Reversible Nano-Scale Phase Separation of Rb$_4$C$_{60}$ under Pressure

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Abstract. The alkali fulleride Rb$_4$C$_{60}$ has been investigated by studies of the resistance and by Raman spectroscopy under pressures up to 2 GPa and 13 GPa, respectively. Our data show a reversible phase separation into metallic Rb$_3$C$_{60}$ and Rb$_6$C$_{60}$ at pressures above 1 GPa. The reversibility indicates that the phase separation primarily occurs on the nanometer length scale. The data explain several puzzling results reported in the recent literature.

1. Introduction

The alkali metal fullerenes show fascinating structural and transport properties related to charge transfer from alkali metal (A) to fullerenes. Among A$_4$C$_{60}$ materials, light alkali compounds (A = Li, Na) form interfullerene covalent bonds and thus doped fullerene polymers [1,2], while the heavier ones (A = K, Rb, Cs) have unpolymerized tetragonal lattices [3]. Because 4 out of 6 electron states are filled, simple theory predicts metallic states, but all A$_4$C$_{60}$ materials are small gap semiconductors [3].

The results from earlier studies of Rb$_4$C$_{60}$ under pressure seem incompatible. NMR data suggested an insulator-to-metal transition at 0.8 GPa [4], while resistance studies indicate a semiconductor up to 2 GPa [5]. Structural studies reveal a transition near 0.5 GPa, but the structure may be either tetragonal [6] or orthorhombic [7] above this. Compton effect results [8] could only be explained by assuming a strong compression of the C$_{60}$ molecules. Recent Raman studies up to 8 GPa [9] show three anomalies, assigned, respectively, to the low-pressure structural transition [6,7], to a subtle second structural anomaly [7], and to molecular deformation. Although such deformations have been deduced from careful compression studies on fullerenes [10], they are very much smaller than those suggested by the Raman and Compton effect studies referred to above. To improve our understanding we have recently carried out Raman studies on well characterized Rb$_4$C$_{60}$ to 13 GPa. As shown here, these studies clearly show that a reversible phase separation occurs in the material, starting above 0.5 GPa.

2. Experimental details

To synthesize Rb$_4$C$_{60}$, we mixed nearly stoichiometric amounts of C$_{60}$ and Rb$_6$C$_{60}$ (produced by a vapor transport method), with a small excess of the latter, and annealed for several weeks. Characterization of the product by Raman scattering, X-ray diffraction and NMR showed that the bulk material...
contained mainly Rb$_4$C$_{60}$, with minor amounts of Rb$_6$C$_{60}$. Rb$_3$C$_{60}$ was only detected in trace amounts on grain surfaces by Raman [5]. Samples were synthesized and handled in Ar gas in a glove-box, and Raman measurements were carried out in a diamond anvil cell (DAC) of the Mao-Bell type, using a Renishaw 1000 Micro-Raman spectrometer with 514.5 nm excitation. No pressure medium was used and the pressure was measured to within ± 0.2 GPa using the standard ruby fluorescence technique. The resistance was measured in a large piston-cylinder device using the four-probe method [5].

3. Experimental results

3.1. Resistance data

In our first study on Rb$_4$C$_{60}$ we carried out measurements of the electric resistance in order to directly detect the insulator-to-metal transition reported in the literature [4]. The results obtained from our recent Raman scattering experiments allow us to extend our conclusions from the published detailed data [5]. For clarity, we repeat here the most important points, adding some previously unpublished details important for understanding the behaviour of Rb$_4$C$_{60}$ under pressure.

It was clear from our data that the resistance $R$ showed an "activated" behaviour ($dR/dT < 0$) at all temperatures $T$ and pressures $p$ in the ranges 90 – 450 K and 0 – 2 GPa, with no insulator-to-metal transition. A second important fact was that we could not fit a single exponential term in $1/T$ to the data over the full range of $T$ at any $p < 2$ GPa. As for other fullerene-based systems we had to use a model in which electrons are excited to the conduction band from both the valence band over the full energy gap $E_g$ and from localized gap states with a characteristic excitation energy $E_2$. In fact, these two components were only sufficient in the early stages of each experiment. Above 0.5 GPa, and during the second or higher pressure cycle, we had to add an additional small conductivity term to obtain a good fit at low temperatures. The final function used for fitting the data was thus

$$S(T) = 1/R = a \exp(E_g/2k_BT) + b \exp(E_2/2k_BT) + c/T,$$

with $a$, $b$ and $c$ constants. The last term was chosen as $c/T$ rather than as a constant because there might be a small amount of metallic Rb$_4$C$_{60}$ in the material. Figure 1 shows experimental data for $S$ versus $T$ obtained at 1.77 GPa, together with the three fitted terms from Eq. (1). The parameter $c$ was observed to increase linearly with $p$ during the first pressure cycle. With decreasing $p$, this change was

![Figure 1](image1.png)

Figure 1. Conductance $S = 1/R$ as a function of $T$ at 1.77 GPa (dots), together with the fit of Eq. (1). The three individual fitted terms of Eq. (1) are also shown, marked $a$, $b$, and $c$, respectively.

![Figure 2](image2.png)

Figure 2. Relative magnitudes of the fitted $c$ (Eq. 1) versus pressure, $p$, for three samples (indicated by different symbols). Filled (open) symbols indicate increasing (decreasing) $p$. 
reversible down to about 0.5 GPa, but below this $c$ increased strongly (not shown in Figure 2). Further heating to above 450 K at 0.1 GPa increased $c$ by an order of magnitude. As reported earlier [5], heating above 480 K under high pressure resulted in a permanent transformation into a metallic state through the formation of a significant fraction of Rb$_3$C$_{60}$ (identified by Raman scattering, X-ray diffraction, and measurement of the critical temperature for superconductivity).

3.2. Raman scattering results
Our recent Raman scattering results shown in Figure 3 are in qualitative agreement with the data of Bellin et al. [9]. Our data reveal two interesting new results: i) the ambient pressure spectra before and after the high pressure run are identical, and the effects of pressures up to 13 GPa (at 293 K) are thus completely reversible [11], ii) even more interesting, above 8 GPa the Raman spectra can be clearly identified as those of Rb$_6$C$_{60}$, for example by a direct comparison with the data of Poloni et al. [12]. A careful analysis of the complete data set [11] reveals that between 1 and 8 GPa, all Raman spectra indicate the presence of a mixture of Rb$_4$C$_{60}$ and Rb$_6$C$_{60}$, and that the material gradually transforms into the latter with increasing pressure. Because no additional rubidium is available we conclude that the formation of Rb$_6$C$_{60}$ must be associated with the simultaneous formation of a compound with a low concentration of Rb. The resistance data suggest the presence of Rb$_3$C$_{60}$, and we thus propose that the reaction taking place is

$$3 \text{Rb}_4\text{C}_{60} \Leftrightarrow 2 \text{Rb}_3\text{C}_{60} + \text{Rb}_6\text{C}_{60}. \quad (2)$$

Because Rb$_3$C$_{60}$ is metallic it has a much smaller Raman cross-section than Rb$_6$C$_{60}$ and is thus much more difficult to observe in the combined spectrum of the Rb$_3$C$_{60}$/Rb$_6$C$_{60}$ mixture. Nevertheless, we do observe weak lines that may possibly be attributed to Rb$_3$C$_{60}$ [11].

4. Discussion and conclusions
A pressure-induced phase separation of Rb$_4$C$_{60}$ under pressure according to Eq. (2), starting already below 1 GPa and completed near 8 GPa, would explain the many puzzling results observed in earlier studies of this material. The driving force behind the reaction is most probably the fact that the phase separation leads to a volume reduction by about 4%, as calculated from the densities at atmospheric pressure.

Figure 3. Raman spectra for (initially) pure Rb$_4$C$_{60}$ at the pressures indicated. Ticks at the top indicate the positions of the Raman modes of pure C$_{60}$ at atmospheric pressure.

Figure 4. Top: the 001 plane of Rb$_4$C$_{60}$ with Rb ions in octahedral sites. Bottom: model for nanophase separation of Rb$_4$C$_{60}$ by Rb diffusion between nearest neighbour sites.
pressure, and we suggest that this separation begins at pressures immediately above the orientational lattice transformation observed at 0.3 – 0.5 GPa [6,7].

The insulator-to-metal transition observed by NMR [4] may be explained by a combination of two effects. Application of pressure deforms the lattice, creating more defects and thus increases the conductivity component arising from localized states with a very small excitation energy \( E_2 \approx 0.1 \) eV, and above 0.5 GPa the phase separation will provide an increasing amount of metallic phase in the form of Rb\(_3\)C\(_{60}\). Below 2 GPa, however, the metallic fraction is never large enough to reach the percolation threshold, which explains why bulk resistivity data always show an activated behaviour.

The combination of an orientational transition at 0.3 GPa [7] and a gradual phase separation at higher pressures probably explains why compressibility data on Rb\(_4\)C\(_{60}\) have been very difficult to analyze, in particular since all samples studied initially contained Rb\(_3\)C\(_{60}\) [6,7] and Rb\(_6\)C\(_{60}\) [6]. The data of Sabouri-Dodaran et al. [6] clearly show an increase in the intensities of peaks from these materials above 1 GPa, supporting our interpretation. It is possible that an increasing fraction of metallic Rb\(_3\)C\(_{60}\) might also explain the puzzling results reported for the electronic structure under pressure [8].

The fact that the phase separation is completely reversible indicates that Rb ions probably diffuse over very short distances, and the high pressure state is thus probably a nanometer-scale composite, adding to the difficulty of identifying phases by diffraction. Raman spectra, on the other hand, are basically molecular spectra even in the solid state. An interesting question is how such a nanostructure may form. There are many possibilities, and Figure 4 shows how a simple lamellar 3/6/3/3/6 structure might be created by movement of Rb ions between nearest neighbour octahedral sites only. (Rb ions in tetrahedral sites are assumed fixed in the lattice, and are not shown in the Figure.)

Finally, we have attributed the appearance of Rb\(_3\)C\(_{60}\) in our samples after heating under pressure to loss of Rb [5]. A different explanation may be that high \( T \) annealing causes growth and merging of the nano-grains, such that for kinetic reasons the Rb\(_3\)C\(_{60}\)/Rb\(_6\)C\(_{60}\) composite can no longer revert to its original Rb\(_3\)C\(_{60}\) structure when \( T \) is lowered.

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