Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

X-Ray Absorption Study of the Local Structure At Potassium and Rubidium in $K_{3-x}Rb_xC_{60}$

G. Nowitzke [a], J. Dumschat [a], G. Wortmann [a], H. Werner [b] & R. Schlögl [b]

[a] Fachbereich Physik, Universität-GH-Paderborn, D-33095, Paderborn, Germany

[b] Institut für Anorganische Chemie, Universität Frankfurt/Main, D-60439, Frankfurt/Main, Germany

Version of record first published: 23 Oct 2006.

To cite this article: G. Nowitzke , J. Dumschat , G. Wortmann , H. Werner & R. Schlögl (1994): X-Ray Absorption Study of the Local Structure At Potassium and Rubidium in $K_{3-x}Rb_xC_{60}$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 245:1, 321-326

To link to this article: http://dx.doi.org/10.1080/10587259408051708

Mol. Cryst. Liq. Cryst. 1994, Vol. 245, pp. 321–326
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

X-RAY ABSORPTION STUDY OF THE LOCAL STRUCTURE AT POTASSIUM AND RUBIDIUM IN $K_{3-x}Rb_xC_{60}$

G. NOWITZKE, J. DUMSCHAT and G. WORTMANN
Fachbereich Physik, Universität-GH-Paderborn, D-33095 Paderborn, Germany

H. WERNER and R. SCHLÖGL
Institut für Anorganische Chemie, Universität Frankfurt/Main, D-60439 Frankfurt/Main, Germany.

Abstract: X-ray absorption fine structure (EXAFS and XANES) studies of the K-edges of potassium and rubidium in K_3C_{60}, K_2RbC_{60} and Rb_3C_{60} reveal the local structure and site preferences of the alkali metals. Both K and Rb ions on tetrahedral interstices exhibit regular positions with respect to the C_{60} neighbours in agreement with crystallographic data, while for Rb ions located on octahedral interstices an off-center position is found. The K_2RbC_{60} sample exhibits a clear preferential site occupation of the octahedral site by Rb, which is also reflected by the lattice constant, and indications for structural rearrangement of the Rb ions on octahedral sites around 50 K.

INTRODUCTION

Among the fascinating properties of the fullerene C_{60} is the appearance of superconductivity in A_3C_{60} compounds (A = K, Rb, Cs) with T_c values up to 31 K [1]. The crystal structure of A_3C_{60} is face-centered cubic (fcc) providing tetrahedral and octahedral interstitial sites in the ratio 2 : 1 for the alkali metals [2,3]. T_c increases with the lattice constant [1,3], which depends on the size of the dopant alkali metals. From the observed lattice constants and size arguments the larger Rb ions were suggested to occupy preferentially octahedral sites, while the smaller K ions prefer the tetrahedral sites in quasi-ternary systems like $K_{3-x}Rb_xC_{60}$. Such a site preference should be observable in an x-ray absorption study of $K_{3-x}Rb_xC_{60}$ at the *K*-edges of potassium and rubidium and is actually observed in the present study for the K_2RbC_{60} system.

SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

The samples were prepared in a two-step procedure, where at first highly purified and ultra-high-vacuum degased C_{60} and the respective alkali metals were reacted to phase-pure A_6C_{60} compounds. These precursors were used with appropriate amounts of C_{60} to prepare the A_3C_{60} compounds. Details of the sample preparation will be given in a forthcoming paper [4]. X-ray diffractogrammes yielded the following lattice constants *a*: 14.234(6) Å, 14.258(4) Å and 14.434(1) Å for K_3C_{60},

K_2RbC_{60} and Rb_3C_{60}, respectively. It is evident from Fig. 1 that the lattice constant of the present K_2RbC_{60} sample does not follow the nearly linear variation of a with x found in previous investigations [1] of the $K_{3-x}Rb_xC_{60}$ system. This points to a strong site preference of the Rb for the octahedral site in the present K_2RbC_{60} sample. It should be mentioned that an K:Rb = 2.3(2):1 ratio was found in this compound by x-ray fluorescence analysis. The superconducting transition curve of this sample with T_c = 21.3 K is as sharp as found for other superconducting single-phase A_3C_{60} materials [5]. It should be mentioned that the potassium content of the present K_3C_{60} sample was found to be slightly lower than 3 [4]. This is reflected by the somewhat smaller lattice constant and the lower transition temperature in comparision with other K_3C_{60} samples [1,3,6].

Since A_3C_{60} samples are extremely reactive with oxygen, all handlings were performed in a purified Ar atmosphere. The samples used in the x-ray absorption experiments were encapsulated in vacuum-tight stainless-steel absorber holders equipped with Be windows. The x-ray absorption studies (XAS) were performed at the EXAFS-II (K *K*-edge at 3600 eV) and RÖMO-II (Rb *K*-edge at 15200 eV) spectrometers at HASYLAB/DESY (Hamburg). Spectra were taken at the potassium and rubidium *K*-edges of $K_{3-x}Rb_xC_{60}$ (x = 0, 1, 3) in the temperature range 10 K - 300 K. In addition, K_6C_{60} and Rb_6C_{60} as well as some reference compounds were investigated.

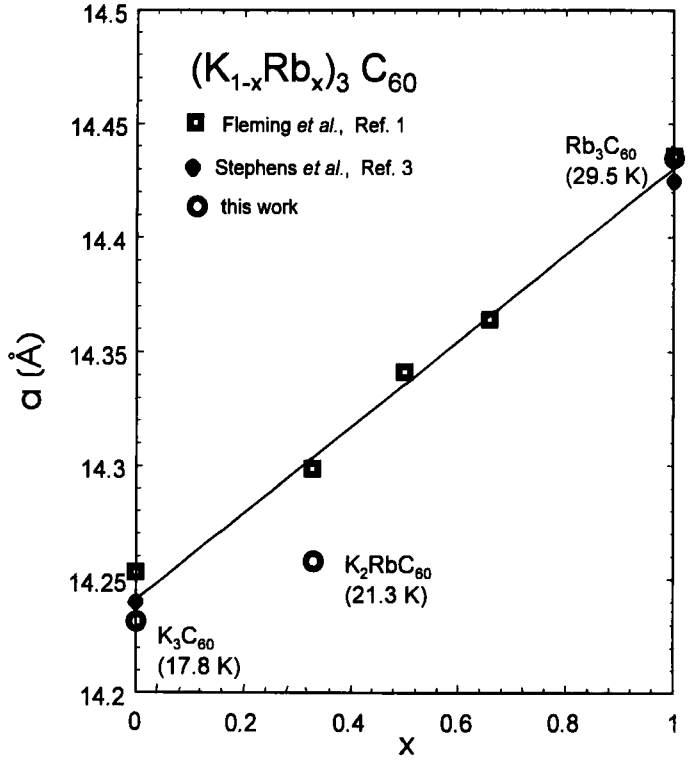

Fig. 1: Lattice constants a of $K_{3-x}Rb_xC_{60}$ as function of the Rb content x. The T_c values of the present samples [5] are given in brackets.

X-RAY ABSORPTION MEASUREMENTS

Before presenting the x-ray absorption measurements, one should mention what kind of informations is obtainable from the applied spectroscopy. From the known structures of K_3C_{60} and Rb_3C_{60} one expects that two third of the potassium or rubidium ions are occupying tetrahedral and one third octahedral interstices. The local surroundings and A-C distances (A = K, Rb) are quite different for the two sites: The alkali atoms at tetrahedral sites are surrounded by four C_{60} molecules with a commensurate position above the hexagons pointing in the (111)-direction. There are, when all C_{60} molecules are rotationally ordered, 24 nearest C neighbours at distances of A_t-C = 3.27 Å and 3.33 Å for K and Rb, respectively [2,3]. These distances are slightly larger than the ones observed in AC_8 graphite intercalation compounds with 12 nearest C neighbours (3.06 Å and 3.18 Å for KC_8 and RbC_8, respectively). For the octahedral sites in A_3C_{60} one derives (for a centrosymmetric position) nearest A_o-C distances of 3.69 Å and 3.72 Å for K_3C_{60} and Rb_3C_{60}, respectively, with 12 nearest C neighbours located pairwise on the edges separating hexagons of 6 neighbouring C_{60} molecules. The octahedral site offers actually more space than needed for the alkali ions; this is reflected by the large thermal factors *B* for K or Rb on these sites derived from Rietveld analyses of XRD data [2,3]. This points to very large thermal displacements and/or, indistinguishable from XRD analysis, to off-center positions of the alkali metals. As a microscopic method, EXAFS analysis should be able to distinguish between these two possibilities from the observed A-C distances as well as from the derived coordination numbers. The same holds for the occupation of tetrahedral and octahedral sites in K_3C_{60} and Rb_3C_{60} as well as for an observation of a preferential site occupation in the investigated K_2RbC_{60} system. The near-edge structures (XANES) should reflect also structurally and chemically different surroundings. We refer the reader to previous XAS investigations of KC_8, RbC_8 and RbC_{24} graphite intercalation compounds [7].

Near-Edge Structure:

Fig. 2 displays the normalized absorption spectra of K and Rb in K_3C_{60}, K_2RbC_{60} and Rb_3C_{60}. The near-edge structure (XANES) of the potassium *K*-edge spectra is better resolved than the corresponding rubidium *K*-edge spectra due to the different lifetimes of the 1s hole in the respective *K* shell. Considering the different resolution, similar spectral features are found for the respective *K*-edge XANES spectra of potassium in K_3C_{60} and K_2RbC_{60} as well as for rubidium in Rb_3C_{60}. The Rb *K*-edge XANES spectrumof K_2RbC_{60}, however, is definitely different from the others. The near-edge structures are less resolved and the first EXAFS oscillations show different positions and in some cases even opposite phases than in Rb_3C_{60}. The near-edge structure of the Rb *K*-edge of K_2RbC_{60} exhibits in addition changes with temperature around 50 K, a quite unusual behaviour pointing to structural changes as a function of temperature.

EXAFS Analysis:

The absorption spectra yield informations in the EXAFS oscillations $\chi(k)$ up to k values of ~10 $Å^{-1}$. Typical Fourier transforms (FT) of $\chi(k)$ are shown in Fig. 3. As already observed for the near-edge structures, the FTs of the potassium *K*-edge

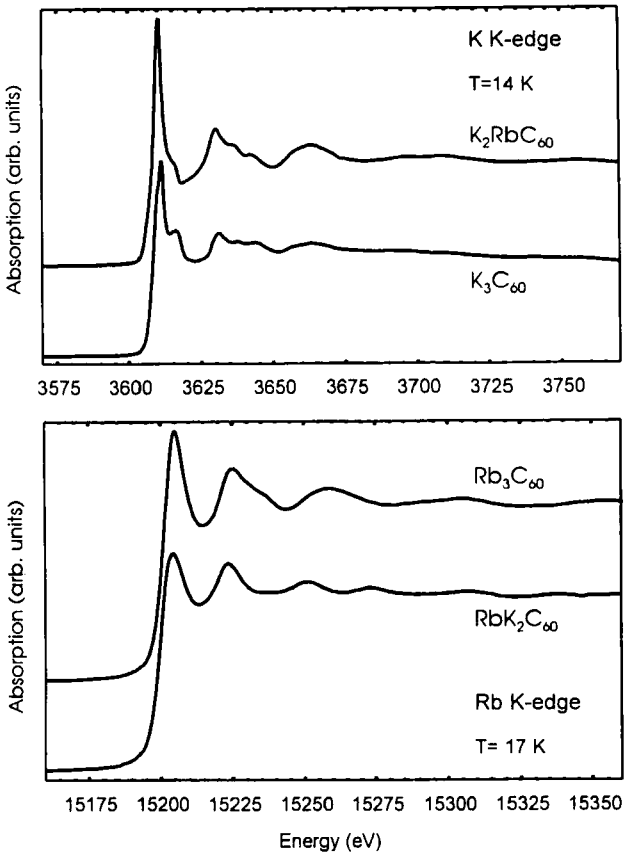

Fig. 2: Near-edge spectra of potassium (left) and rubidium (right) in $K_{3-x}Rb_xC_{60}$ taken at low temperature.

spectra of K_3C_{60} and K_2RbC_{60} as well as of the rubidium *K*-edge spectrum of Rb_3C_{60} resemble each other. They exhibit a dominant structure at a distance expected for tetrahedral sites (near 3 Å in the FTs, which are not corrected for phase shifts). Surprisingly, there are no significant structures in the FTs of K_3C_{60} and Rb_3C_{60}, which can be attributed to octahedral sites (the second peak in the FTs near 4 Å can be attributed to the next-nearest C shell for tetrahedral sites and/or to multiple scattering effects). Attempts to extract reliable A_t-C and A_o-C distances for both the tetrahedral and octahedral sites in the A_3C_{60} systems by a two-shell fit were not successful up to now. On the other hand, single-shell fits of the FTs of the A_3C_{60} systems yielded reliable results for the tetrahedral sites: A_t-C = 3.27(1) Å and 3.33(1) Å for K_3C_{60} and Rb_3C_{60}; the coordination numbers of the C neighbours, however, were systematically too low. The reason for this behaviour is evidenced in the analysis of the spectra of the K_2RbC_{60} system.

The potassium *K*-edge near-edge spectra and FTs of K_2RbC_{60} are, as shown in Figs. 2 and 3, very similar to the ones of K_3C_{60} and Rb_3C_{60}. The near-edge spectra and

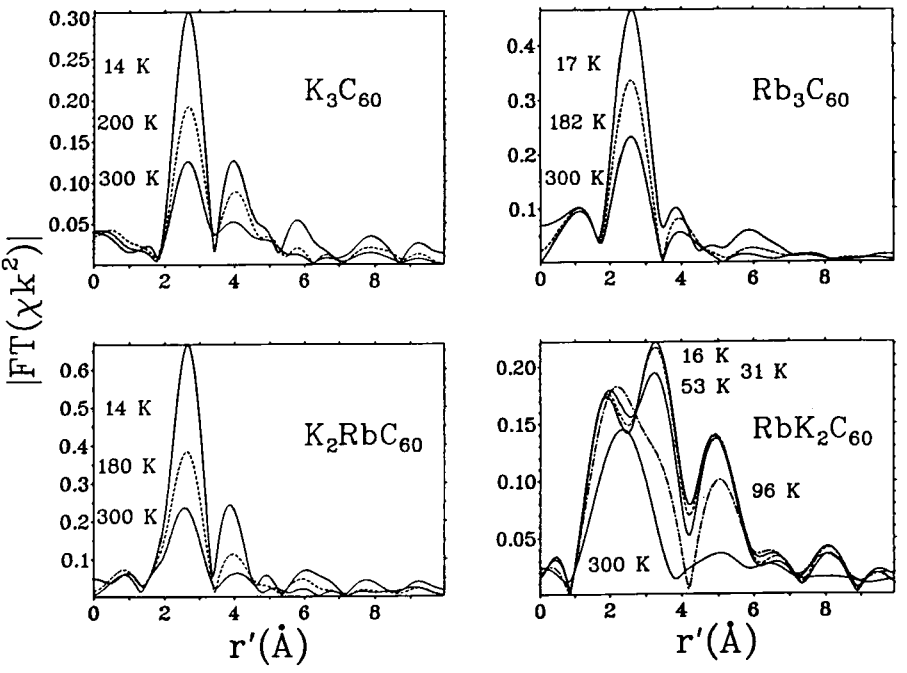

Fig. 3: Fourier transforms of the potassium (left) and rubidium right) EXAFS in $K_{3-x}Rb_xC_{60}$ measured at various temperatures.

FTs of the rubidium *K*-edge spectra of K_2RbC_{60}, however, are drastically different from the corresponding potassium spectra. The FTs exhibit now, clearly resolved at low temperatures, at least two different Rb-C distances, with the first shell at a smaller distance than observed for the tetrahedral sites. Correspondingly, the respective amplitudes of the various shells in the FT-spectra are only about one third of those observed in Rb_3C_{60} . The Rb EXAFS-FTs of K_2RbC_{60} exhibit, in contrast to the other FTs shown in Fig. 3, a strong temperature dependence in their spectral features: the resolved structures visible in the FTs at low temperatures disappear at temperatures above 53 K. From this we conclude that the Rb ions on the octahedral sites are in a (obviously temperature-dependent) off-center position. Preliminary two-shell fits yield defined Rb-C distances around 2.7(1) and 3.8(1) Å at low temperatures, pointing to a considerable off-center position. Such a highly distorted position with respect to the 12 C neighbours leads to a distribution in Rb-C distances and to a strong loss in the EXAFS signal, especially at higher k values. Similar features in the Rb EXAFS-FT were previously observed in stage-2 RbC_{24}, where an incommensurate position of Rb with respect to the carbon hexagons leads also to a dramatic loss in the Rb EXAFS signal [7]. We conclude that in the present case the off-center position of Rb (and presumably also of K) on the octahedral sites reduces the contributions to the EXAFS signals and explains the virtual disappearance of the octahedral sites in the EXAFS analysis of Rb_3C_{60} and K_3C_{60}. This explains also why a single-shell analysis of the corresponding spectra provides reliable A_t-C distances for the tetragonal sites, but too low coordination numbers.

(Disorder effects of the C_{60} molecules can also lead to a reduced coordination number of C neighbours at the tetragonal sites; these effects will be discussed elsewhere [4]).

From the above findings and other results not shown here we conclude that at least 85% of the Rb ions occupy octahedral sites in the investigated K_2RbC_{60} sample, a behaviour already reflected in the XRD data. This strong site preference enables a more detailed analysis of the K_3C_{60} and Rb_3C_{60} spectra by creating difference spectra from the respective normalized K_3C_{60}, Rb_3C_{60} and K_2RbC_{60} spectra (taken at the same temperature). The resulting Rb K-edge Rb_3C_{60}/K_2RbC_{60} difference spectra are now exhibiting exclusively the properties of Rb on tetrahedral sites (like the potassium EXAFS spectra of K_2RbC_{60}). Single-shell EXAFS analyses yielded Rb-C distances *and* coordination numbers in reasonable agreement with the values expected from the XRD data. A detailed report of the EXAFS analyses of alkali metal ions on tetrahedral and octahedral sites and their temperature dependence in $K_{3-x}Rb_xC_{60}$ and Rb_2CsC_{60} will be given elsewhere [4].

One should finally comment on recent ^{87}Rb- and ^{133}Cs-NMR studies of A_3C_{60} systems. Maniwa et al. [8] found from a ^{133}Cs-NMR study in the $Rb_{3-x}Cs_xC_{60}$ system also a site preference for the octahedral site, but now, as expected, for the larger Cs ions. Walstedt et al. [9] investigated Rb_3C_{60} and $K_{1.5}Rb_{1.5}C_{60}$ with ^{87}Rb NMR. They found a prefered occupation of the octahedral site by Rb and discuss a possible off-center position of Rb on the octahedral site connected with the appearance of an additional NMR line attributed to Rb on a modified tetrahedral site. Zimmer et al. [10] performed a similar ^{87}Rb-NMR study on Rb_3C_{60}. They observe also the additional line/site and found, with a very pronounced hysteresis, evidence for a structural phase transition around 50 K. Both ^{87}Rb-NMR studies as well as a recent ESR study [6] find their correspondence in the present finding that the Rb ions on the octahedral sites exhibit a change in their off-center position above 50 K.

This work was supported by the BMFT (projects No 05 5PPACB and No 2654/92-13N6075 2) and the DFG (Sfb-337, TP B2). We acknowledge the help of Dr. J. Freund and Dr. J. Röhler in the XAS measurements. The superconducting properties of the samples were measured by M. Baenitz (Freie Universität Berlin).

REFERENCES

[1] R.M. Fleming *et al.*, Nature 352, 787 (1991).
[2] P.W. Stephens *et al.*, Nature 351, 632 (1991)
[3] P.W. Stephens *et al.*, Phys. Rev. B 45, 543 (1992).
[4] G. Nowitzke et al., in preparation.
[5] M. Baenitz *et al.*, in: Fullerenes Science and Technology (M. Dekker, New York, 1993), in print.
[6] K. Holczer and R.L. Whetten, Carbon 30, 1261 (1992).
[7] D. Bonnin *et al.*, J. de Physique 47, Colloq. C8-865 and C. Fretigny *et al.*, *ibid.*, C8-869 (1986).
[8] Y. Maniwa *et al.*, Solid State Commun. 82, 783 (1992).
[9] R.E. Walstedt, D.W. Murphy, M. Rosseinsky, Nature 362, 611 (1993).
[10] G. Zimmer *et al.*, in: Springer Series of Solid State Sciences (Proc. IWEPNM'93 Kirchberg/Austria, 1993), in print.