DiVA – Digitala Vetenskapliga Arkivet <http://umu.diva-portal.org>

This is an author produced version of a paper presented at **New Diamond and Nano Carbon 2010 (NDNC 2010), Suzhou, May 2010**. This paper has been peer-reviewed but does not include the final publisher proof-corrections or journal pagination.

Citation for the published paper:

Bertil Sundqvist; Thomas Wågberg; Mingguang Yao

High pressure studies of alkali metal doped fullerenes A_4C_{60}

Diamond and Related Materials, 2011 Vol. 20, Issue: 4 pp 600-603

DOI: 10.1016/j.diamond.2011.01.009

Access to the published version may require subscription. Published with permission from:
Elsevier

High pressure studies of alkali-metal doped fullerenes A_4C_{60}

Bertil Sundqvist^{a,*}, Thomas Wågberg^a and Mingguang Yao^{a,b,c}

^a Department of Physics, Umeå University, SE-90187 Umeå, Sweden

^b LPMCN, Université de Lyon 1 et CNRS, F-69622 Villeurbanne Cédex, France

^c State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, P.R. China

Abstract:

The electrical resistance R of K_4C_{60} and Li_4C_{60} has been measured between 100 and 300 K under pressures up to 1 and 2 GPa, respectively. For both materials, the temperature coefficient of R is negative at all pressures and temperatures in this range. The transport properties of Li_4C_{60} at low pressure are compatible with a recent observation of high ionic conductivity, but surprisingly this conductivity term increases strongly with increasing pressure, contradicting an intuitive model. For K_4C_{60} we see no sign of a recently suggested structural phase transformation at low temperature, nor can we find any convincing evidence for a lattice disproportionation as recently observed for Rb_4C_{60} .

Keywords: 1. fullerenes 4. vibrational properties characterization 5. electrical conductivity,
vibrational properties

Present e-mail addresses:

* Corresponding author;

bertil.sundqvist@physics.umu.se, tel. +46 90 7867488, fax +46 90 7866673

thomas.wagberg@physics.umu.se

yaomg@jlu.edu.cn

1. Introduction

Intercalation of alkali metals (A) into fullerenes such as C_{60} leads to charge transfer, in most cases with one electron being transferred to the fullerene conduction band for every alkali metal ion inserted. The conduction band of C_{60} can accommodate up to six electrons per fullerene molecule, and the C_{60} lattice can also accommodate up to six alkali metal ions per fullerene (except for the very small Li^+ ion, which may be inserted in much larger numbers). The saturated A_6C_{60} compounds are thus insulators, while lower alkali metal concentrations result in fulleride compounds with interesting physical properties, in some cases (A_3C_{60}) even including high transition temperature superconductivity [1]. From a simple band model the A_4C_{60} compounds would also be expected to be metallic, but all are found to be small bandgap semiconductors. For the light compounds ($A = Li, Na$), charge transfer leads to formation of covalent interfullerene bonds (polymerization), which modifies the band structure, while for the heavier ones ($A = K, Rb$) a Jahn-Teller molecular distortion leads to opening of a small band gap at the Fermi surface [2]. Several years ago, NMR data were reported to show that Rb_4C_{60} underwent an insulator-to-metal transition near 1 GPa [3] at room temperature, and to investigate this interesting behaviour further we recently carried out measurements of the electrical conductivity over a wide range of temperatures up to 2 GPa [4]. Surprisingly, no such metallization was found, but a later Raman investigation on the same material showed [5] that the Rb_4C_{60} actually disproportionated reversibly into the more stable phases Rb_3C_{60} and Rb_6C_{60} under pressure. The first of these phases is metallic, explaining the earlier NMR results in a natural way. For the structurally very similar compound K_4C_{60} , data from infrared spectroscopy also recently showed the possibility of a

phase transition below 250 K [2]. Interest in the A_4C_{60} compounds has continued to increase even further recently, mainly due to the discovery that Li_4C_{60} has a unique, layered two-dimensional polymeric structure at room temperature [6]. Recent investigations of the conduction properties of this phase have indicated a very high ionic conductivity with an excitation energy of only 0.23 eV [7].

In this short report we present recent results for the electrical conductivities of Li_4C_{60} and K_4C_{60} as functions of temperature in the range 100 K to room temperature, at pressures up to 2 and 1 GPa, respectively. Full results for Li_4C_{60} will be presented elsewhere [8], but we show here that the results for this material are not fully compatible with the suggested ionic conduction mechanism. We also show very recent data for K_4C_{60} , which we have investigated to see whether we can see i) any indications of a low temperature structural transformation, or ii) any indications of a disproportionation of the material, similar to that found for Rb_4C_{60} . For the latter material a good fit to the low temperature conductivity data could only be obtained if a metallic term was added during the fitting procedure, and the magnitude of this term varied reversibly [4, 9] with applied pressure.

2. Experimental details

The compounds studied were synthesized from sublimed C_{60} with a nominal purity better than 99.98 %, which was first treated at temperatures above 200°C for more than 48 h under dynamic vacuum to remove water and atmospheric gases. A turbomolecular pump was used during most of the treatment period to obtain the best possible vacuum. The Li_4C_{60} was synthesized by directly mixing stoichiometric amounts of metallic lithium and C_{60} . The mix

was then annealed at 350°C or higher for several weeks with intermediate grinding and re-mixing. To synthesize K_4C_{60} , we applied the same two-step procedure as used for synthesizing Rb_4C_{60} [4]. Saturated K_6C_{60} was first produced by a gas phase intercalation method. A known amount of C_{60} and an excess amount of K metal were inserted at the two ends of a sealed, evacuated Pyrex tube which was kept at 300°C for three weeks. A small temperature gradient kept the potassium from condensing on the fullerene powder. Near stoichiometric amounts of C_{60} and K_6C_{60} were then well mixed and annealed together in another evacuated and closed tube at the same temperature for a month to obtain the final reaction product. It should be noted that for the nominal K_4C_{60} (as for Rb_4C_{60} earlier) we kept the K content on the high side to avoid formation of metallic K_3C_{60} . The presence of a small amount of insulating K_6C_{60} should have little effect on the measured conductivity.

After synthesis, the materials were characterized by X-ray diffraction and Raman scattering. Due to their sensitivity to air and water, the samples were protected in thin glass capillaries which degraded the signal-to-noise ratios. We show in Figures 1a and 1b a Raman spectrum and an X-ray diffraction diagram for K_4C_{60} . In the latter case, the background from the glass capillary has been removed but the peaks are broadened because of the experimental geometry. In Figure 1a we also show, for comparison, a Raman spectrum for Rb_4C_{60} , synthesized by the same method for our earlier investigation [4]. The spectra are in excellent agreement, showing very similar peak shifts (relative to peaks for pure C_{60}) for the $A_g(1)$ and $A_g(2)$ modes at 496 and 1445 cm^{-1} , respectively. Both methods agree that all samples contain the expected majority phases, although for nominal K_4C_{60} both Raman spectroscopy and X-ray diffraction also show the presence of a small amount of K_6C_{60} , as intended.

As before [4], the electrical resistance R was measured using a DC method in a four-probe geometry, filling the loose powder into grooves machined in the bottom of the Teflon cells used. Nickel alloy (Nickel 200™) wires were used for both current and potential contacts. Pressure was created in a piston-and-cylinder device, 45 mm in internal diameter, using a hydraulic press. The pressure was estimated from the press load, using an earlier calibration, and temperature was measured using a type K thermocouple. The pressure cell could be cooled down to about 100 K using liquid nitrogen. Raman spectra were collected using a Renishaw 1000 micro-Raman spectrometer and X-ray diffraction data were obtained using a Siemens/Bruker D5000 diffractometer system.

3. Experimental results and discussion

3.1. General considerations on measurements and analysis

Measurements have been carried out on at least two samples of each type, and at room temperature and below the results have been found to be quite repeatable and stable, with the exception of the data from the initial phase of the experiment when the powder samples are compressed into solid lumps. None of the A_4C_{60} compounds has been found to be stable on heating to above 400 K, and in the present paper we limit the discussion to the low-temperature range. (Effects of heating will be discussed further elsewhere [8].)

Data for the conductance $G = 1/R$ have been fitted to equations of the type

$$G(T) = A \exp(-B/T) + C \exp(-D/T) \text{ (+ further terms).} \quad (1)$$

As discussed in detail earlier [4,8], it is usually not possible to fit conductance data for this type of compounds by a single exponential term, since carriers may be excited through

different mechanisms. The fitted parameters may be identified in different ways depending on the conduction mechanism assumed. Taking the first term in Eq. (1) as our model, in the case of ionic conductivity, as identified by Riccò *et al.* [7], we may calculate the activation energy, E_a , from $B = E_a/k_B$. For electronic conduction, the exponential terms will yield either the band gap energy, E_g , from $B = E_g/2k_B$, or the energy E_s of localized electronic states in the gap as $B = E_s/2k_B$. For Rb_4C_{60} [4] we found a band gap value of $E_g = 0.7$ eV. in good agreement with literature data, but below room temperature the conductivity was actually dominated by electrons excited from localized states with energies E_s just above 0.1 eV. Such a behaviour is observed also for pure fullerenes, such as C_{60} [10], and for other fullerene compounds [8]. Although the "further terms" indicated in Eq. (1) may be further exponential terms, for Rb_4C_{60} it was necessary to add a "metallic" conductivity term f/T , indicating the presence of a small amount of metallic Rb_3C_{60} . The fitting procedure used is discussed in detail elsewhere [4,8] and below we only present the results of the fitting in terms of band gaps or activation energies.

3.2. Results for Li_4C_{60}

Measurements were carried out on well characterized Li_4C_{60} , in order to investigate whether we could observe the ionic conductivity term identified by Riccò *et al.* [7]. Experimental results between 100 and 300 K, and up to 2 GPa, for one sample are shown in Figure 2. (The extra curvature below 115 K at 0.1 GPa is caused by the input impedance of the measurement system, and must be corrected for.) At all pressures, Eq. (1) could be fitted to the data provided at least two terms were used, and we always found one term which could

be interpreted in terms of an activation energy E_a near 0.23 eV, in excellent agreement with the report by Riccò *et al.* [7]. In addition, we also found a second term, dominant below 240 K, which we could interpret in terms of electrons, excited from localized states in the band gap, as for other fullerenes investigated. At low temperature we also observed other terms with even lower energies, but these terms were less well defined because of the narrow temperature range where they could be observed. In no case did we need to use a "metallic" term f/T in Eq. (1), but we note that a metallic phase has actually been observed in Li_4C_{60} at high temperatures [11].

With increasing pressure the activation energy of the "ionic" term steadily decreased, while all other excitation energies were constant within the experimental scatter. A calculation of the magnitudes of the two (or three) fitted conductance terms in Eq. (1) showed that all terms increased in magnitude with increasing pressure, and the relative increase was very similar for the two dominant terms; in fact, the "ionic" term increased by a factor of eight from 0.1 to 2 GPa, while the electronic term increased by a smaller factor of five. Further details will be given in a separate publication [8].

The high pressure results are quite unexpected, since intuitively we would not expect ionic conductivity to increase under pressure when compression of the lattice makes less space available for diffusion of the ions. In some amorphous materials the free volume initially increases under pressure, causing a peak in their ionic conductivities, but it is difficult to see such a mechanism at work in the present crystalline structure. Possible reasons for the observed behaviour might be either that plastic deformation of the sample opens new macroscopic diffusion paths, or that the carbon-lithium interaction decreases under pressure.

If the results would be interpreted instead in terms of an electronic conduction mechanism with $E_g = 2 E_a = 0.46$ eV, the increased conductivity is a natural consequence of the expected (and, in this model, observed) decrease in band gap with increasing pressure, as the increasing intermolecular interactions broaden the valence and conduction bands.

Clearly, the present study has created more new questions than it has answered, and further studies are definitely required in order to understand the conduction properties of this material under high pressure.

3.3. Results for K_4C_{60}

Very recently, we also carried out a corresponding investigation of the electrical transport properties of K_4C_{60} below room temperature and under pressures up to 1 GPa. The aim of this investigation was to find out whether this material, like the structurally very similar compound Rb_4C_{60} , is susceptible to disproportionation under pressure. However, we also wanted to see if we could find any electrical anomalies that could be attributed to the possible structural transformation suggested by Kamarás *et al.* [2]. Since the changes in the IR spectrum found by Kamarás *et al.* were observed at zero pressure our search has been focused on the low pressure range, and we show in Figure 3 the electrical resistance of one sample of K_4C_{60} at 0.1, 0.5, and 1.0 GPa. The data shown were in all cases obtained during cooling, i.e. for decreasing temperature. The resistance is a smooth function of temperature at all pressures. It is also clear that the resistance has a negative temperature coefficient at all pressures and temperatures and thus shows an "activated" or "semiconductor-like" behaviour like all other A_4C_{60} compounds investigated. Again, as for the other A_4C_{60} compounds it is

impossible to fit a single exponential term in T^{-1} to the data. This is obvious from the near linearity of R (logarithmic scale) versus T in the Figure, and plotting each isobaric data set as $\ln R$ (or $\ln G$) versus $1/T$ gives a very strong curvature instead of a straight line. On the other hand, Eq. (1) can again be fitted to the data for G with excellent results, using two conduction terms. The addition of a small extra "metallic" conductance term does not improve the global fit significantly, but there is a noticeable improvement in the agreement between the data and the fitted function (especially regarding dG/dT) below about 140 K. However, on the scale of the figure the difference is such that both types of curves fall well within the symbols shown, and although the magnitudes of the fitted "metallic" terms increase with pressure there is no clear evidence for disproportionation.

The fitted energy levels are surprising low. In the range studied, the *higher* of the fitted energy levels is about 0.23 eV, while the lower is about an order of magnitude smaller. A very small energy gap of 50 meV, in reasonable agreement with our results, was reported for K_4C_{60} by Ruani *et al.* [12] based on resonant Raman scattering studies. However, later direct optical measurements [13] have shown that the actual band gap is close to 0.5 eV, about twice the value of the highest energy level found here. Early band structure calculations by both LDA-DFT [14] and tight-binding [15] methods indicated that K_4C_{60} should be metallic, but at present there is a consensus that a gap opens at the Fermi surface due to a Jahn-Teller distortion of the C_{60} molecules [2, 13]. Because no ionic conductivity is expected from the large, heavy K^+ ions and because the band gap is quite large, both energy levels observed in this work probably correspond to localized states in the band gap. The very low excitation energies also imply that the total change in resistance between 100 and 300 K is only about

one order of magnitude (see Figure 3). The magnitude of the resistivity is low and we thus conclude that the number of carriers is high, suggesting that there must be a very large concentration of localized defect states in the band gap. Due to the high conductivity arising from this term, any effect from electrons excited over the actual band gap is completely masked at and below room temperature.

Returning to the question of a possible phase transformation in K_4C_{60} , as suggested by Kamarás *et al.* [2], we note that the rotational transition in pure C_{60} gives rise to a step change in the measured resistance by about a factor of two [16]. Such an anomaly would be easily discernible in our data, but we find that the measured resistance is a smooth function of temperature at all pressures up to 1 GPa, with no sharp anomalies that can be attributed to structural phase transformations. We thus conclude that there are probably no structural phase transformations, involving positional changes in the molecular lattice, in the ranges investigated. Rotational or orientational transitions involving the molecular ions can probably also be ruled out, unless smeared over a large range in temperature. Kamarás *et al.* [2] speculate that the IR anomalies observed might arise from either a true structural lattice transformation, or from more subtle changes from a static Jahn-Teller molecular distortion at low temperature to a dynamic Jahn-Teller effect at high T. It is probable that the latter type of transition, involving rather the shape of an individual molecule than its position, would have a much smaller effect on the transport properties and would not be easy to observe in a temperature range where conduction is dominated by electrons excited mainly from localized states in the gap.

Further measurements, over wider ranges in pressure and temperature, are in progress, and might possibly shed further light on the behaviour of K_4C_{60} under high pressure.

4. Conclusions

Recent measurements show that high pressure transport properties of the anomalous A_4C_{60} compounds may reveal many interesting and unexpected properties of the materials. For the fulleride polymer Li_4C_{60} we observe a conduction mechanism which may be identified with the ionic mechanism observed in a recent publication [7]. High pressure studies, however, show that this conduction term increases with increasing pressure at a rate very similar to that of other conduction terms which we identify as having an electronic origin. Because ionic conduction would intuitively become less easy when ion diffusion paths are closed by the compression of the lattice, we find it difficult to explain this observation in terms of purely ionic conduction.

For K_4C_{60} , we see no resistance anomalies that may be connected with the low-temperature structural lattice transformation suggested by Kamarás et al. [2], and neither do we observe any significant metallic component in the conductivity, indicating the existence of a structural disproportionation as observed in the related compound Rb_4C_{60} [5].

Acknowledgements

This work was financially supported by the Swedish Research Council through grant dnr 621-2007-5319.

References:

- [1] K. Prassides, S. Margadonna, Structures of fullerene-based solids, in: K.M. Kadish, R.S. Ruoff (Eds.), *Fullerenes: Chemistry, Physics, and Technology*, Wiley Interscience, New York, 2000, pp. 555-610.
- [2] K. Kamarás, G. Klupp, D.B. Tanner, A.F. Hebard, N.M. Nemes, J.E. Fischer, *Phys. Rev. B* 65 (2002) 052103.
- [3] R. Kerkoud, P. Auban-Senzier, D. Jérôme, S. Brazovskii, I. Luk'Yanchuk, N. Kirova, F. Rachdi, C. Goze, *J. Phys. Chem. Solids* 57 (1996) 143.
- [4] A. Iwasiewicz-Wabnig, T. Wågberg, T.L. Makarova, B. Sundqvist, *Phys. Rev. B* 77 (2008) 085434.
- [5] M.G. Yao, T. Wågberg, B. Sundqvist, *Phys. Rev. B* 79 (2009) 081403(R).
- [6] S. Margadonna, D. Pontiroli, M. Belli, T. Shiroka, M. Riccò, M. Brunelli, *J. Am. Chem. Soc.* 126 (2004) 15032.
- [7] M. Riccò, M. Belli, M. Mazzani, D. Pontiroli, D. Quintavalle, A. Jánossy, G. Csányi, *Phys. Rev. Lett.* 102 (2009) 145901.
- [8] M.G. Yao, T. Wågberg, B. Sundqvist, *Phys. Rev. B* 81 (2010) 155441.
- [9] M.G. Yao, T. Wågberg, A. Iwasiewicz-Wabnig, T.L. Makarova, B. Sundqvist, *J. Phys.: Conf. Series* **215** (2010) 012020.
- [10] T.L. Makarova, *Semiconductors* 35 (2001) 243.
- [11] M. Riccò, M. Belli, D. Pontiroli, M. Mazzani, T. Shiroka, D. Arčon, A. Zorko, S. Margadonna, G. Ruani, *Phys. Rev. B* 75 (2007) 081401.
- [12] G. Ruani, P. Guptasarma, C. Taliani, J. Fischer, *Physica C* 235-240 (1994) 2477.

- [13] M. Knupfer and J. Fink, Phys. Rev. Lett. 79 (1997) 2714.
- [14] S.C. Erwin, C. Bruder, Physica B 199&200 (1994) 600.
- [15] O. Gunnarsson, S.C. Erwin, E. Koch, R.M. Martin, Phys. Rev. B 57 (1998) 2159.
- [16] S. Matsuura, T. Ishiguro, K. Kikuchi, Y. Achiba, I. Ikemoto, Fullerene Sci. Technol. 3 (1995) 437.

Figure captions:

Figure 1 a. Raman spectra for K_4C_{60} (synthesized for this work) and for Rb_4C_{60} synthesized in an earlier investigation [4]. Both spectra were obtained using HeNe laser excitation at 632.8 nm and have been shifted vertically for clarity. The triangular feature between 300 and 400 cm^{-1} is a known experimental artifact in our spectrometer.

Figure 1b. X-ray diffraction diagram for nominal K_4C_{60} . Ticks indicate expected peak positions; top for K_4C_{60} ($I4/mmm$, $a = 1.186$ nm, $c = 1.076$ nm), bottom for K_6C_{60} ($Im3$, $a = 1.139$ nm). Two weak peaks for pure C_{60} can also be identified, near 17.8 and 21.0 degrees. A strong background from the glass capillary has been removed for clarity.

Figure 2. Electrical resistance of a Li_4C_{60} sample as a function of temperature at the pressures indicated.

Figure 3. Electrical resistance of a K_4C_{60} sample as a function of temperature at the pressures indicated.

Figure 1a

Figure 1 b

Figure 2

Figure 3