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## ALKALI INTERCALATED C<sub>60</sub>: NMR AND MAGNETIC SUSCEPTIBILITY STUDIES

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We report on <sup>13</sup>C NMR measurements on potassium intercalated C<sub>60</sub> compounds. By using high resolution NMR technique we were able to characterize the different thermodynamically stable phases. The effects of the intercalation on the molecular dynamics as well as on the electronic properties will be discussed. We also performed the magnetic susceptibility measurements on Rb<sub>4</sub>C<sub>60</sub> compound, which reveal the activation temperature behavior with the activation energy about 1200 K. By comparison with the NMR and ESR data of the same sample we conclude that the additional electrons are localized on the C<sub>60</sub> molecule and form the spin singlet ground state.

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### 1. Introduction

The discovery of distinct phases with unusual properties in alkali fullerides has raised fundamental questions about their physical and chemical structure [1-3]. For the alkali metals K, Rb thermodynamically stable phases A<sub>x</sub>C<sub>60</sub> with  $x = 1, 3, 4$  and  $6$  exhibiting different crystal structures have been well established through structural investigations [4-7]. Since each of these phases exhibits a distinctive behaviour, it is highly desirable to characterize and elucidate their properties. In this respect nuclear magnetic resonance is a powerful tool because it supplies a microscopic probe which allows for studying the electronic structure as well as the molecular dynamics of the different phases. Although many NMR investigations in pristine and doped fullerene have been performed [8, 9], the number of high-resolution studies in the solid state, especially for the doped compounds, has been rather limited [10-12]. This is mainly due to the fact that these samples are very air-sensitive which requires a special NMR probehead and spinner design, not achievable with standard commercial magic angle spinning (MAS) probeheads.

In this paper we report the results of  $^{13}\text{C}$  nuclear magnetic resonance on different phases  $\text{K}_x\text{C}_{60}$  compounds by using magic angle spinning at room temperature and discuss their distinctive features in terms of chemical and/or Knight shifts. One of the important questions to clarify in alkali doped fullerides is the nature of the ground state of carriers. The various thermodynamically stable phases in these compounds provide a good opportunity to investigate the effects of electron-electron correlations. We report here the bulk magnetization measurements in  $\text{Rb}_4\text{C}_{60}$  in order to get information about the electronic structure in this phase.

## 2. Experiment

Powder samples of  $\text{K}_x\text{C}_{60}$  and  $\text{Rb}_x\text{C}_{60}$  with  $x = 3, 4$  and  $6$  were synthesized by preparing in the first step the compound  $\text{A}_6\text{C}_{60}$  using a vapour transport method similar to that described in the literature [2]. The sample structures were checked by X-ray diffraction. NMR spectra were recorded at a  $^{13}\text{C}$  frequency of 50.3 MHz (4.7 T field) on a Bruker ASX 200 spectrometer. The NMR signal was obtained as the Fourier transform of the free induction decay after a  $\pi/2$  r.f. pulse. All chemical shifts were referenced to tetramethylsilane (TMS). We applied magic angle spinning by using a homebuilt NMR probehead and a specially designed spinner which allows air-sensitive samples to be spun in sealed NMR tubes with frequencies up to 3 kHz. Approximately 30 mg of material was filled in the NMR tubes.  $T_1$  values were determined with the inversion-recovery technique.

The magnetic susceptibility  $X(T)$  of  $\text{Rb}_4\text{C}_{60}$  sample was obtained from dc magnetization measurements between 50 G and 40 kG using a Quantum Design SQUID magnetometer. The sample contains about 20% of the phase  $\text{Rb}_3\text{C}_{60}$ . The onset of superconducting phase transition in the fraction of  $\text{Rb}_3\text{C}_{60}$  at  $T_c = 30$  K restricts the low temperature magnetization measurements below  $T_c$ . The correction of the sample holder contribution to the susceptibility was made by the independent measurement of the susceptibility of the empty Pyrex tube. We also corrected for the 20% content of the  $\text{Rb}_3\text{C}_{60}$  phase, assuming  $X_{\text{Rb}_3\text{C}_{60}} = 14.7 \times 10^{-4}$  emu/mol [13].

## 3. Results and discussion

Figure 1a shows the isotropic parts of the high-resolution  $^{13}\text{C}$  MAS-NMR spectra for the different phases of potassium doped  $\text{C}_{60}$  at ambient temperature, which were all obtained with the same spinning frequency of about 2.5 kHz. As can be clearly seen each phase is well discernible by its characteristic resonance with the following values for the shifts  $d$  (relative to TMS)  $\text{K}_6\text{C}_{60}$  (156 ppm),  $\text{K}_4\text{C}_{60}$  (180 ppm) and  $\text{K}_3\text{C}_{60}$  (187 ppm). The arrow marks the resonance of undoped  $\text{C}_{60}$  (143.6 ppm) for reference. For the spinning frequency used  $\text{K}_3\text{C}_{60}$  and  $\text{K}_4\text{C}_{60}$  yield a single line shifted 44 ppm and 37 ppm downfield from undoped  $\text{C}_{60}$ , respectively, whereas the spectrum of  $\text{K}_6\text{C}_{60}$  shows three peaks, indicating the existence of three magnetically non-equivalent carbon sites in this compound [10]. Note that the full width at half maximum (FWHM) of the resonance in  $\text{K}_3\text{C}_{60}$  is distinctly larger

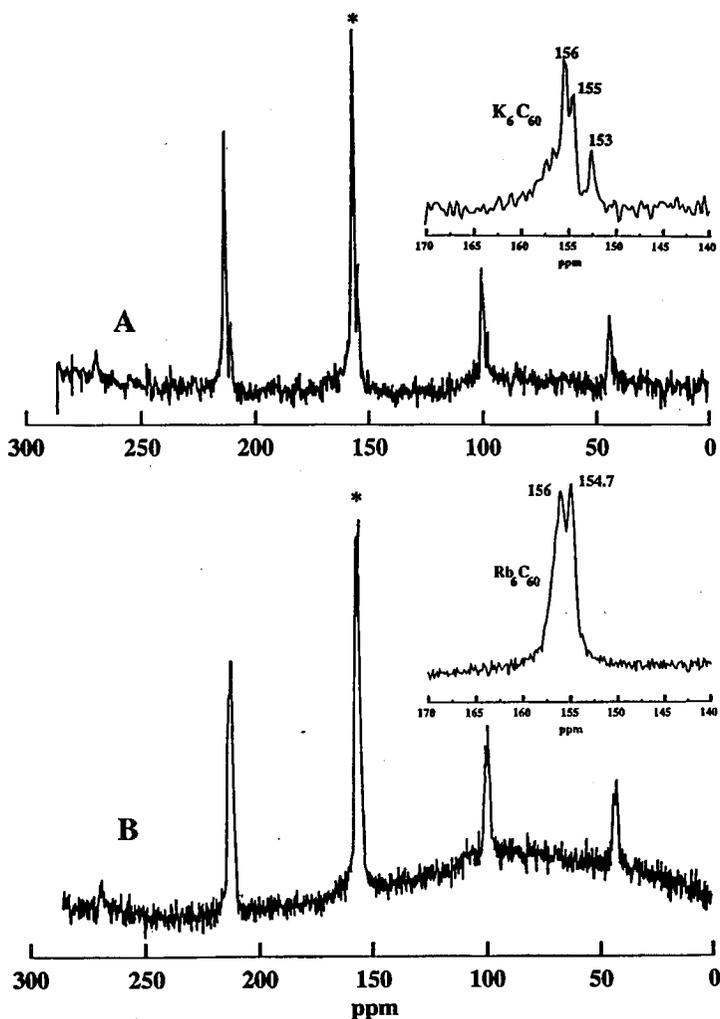


Fig. 1. (a) High-resolution  $^{13}\text{C}$  MAS-NMR room temperature spectra of the different phases in potassium-doped fullerene  $\text{K}_x\text{C}_{60}$  ( $x = 3, 4, 6$ ) showing the different isotropic lines. The arrow marks the resonance position of pure  $\text{C}_{60}$ . Frequencies are in ppm with respect to tetramethylsilane. (b)  $^{13}\text{C}$  room temperature of  $\text{K}_6\text{C}_{60}$  spinning at the magic angle with a frequency of 2.8 kHz. The inset shows the isotropic line in more detail (see text).

( $\Delta H \approx 4$  ppm) as compared to the FWHM of the lines in  $\text{K}_4\text{C}_{60}$  and  $\text{K}_6\text{C}_{60}$  ( $\Delta H \approx 1$  ppm).

In Fig. 1b we have plotted the full  $^{13}\text{C}$  MAS-NMR spectra for  $\text{K}_6\text{C}_{60}$  showing in addition to the isotropic line a whole series of equally spaced spinning sidebands. The sidebands extend over roughly 300 ppm indicating the large chemical shift

anisotropy (CSA) which leads to the broad characteristic powder pattern in static measurements. It is noteworthy that we obtain for  $\text{Rb}_6\text{C}_{60}$  compound essentially identical spectra. This indicates that the saturated phases are principally ionic, exhibiting only weak hybridization between  $\text{C}_{60}$  and alkali metal states. Their properties are largely molecular and due to the  $\text{C}_{60}^{6-}$  ions, whereby this conclusion has also been confirmed by other, e.g. optical experiments [14]. The fact that distinct resonances within the isotropic lines are observed proves the existence of an orientationally ordered phase in the  $\text{A}_6\text{C}_{60}$  compounds in agreement with structural investigations [4]. According to these investigations the  $\text{C}_{60}$  molecules in the body centered cubic (bcc) lattice are orientationally ordered with their twofold axes directed along the edges of the cubic elementary cell. Within the  $Im\bar{3}$  space group there are only three crystallographically non-equivalent carbon positions C1, C2 and C3 (one g and two h positions) with a ratio of 1:2:2, respectively. By simulating the observed spectra we obtained the following lineshifts for  $\text{K}_6\text{C}_{60}$ : 155.9 ppm (C3), 155 ppm (C2) and 153.1 ppm (C1), where the intensity of the C1-line is indeed only half the intensities of the other two lines (see inset in Fig. 1b).

The high-resolution NMR spectra in  $\text{C}_{60}$  and  $\text{A}_6\text{C}_{60}$  allow to pick up finer details between these compounds. The averaged isotropic value in  $\text{A}_6\text{C}_{60}$  is shifted downfield by 13 ppm with respect to  $\text{C}_{60}$ . This shift is attributed to the six additional electrons donated by the alkali anions and occupying the threefold degenerate lowest unoccupied molecular orbital (LUMO). This paramagnetic downfield shift is quite unusual for aromatic compounds. The additional charges cause in general several effects: (i) The shielding effect reduces the expectation value of the inverse cube of the distance between a  $2p$  electron and the nucleus and yields consequently a diamagnetic contribution to the overall shift. The numerical value of this effect is estimated to be 160 ppm per electron and carbon atom [15]. (ii) The matrix elements are changed due to the occupation of other orbitals and (iii) the ring currents are also altered. In benzene, for example, an additional charge is distributed over six C atoms yielding a diamagnetic shift of  $160/6 \approx 26$  ppm per electron and C atom. This contribution dominates over the effects (ii) and (iii). Applying the same qualitative estimation in the case of  $\text{A}_6\text{C}_{60}$  we obtain a value of 2.6 ppm per electron and C atom. Obviously, this small value seems not to dominate over the other contributions. Therefore, to explain the "anomalous" paramagnetic shift in  $\text{A}_6\text{C}_{60}$  with respect to  $\text{C}_{60}$  a detailed quantum chemical calculation applying gauge invariant orbitals is required.

Turning now to phase  $\text{A}_4\text{C}_{60}$ , we present in Fig. 2 the  $^{13}\text{C}$ -NMR spectra for  $\text{K}_4\text{C}_{60}$  at different spinning rates. In Fig. 2a we have plotted the static spectrum which shows a drastically reduced spectral spread of about 25 ppm compared to the roughly 300 ppm in  $\text{A}_6\text{C}_{60}$ . This indicates the presence of molecular motion of the molecules, averaging to a high degree the anisotropies already at room temperature. Spinning the sample at slow speed (Fig. 2b) leads to a typical sideband pattern, which mimics the form of the static spectrum. At higher spinning rates (Fig. 2c) we are able to remove completely the anisotropies, thereby observing a single, very sharp isotropic line at 180 ppm with a FWHM of about 1 ppm. Again, the results for  $\text{Rb}_4\text{C}_{60}$  are very similar. The isotropic line of  $\text{Rb}_4\text{C}_{60}$  appears at 182 ppm. The most interesting fact is the very large spin-lattice relaxation (SLR)

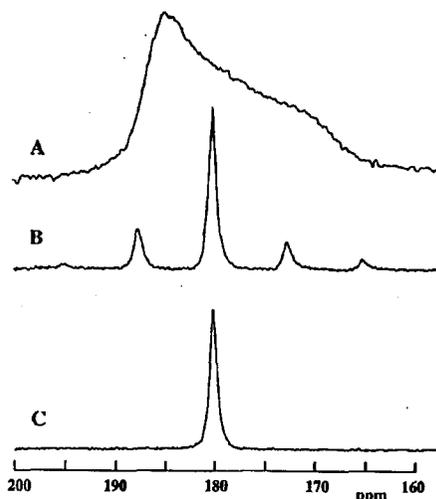


Fig. 2. (a)  $^{13}\text{C}$  NMR spectrum of  $\text{K}_4\text{C}_{60}$  at room temperature. (b)  $^{13}\text{C}$  MAS NMR spectrum with a spinning frequency of 370 Hz. (c) Same as (b) with spinning frequency of 3.1 kHz.

rate in these compounds. The  $T_1$  values at ambient temperature are 110 ms and 80 ms for  $\text{K}_4\text{C}_{60}$  and  $\text{Rb}_4\text{C}_{60}$ , respectively, and are even shorter than the ones in the conducting  $\text{A}_3\text{C}_{60}$  phases. Furthermore, detailed measurements on the temperature dependence of the  $^{13}\text{C}$  SLR rate reveal a strong deviation from a Korringa-like behaviour [15]. With decreasing temperature  $T_1$  increases to several seconds at 100 K. This can consistently be explained by the freezing out of different types of motion at low temperatures as will be discussed in a separate publication [15]. There is no sign of a metallic state. Simple rigid-band models or band structure calculations however, predict that the  $\text{A}_4\text{C}_{60}$  compounds should be metallic with four electrons occupying the threefold degenerate LUMO band [16] which, on the other hand, is in striking contrast to experimental results. Recent low-temperature ultraviolet photoemission spectroscopy with high energy-resolution has revealed that  $\text{K}_4\text{C}_{60}$  is a semiconductor with an energy gap of more than 200 meV [17].

The resulting temperature dependence of the magnetic susceptibility of  $\text{Rb}_4\text{C}_{60}$  is shown in Fig. 3. Two conclusions are reached: (i)  $\chi$  increases with temperature, (ii) the characteristic scale of  $\chi(T)$  is much smaller than the susceptibility of the conducting  $\text{Rb}_3\text{C}_{60}$ . Hence in  $\text{Rb}_4\text{C}_{60}$  the additional electrons at LUMO level form a localized rather than a paramagnetic metallic state. The preliminary EPR experiments show the same temperature dependence of the EPR susceptibility [18]. This confirms the spin paramagnetic origin of the temperature dependent part of  $\chi(T)$ . Our magnetization measurements agree with the NMR properties of  $\text{A}_4\text{C}_{60}$  which are also quite different from those for the Pauli paramagnetic metallic phase  $\text{A}_3\text{C}_{60}$ . The NMR shift of  $\text{K}_4\text{C}_{60}$  which seems to be provided by contact hyperfine coupling of  $^{13}\text{C}$  with spins of additional elec-

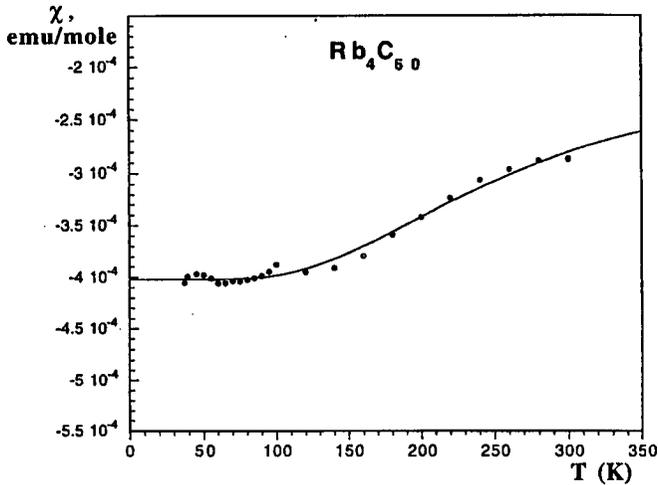


Fig. 3. Temperature dependence of the magnetic susceptibility of  $\text{Rb}_4\text{C}_{60}$  obtained using a SQUID magnetometer.

trons, weakly decreases with temperature [19] in the same fashion as  $X(T)$ . In order to perform the numerical fitting of the experimental data we assume that either the crystal field or Jahn–Teller distortions are relevant to the formation of the spin singlet ground state [20]. From the curve  $X(T)$  (Fig. 3) we estimated a Curie constant of  $C = 0.8$  emu K/mol (for  $g = 2$ ), the activation energy as  $\Delta = 1200 \pm 50$  K and a temperature independent diamagnetic contribution of  $X_d = -4.2 \times 10^{-4}$  emu/mol. Correcting the diamagnetic contribution by the core susceptibility of the neutral  $\text{C}_{60}$  molecule ( $-2.5 \times 10^{-4}$  emu/mol) [21] and four ions of  $\text{Rb}^+$  ( $X_{\text{Rb}^+} = -0.22 \times 10^{-4}$  emu/mol) [22] we obtain the diamagnetic contribution due to four additional electrons as  $-0.8 \times 10^{-4}$  emu/mol. This value derives from the diamagnetic shielding orbital ring currents which are shown [23] to contribute significantly to the susceptibility of the ionic  $\text{C}_{60}^{2-}$ . Consequently, the parameters we obtained from the bulk magnetization measurements reveal the qualitatively new electronic properties of the phase  $\text{Rb}_4\text{C}_{60}$  with respect to other alkali doped fullerenes. We found that  $\text{Rb}_4\text{C}_{60}$  is an insulator in which the four on-site localized electrons form a spin singlet ground state. The observed paramagnetic properties are due to the thermally activated electrons. The experimental results are in good agreement with the existence of the Jahn–Teller or crystal field distortions, providing the lifting of the LUMO level degeneracy. The excitation energy between the ground and the excited spin paramagnetic state is found to be about 1200 K. Similar conclusions were also obtained from NMR experiments on the same sample [19].

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