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Effect of high pressure on electrical transport in the Li_4C_{60} fulleride polymer from 100 to 400 K

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In situ resistance measurements have been carried out on Li_4C_{60} under pressures up to 2 GPa at temperatures from below 100 to 400 K. In agreement with recent reports we find an Arrhenius law behavior for the conductivity, which can be interpreted in terms of Li^+ ionic conduction with an activation energy near 225 meV. The activation energy decreases with increasing pressure at an initial rate of about $-11\%/\mathrm{GPa}$ and the room-temperature conductivity increases by a factor of about 6 from 0.1 to 2 GPa. We also observe conductivity terms with a lower excitation energy, most probably associated with conduction by electrons excited from defect-induced states in the main band gap. We discuss this conduction behavior in the context of recent measurements on both Li_4C_{60} and other alkali-metal intercalated phases such as Rb_4C_{60}, Na_2C_{60}, and Na_4C_{60}. After heating to 400 K at 2 GPa the conduction behavior changes drastically, manifested by a change in the slopes of R versus T curves signifying newly created gap states. Postexperimental characterization by Raman spectroscopy and x-ray diffraction indicate the loss of Li especially from the grain surfaces. Finally, high-pressure Raman studies suggest a possible metallization transition above 9 GPa.

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I. INTRODUCTION

The transport properties of intercalated fullerides show a strong correlation with crystal structure. They can exhibit insulating, semiconducting, metallic, or even superconducting properties depending on the intercalated metal and on doping concentration.[1–3] The smallest alkali-metal ion, lithium, can be intercalated into C_{60} up to a stoichiometry of $Li_{28}C_{60}$.[4] At high doping levels (typically for $x>7$) lithium clusters form, located in the largest interstices of the original fcc lattice of C_{60}.[5] Li_4C_{60} is a particularly interesting compound among the Li-intercalated fullerides due to its unique, stable structure and its interesting properties.[6–11] The two-dimensional monoclinic polymer structure is based on two types of differently bonded fullerene chains, with one and two covalent interfullerene C-C bonds, respectively, running perpendicular to each other in the *ab* basal plane.[6] The only other covalently bonded A_4C_{60} compound is Na_4C_{60} where each fullerene molecule is linked to four others by single covalent C-C bonds.[12] Li_4C_{60} is a band-gap insulator at ambient pressure, indicating that the electrons involved in the covalent bonds are fully localized between the fullerene molecules.[7–9] Above ~470 K it transforms by a gradual depolymerization into a monomeric fcc high-temperature structure. At even higher temperatures Li_4C_{60} is found to be metallic at 673 K with a fcc structure[9,10] similar to that of the A_3C_{60} compounds. The small size of the Li^+ ions and the large free space in the structure (two tetrahedral and one larger octahedral interstitial voids per molecular unit in the fcc C_{60} crystal lattice) should enable the ions to move in three dimensions in the lattice and recent studies report an extraordinary superionic conductivity in Li_4C_{60}.[10,11] At low temperatures the Li^+ ions are statically disordered but at $T>130$ K they are observed to start to diffuse.[10,11] However, from the measured band gap[8] of Li_4C_{60} it is also reasonable to expect that an electronic conduction channel should exist in parallel to the ionic conduction, with a conductivity magnitude similar to what is found in other alkali-metal fullerides.[13,14]

The possible existence of two parallel conduction channels makes Li_4C_{60} a very interesting material. One possible way to tune these conduction mechanisms would be to apply an external pressure. We know that an applied pressure leads to a slow closing of the band gap and an increased electronic conductivity in most fullerides, and, in particular, in the related compounds Na_4C_{60} (Ref. 14) and Rb_4C_{60}.[13,15,16] On the other hand we intuitively expect that ion diffusion should be slowed down by the narrowing of the intermolecular channels under pressure, leading to a reduced ionic conductivity.

In the current study we present a series of dc resistance measurements on Li_4C_{60} over a wide range of temperatures at pressures from 0.1 to 2 GPa. We show that the results may be interpreted in terms of an ionic conductivity component with an activation energy near 225 meV, in excellent agreement with the ionic conduction mechanism identified by Riccò *et al.*[10,11] Above 240 K this conduction mechanism dominates the total conductivity while below 240 K a second term, tentatively identified as an electronic term with a very similar activation energy, dominates. With increasing pressure, and at very low temperatures, we observe effects that are best described by a further conduction channel characterized by an additional, lower activation energy near 130 meV, similar to that previously observed for the defect state conductivity in Na_4C_{60} (Ref. 14) and Rb_4C_{60}.[13] Surprisingly, we find that the application of a pressure of 2 GPa induces a very rapid, order-of-magnitude increase in all three fitted conduction components. Such an increase is intuitively difficult to reconcile with ionic conduction. Although we may find arguments in favor of such a model, we also suggest as an alternative that electronic conduction might become increasingly important with increasing pressure.

Heating at high pressure results in a transformation into a state where the conductivity shows a much lower dominant excitation energy and a very weak pressure dependence, which we believe is mainly associated with an increased contribution from carriers excited from defect states caused by a small loss of Li. The strong pressure dependence observed for the dominant carrier excitation energy may imply a pos-

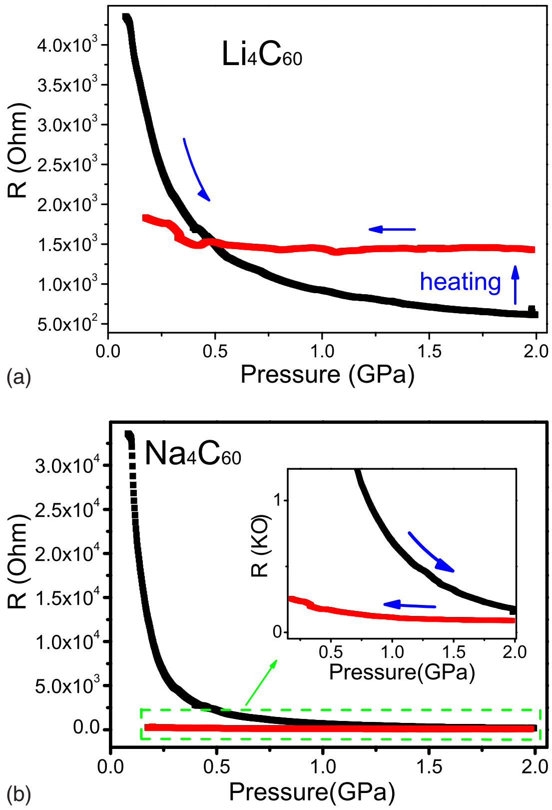

FIG. 1. (Color online) (a) Resistance as a function of pressure for one sample of Li_4C_{60}, first for increasing pressure up to 2 GPa at room temperature, then for decreasing pressure after heating at 2 GPa. (b) Data obtained in the same pressure run for Na_4C_{60}, with the high-pressure behavior shown on an enlarged scale.

sible metallization at high pressure and we finally present Raman measurements which indeed indicate that such a metallization may occur at pressures above about 9 GPa.

II. EXPERIMENTAL DETAILS

To produce Li_4C_{60}, sublimed C_{60} powder with a nominal purity of 99.98%, obtained from Term-USA (Fort Bragg, CA, USA) was heated for 12 h under dynamic vacuum to remove O_2 and N_2. Well mixed stoichiometric amounts of C_{60} and alkali metal were loaded into copper or stainless-steel crucibles with tight-fitting covers and then annealed at elevated temperatures (350 °C) for about 1 month in an oxygen-free glove box. The samples were reground once every week. The progress of the reaction was monitored by x-ray diffraction and Raman spectroscopy. The final products were confirmed to be single phase Li_4C_{60}, having the same structural and spectroscopic features as observed in earlier work.[6,17] For the resistance measurement, the powder samples were compressed into linear grooves in a Teflon plate with Ni resistance probes, using the same piston-cylinder high-pressure device and the same measurement system as in our earlier work on Rb_4C_{60} and Na_2C_{60}.[13,18] The pressure vessel was cooled by liquid nitrogen and the cell had an internal heater which enabled us to reach temperatures up to 500 K. The electric resistivity was measured using a four-probe dc method with nickel wire contacts. As mentioned above, Riccò *et al.*[10,11] have found a strong ionic conductivity in Li_4C_{60} and to avoid Li^+ ion migration they used a quasi-dc method with current inversion every 200 ms. We have carefully checked the time dependence of the measured resistance to find any evidence for errors due to such an effect. We find no such evidence and we conclude that the dc method is sufficiently accurate for our purposes. The *in situ* high-pressure Raman measurements were carried out in a diamond-anvil cell with 0.75 mm culets, using the standard ruby method for pressure calibration.

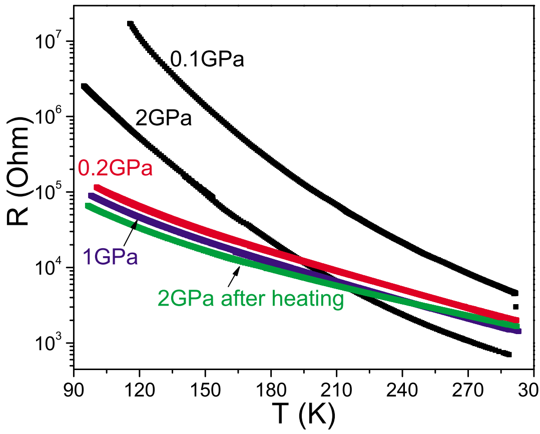

FIG. 2. (Color online) The resistance of Li_4C_{60} as a function of temperature between 100 and 300 K at the pressures indicated. Data were taken in the sequence 0.1 and 2 GPa (black), then, after heating to high temperature, at 0.2, 1, and 2 GPa (red, blue, and green curves).

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Results for the ambient-pressure phase of Li_4C_{60}

High-pressure resistance measurements were carried out on two well characterized, homogeneous Li_4C_{60} samples. In the first experiment, we started by a cooling run at 0.1 GPa to identify the initial low-pressure transport properties of the material. The pressure was then increased from 0.1 to 2 GPa at room temperature at a rate of 1 $GPa\ h^{-1}$ (Fig. 1). In this pressure range the resistance had negative temperature and pressure coefficients at all pressures and no signs of phase transformations could be observed. At 2 GPa, another cooling run was made, followed by heating to about 400 K to find any conductivity terms with higher excitation energies. After this heating run the sample showed a very different behavior, with much smaller variations in resistance with temperature and pressure, as shown in Figs. 1 and 2. To investigate this state further a second cooling run was carried out before the pressure was decreased back to atmospheric pressure. On the way back to atmospheric pressure cooling runs were performed first at 0.2 GPa, then at 1 GPa, with a final heating run at 1 GPa before the pressure was released.

To verify the results we carried out a second experiment. The resistance of sample 2 was first studied by making cooling runs between 100 and 290 K at 0.1, 1, and 2 GPa. At 2 GPa we heated the sample to 400 K in the same way as in the first experiment, after which we made another low-temperature run which verified that the resistance behavior had changed in the same way as before. Finally, we decreased the pressure to 0.2 GPa and made another cooling run. However, in order to ascertain that the lattice structure of the heat transformed sample was preserved to atmospheric pressure we did not repeat the heating cycle at this pressure.

The resistance data of the two Li_4C_{60} samples were highly reproducible with very similar pressure and temperature dependences. In contrast to Riccò *et al.*,[11] who found a sharp change in dR/dT near 130 K and correlated this anomaly with a freezing of Li^+ ion diffusion, we see only a gradual change in slope in R versus T in this temperature range because of the presence of additional conductance terms (see below).

The semiconductorlike resistance observed in the initial low temperature runs up to 2 GPa, which can be fitted rather well by an Arrhenius-type law (see below), is similar to the semiconducting behavior reported for Rb_4C_{60} and Na_4C_{60}.[13,14] In the same way as for those materials we find that a single exponential function is not able to provide a good fit to the data and that at least two conduction mechanisms or terms must be used for this material. The total conductivity σ ($=1/\rho$, where ρ is the resistivity) can then be written as the sum of two (or several) additive terms acting effectively in parallel. Using the same fitting method and software as in previous studies we thus write

$$\sigma(T) = A_1 \exp(-E_1/2k_BT) + A_2 \exp(-E_2/2k_BT) \times (+\text{possible further terms}). \quad (1)$$

The exponential terms describe the thermal excitation of carriers and the constants A_i include all geometrical factors, mobilities, etc. In practice, we fit Eq. (1) to the conductance $G=R^{-1}$ which differs from σ only by a constant (geometrical) factor.

The factors of 2 in the exponentials of Eq. (1) actually imply a semiconductor model with electronic conduction, and in our earlier studies of Rb_4C_{60} and Na_4C_{60} (Refs. 13 and 14) the two terms in Eq. (1) were attributed to contributions from carriers excited over the band gap $E_g(E_1=E_g)$ and from carriers excited from localized states with energy E_2 in the gap. For Li_4C_{60}, recent work has identified an ionic conduction mechanism in which σ has also been shown to follow an Arrhenius law behavior[11] with an excitation energy near 220 meV. However, in this case the ionic conduction term σ_i should be written

$$\sigma_i = A_i \exp(-E_i/k_BT). \quad (2)$$

The excitation energies will thus have different values, depending on the conduction mechanism assumed, but the general mathematical expression fitted to the data will be the same for both types of conduction. Because Li_4C_{60} is reported to be a semiconductor with a band gap similar to that of other A_4C_{60} compounds[8] some care must be taken when assigning the fitted excitation energies. Although we expect to find an ionic term [Eq. (2)] with an excitation energy of about 220 meV, corresponding to twice this value in the fit to Eq. (1), other terms are also observed. For these we could make similar assignments as in our earlier work. Recent electron paramagnetic resonance measurements[10] and ^7Li NMR measurements[19] have shown the presence of localized states in the band gap, originating from broken C_{60}-C_{60} bonds or local Li off-stoichiometry. In a similar way, NMR measurements also showed the existence of donor gap states in Rb_4C_{60} (Ref. 20) and the same model has been successfully used to interpret the conductivity in pure C_{60} (Ref. 21), in Rb_4C_{60},[13] and in Na_4C_{60}.[14] It should be noted that in the present material we have an interesting case with both electronic and ionic conduction, possibly with quite similar excitation energies, but we have no way of distinguishing between these mechanisms from our dc measurements.

Before discussing the actual results, we need to discuss briefly the fitting and analysis procedures. In our earlier studies of Rb_4C_{60} and Na_4C_{60}, fitting Eq. (1) to the data gave well-separated values for E_1 and E_2 but for Li_4C_{60} curve fitting was more difficult because the observed energy levels were rather closely spaced. Also, exponential functions are notoriously difficult to fit by the least-square method because this procedure minimizes the absolute deviation of the data from the fitted function. In our case the resistance varies by three orders of magnitude at each pressure. From Fig. 2 we see that an average least-square deviation of 10 kΩ will correspond to about 0.1% of R at low T but about 100% near room temperature. As a rule of thumb, fitting any function to our data for $R(T)$ will give very high relative accuracy at *low* temperatures while fitting the corresponding function to the same data in the form of conductance $G(T)$ will give high accuracy at *high* T. Of course, if we assume a *single* exponential term of the form given in Eq. (1) and (2) we can easily obtain the local energy parameter E from the slope of $\ln \rho$ (or $\ln \sigma$) versus T^{-1}. When more than one term is involved such a procedure gives an effective value $E(T)$ at any chosen T. However, only in those ranges of T where any single term dominates the magnitude of σ do the values fitted in this way correspond to true physical properties of the material. For the data in Fig. 2, for example, values of E_1 and E_2 derived from the slopes at the highest and lowest temperatures should be good approximations to the values obtained by a direct fit of Eq. (1).

Taking these difficulties into account, a reasonable strategy for fitting Eq. (1) to the data over wider ranges in T is to use the two-step procedure illustrated in Fig. 3. We first fit a single exponential function to the data for $R(T)$ at low temperatures to find the smaller exponent E_2 [Fig. 3(a)]. After this, the data are inverted and we fit Eq. (1) to the conductance $G(T)=R^{-1}$, with E_2 fixed at the value found in the first step, to find the remaining coefficients (green curve in Fig. 3). With such a procedure, which has also been used in previous studies,[18] a very good agreement can be found between the measured data and the fitted four-parameter functions at most temperatures.

When analyzing the data shown in Fig. 2 we found that a reasonable fit required the use of two terms in Eq. (1) above, and to minimize deviations from the fitted curves we also had to limit the range to temperatures higher than 115–130 K, depending on pressure. In the remaining narrow temperature range below this the data could be fitted by a single exponential term in T^{-1} with an even smaller value for the

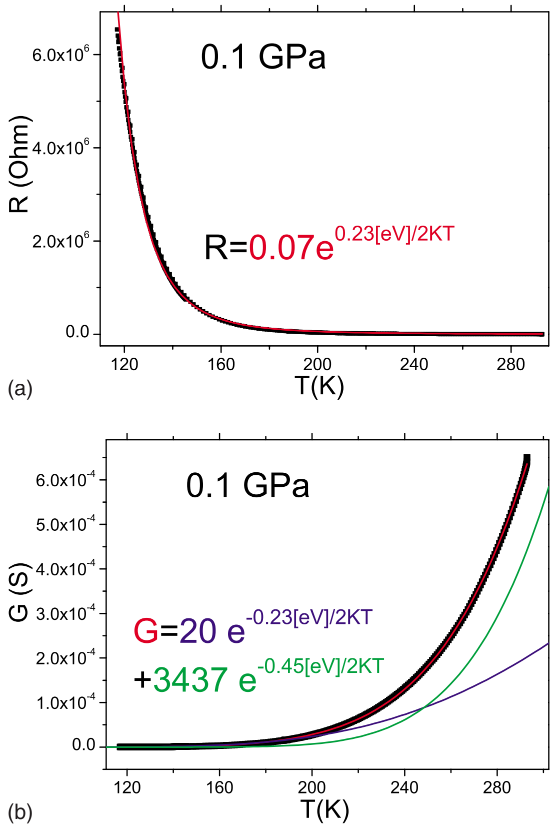

FIG. 3. (Color online) (a) Single exponential function $R = A_2 \exp(E_2/2k_BT)$ fitted to the data for the resistance $R(T)$ to yield E_2 in the temperature range 115–295 K and (b) Eq. (1) fitted to the same data set, inverted to the form $G = 1/R$. The two fitted energy constants are $E_g = 0.45$ eV and $E_2 = 0.23$ eV.

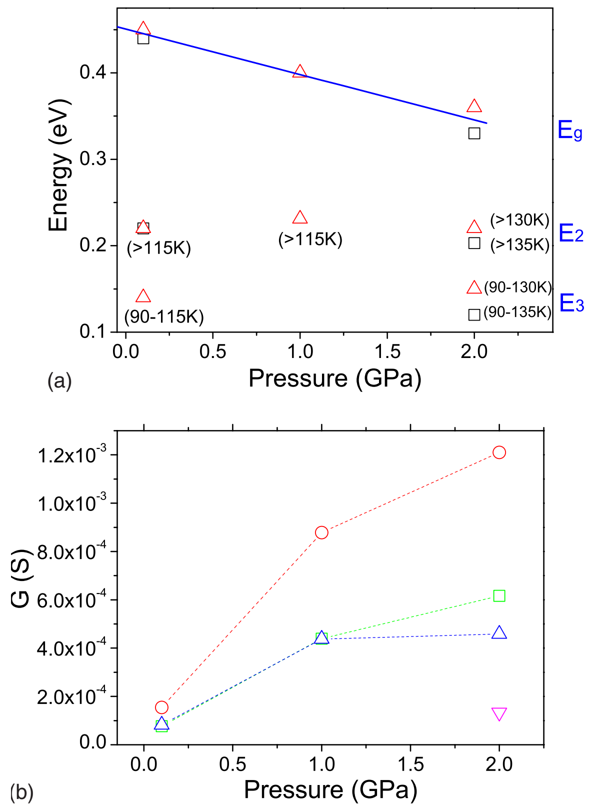

FIG. 4. (Color online) (a) Fitted excitation energies as functions of pressure. The fitted straight line has a slope −52 ± 7 meV GPa^{-1} and (b) magnitudes of the total conductance and of the conduction terms corresponding to each excitation energy as functions of pressure at 245 K. Circles represent the total conductance, inverse triangles, triangles, and squares the magnitudes of the 0.13, 0.23, and 0.45 eV terms, respectively. The term corresponding to gap states ($E_3 = 0.13$ eV) is very close to zero at 0.1 and 1 GPa and is not plotted at these pressures.

excitation energy, in qualitative agreement with the results of Riccò *et al.*[11]

The fitted excitation energies obtained from Eq. (1) for the two experiments are shown in Fig. 4(a) as functions of pressure. We find that three exponential terms with similar characteristic energies of $E_1 = 0.45$, $E_2 = 0.23$, and $E_3 = 0.13$ eV, respectively, are needed to completely describe the conductivity of our material at the lowest pressure. The two smaller energies probably correspond to the energies of localized electronic states in the gap, as found for other fullerides. The term with the largest excitation energy could be interpreted as the ionic conduction term identified by Riccò *et al.*,[11] with an excitation energy of 0.225 eV [Eq. (2)], very close to the value found by Riccò *et al.* However, in principle, both ionic and electronic conduction might contribute to this term and if it is associated with electronic conduction it would correspond to a band-gap energy of 0.45 eV. The conductivity of Li_4C_{60} thus seems to be quite complex, possibly with both ionic and electronic conduction acting in parallel. Note that in Fig. 4(a) we plot the energy values as obtained by fitting Eq. (1) to the data, such that the E_1 term is plotted at 0.45 eV (in principle corresponding to electronic conduction) rather than at 0.225 eV (ionic conduction). This is done intentionally in order to avoid confusing this term with the E_2 term near 0.23 eV since the two terms have a quite different dependence on pressure. Whereas E_2 is almost independent of pressure, E_1 decreases rapidly with increasing pressure. We return to this fact below.

Each of the three terms dominates in a certain temperature region. At low pressure we can obtain a quite good fit to the data from 130 K to room temperature using only the terms with $E_1 = 0.45$ eV (corresponding to an ionic term with energy 0.225 eV) and $E_2 = 0.23$ eV but fitting the data below 130 K (where these terms are very small) we also find a small term with $E_3 = 0.13$ eV which we must assume corresponds to excitation of localized electron states in the gap associated with deformation-induced defects. Such a term dominates the resistivity in the low-T region for other alkali-metal fullerides investigated[13,14,18] and is also discussed by Riccò *et al.*[11] for Li_4C_{60} at low T. The term corresponding to E_2 dominates at intermediate temperatures (from 130 to about 240 K at 0.1 GPa), above which the term due to E_1 grows rapidly. For our sample, which has been strongly deformed by the application of pressure, these defect-induced terms are much larger than in the work of Riccò *et al.*[11] As a consequence, the total change in conductivity with temperature is about an order of magnitude smaller for our sample than for that of Riccò *et al.*, where only the term with the highest excitation energy is active and the sharp freezing of the ion conduction term reported by Riccò *et al.* is hidden by the much larger, smooth electronic term.

To show the evolution of each of these conduction terms with pressure, their magnitudes are shown in Fig. 4(b) as functions of pressure at an intermediate temperature of 245 K. The small 0.13 eV defect term increases most strongly, by about two orders of magnitude, from 0.1 to 2 GPa. (The magnitude of this term is not shown at and below 1 GPa because it is zero on the scale of the figure.) The other two terms also increase strongly by factors of about 8 and 5.

If we interpret the term with the largest fitted excitation energy as arising from ionic conductivity, the observed increase in the conductance with increasing pressure is quite unexpected. Intuitively, we would expect a *decrease* in such a term under pressure because an applied pressure decreases the intermolecular distances and thereby shrinks the diameters of the available channels for Li diffusion. Also, not only does the magnitude of the conduction term increase under pressure but the fitted excitation energy also decreases [Fig. 4(a)] by about 11%/GPa, suggesting that the mobility of the ions increases rapidly under pressure. Although such effects seem unlikely, it has been observed for several superionic oxide conductors that their conductivities increase by an order of magnitude under pressures in the range studied here. However, it is uncertain whether it is possible to make a direct comparison between pressure effects in glassy or structurally complex oxides and in a crystalline carbon-based conductor such as Li_4C_{60}. On the other hand, we know that the Li-C interaction changes strongly under pressure since three times more Li can be intercalated into graphite at 5 GPa as compared to at zero pressure,[22] and it is mainly the in-plane diffusion channels that should be closed by compression due to the layered structure of Li_4C_{60}. In principle, the creation of lattice defects might also create new diffusion paths for the ions but the probability is high that the number of paths created and the number of paths closed by defects are similar. The results obtained for the pressure dependence of this conduction term are difficult to understand at an intuitive level and calculations or further experiments are clearly needed to shed light on this behavior.

As mentioned above, an alternative interpretation of this term in a semiconductor model is also possible. In such a case, a strong increase would be expected. E_1 would then correspond to the band-gap energy and the strong increase in σ would correlate with a rapid decrease in band gap with increasing pressure, as shown in Fig. 4(a). The band gap of Li_4C_{60} would be $E_1 = E_g = 0.45$ eV near atmospheric pressure, very close to the value 0.4 eV found for the polymer Na_4C_{60},[14] and also in reasonable agreement with data that we obtained for Li_4C_{60} in a recent ^{13}C NMR study (unpublished). It is noticeably smaller than the band gap 0.7 eV found in the unpolymerized compound Rb_4C_{60},[13] as would be expected since both theory[23] and experiments[24] agree that fullerene-based polymers usually have significantly smaller band gaps than the corresponding unpolymerized compounds. However, the gap is significantly smaller than the value 0.8 eV recently found by Macovez *et al.*[8] from electron energy loss and photoemission spectra on Li_4C_{60} thin films. The existence of an electronic conduction channel is not discussed by Riccò *et al.* but an increase in the slope of ln R versus T^{-1} near room temperature is clearly noticeable in their Fig. 1. The measured energy E_g for our samples decreases from 0.44 eV at 0.1 GPa to about 0.34 eV at 2 GPa [see Fig. 4(a)]. A linear fit yields a pressure dependence of -0.052 eV GPa^{-1}, corresponding to an initial pressure coefficient of $d(\ln E_g)/dp = -0.114$ GPa^{-1}. A linear extrapolation indicates a possible closing of the gap already near 9 GPa. To compare the pressure dependence of this E_g with that of other materials we need data for the compressibility of Li_4C_{60}. This property has not been measured but the two-dimensional polymeric structure of the material, with covalent intermolecular bonds in two directions, should imply a rather low and anisotropic compressibility dominated by interactions between the polymeric fullerene layers. To a first approximation we would thus expect the bulk modulus B_0 to be about three times higher than for pure C_{60} [$B_0 = 9.6$ GPa (Refs. 25 and 26)] and similar to those of tetragonal C_{60}, 34.8 GPa (Refs. 25 and 27) and graphite, 33.8 GPa.[28] The very small Li^+ ions should have only a minor effect on the compressibility but could in principle lead to a higher value for the bulk modulus. The band gap in pure C_{60} also closes under pressure, at an initial rate of $dE_g/dp = -0.14$ eV GPa^{-1} (Refs. 25 and 29) and considering the difference in compressibility we see that the two gaps have rather similar dependences on changes in crystal volume. We note here that Na_4C_{60} is significantly less compressible than this, with a bulk modulus $B_0 = 73$ GPa,[30] probably because the larger Na^+ ions interact strongly with the fullerene cages on compression.

The pressure dependence of the conductivity is thus much easier to reconcile with an electronic mechanism than with ionic conductivity. However, there are still many open questions which our dc measurements cannot answer, and as already stated above further experiments and calculations are needed in order to understand whether we observe a novel behavior for an ionic mechanism in a crystalline solid or a transition from an ionic mechanism at low pressure to an electronic transport mechanism with a very similar activation energy at higher pressures.

For the energy parameters E_2 and E_3, assumed to correspond to localized states in the gap, the scatter in the data is too large to allow a numerical estimate of their pressure dependence and we only note that they depend weakly on pressure. We have found in our earlier studies on Rb_4C_{60} and Na_4C_{60} that the pressure dependence for the excitation energy for the localized electrons was also quite small and that both this energy and E_g decrease with increasing pressure. The rapid increase in the conduction terms corresponding to E_2 and E_3 probably arises from the creation of further defects with increasing nonhydrostatic pressure in the experiment. Whether two well-defined activation energies really exist is another interesting question; it is quite possible that the results obtained instead correspond to a smooth distribution of low excitation energies. This would not, of course, change the main conclusions.

Finally, we return to the pressure dependence of the total resistance, shown in Fig. 1. The inset in this figure shows data for Na_4C_{60} measured simultaneously in the same pressure cell. The starting resistance of Li_4C_{60} at room temperature is one order of magnitude lower than that of Na_4C_{60}, which can be related either to the different structures of these two compounds or to the ionic conduction possibly present in Li_4C_{60}. It has been suggested that the resistance of fullerene polymers decreases with an increase in the degree of polymerization,[23] which rationalizes our results considering the higher density of intermolecular bonds in Li_4C_{60} as compared with Na_4C_{60}. However, it is interesting to note that up to 2 GPa the resistance of Li_4C_{60} drops to 15% of the zero-pressure value while in Na_4C_{60} it drops to only 0.6% of the initial value. (As a comparison, the resistivity of single crystal C_{60} drops by about one order of magnitude up to 1 GPa,[31] rather closer to the results for Na_4C_{60} than to those for Li_4C_{60}.) This result has been reproduced in two different experimental runs and thus a random geometrical effect can be excluded. The pressure dependence of the resistance is thus an order of magnitude stronger for Na_4C_{60} than for Li_4C_{60}. This is probably not related to structural changes since Na_4C_{60} has a quite low volume compressibility, which should imply small pressure effects, and the band gap of Li_4C_{60} should also be more sensitive to pressure than that of Na_4C_{60}.

B. Results for Li_4C_{60} heated to 400 K at 2 GPa

After heating at 2 GPa, the resistance of both samples showed a completely different behavior, characterized by a much weaker dependence on both temperature and pressure (Figs. 1 and 2). In addition, after heating the room-temperature resistance increases by about 100% in Li_4C_{60} while that of Na_4C_{60} decreases by ~50%, indicating that the high-temperature treatment at high pressure has induced different changes to the two materials. It is also interesting to note that it is no longer possible to fit the $R \sim T$ data in the same way as before. In particular, the 0.2 eV term is no longer observed. A reasonable fit again requires more than one low-energy term with energies near or below 0.1 eV but the energies are very close together indicating that the low-energy state no longer has a well-defined energy but rather should be described by a distribution of energy values. We also tried to apply a variable-range hopping model but without success. Because of the larger uncertainties we do not give fitted values for the various parameters for the samples after heating.

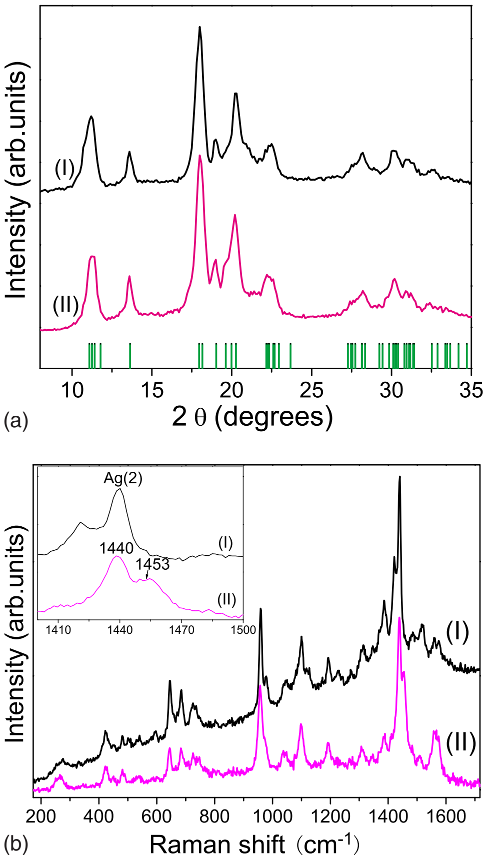

FIG. 5. (Color online) (a) X-ray diffraction patterns of Li_4C_{60}, (i) at zero pressure before the experiment and (ii) after high pressure and high-temperature treatment. Ticks show line positions for Li_4C_{60} (bottom, green) calculated from literature data (Ref. 6); (b) Raman spectra of Li_4C_{60}, (i) at zero pressure before the experiment and (II) after high pressure and high-temperature treatment. Inset shows the $A_g(2)$ modes.

To study what happened in the samples during the treatment at high pressure and high temperature, the entire high-pressure cell was transferred to a glove box and opened under argon. The sample was then loaded into a capillary for Raman and x-ray characterization. Figure 5 shows the ambient condition x-ray pattern and Raman spectra of this sample, as well as those of as-produced Li_4C_{60} for comparison. There are only minor differences between the two x-ray patterns, consistent with a literature report[4] that Li_4C_{60} shows similar x-ray patterns before and after treatment under 5 GPa at 573 K. However, in the Raman spectrum a well-resolved shoulder is observed in the $A_g(2)$ mode, with the peak center located at 1453 cm^{-1}. This can be considered as a component with lower Li doping concentration or even as the presence of a polymerized pure C_{60} component formed in the sample.[32] In either case this implies that at these conditions (400 K, 2 GPa) lithium is lost from the sample. This should give a large effect on possible ionic transport and indeed we observe a virtually complete disappearance of the 0.2 eV conductivity term. However, since little change was found in the x-ray pattern, which reflects the structure of the bulk material, we suggest that the loss of Li mostly occurs on the surface of the sample grains while the bulk still preserves the initial structure. Whether Li was lost due to enhanced diffusion by a reaction with metal contacts or trapped air/water or by an increased electromigration at high temperature is not known. The loss of Li from Li_4C_{60} should induce more defects, such as the breaking of some polymeric C_{60}-C_{60} bonds and local Li off-stoichiometry create more gap states and even create insulating surface barriers between individual grains, consistent with the semiconductor model analysis above and the observation that it is impossible to fit the low-temperature $R \sim T$ curves with a single exponential function. The high, almost pressure-independent conductivity observed is consistent with such a high, pressure-independent defect density.

C. Possible metallization of Li_4C_{60} under high pressure

As discussed above, the rapid decrease in E_1 under pressure might be interpreted as a strong pressure dependence of

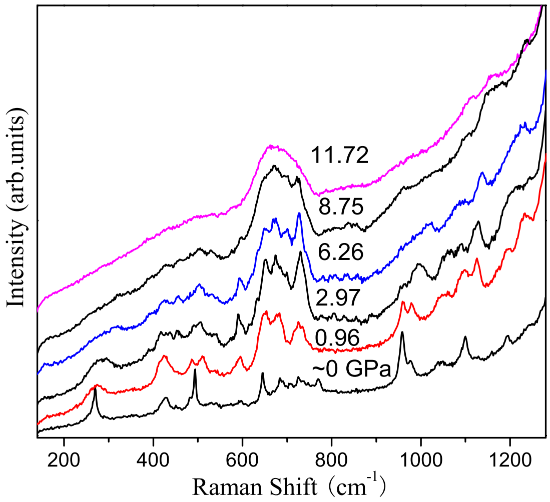

FIG. 6. (Color online) Raman spectra for Li_4C_{60} at the pressures (in gigapascal) indicated.

the band-gap energy, about -52 ± 7 meV GPa^{-1}, corresponding to about 11%/GPa. Such a rapid closing of the band gap under pressure should lead to an insulator-metal transition at about 9 GPa. To search for a pressure-induced insulator-metal transition we have carried out a high-pressure Raman experiment on Li_4C_{60} under pressures up to 12 GPa. Generally an increased electron-phonon coupling, which is expected in a metallic fulleride phase, broadens especially the H_g-derived Raman modes. This, in combination with other effects such as a weakening of all signals due to a metallization-induced reflection of the incident excitation light, makes Raman spectroscopy a sensitive tool to detect such a transition, if present. The results obtained are shown in Fig. 6. Below 8 GPa we can see all zero-pressure Raman modes and peak positions change progressively with increasing pressure. At 8–10 GPa, all Raman modes become too weak to be detected due to broadening and weakening, except for a "bump" around 600–800 cm^{-1}. A similar effect of the Raman modes is often observed for other fullerides or fullerenes but usually at much higher pressures, at least 15 GPa for Na_4C_{60} or polymeric C_{60}, and usually indicates an irreversible polymerization or amorphization. The low pressure observed for Li_4C_{60} clearly points to a different explanation, and this is also indicated by the rapid weakening and disappearance of the Raman peaks characteristic for the intermolecular (polymer) bonds near 960 cm^{-1} which may indicate a depolymerization just below 8.7 GPa. Furthermore, upon pressure release from 12 GPa the Raman spectra of the sample are clearly reversible, excluding the possibility that the changes result from an amorphization due to destruction of the C_{60} molecules. These observations give strong support for either a pressure-induced metallization of Li_4C_{60}, possibly associated with depolymerization or to a further enhancement of the Li^+-C interactions. Such an enhancement could result in the partial hybridization of Li and C p_z orbitals, thus changing the C_{60} molecular features and the Raman modes. A full explanation must await theoretical calculations of the band structure of Li_4C_{60} under pressure.

IV. CONCLUSIONS

In summary, *in situ* resistance measurements on Li_4C_{60} under pressures up to 2 GPa show that the resistivity of Li_4C_{60} is dominated by an Arrhenius-type activated mechanism. The data can be interpreted in terms of an ionic conduction mechanism, associated with an activation energy of about 0.23 eV, as identified in recent work by Riccò *et al.*,[11] acting together with at least one electronic mechanism. The latter are associated with smaller activation energies and probably with defects produced by deformation under pressure, and this identification is strengthened by the observation of a very rapid increase in the conductivity with increasing pressure. Although we intuitively expect the application of high pressure to close the diffusion paths for the Li^+ ions, we find that the magnitude of the ionic term increases by a factor of 8 between 0.1 and 2 GPa. Although we can find arguments why this might be possible, we also present an alternative model in terms of an electronic conduction mechanism which we find easier to reconcile with the data. In this model the band gap shows a strong pressure dependence, about –0.05 eV GPa^{-1}, while the other excitation energies are almost independent of pressure. The fitted low excitation energies may in reality represent a distribution of gap state energies and correspond to electronic conduction at all pressures. A third possible interpretation is that ionic conduction exists under ambient conditions but decreases under pressure where the conduction is dominated by electrons excited both over the full band gap and from strain-induced localized defect states in the gap.

Heating at 2 GPa leads to the loss of Li from Li_4C_{60}, especially from the surface of the grains, creating more defects and thus more localized states in the band gap, which completely changes the conduction behavior of the sample. However, this transformation results in surprisingly small changes in the bulk structure.

Finally, guided by the strong pressure dependence observed for the band gap we have carried out a Raman study under high pressure to look for a possible closing of the band gap and a metallization transition. Our data show anomalies in the Raman data near 8–10 GPa which can be interpreted in terms of an insulator-to-metal transition in this range, in very good agreement with the observed rate of decrease for the band-gap energy.

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