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INSULATOR–METAL TRANSITION IN Rb_4C_{60} UNDER PRESSURE FROM ^{13}C-NMR

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Abstract—We present an NMR study of Rb_4C_{60} performed under pressure up to 12 kbar. The temperature dependence of the ^{13}C spin-lattice relaxation rate is activated at ambient pressure and becomes Korringa-like under pressure. The behaviour of the relaxation is interpreted in terms of one channel due to excited intramolecular triplet states above the Jahn–Teller ground state plus another one related to electron-hole excitations through an indirect band gap. In spite of a finite value of the density of states at the Fermi level indicated by the NMR data under pressure, no superconductivity could be detected at 15 kbar above 0.4 K.

Keywords: A. fullerenes, C. high pressure, D. nuclear magnetic resonance (NMR), D. superconductivity

1. INTRODUCTION

In A_4C_{60} compounds (where A is an alkali atom) four levels among the six threefold-degenerate lowest unoccupied molecular orbitals (LUMO), t_{1u}, are occupied by electrons provided by alkali metal atoms implying a partial filling of the band in the solid. The situation is similar in A_3C_{60} (half-filled band) where it leads to metallic and superconducting compounds at variance with insulating A_6C_{60} where the LUMO level is completely filled. However, the metallic character which could be expected because the partial band filling [1], is not observed in A_4C_{60}. As a matter of fact, a rigid-band model does not seem to be valid for A_xC_{60} compounds as shown in photoemission spectra from the growth of a new broad band near the Fermi level, E_F, as x increases [2]. More precisely, a photoelectric yield spectroscopy study of K_xC_{60} compounds has clearly identified a Fermi band edge for $x = 3$ confirming its metallic character, whereas E_F is located in the band tail for $x = 4$ and 6, indicating an insulating character for these last compounds [3]. This situation is confirmed by optical conductivity data [4]. Moreover, muon spin relaxation (μSR) [5] and ESR spin susceptibility [6] measurements performed on K_4C_{60} and K_6C_{60} compounds show that both systems are non-conducting and non-magnetic at low temperature. Finally, resistivity measurements performed on C_{60} thin films exposed to alkali vapour have provided for A_4C_{60} a resistivity value at room temperature which is intermediate between those found for A_3C_{60} and A_6C_{60} stoichiometries and an insulating-like temperature dependence [7, 8]. Whereas the insulating nature of A_6C_{60} can be readily understood in terms of a gap between the completely filled t_{1u} valence band and the empty t_{1g} conduction band, the rigid-band model has failed to explain the non-conducting nature of A_4C_{60}. Furthermore, recent resonant Raman spectroscopy experiments in K_4C_{60} have identified a gap in the band structure of the order of 50–70 meV attributed to a splitting within the t_{1u} manifold [9]. An exponential temperature dependence of the NMR spin-lattice relaxation rate (T_1^{-1}) of K_4C_{60} has been reported with an activation energy also in the range of 50 meV [10].

One of the differences between stoichiometries 3 and 4 is related to the crystalline structure. While A_3C_{60} compounds retain the face-centered cubic structure of C_{60} crystals with alkali atoms occupying all interstitial sites, A_4C_{60} compounds adopt a body-centered tetragonal (bct) structure leading to smaller intermolecular overlaps. An orientational disorder (of random or merohedral type) is also necessary to preserve this structure when the molecular reorientations are frozen at low temperature [11, 12]. If the semi-conducting behaviour of A_4C_{60} is related to a less compact structure as compared to A_3C_{60}, an applied pressure could remove this difference and increase the density of states at the Fermi level. Therefore, we anticipate that the role of pressure on T_1^{-1} could clarify the origin of the energy gap and discriminate between intramolecular (Jahn–Teller