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STUDIES OF THE SYSTEM C_{60}-Pb BY TUNNELING SPECTROSCOPY

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ABSTRACT

In the present work we report tunneling experiments on junctions of the type Al-oxide-C_{60}-Pb, and Pb-oxide-C_{60}-Pb. At low temperatures we observed a well defined and narrow semiconducting gap with a magnitude of the order of 6-7 meV. This gap corresponds to the semiconductor formed by C_{60} doped with Pb.

Since the discovery of superconductivity in the alkali doped fullerenes,[1] great effort has been devoted to the study of the microscopic mechanisms involved in the superconductivity of these materials, and to the discovery of new superconducting compounds related to the C_{60}.[2,3] To date, apart of the superconductive compounds obtained with alkaline and alkaline earth ions, only a few new superconducting compounds have been synthesized using other elements; such as Sm[4] and Yb.[5] Other compounds based on Sn,[6] and Cu[7] have been claimed to be superconductors, but to date there are not conclusive evidences for these assertions.

In the case of K_nC_{60}, the system transits from an insulator state (n=0) to another insulator state (n=6), through a metallic (and superconducting) state

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for n=3.[8–10] An important effect on this situation is the transfer of electrons from K to the band derived from the lowest unoccupied molecular orbital of the C_{60}.

Other system where electronic transfer has been observed is in the C_{60}-metal bilayers in close contact. The charge transfer to the C_{60} molecules has been studied in monolayers of C_{60} deposited on metallic or semiconducting surfaces,[11–13] as well as in bilayers of metal-C_{60}.[14,15] To date, still it is not very clear how much charge can be transferred from the metal film to the C_{60}. In the case of the charge transfer experiments in Al-C_{60} interfaces, some studies indicate that up to six electrons per C_{60} may be transferred from the Al layer,[14] but more recent studies indicate that approximately 0.2 electrons per C_{60} molecule are transferred and the effect is limited to the first monolayer of C_{60} which is in contact with the Al film.[15] An important conclusion derived from these previous works is that the interplay of the materials used in the metal-fullerene layered systems, and the morphology of the interfaces, determine the properties measured in the system. One example of this interplay can be found when Al is deposited on the C_{60}, in this case Al diffuse in to the C_{60} more than in the opposite situation.[14,15]

Before going to the experimental details, let us introduce some information related to the experimental technique that we used in our studies and mention some of the information that this can provide.

Tunneling spectroscopy is one useful technique to study processes that occur close to the Fermi surface of a material, such as energy gaps, and elementary excitations. In general is very frequently used to study some of the microscopic phenomena that give place to the superconducting state. Particularly was used in the past to study weak and strong coupling superconductors. In these last type of superconductors, it can provide the most detailed information about the electron-phonon interaction and the nature of the excitations that form the Cooper pairing. Also can be used to study the physical changes that occur close to the Fermi surface in metals, in Charge Density Waves and Spin density Waves systems, magnetic excitations, Kondo systems, etc. In semiconductors and disordered systems it is also appropriated to probe in the most direct manner the size of the energy gap, or pseudogaps, particularly if the gaps or pseudogaps are small and could be smeared by effects of temperature. That situation make the technique particularly very useful if the size of the gap is comparable to the thermal energy. When this experimental conditions occur then will be convenient to perform the measurements of the tunnel junctions at low temperatures, because in this way the smearing by thermal fluctuations will be reduced to a minimum. Under these conditions we may obtain very definite and sharp features indicating with great clarity not only the size of the energy gap, but showing other features that occur at the edge of the Fermi level.

In the present work we explore the electronic behavior of C_{60}-Pb bilayers using the technique of tunneling spectroscopy. In order to perform the experimental studies we fabricated two types of tunnel junctions, which were made with thin films. These are of the form: Al-oxide-C_{60}-Pb, and Pb-oxide-C_{60}-Pb. The main result of the experiments that are reported in this paper, is the determination of the existence of a narrow semiconducting gap in the C_{60}-Pb bilayer. This semiconducting effect is produced probably, by the interdiffusion of Pb into the C_{60} layer, and the subsequently electronic transference by Pb to C_{60}.

The junctions used to study the C_{60}-Pb bilayer were fabricated on glass substrates by thermal evaporation in vacuum at pressures less than $6\text{x}10^{-6}$ Torr. Firstly, it was evaporated an Al or Pb film (6N purity) as the first electrode. This film was exposed to the laboratory atmosphere for a small period of time of about 3 min., with the purpose to form the insulating oxide barrier for the tunnel junction. Secondly, a C_{60} film (purity > 99.5%, from MER Corporation) was evaporated on the oxidized Al or Pb films. Finally, a

Pb film was evaporated transverse to the first Al or Pb films; the intersection between the Al or Pb and the top Pb films form the tunnel device. The area of these junctions were ~1x0.3 mm^2. The thickness of the films was monitored in situ by a quartz-crystal microbalance. Approximately typical thickness of the Al or Pb films were ~700 Å, for the C_{60} films were ~120 Å. Larger thickness than 120 Å of the C_{60} film produced very resistive tunnel junctions which are not appropriates for our measurements, due to noise, and lack of reproducibility. Lower thickness of the films were difficult to control mainly limited by the sensitivity of the quartz microbalance, and also for the control on the power that heat the tungsten boat used to make the evaporation of the C_{60}. Once we completed the sequence of evaporation of the tunnel junctions, we make the appropriate electrical wiring and connections, and then the devices were introduced as soon as possible into liquid helium.

The measurements of the tunneling characteristics, the differential resistance (dV/dI) versus the bias voltage V, the d^2V/dI^2 versus bias voltage V, were performed using the standard lock-in and modulation technique. We measured about 30 tunnel junctions, from which 12 presented a clear developing of the features related with the superconducting energy gap of Pb when the junction was cold down to below the superconducting transition temperature (T_c = 7.2 K). In the case of tunnel junctions of the type Pb-oxide-C_{60}-Pb, changes in the differential resistance at zero bias between the superconducting state and the normal state were at least of about one order of magnitude. Beside these devices, we also fabricated Pb-oxide-Pb tunnel junctions (without C_{60}) to check the position of the Pb phonon structure and the size of the energy gap, in this case the junctions fulfilled the Rowell criteria.[16]

In Fig. 1 we show a series of curves of the differential resistance versus bias voltage applied to the junction taken at different temperatures, for one of the sets of our tunnel junctions of the type Al-oxide-C_{60}-Pb. At high temperatures we can see the normal, almost parabolic background of a typical

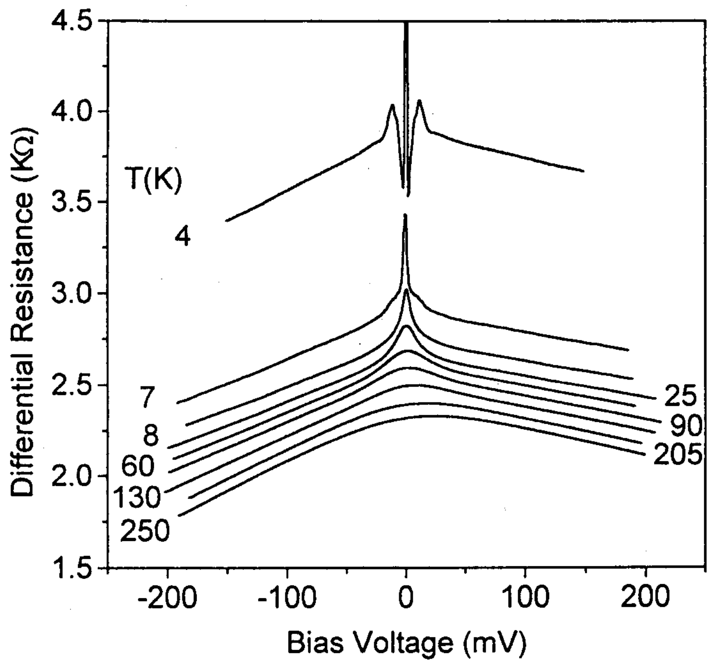

Figure 1: Tunneling characteristics of a junction of the type: Al-oxide-C_{60}-Pb. Set of curves of the differential resistance as a function of the bias voltage for different temperatures. The curves are vertically shifted for clarity.

tunnel junction between two metallic electrodes. However, in lowering the temperature, this parabolic background start to be distorted mainly around the zero bias voltage of the tunneling characteristic. We can note in the Fig. 1, that this new feature start to be well defined at a temperature of around 130 K, and it continuously increases as we follow decreasing the temperature. At about 8 K the feature looks clearly well defined, indicating the presence of an anomaly close to the Fermi surface of the material under study. At about 7 K the zero bias anomaly, presents an extra feature, indicating the opening of the superconducting gap of Pb. For temperatures below the superconducting transition temperature of Pb (T_C=7.2 K), the feature that emerges around zero bias is produced by the superconducting energy gap of lead. The upper part of the curve for T=4 K is out of scale due to the large anomaly produced by a well developed superconducting energy gap. It is worth mentioning that the magnitude of the superconducting gap is zero at T_C and increases as the temperature is lowered. The size of the gap was of ~2.6 meV at 4 K, the tunnel characteristic also shows the phonon structure of Pb, when the d^2V/dI^2 versus V is extracted.

For T=7 K (just below the T_C of Pb) we observed the presence of the superconducting gap of Pb and the semiconducting gap of C_{60}-Pb is clearly observed in the Fig. 2.

It is worth mentioning that theoretical studies of Altshuler and Aronov[17] show that in disordered semiconductors the zero bias anomaly observed in the differential resistance of tunnel junction can be due to the formation of a pseudogap or the arising of a small gap due to electron-electron interaction. It is noteworthy that also in a work by McMillan et al. they believe that this feature may be originated by localization effects near the metal-insulator transition in disordered materials.[18,19]

This zero bias anomaly observed in our junctions above the superconducting transition of Pb, resembles the existence of such a kind of feature arising in the density of states close to the Fermi surface of the formed C_{60}-Pb compound.

To observe in more detail the feature at zero bias above the superconducting temperature of Pb that we related with a pseudogap or a small semiconducting gap of the C_{60}-Pb bilayer, in Fig. 3 we present the derivative of the differential resistance against bias voltage for temperatures above T_C. Here we can associate the separation in voltage, between the maximum at negative bias and the minimum at positive bias, as the magnitude of the energy gap of the bilayer formed by C_{60} and Pb. For example, at temperatures of around T=8 K this magnitude is of the order of 6 meV. At higher temperatures thermal smearing hides the structure and this apparently disappears.

To get more insight about the nature of the mentioned feature that we are observing, in Fig. 4 we have plotted a Log-Log graph of the normalized

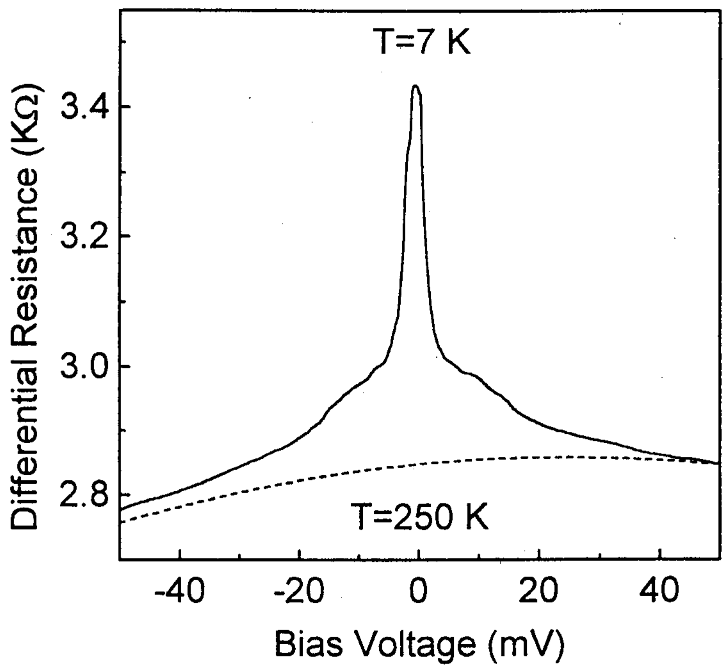

Figure 2: Tunneling characteristic of a junction of the type Al-oxide-C_{60}-Pb measured at 7 K; note the presence of the superconducting gap of Pb and the semiconducting gap, the dashed line corresponds to the characteristic measured at 250 K.

conductance versus bias voltage for T=8 K. We show in this plot the clearly amplified pseudogap or gap feature, possibly originated by localization effects near the metal-insulator transition in disordered materials.[18,19] If such is the case, we would expect a dependence of the density of states of the form $D(E) = D(0)(1 + \sqrt{E/\Delta})$, being $D(0)$ the density of states at the Fermi level and Δ the as called correlation gap.[18,19] At lower temperatures we expect that the conductance follows the form of that density of states.[18] As it is clearly observed in Fig. 4. However we did not see that predicted behavior, instead we can argue that other power laws can be associated to different regions of voltages. Only for comparison purposes in Fig. 4 we have plotted a curve which goes as $V^{1/2}$, note that this adjusts to the experimental points only in a very limited range of voltages.

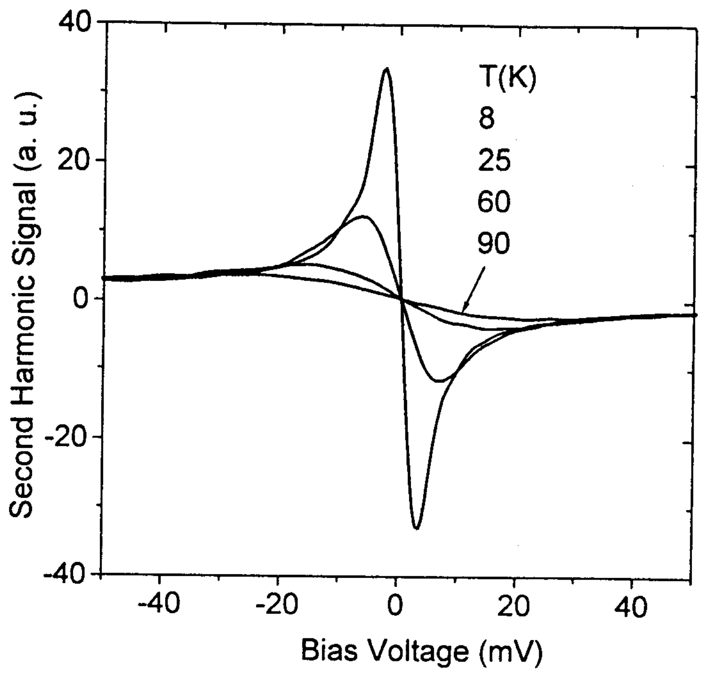

Figure 3: Derivative of the differential resistance for various temperatures above 7.2 K. We take the magnitude of the semiconducting gap as the separation in voltage between the maximum at negative bias and the minimum at positive bias.

In spite of this observation, it is worth mentioning that in the tunneling literature (see for example [18]), other kind of effects have been associated to the zero bias anomaly; such as superconductivity in granular systems or to magnetic impurities. We discarded any of those effects because with the application of magnetic fields up to 5 Teslas, and temperatures above the superconducting transition temperature of Pb the structure around zero bias remains unchanged. In addition, we observed that the differential conductance at zero bias as a function of temperature does not follow a linear behavior, such as has been observed in granular systems in the normal state.[18]

Further evidence of the existence of a gap in the density of states in the C_{60}-Pb bilayer is presented in Fig. 5. Here we used other set of tunnel junctions,

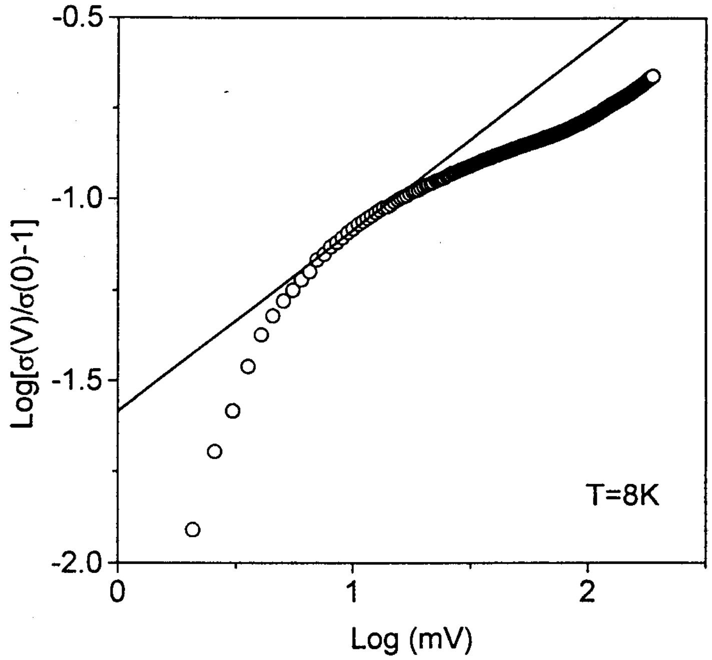

Figure 4: Log-Log plot of the normalized conductance, [σ(V)/σ(0)]-1, at T=8 K, where $\sigma(0)$ is the conductance at zero bias. The straight line corresponds to a $V^{1/2}$ behavior.

now of the type Pb-oxide-C_{60}-Pb. In this figure we plotted the derivative of the differential resistance against bias voltage for a tunnel junction measured at T=7.5 K. In the inset appears the differential resistance at zero bias as a function of the temperature. The dramatic change in this curve at T=7.2 K is due to the opening of the superconducting energy gap of Pb. The magnitude of the energy gap associated to the C_{60}-Pb bilayer, with value about 7 meV, is also in this case similar to the observed in Fig. 3 for junctions of Al-oxide-C_{60}-Pb.

In summary, the feature related with a semiconducting energy gap or pseudogap observed in our experiments, is associated to the system formed by C_{60}-Pb. Due to the thickness of the C_{60} layer (approximately 10 monolayers of C_{60}), many Pb atoms diffuse into this layer forming a semiconducting

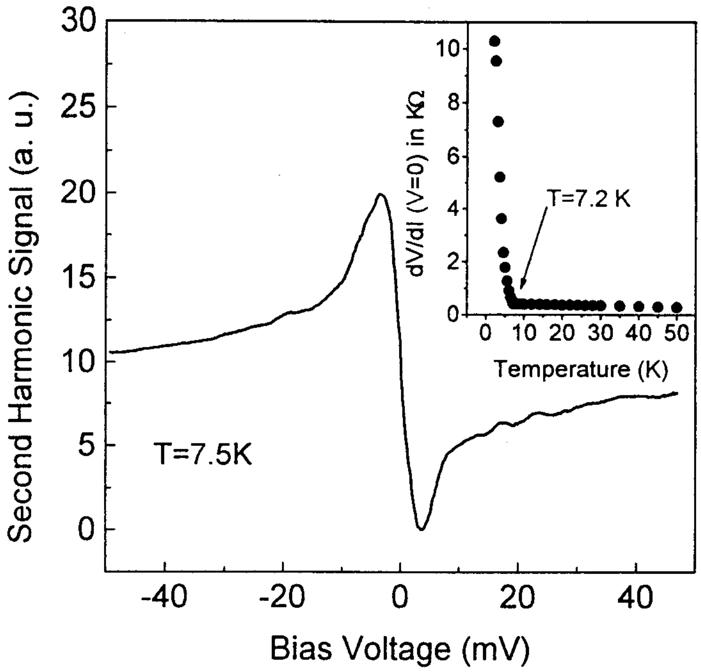

Figure 5: Derivative of the differential resistance against bias voltage for a tunnel junction of the type Pb-oxide-C_{60}-Pb taken at 7.5 K. The inset shows the zero bias resistance as a function of the temperature; the abrupt change observed at 7.2 K corresponds to the opening of the superconducting energy gap of Pb.

phase with a narrow gap in its density of states. We recall that tunneling spectroscopy has been proved to be very sensitive to interface states(see for example [18]); and this is the reason for which we clearly observed the gap feature, even when only some monolayers of C_{60} have been doped with Pb. We should remark that when other metallic layers are deposited on to a C_{60} layer, a strong process of interdiffusion has been observed.[14,15] Then we can conclude that this kind of process is also occurring in the C_{60}-Pb bilayers.

Finally we should mention that semiconducting systems has been found in C_{60} doped with In or Sb, the finding in those works is that the conductivity of the new system were increased many orders of magnitude compared to pure C_{60}.[20]

In conclusion, using tunneling spectroscopy we have found a narrow semiconducting gap or pseudogap (~6-7 meV wide) in the C_{60}-Pb bilayer which may be due to the doping of C_{60} by Pb atoms.

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References

[1] Hebard, A. F., Rosseinsky, M. J., Haddon, R. C., Murphy, D.W., Glarum, S. H., Palstra, T. T. M., Ramirez, A. P., and Kortan, A. R., Nature, 1991, 350, 600.

[2] Fleming, R. M., Ramirez, A. P., Rosseinsky, M. J., Murphy, D. W., Haddon, R. C., Zahurak, S. M., and Makhija, A. V., Nature, 1991, 352, 787.

[3] Haddon, R. C., Acc. Chem. Res., 1992, 25,127.

[4] Chen, X. H., and Roth, G., Phys. Rev. B, 1995, 52, 15534.

[5] Özdas, E., Kortan, A. R., Kopylov, N., Ramirez, A. P., Siegrist, T., Rabe, K. M., Bair, H. E., Schuppler, S., and Critin, P. H., Nature, 1995, 375, 126.

[6] Zhennan, G., Jiuxin, Q., Zhaoxia, J., Xihuang, Z., Sunqi, F., Wensheng, Z., and Xing, Z., Solid State Commun., 1992, 82, 167.

[7] Masterov, V. F., Popov,B. P., and Prikhod'ko, A. V., Phys. Solid State, 1995, 37,1371.

[8] Benning, P. J., Martins, J. L., Weaver, J. H., Chibante, L. P. F., and Smalley, R. E., Science, 1991, 252 1417.

[9] Wertheim, G. K., Rowe, J. E., Buchanan, D. N. E., Chaban, E. E., Hebard, A. F., Kortan, A. R., Makhija, A. V., and Haddon, R. C., Science, 1991, 252, 1419.

[10] Chen, C. T., Tjeng, L. H., Rudolf, P., Meigs, G., Rowe, J. E., Chen, J., McCauley Jr, J. P., Smith III, A. B., McGhie, A. R., Romanow, W. J., and Plummer, E. W., Nature, 1991, 352, 603.

[11] Ohno, T. R. , Chen, Y., Harvey, S. E., Kroll, G. H., Weaver, J. H., Haufler, R. E., and Smalley, R. E., Phys. Rev. B, 1991, 44, 13747.

[12] Hashizume, T., Motai, K., Wang, X. D., Shinohara, H., Saito, Y., Murayama, Y., Ohno, K., Kawasoe, Y., Nishina, Y., Pickering, H. W., Kuk, Y., and Sakurai, T., Phys. Rev. Lett., 1993, 71, 2959.

[13] Rong, Z. Y., and Rokhinson, L., Phys. Rev. B, 1994, 49, 7749.

[14] Hebard, A. F., Eom, C. B., Iwasa, Y., Lyons, K. B., Thomas, G. A., Rapkine, D. H., Fleming, R. M., Haddon, R. C., Phillips, J. M., Marshall, J. H., and Eick, R. H., Phys. Rev. B, 1994, 50, 17740.

[15] Owens, D. W., Aldao, C. M., Poirier, D. M., and Weaver, J. H., Phys. Rev. B, 1995, 51, 17068.

[16] See for example: McMillan, W. L., and Rowell, J. M., in "Superconductivity", vol. 1, chapter 11. Marcel Dekker, Inc. New York 1969.

[17] Altshuler, B. L., and Aronov, A. G., Solid State Commun., 1979, 30, 115.

[18] Wolf, E. L., "Principles of Electron Tunneling Spectroscopy", Oxford University Press, New York, 1989.

[19] McMillan, W. L., Phys. Rev. B, 1981, 24, 2739.

[20] Hoshimono, K., Fujimori, S., Fujita, S., and Fujita, S., Jpn. J. Appl. Phys., 1993, 32, L1070.

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