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Electrical transport properties of Na_2C_{60} under high pressure

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We present direct resistance measurements on Na_2C_{60} under high pressure up to 2 GPa in the temperature range ~90–500 K. We show that fresh, nominally pure Na_2C_{60} exhibits a semiconductor-type conduction behavior at all experimental conditions, with a 1.2 eV band gap and a conduction strongly influenced by defect gap states. Contrary to Rb_4C_{60} and Na_4C_{60}, both band gap and gap states have large pressure dependences. In contrast, a Na_2C_{60} sample preserved in an oxygen-free environment for several months shows conduction by another mechanism, variable range 3D hopping. This is consistent with recent findings of nanoscale phase segregation in Na_2C_{60} and can be understood in terms of conduction by intergrain hopping. Heating the sample at 2 GPa leads to a significant change in the resistivity, suggesting a structural transition. By characterizing the sample after the phase transformation with Raman spectroscopy and x-ray diffraction we identify a phase separation of the material into two main structures, linearly polymerized orthorhombic C_{60} and two-dimensionally polymerized Na_4C_{60}.

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I. INTRODUCTION

In alkali fullerides A_xC_{60}, the crystal structures and electronic properties are strongly related to the doping concentration and the size of the alkali metal ions.[1–3] Among the alkali fullerides, Na-doped C_{60} (Na_xC_{60}) exhibits structures and physical properties different from those of the other alkali-doped A_xC_{60} (A=K, Rb, and Cs) fullerides. Na_3C_{60} is metallic with a face-centered cubic (fcc) structure but is not a superconductor like Rb_3C_{60} and K_3C_{60}.[4] Na_4C_{60} is a small-gap semiconductor and forms a two-dimensional single-bonded polymer structure, in contrast to the A_4C_{60} monomers of the heavy alkali fullerides.[5–10] The saturated phase is $Na_{10}C_{60}$, with the same fcc lattice as the pure host,[11] while heavy-alkali systems saturate as A_6C_{60} in a bcc lattice.[12] Moreover, Na_2C_{60} is currently the only divalent fulleride that has been successfully synthesized.[13,14] It retains its monomeric fcc structure and has a lattice constant close to that of pristine C_{60}. Since the two Na^+ ions occupy the tetrahedral sites, leaving the larger octahedral sites unoccupied, it can be further intercalated by a heavy alkali metal (K, Rb, Cs). The expanded fcc lattice in combination with a transfer of three electrons to each C_{60} molecule turn these systems into superconductors with particularly high T_cs.[4] Due to the various unique intermolecular interactions between Na^+ and C_{60}^{-n}, a rich variety of structural and dynamical phenomena is expected in Na_2C_{60}.[13,15–17] Early photoemission studies revealed that this compound was metallic[15] and Electron Spin Resonance and Raman scattering indicated a metal-insulator (M-I) transition at 50 K.[16] However, recent studies suggest that the electronic structure of A_2C_{60} salts should be related to that of A_4C_{60} by electron-hole symmetry, and the materials should, thus, be insulators due to the Jahn-Teller distortion in the C_{60}^{2-} ions.[18–21] Regarding structural aspects, an orientational ordering transition was observed at 325 K, a temperature significantly higher than the corresponding value of 260 K for pure C_{60}. The high transition temperature can be explained by Coulomb interactions between C_{60} molecules and Na ions.[13] A reversible phase transition from the cubic $Pa\bar{3}$ structure of as-prepared Na_2C_{60} to a new low-symmetry distorted phase was observed by neutron diffraction under high Ne gas pressure, $p>100$ MPa, above $T>200$ K,[17] and by considering the observed compressibility and the interactions between the ions the authors predicted a further phase transition from $Pa\bar{3}$ to $Fm\bar{3}m$ below 1.7 GPa at room temperature.

In a search for a deeper understanding of both the structural transitions and the transport properties of Na_2C_{60}, we have carried out electronic transport measurements up to 2 GPa in the range 90–500 K. Similar resistance measurements have been carried out for A_4C_{60} (A=Li,Na,Rb).[5,8] Our data show that Na_2C_{60} is semiconducting with a wide band gap containing localized gap states far away (~0.5 eV) from the band edges. The band gap and the gap states exhibit large pressure dependences, in contrast to what was observed for Na_4C_{60} (Ref. 5) and Rb_4C_{60}.[8] Heating under high pressure leads to drastic resistance changes suggesting a structural transition. From evidence provided by *in situ* resistance measurements and *ex situ* studies by Raman spectroscopy and x-ray diffraction (XRD), we interpret these changes as evidence for a phase separation in association with the formation of at least two polymeric phases, Na_4C_{60} and an orthorhombic phase with a zero (or low) Na concentration.

In addition, in order to investigate a recently suggested nanophase segregation in Na_2C_{60} stored for an extended period of time,[14] and since minor differences in phase stoichiometry can lead to drastic changes in material properties,[22] we also carried out similar resistance measurements on aged Na_2C_{60}, stored for a long period of time. We did, indeed, observe a different conduction behavior in this sample; instead of a typical semiconducting behavior we observed a temperature dependence typical for a three dimensional (3D) hopping mechanism.

II. EXPERIMENTAL DETAILS

Na_2C_{60} was prepared by a common solid-solid reaction route in an Argon filled glove box.[14] Prior to use, pristine C_{60}

was heated for 12 h under dynamic vacuum to remove absorbed gas. Stoichiometric amounts of C_{60} and sodium were mixed in copper or stainless steel crucibles and heated at 350 °C for three weeks. The sample was then heated to 450 °C for an additional week. During the heat treatment, the samples were ground about once every five days to increase homogeneity. Two types of samples were used in our studies. Both samples were quenched by rapid cooling from 450 °C, which is reported to produce a homogeneous metastable state Na_2C_{60} that can be stable for ~2 weeks.[14] One of the samples was used directly after being synthesized, while the other was used after storage in oxygen-free condition for several months at room temperature. This type of storage is supposed to transform Na_2C_{60} into a phase segregated material.[14] The samples were characterized by XRD on a Siemens/Bruker D5000 powder diffractometer with Cu K_α radiation and by Raman spectroscopy (Renishaw 1000 micro-Raman spectrometer, with excitation laser wavelengths of 514.5 and 633 nm). All characterization was performed on samples protected inside glass capillaries. XRD analysis of the synthesized samples could within the spatial resolution of the XRD establish a *single* $Pa\bar{3}$ phase with a lattice constant of 14.19 Å, similar to that reported earlier.[13] For high pressure resistance measurements, the equipment and techniques were identical to those used in earlier works on Rb_4C_{60}, Na_4C_{60}, and Li_4C_{60}, and it is described more extensively in Refs. 5 and 8. In brief, the powder samples were compressed into linear grooves in a Teflon plate with Ni resistance probes, using a piston-cylinder high pressure device and a four-pole resistance measurement system. The pressure vessel was cooled by liquid nitrogen and the cell contained an internal heater to reach temperatures up to above 500 K. Because the structural transitions reported earlier at 0.4 and 1.7 GPa[17] were observed or predicted at room temperature or below, and to avoid any heating-induced irreversible transition in the sample under pressure, resistance measurements were made on both types of pristine samples during the pressure increase by carrying out cooling/heating cycles between room temperature and 100 K at pressures of 0.1, 0.3, 0.5, and 2 GPa. After the final pressure increase to 2 GPa and the subsequent cooling run, the sample was heated to above 400 K and then cooled to room temperature before decreasing the pressure. During the pressure decrease, different cooling/heating treatment cycles were carried out for different samples.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Resistance of Na_2C_{60} under pressure

Figure 1 shows experimental data for the resistance R of Na_2C_{60} (on a logarithmic scale) as a function of temperature between 100 and 310 K, collected at several pressures during the pressure increase, as described above. At all pressures, including the lowest pressures where the high resistance only allows a limited measurement range, the resistance of Na_2C_{60} is semiconductor-like, i.e., the resistance has an exponential dependence on $1/T$. Carriers are thus thermally excited, either over the full band gap from the valence band, or from disorder-induced localized states within the band gap. Similar behavior has been observed earlier both for pure C_{60} (Ref. 23) and for the previously studied fullerides Li_4C_{60}, Na_4C_{60}, and Rb_4C_{60}.[5,8] The existence of donor (or possibly acceptor) gap states has also been observed in these related systems by NMR measurements,[24] and both EPR[25] and NMR[26] reveal the presence of local Li off-stoichiometry and, in the polymeric phases, intrinsic centers originating from broken C_{60}-C_{60} bonds that could create band gap states and account for the complex temperature dependence of the spin susceptibility as well as the residual temperature dependence of the ^{7}Li NMR shift.[25] The total conductivity σ ($=1/\rho$, where ρ is the resistivity) can be written as the sum of (at least) two components,

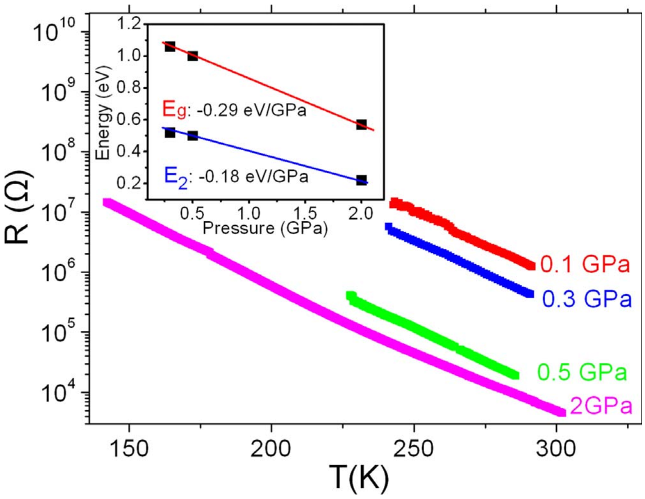

FIG. 1. (Color online) Resistance of Na_2C_{60} (on a logarithmic scale) as a function of temperature at the pressures indicated. Inset shows band gap and localized gap state energy for Na_2C_{60} as functions of pressure as obtained from fitting Eq. (1) to the resistance data.

$$\sigma(T) = A_1 \exp(-E_g/2k_BT) + A_2 \exp(-E_2/2k_BT), \qquad (1)$$

where the exponential terms describe the thermal excitation of carriers and the constants A_i include all geometrical factors, mobilities, etc. We choose to let the first term denote the true band gap E_g while the second term represents the contribution from carriers excited from states in the gap. In Rb_4C_{60} (Ref. 8) the measured conductivity is dominated by carriers excited from gap states over most of the temperature range studied, except at very high temperatures. At very low temperature the fit of the conductivity function to the data is often improved by the addition of a small metallic component ascribed to Rb_3C_{60}. Fresh Na_2C_{60} is not expected to contain any metallic component and thus the low-temperature conductivity should be dominated by low-energy gap states. Indeed, a single exponential function $R = A\exp(E_2/2k_BT)$ gives an excellent fit at low temperatures for the R-T curves measured from 0.1 to 2GPa (without heating). From this low-T fit we can find E_2, and then insert this term into Eq. (1) to calculate the band gap E_g which gives good fits for the high-T part of the σ-T curves.

Fitting Eq. (1) to our data reveals that both the band gap E_g and the energy E_2 of the localized states have relatively large pressure dependences (see inset in Fig. 1). For E_g, we estimate $dE_g/dp=-0.29$ eV/GPa, while for the gap states $dE_2/dp=-0.18$ eV/GPa. Since the width of the band gap in a semiconducting material is correlated with the size of the first Brillouin zone, which is inversely proportional to the size of the unit cell, one could expect that a large compressibility should be accompanied by a large pressure dependence of the band gap energy. Indeed we see that the relatively "soft" Na_2C_{60} and pure C_{60}, with volume compressibilities $\kappa=5.1\times10^{-2}$ GPa^{-1} (Ref. 17) and $\kappa=6.7\times10^{-2}$ GPa^{-1},[27] respectively, both have band gap energies with large pressure dependences, $dE_g/dp=-0.29$ eV/GPa and -0.15 eV/GPa, respectively, corresponding to pressure coefficients $E_g^{-1}\, dE_g/dp$ of -0.25 GPa^{-1} and -0.10 GPa^{-1}. This can be compared with the band-gap energy of the polymer Na_4C_{60} which is almost independent of pressure, in agreement with its much lower (but anisotropic) compressibility[28] $\kappa=1.43\times10^{-2}$ GPa^{-1}. If we extrapolate the value of the band-gap energy to higher pressures for Na_2C_{60}, the slope would imply a possible metal-insulator transition above 4–5 GPa.

Our direct resistance measurements unambiguously show that both Na_2C_{60} and Na_4C_{60} (Ref. 5) are semiconductors but that Na_2C_{60} has a larger band gap and a conductance more influenced by gap states. A few years ago Klupp *et al.* suggested that Na_2C_{60} is not a simple electron-hole analog of C_{60}^{4-}, but rather another example of an inhomogeneous charge distribution on the nanoscale.[14] They suggested that a phase segregation could reappear in rapid-cooling-quenched homogeneous Na_2C_{60} after about 2 weeks at room temperature. Very recently we also observed a pressure-driven phase separation in heavy-alkali-metal-doped nonpolymerized Rb_4C_{60},[29] an effect which obviously affects also the conduction behavior of the material.[8] To see if such a nanoscale phase separation could influence the conduction behavior we performed a resistance measurement similar to those described above on a sample that had been stored in the glovebox for several months. Interestingly, this sample shows a completely different electronic transport behavior, which cannot be fitted by the standard semiconductor behavior given by Eq. (1).

The measured resistivity was about one order of magnitude lower than that of the fresh Na_2C_{60} sample and decreased with increasing T from 100 to 400 K. The resistance data (Fig. 2) show an excellent fit to a 3D variable range hopping (VRH) model[30] at all pressures up to 2 GPa. In such a model

$$\rho(T)=\rho_0\exp(T_0/T)^{1/4}, \tag{2}$$

where $T_0=512/9\pi k_B\,\mathrm{N}(E_F)\xi^3$, ξ is the localization length, $\mathrm{N}(E_F)$ is the density of states at the Fermi level and ρ_0 is proportional to the phonon energies, scaling as v_{Ph}^{-1}. For resistances exceeding 10 MΩ systematic deviations are observed, but we believe these are due to systematic errors arising from the high resistance values.

Based on the 3D hopping model, T_0 has a characteristic value ∼200 K and decreases with increasing pressure (198, 181, and 155 K at 0.1, 1, and 2 GPa, respectively). The results may be understood in the framework of the variable range hopping model between localized states near the Fermi level. The origin of the VRH behavior is probably the structure of the material, which should be a nanoscale composite of C_{60} (insulating) and Na_3C_{60} (metallic) grains, as suggested by Klupp *et al.*,[14] with electronic hopping conduction occurring between the metal grains. The average size of the nanograins is expected to be in the range of 3–10 nm.[14] Assuming a hopping distance of 10 nm, the same as the phase-separation grain size, the 3D density of states becomes $\mathrm{N}(E_F)|3\mathrm{D}\sim1.04\times10^{21}$ $eV^{-1}\,cm^{-3}$ (a grain size of 3 nm gives $\mathrm{N}(E_F)|3\mathrm{D}\sim3.85\times10^{22}$ $eV^{-1}\,cm^{-3}$), i.e., in the range also found for amorphous semiconductor VRH systems such as Si and Ge.[30]

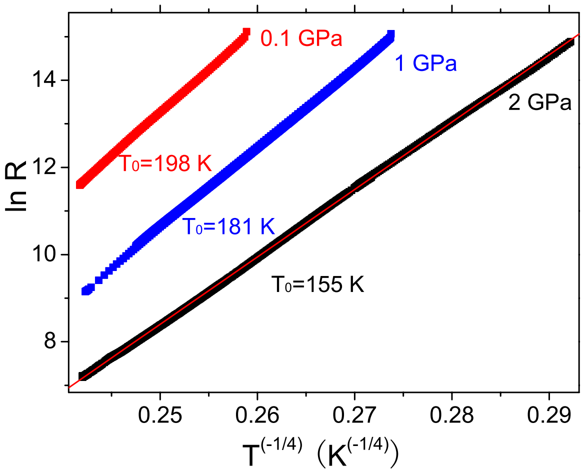

FIG. 2. (Color online) Logarithm of the resistance of phase-separated Na_2C_{60} vs $T^{-1/4}$.

B. Structural transition after heating at 2 GPa

Numerous experiments on both pristine[31] and intercalated[32] C_{60} have shown that a combination of elevated temperature and high pressures can lead to dramatic changes in the crystal and molecular structures. This was the reason why we first chose to explore the electrical conduction of Na_2C_{60} by only cooling at elevated pressures. However, at 2 GPa, after having fully explored the conducting properties below 300 K, we also started to increase the temperature. After heating, both our samples show indeed a complete change in their conduction behavior.

The resistivity change is clearly shown in Fig. 3(a), presenting the resistance data of the "fresh" sample at 2.0 GPa when heated to 414 K, then cooled back to 293 K. The aged sample shows a similar behavior, but starting from a lower resistivity. After heating it was not possible to get a very good fit to the data using any conductance model, but a reasonable agreement could be obtained using a 1D (or 2D) VRH model. To understand the cause of the abrupt resistance change after heating, one of the samples (initially "aged" Na_2C_{60}) was unloaded after the heat treatment and characterized by x-ray diffraction and Raman spectroscopy.

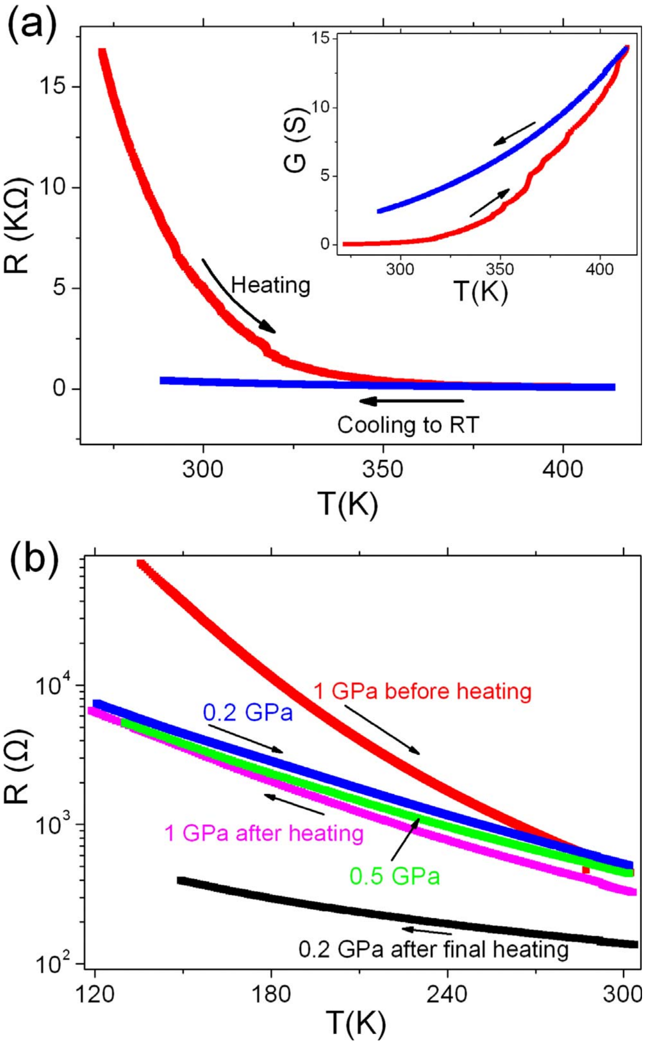

FIG. 3. (Color online) (a) Resistance R of Na_2C_{60} versus temperature at 2.0 GPa. Inset shows the conductance $(G = 1/R)$ versus temperature. (b) Resistance versus temperature at several pressures after heating at 2 GPa. See text for details.

The x-ray diffraction and Raman spectroscopy data in Figs. 4 and 5, respectively, give very strong support to the theory that the abrupt change in resistivity after heating the sample at 2.0 GPa is related to a polymerization and phase separation of the Na_2C_{60} into a mixture of mainly 1D (linear chain) polymerized orthorhombic C_{60} and possibly 2D polymerized Na_4C_{60}. The x-ray diffraction pattern of the heated and recovered sample is a clear superposition of mainly polymeric orthorhombic C_{60} (Ref. 33) and polymeric Na_4C_{60}.[34] In addition there are indications of minor amounts of Na_2C_{60}. The low resolution of the x-ray diffraction data and the complexity of the x-ray diffraction patterns resulting from the many similar phases in the sample make it difficult to determine if the orthorhombic structure is exactly similar to the orthorhombic 1D phase obtained for pure C_{60} at high pressure and high temperature[33,35,36] or whether it contains some sodium ions and thus represent a charged 1D orthorhombic structure.

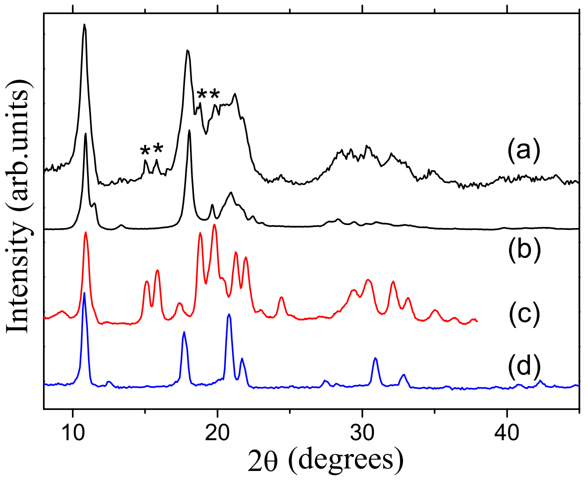

FIG. 4. (Color online) X-ray diffraction diagrams for (a) Na_2C_{60} after HPHT, (b) orthorhombic C_{60}, (c) Na_4C_{60}, and (d) nominally pure Na_2C_{60}.

The Raman spectrum also supports the separation into polymer structures, most strongly evidenced by the observation of a distinct mode around 960 cm^{-1}.[34] In brief, the Raman spectrum of Na_2C_{60} after heating at 2.0 GPa shows the presence of orthorhombic C_{60}, Na_4C_{60}, as well as some other Na_xC_{60} structures. The $A_g(2)$ mode contains several components shifted to lower wave numbers, which is a well-known phenomenon for both polymeric and doped C_{60} structures. The Raman peak at 1457 cm^{-1} could be attributed to the $A_g(2)$ mode of an orthorhombic phase that has experienced a charge induced shift from its normal value of 1460 cm^{-1} in undoped orthorhombic C_{60}. The possibility of a doped orthorhombic structure can also be rationalized by other arguments. During the heating of the sample at 2.0 GPa the resistance starts to drop already at 300 K and as shown in the figure a clear transformation seems to have occurred already around 360 K. This temperature is significantly lower than the fcc-to-orthorhombic phase transition temperature for un-

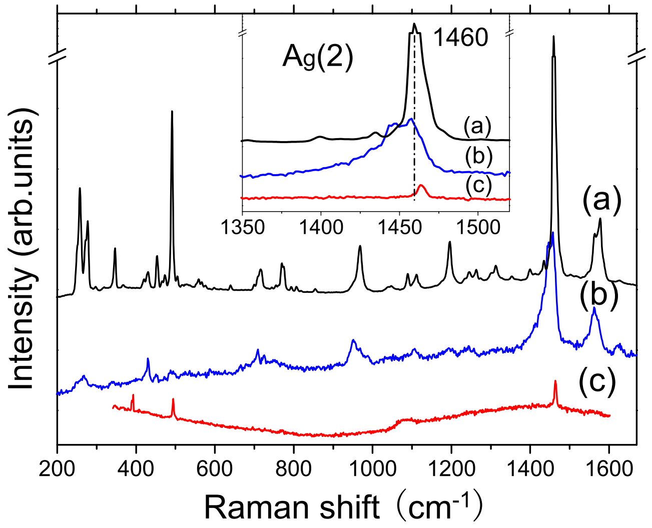

FIG. 5. (Color online) Raman spectra of (a) orthorhombic C_{60}, (b) Na_2C_{60} after HPHT treatment, (c) nominally pure Na_2C_{60} before the high pressure experiment. Inset shows the $A_g(2)$ mode positions on an expanded scale.

doped pristine C_{60} at this pressure.[37] The polymer transition might therefore be catalyzed by the charge transfer to the C_{60} molecules, a mechanism well known to trigger polymerization.[38] However, all indications of a formation of a *doped* orthorhombic structure in the pressure-heat treatment are weak and we can only provide substantial evidence for a normal orthorhombic polymer structure.

The other sample heat treated at 2 GPa was submitted to cooling cycles down to about 100 K at 2 and 1 GPa [Fig. 3(b)], and was then heated again at 1 GPa to a peak temperature of 491 K. After this heating the slope of R versus T decreased significantly, as shown in Fig. 3(b), and further cooling/heating cycles at 0.5 and 0.2 GPa to lower peak temperatures (423 K) did not change the general behavior. The resistance became nearly pressure independent, and again Eq. (1) could be fitted to the data, this time with almost pressure independent gap state energies near 0.2 eV and a band gap that increases with decreasing pressure and reaches a value $E_g \sim 1.6$ eV at 0.2 GPa. From previous knowledge about the effect of high temperature, high pressure conditions on C_{60}, and from the data obtained from the Raman and XRD investigations, we conclude that these changes are probably related to a complete transformation of the sample into a mixture of polymeric phases. The diffraction and Raman results discussed above show that heating at 2 GPa resulted in a phase separation into a mixture of C_{60}, probably in the orthorhombic polymer phase, and Na_4C_{60}, but the resistance data indicate a very strong disorder and probably a phase separation only on the micro- or nanometer scale. Heating to higher temperature (at 1 GPa) enables the formation of larger volumes of well-crystallized material of both types and makes it possible to identify the materials as normal semiconductors.

The fitted parameters are consistent with such a mixture; a band gap of about 1.6 eV might correspond to orthorhombic C_{60},[39] while almost pressure independent gap state energies near 0.15 eV have been observed for Na_4C_{60}.[5]

To verify our hypothesis of a polymerization transition and to study the dynamic transport behavior during the possible depolymerization process, the sample was then heated to 538 K at 0.2 GPa before the pressure was reduced to atmospheric. Figure 6 shows the conductance as a function of temperature during this process. Around 500 K, there is a sharp decrease in the conductivity. This transition temperature agrees very well with the depolymerization temperature reported by Nagel *et al.*[40] and thus gives strong support for our interpretation of a polymerization transformation in the divalent fcc C_{60} fulleride Na_2C_{60} under high pressure, high-temperature conditions.

To conclude, we have presented experimental data for the resistance of Na_2C_{60} at pressures up to 2.0 GPa in the temperature range 100–500 K. The overall picture shows that Na_2C_{60} is a semiconductor with a band gap of about 1.2 eV, but with a conductivity strongly influenced by (defect) gap states. In contrast, Na_2C_{60} stored in an oxygen-free environment for several months shows a different conduction behavior which can instead be described by a 3D variable range hopping model. Contrary to suggestions by Yildrim *et al.*[17] we do not observe any signs of a phase transition at pressures below 2.0 GPa and temperatures below room temperature. However, for both types of samples, heating at 2.0 GPa induces a transformation into a metastable phase separated system containing Na_4C_{60} and orthorhombic polymeric C_{60}, or possibly Na-doped orthorhombic polymeric C_{60}. This conclusion is supported by x-ray diffraction data, Raman data, and the results from a depolymerization experiment performed at 0.2 GPa. The fact that the phase separation behavior is different at atmospheric pressure, where Na_2C_{60} disproportionates into C_{60} and Na_3C_{60},[14] and under high pressure (polymeric C_{60} and Na_4C_{60}, shown here) is probably due to the fact that the two polymer phases are thermodynamically preferred under high-pressure conditions because of their higher densities. The conduction behavior of the polymeric phase mixture is complex and depends on the actual conditions used, but is in general consistent with the observed structure of the sample polymerized under high pressure and temperature.

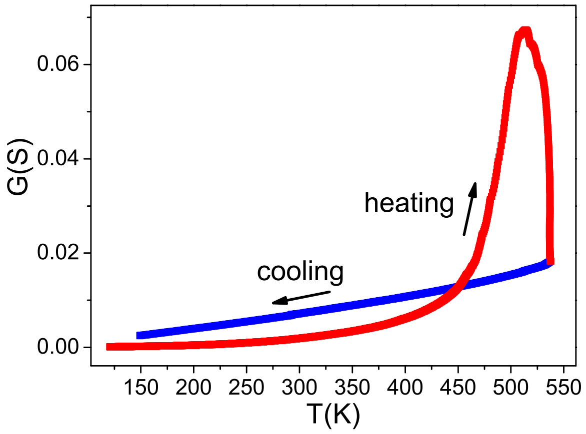

FIG. 6. (Color online) Conductance versus temperature at 0.2 GPa.

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