a negative slope is designated as the beginning of region II at approximately 1.65 eV that is characterized by a “knee” followed by some structure. The next region III with a clearly defined negative-slope signal starts at about 2.3 eV.

Region I is attributed to a subgap photoexcitation. Taking into account the results of photoemission and inverse photoemission room-temperature measurements of the band gap of  $C_{60}$  fullerite as of 2.3 eV,<sup>26</sup> the SPV signal in region III was previously<sup>12,13</sup> attributed to a valence-to-conduction interband photoinduced excitation. The results of the combined experiment of photoconductivity, photoluminescence, photoinduced absorption excitation spectroscopy, resonant Raman spectroscopy, and electroabsorption,<sup>27</sup> and the comparative study of optical absorption and photoconductivity spectra,<sup>28</sup> confirmed that the main threshold in optical absorption and photoinduced carrier generation of  $C_{60}$  films is at 2.3 eV. However, the authors of Refs. 27 and 28 attributed this signal to the lowest charge-transfer excitation state in solid  $C_{60}$  (formed by a Coulomb bound electron and hole located on different molecules) while the single-particle band gap of solid  $C_{60}$  is expected to be at 2.6 eV.

The origin of near-gap optical absorption and, in particular, of region II in the SPV spectra is still under discussion. The optical absorption of  $C_{60}$  thin films is known to extend from the gap energy forming a tail on the lower energy side.<sup>29</sup> A series of weak absorption structures have been observed in the tail of the optical and photoacoustical spectra.<sup>30,31</sup> These structures have been ascribed to either exciton levels or the splitting due to vibronic modes of the molecules. Specifically, the absorption at 1.65 eV has been related to  $h_u \rightarrow t_{1u}$  intramolecular excitation.<sup>32–34</sup> It is well known that pristine solid  $C_{60}$  exhibits semiconductor-like behavior in its optical absorption and electron transport properties and yet retains a molecular character. To describe the tail in optical absorption and, in particular, region II of the SPV spectra, we adopt an approach similar to that used in amorphous semiconductor physics.<sup>35</sup> The corresponding simplified model of the electronic structure of  $C_{60}$  fullerite including a room temperature mobility gap of about 2.3 eV, and a photoconduction gap of 1.6–1.7 eV has been recently suggested. The model and our arguments for the presence of tails of localized electronic states extending towards the forbidden gap as well as a discussion of the possible origins of the tails have been presented elsewhere.<sup>12</sup> In addition to the above-mentioned origins, a dynamic disorder (related to dynamics of  $C_{60}$  molecular rotation, above  $T_c$ ),<sup>12,36</sup> and static orientational disorder, below  $T_c$ ,<sup>37</sup> have been suggested. It is obvious that the disorder/order phase transition must have an influence on these phenomena and, in turn, on both the SPV signal and the energy position of region II.

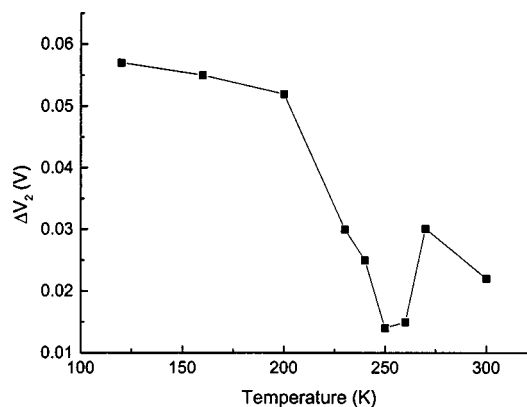


FIG. 3. Temperature dependence of the absolute value of the SPV signal change along the main knee in region II. The data have been obtained by processing of the SPV spectra presented in Fig. 2.

Regions II and III are present in all of the SPV spectra we measured on different  $C_{60}$  films.<sup>12,13,38</sup> The negative slope of these signals indicates an  $n$  type of the conductivity of the  $C_{60}$  films. The SPV signal in region I may vary considerably depending on the crystalline structure and “history” of the film.<sup>12,13</sup> This is consistent with similar behavior of the subgap optical absorption of  $C_{60}$  films.<sup>39</sup>

Each of the above-mentioned regions (I, II and III) in the SPV spectra coincides with the corresponding well-defined features in the photoconductivity spectra of our samples<sup>40</sup> and the photoconductivity spectra reported by other groups.<sup>36</sup> In general,<sup>11</sup> the SPV signal may indicate a population/depopulation of surface states or/and localized states in the bulk of the film near the surface. The clear correlation between the SPV spectra and such a bulk property as photoconductivity suggests that SPV spectroscopy is capable of scanning bulk electronic structure of  $C_{60}$  films.

At room temperature the concentration of the deep states in the gap for the studied highly crystalline  $C_{60}$  film is too small to be detected by the method. This explains the absence of the sub-band-gap SPV response (in region I) at 300–270 K. However, starting from a certain temperature between 270 and 260 K a positive signal was observed in this region and its intensity increased with decreasing temperature.<sup>38,41,42</sup>

Before going into details of the temperature variations of the main SPV signals (in regions II and III), we draw attention to their nonmonotonic character. To make this behavior apparent we plotted an absolute value of the signal change along the main knee in region II,  $\Delta V_2$ , as a function of temperature (Fig. 3). One can see a pronounced dip in the vicinity of the orientational phase transition with a clear minimum near  $T_c = 250$  K against the natural growing background of the SPV intensity with temperature decreasing owing to the well known increased SPV sensitivity.<sup>11</sup> The signal in region III (not shown) exhibits a similar behavior. Critical behavior of the SPV signal near  $T_c$  qualitatively reproduces the temperature dependence of conductivity and photoconductivity in the corresponding temperature range recently observed for similar highly crystalline  $C_{60}$  films<sup>8</sup> and, therefore,



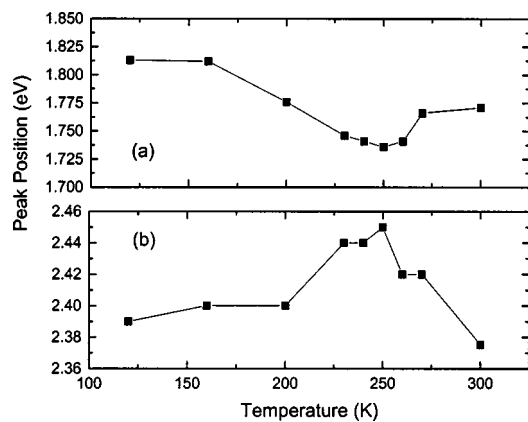


FIG. 4. Temperature dependence of the energy positions of the SPV signal onsets in regions II (a) and III (b). The data have been obtained by processing of the SPV spectra presented in Fig. 2 assuming that the positions of these onsets coincide with the minima in the negative derivative of the SPV curves in the corresponding spectral ranges.

may be explained by the effect of the phase transition on the electrical transport in the material.

SPV spectroscopy is very sensitive to any changes in the electronic structure, such as the band bending shape near a semiconductor's surface, the position of the Fermi level, etc. The effect of the phase transition on the electronic structure of  $C_{60}$  films requires further systematic investigation. Here, we would like to demonstrate only one example of such an effect recorded by SPV spectroscopy. Figures 4(a) and 4(b) show the temperature dependence of the energy positions of the edges of regions II and III,  $E_2$  and  $E_3$ , respectively, as derived from Fig. 2. To be more quantitative, we assume that the positions of these edges coincide with the minima in the negative derivative of the SPV curves in the corresponding spectral ranges. According to our interpretation of the SPV signal in region II, a redshift of  $E_2$  should indicate a broadening of the tails, and vice versa. Figure 4(a) demonstrates a general blueshift trend of  $E_2$  with decreasing temperature below  $T_c$  (narrowing of the tails). This is consistent with the tail width behavior inferred previously from the temperature dependence of the optical transmission,<sup>39,43</sup> photothermal deflection,<sup>39</sup> and photoconductivity<sup>43,44</sup> spectra of  $C_{60}$  films and single crystals as well as with the general knowledge on the rotational states of  $C_{60}$  molecules in fullerite. Indeed, it is well known<sup>3,45</sup> that below  $T_c$  the molecular rotations are partially locked with the fivefold symmetry axes  $C_5$  having specific orientations. Even though the orientations  $\langle 111 \rangle$  of the  $C_5$  axes remain fixed, at temperatures below  $T_c$  down to roughly 90 K, the molecules execute turns around the threefold axes  $C_3$  finishing every turn so that the same or another  $C_5$  is aligned along  $\langle 111 \rangle$  direction. As a result, there are two slightly different mutual orientations of a pair of  $C_{60}$  molecules in the  $C_{60}$  solid. They differ in that in the more favorable one the closest electron-rich double bond of one molecule faces the electron deficient pentagon element of the other while in the less favorable orientation this double bond is opposite the electron-rich hexagon element of the other molecule. These mutual orientations are termed pentagonal and hexagonal,

respectively. It is worth noting that free rotations above  $T_c$  provide a dynamic disorder but ensure the least possible orientation-related static disorder. On the contrary, below  $T_c$  the orientations are (at least partially) ordered, however, the presence of unequivalent mutual (hexagonal and pentagonal) orientations entails an extra static disorder. Since the pentagon to hexagon number ratio increases (from  $\sim 60\%$  near 260 K to  $\sim 84\%$  at 90 K),<sup>45</sup> and the frequency of the turns, decreases with temperature reduction, both the dynamic and static disorders should diminish with temperature reduction below  $T_c$ . This behavior may well explain the above-mentioned narrowing of the tail.

On the other hand, contrary to the above-mentioned results<sup>39,43,44</sup> the redshift of  $E_2$  (broadening of the tails) with decreasing temperature is in evidence just above  $T_c$  that manifests in the minimum in  $E_2$  near  $T_c = 250$  K. Meanwhile, the  $E_3$  has a maximum near  $T_c$  [Fig. 4(b)]. The temperature dependencies of  $E_2$  and  $E_3$  demonstrate good mirror symmetry. Similar mirror symmetry has previously been demonstrated<sup>39</sup> for the temperature dependencies of the Tauc optical band gap<sup>46</sup> of  $C_{60}$  films and the corresponding Urbach-tail width. The latter can be explained quite reasonably assuming that a redshift of the optical band gap occurs simultaneously with tail broadening. At the same time, the demonstrated temperature dependencies of the  $E_2$  and  $E_3$  onsets, and in particular their mirror symmetry, still need further experimental and theoretical clarification including a deeper insight into SPV formation mechanisms in  $C_{60}$  fullerite and its dependence on the orientational state of this molecular crystal.

#### IV. CONCLUSIONS

We report nonmonotonic temperature variations in the SPV spectra of polycrystalline  $\langle 111 \rangle$ -textured  $C_{60}$  thin films in the vicinity of the first-order orientational phase transition at  $T_c = 250$  K, as recorded by XRD. Absolute values of both the band-to-band and band (or band tail) -to-band tail SPV signals are shown to exhibit a clear minimum at  $T_c = 250$  K in contrast to the well-known growing background of the SPV intensity with decreasing temperature. The temperature dependence of the intensities of these SPV signals near  $T_c$  qualitatively reproduces the temperature dependence of conductivity and photoconductivity in the corresponding temperature range recently observed for similar highly crystalline  $C_{60}$  films and, therefore, may be attributed to the effect of the phase transition on the electrical transport in the material. In addition, the energy positions of the thresholds of the band-to-band and band (or band tail) -to-band tail regions in the SPV spectra also exhibit a critical behavior with a mirror symmetry and distinct extrema near  $T_c$ . Such behavior manifests the effect of the phase transition on the electronic structure of the  $C_{60}$  fullerite. In particular, the observed narrowing of the tails of localized electronic states with decreasing temperature below  $T_c$  is discussed in terms of the reduction of both the dynamic and static disorders in this molecular crystal due to changes in the orientational state of  $C_{60}$  molecules.

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- <sup>1</sup>R. Tycko, G. Dabbagh, R. M. Fleming, R. C. Haddon, A. V. Makhia, and S. M. Zahurak, *Phys. Rev. Lett.* **67**, 1886 (1991).
- <sup>2</sup>J. P. Lu, X.-P. Li, and R. M. Martin, *Phys. Rev. Lett.* **68**, 1551 (1992).
- <sup>3</sup>P. A. Heiney, J. E. Fisher, A. R. McGhie, W. J. Romanow, A. M. Denes-tejn, J. P. McCauley, Jr., A. B. Smith III, and D. E. Cox, *Phys. Rev. Lett.* **66**, 2911 (1991).
- <sup>4</sup>T. Arai, Y. Muracami, H. Suematsu, K. Kikuchi, Y. Ashiba, and I. Ikemoto, *Solid State Commun.* **84**, 827 (1992).
- <sup>5</sup>D. Barancok, M. Haluska, V. Nadazdy, and J. Vajda, *Solid State Commun.* **94**, 597 (1995).
- <sup>6</sup>K. C. Chiu, J. S. Wang, Y. T. Dai, and Y. F. Chen, *Appl. Phys. Lett.* **69**, 2665 (1996).
- <sup>7</sup>E. Frankevich, Y. Maruyama, and H. Ogata, *Chem. Phys. Lett.* **214**, 39 (1993).
- <sup>8</sup>E. A. Katz, D. Faiman, K. Iakoubovskii, A. Isakina, K. A. Yagotintsev, M. A. Strzhemechny, and I. Balberg, *J. Appl. Phys.* **93**, 3401 (2003).
- <sup>9</sup>K.-C. Chiu, Y.-C. Su, R.-S. Chen, Y.-J. Lin, W.-R. Cheng, and S.-J. Tang, *Jpn. J. Appl. Phys., Part 1* **41**, 6028 (2002).
- <sup>10</sup>C. L. Balestra, J. Lagowski, and H. C. Gatos, *Surf. Sci.* **26**, 317 (1971).
- <sup>11</sup>L. Kronik and Y. Shapira, *Surf. Sci. Rep.* **37**, 1 (1999).
- <sup>12</sup>B. Mishori, E. A. Katz, D. Faiman, and Y. Shapira, *Solid State Commun.* **102**, 489 (1997).
- <sup>13</sup>E. A. Katz, D. Faiman, B. Mishori, Yoram Shapira, A. I. Shames, S. Shtutina, and S. Goren, *J. Appl. Phys.* **84**, 3333 (1998).
- <sup>14</sup>E. A. Katz, D. Faiman, S. Shtutina, and A. Isakina, *Thin Solid Films* **368**, 49 (2000).
- <sup>15</sup>H. Kasatani, H. Terauchi, Y. Hamanaka, and S. Nakashima, *Phys. Rev. B* **47**, 4022 (1993).
- <sup>16</sup>S. Fomenko, V. D. Natsik, S. V. Lubenets, V. G. Lirtsman, N. A. Akse-nova, A. P. Isakina, A. I. Prokhvatilov, M. A. Strzhemechny, and R. S. Ruoff, *Fiz. Nizk. Temp.* **21**, 465 (1995); [*Low Temp. Phys.* **21**, 364 (1995)].
- <sup>17</sup>E. A. Katz, D. Faiman, S. Shtutina, A. Isakina, and K. A. Yagotintsev, *Mater. Res. Soc. Symp. Proc.* **675**, W7.6.1 (2001).
- <sup>18</sup>N. A. Aksenova, A. P. Isakina, A. I. Prokhvatilov, M. A. Strzhemechny, and V. N. Varyukhin, in *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, edited by K. M. Kadish and R. S. Ruoff (The Electrochemical Society, Pennington, 1994), **PV94-24**, 1543 (1994).
- <sup>19</sup>K. Matsuishi, K. Tada, S. Onari, and T. Arai, *Philos. Mag. B* **70**, 795 (1994).
- <sup>20</sup>F. Yan, Ye-N. Wang, and M. Gu, *J. Phys.: Condens. Matter* **10**, 6875 (1998).
- <sup>21</sup>X. Li, Y. J. Tang, H. W. Zhao, W. S. Zhan, H. Wang, and J. G. Hou, *Appl. Phys. Lett.* **77**, 984 (2000).
- <sup>22</sup>Y. Yoneda, K. Sakaue, and T. Terauchi, *J. Phys.: Condens. Matter* **9**, 2851 (1997).
- <sup>23</sup>A. Glebov, V. Senz, J. P. Toennies, and G. Gensterblum, *J. Appl. Phys.* **82**, 2359 (1997).
- <sup>24</sup>A. Fartash, *Phys. Rev. B* **54**, 17215 (1996).
- <sup>25</sup>A. Goldoni, C. Cepek, and S. Modesti, *Phys. Rev. B* **54**, 2890 (1996).
- <sup>26</sup>R. W. Lof, M. A. van Veenendaal, B. Koopmans, H. T. Jonkman, and G. A. Sawatzky, *Phys. Rev. Lett.* **68**, 3924 (1992).
- <sup>27</sup>X. Wei, D. Dick, S. A. Jeglinski, and Z. V. Vardeny, *Synth. Met.* **86**, 2317 (1997).
- <sup>28</sup>R. Konenkamp, G. Priebe, and B. Pietzak, *Phys. Rev. B* **60**, 11804 (1999).
- <sup>29</sup>A. Skumanich, *Chem. Phys. Lett.* **182**, 486 (1991).
- <sup>30</sup>C. Reber, Y. Lee, J. McKiernan, J. I. Zink, R. S. Williams, W. M. Tong, D. A. A. Ohlberg, R. L. Whetten, and F. Diederich, *J. Phys. Chem.* **95**, 2127 (1991).
- <sup>31</sup>S. Matsuura, T. Tsuzuki, T. Ishiguro, H. Endo, K. Kikuchi, Y. Achiba, and I. Ikemoto, *J. Phys. Chem. Solids* **55**, 835 (1994).
- <sup>32</sup>R. R. Hung and J. J. Grabovski, *J. Phys. Chem.* **95**, 6073 (1991).
- <sup>33</sup>M. Terazima, N. Hirota, H. Shinohara, and Y. Saito, *J. Phys. Chem.* **95**, 9080 (1991).
- <sup>34</sup>C. Wen, T. Aida, I. Homna, H. Komiyama, and K. Yamada, *J. Phys.: Condens. Matter* **6**, 1603 (1994).
- <sup>35</sup>N. F. Mott and E. A. Davis, *Electronic Processes in Noncrystalline Mate-rials* (Clarendon, Oxford, 1979).
- <sup>36</sup>A. Hamed, in *Organic Conductive Molecules and Polymers*, edited by H. S. Nalwa (Wiley, Sussex, 1997), p. 486.
- <sup>37</sup>M. P. Gelfand and J. P. Lu, *Phys. Rev. Lett.* **68**, 1050 (1992).
- <sup>38</sup>E. A. Katz, D. Faiman, S. Shtutina, A. Shames, S. Goren, B. Mishori, and Y. Shapira, *Mater. Res. Soc. Symp. Proc.* **485**, 113 (1998).
- <sup>39</sup>T. Gotoh, S. Nonomura, H. Watanabe, and S. Goto, *Phys. Rev. B* **58**, 10060 (1996).
- <sup>40</sup>E. A. Katz, D. Faiman, K. Iakoubovskii, A. Bozhko, and I. Balberg, in *Proceedings of the 24th International Conference on the Physics of Semi-conductors*, Jerusalem, 2-7 August, edited by D. Gershoni (World Scien-tific, Singapore, 1999), CD-RDM.
- <sup>41</sup>The sub-band-gap SPV signal has a positive sign and, at low temperatures, may be even stronger than the main C<sub>60</sub> super-band-gap SPV signals. Therefore, we tend to conclude that this signal originates from the back C<sub>60</sub>/Ag interface (for detailed argumentation see Refs. 38 and 42). We believe that the increase of this signal with temperature reduction is caused by filling of interface states by electrons with the reduction of temperature.
- <sup>42</sup>E. A. Katz, D. Faiman, S. Shtutina, B. Mishori, and Y. Shapira, *AIP Conf. Proc.* **442**, 527 (1998).
- <sup>43</sup>K.-C. Chiu, J.-S. Wang, and Y.-J. Lin, *J. Appl. Phys.* **79**, 1784 (1996).
- <sup>44</sup>R. Konenkamp, J. Erxmeyer, and A. Weidinger, *Appl. Phys. Lett.* **65**, 758 (1994).
- <sup>45</sup>W. I. F. David, R. M. Ibberson, T. J. S. Dennis, J. P. Hare, and K. Pras-sides, *Europhys. Lett.* **18**, 219 (1992).
- <sup>46</sup>G. D. Cody, *Semicond. Semimetals* **21**, 11 (1984).