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G. Faigel, M. Tegze, G. Bortel, L. Forró, G. Oszlányi, et al.. Parallel beam powder diffraction study on the AlC60 system (A=K, Rb). Journal de Physique IV Proceedings, 1994, 04 (C9), pp.C9-109-C9-112. 10.1051/jp4:1994914 . jpa-00253474

HAL Id: jpa-00253474

<https://hal.science/jpa-00253474>

Submitted on 1 Jan 1994

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Parallel beam powder diffraction study on the A_1C_{60} system ($A=K, Rb$)

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Abstract: We report x-ray powder diffraction studies on Rb_xC_{60} and K_xC_{60} . It is shown that at room temperature there exist stoichiometric compounds in the Rb_xC_{60} and K_xC_{60} systems at the $x \approx 1$ composition. Their equilibrium structures are pseudo body centered orthorhombic. The C_{60} - C_{60} intermolecular separation (9.1 Å) is the shortest among the known alkali- fullerides. A first order phase transition is observed at about 380 K from the high temperature fcc phase to the room temperature orthorhombic phase.

1. INTRODUCTION

Among the alkaline metal doped fullerenes many phases appear with different compositions. Most of the efforts were concentrated on the A_3C_{60} type compounds since they show superconductivity. However, recently the interest turned to the A_1C_{60} compounds, since they have unusual phase transitions accompanied with drastic changes of the transport properties [1-5].

Zhu et al. [1] have prepared first single-phase samples of Rb_1C_{60} as well as K_1C_{60} and Cs_1C_{60}

They find that these have an fcc (rock salt) structure at elevated temperatures, and suggested a rhombohedrally distorted fcc lattice for both Rb_1C_{60} and K_1C_{60} at room temperature, but structural details were not given.

In this work we present detailed structural studies of Rb_1C_{60} and K_1C_{60} . We show that the room temperature lattice of Rb_1C_{60} and K_1C_{60} is orthorhombic with an unusually short C-C intermolecular separation (9.1 Å).

2. EXPERIMENTS

Samples were prepared by a solid state reaction of high purity C_{60} powder and alkali metal in sealed quartz capillaries at 260 °C for 80 days. The samples used in our studies had nominal compositions: $Rb_{0.5}C_{60}$, Rb_1C_{60} and K_1C_{60} . Parallel beam x-ray powder diffraction measurements were performed at the X3B1 beamline of the Brookhaven National Synchrotron Light Source. X-ray optics consisted of a double Si(111) single crystal monochromator and a perfect Ge single crystal analyzer. This arrangement allowed to take high quality powder data which was crucial for Rietveld refinement.

3. RESULTS

The high temperature (465 K) diffraction pattern of the Rb_1C_{60} sample is shown in Fig. 1. Three phases can be clearly distinguished: pure C_{60} , Rb_1C_{60} and Rb_3C_{60} .

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Fig. 1. The diffraction pattern and the Rietveld fit of the Rb_1C_{60} sample at 465 K.

All three have fcc structures with lattice parameters

$$\begin{aligned} a(\text{C}_{60}) &= 14.172(5) \text{ \AA}, \\ a(\text{Rb}_1\text{C}_{60}) &= 14.077(5) \text{ \AA}, \\ a(\text{Rb}_3\text{C}_{60}) &= 14.466(5) \text{ \AA}. \end{aligned}$$

The room temperature diffraction data of the same sample leads to surprising new results. Fig. 2 shows the powder pattern of the sample after slow cooling to room temperature. Three phases can be identified again: pure C_{60} , a new orthorhombic phase of Rb_1C_{60} and Rb_3C_{60} . The refined lattice parameters are:

$$\begin{aligned} a(\text{C}_{60}) &= 14.152(5) \text{ \AA}, \\ a(\text{Rb}_1\text{C}_{60}) &= 9.134(10) \text{ \AA}, \\ b(\text{Rb}_1\text{C}_{60}) &= 10.099(10) \text{ \AA}, \\ c(\text{Rb}_1\text{C}_{60}) &= 14.234(10) \text{ \AA}, \\ a(\text{Rb}_3\text{C}_{60}) &= 14.417(5) \text{ \AA}. \end{aligned}$$

In the orthorhombic Rb_1C_{60} structure (see Fig. 3) the 9.13 Å interfullerene separation along a is unusually short. The most likely space groups are Immm or Pnnm, depending on the orientation of the fullerene molecules. The short intermolecular separation suggests chemical bonding (formation of polymer chains along the (100) direction [6]) which would be compatible with space group Immm.

In the case of K_1C_{60} a result similar to Rb_1C_{60} was obtained (Fig. 4). The room temperature equilibrium phase of K_1C_{60} is pseudo body centered orthorhombic with lattice parameters:

$$\begin{aligned} a &= 9.093(10) \text{ \AA}, \\ b &= 9.994(10) \text{ \AA}, \\ c &= 14.425(10) \text{ \AA}. \end{aligned}$$

In order to determine how the phase transition takes place, we carried out a series of short x-ray diffraction scans as a function of the temperature on the Rb_1C_{60} sample. Three typical spectra are shown in Fig. 5. The phase transition takes place at 380 K. The evolution of the phase transition can be followed in Fig. 6 where the integrated intensity of the peaks corresponding to the high temperature fcc and room temperature orthorhombic phases are shown as a function of

Fig. 2. The diffraction pattern and the Rietveld fit of the Rb_1C_{60} (upper panel) and the $\text{Rb}_{0.5}\text{C}_{60}$ (lower panel) samples at room temperature.

Fig. 3. The connection between the high temperature fcc and the room temperature orthorhombic cell.

Fig. 4. The diffraction pattern and the Rietveld fit of the K_1C_{60} sample at room temperature.

Fig. 5. A characteristic 2θ range of the powder pattern of the Rb_1C_{60} sample above, at, and below the phase transition temperature.

the temperature. The hysteretic difference between the data collected on heating and cooling is characteristic to a first order phase transition.

4. SUMMARY

In this paper we showed that the room temperature equilibrium structure of both Rb_1C_{60} and K_1C_{60} is orthorhombic. This result is based on detailed Rietveld refinement studies. In these structures the intermolecular separation is the shortest among all the known C_{60} compounds. The phase transition from the high temperature fcc to the room temperature orthorhombic structure is shown to be of first order.

5. ACKNOWLEDGEMENTS

This work has been supported by OTKA grants under contract numbers 2943 and E-012313. The SUNY X3 beam line at NSLS is supported by the DOE under grant No. DEFG-0286-ER-45231. Part of this research was carried out at the National Synchrotron Light Source which is

Fig. 6. The peak areas of the fcc Rb_1C_{60} on heating (empty circles), on cooling (empty triangles) and the orthorhombic Rb_1C_{60} on heating (full circles), on cooling (full triangles) versus the temperature.

supported by U.S. DOE, Division of Material Sciences and Division of Chemical Sciences. Work at SUNY was supported by the National Science Foundation Division of Materials Research under grant No. DMR 92-02528.

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