

INFLUENCE OF LOCAL C₆₀ ORIENTATION ON ELECTRONIC PROPERTIES OF A₃C₆₀ COMPOUNDS

Thesis Booklet

PÉTER MATUS

Supervisors

HENRI ALLOUL

directeur de recherche

Laboratoire de Physique
des Solides, Université Paris-Sud
Orsay, France

GYÖRGY KRIZA

scientific advisor

Research Institute for Solid State Physics
and Optics, Hungarian Academy of Sciences
Budapest, Hungary

**RESEARCH INSTITUTE FOR SOLID STATE PHYSICS AND OPTICS
of the Hungarian Academy of Sciences**

BUDAPEST

2006

Introduction

The discovery of fullerenes, *i.e.*, cage-like all-carbon molecules in 1985 by Kroto and his coworkers was welcome by the scientific community as an astonishing breakthrough [Kroto *et al.*, 1985]. The advent of large-scale fullerene science dates to 1990, when the arc-vaporization method for the mass production of fullerenes was developed [Krätschmer *et al.*, 1990]. The discovery of superconductivity in alkali fullerene compounds [Hebard *et al.*, 1991] with surprisingly high transition temperature opened a new avenue in fullerene research.

The dimensions of interstitial voids in the C_{60} crystal structure and the high electron affinity of the C_{60} molecule motivated the research of intercalating alkali atoms into the fullerene structure. Indeed, a series of alkali fulleride materials A_nC_{60} can be synthesized, where A is an alkali metal and $n = 1, 2, 3, 4,$ or 6 . The fact that the electrons in the conduction band are mainly concentrated on the fullerene molecules results in ineffective electron screening and a strong on-site Coulomb repulsion. The interplay of molecular and band physics leads to diverse properties of these compounds ranging from Mott–Jahn–Teller insulators [Fabrizio *et al.*, 1997] to superconducting metals [Gunnarsson *et al.*, 1997].

The energy associated with the electronic interactions between the fullerene molecules as well as between the fullerene molecules and alkali ions is minimized in a structure in which the orientation of the C_{60} molecules is ordered. At high enough temperature, however, the entropy associated with the rotational freedom of the molecules dominates over these electronic interactions leading to an almost free rotation of the molecule, *i.e.*, to a plastic crystal. Even in the low-temperature orientationally ordered phase, molecular reorientations are frequent and orientational defects are abundant.

In all A_3C_{60} superconductors the C_{60} molecules sit on the vertices of a face centered cubic (fcc) lattice. Depending on the size of the alkali atoms, however, two different kinds of orientational order may form at low temperature. In one class of A_3C_{60} compounds the Bravais lattice is fcc [Stephens *et al.*, 1991] while in some other A_3C_{60} compounds the order

is simple cubic (sc) [Prassides *et al.*, 1994] similarly to the pure C_{60} crystal. Although the only difference between the two structures is the orientational order, the superconducting properties are remarkably different. Most studies of A_3C_{60} compounds have been carried out on fcc systems; in the present work we turn our attention to the sc phase.

The present thesis is a result of a French–Hungarian cooperation which rooted deeply in the past. The experiments were done in the Laboratoire de Physique des Solides, Orsay supported by Marie Curie fellowship of the EU 5th framework. The high quality powder samples were synthesized by Slaven Garaj in the research group led by László Forró in EPFL, Lausanne.

Objectives

A big surprise of fullerene research came from alkali nuclear magnetic resonance (NMR) investigation of A_3C_{60} fullerides. Walstedt and his coworkers [Walstedt *et al.*, 1993] investigated Rb_3C_{60} by ^{87}Rb NMR. One expects two ^{87}Rb lines, one for the octahedral (O) and one for the tetrahedral (T) site symmetry with intensity ratio 1 : 2 according to stoichiometric ratio. This is exactly what is seen above 370 K. Below that temperature, however, the NMR line associated with the tetrahedral site is split into two lines (T and T') with relative weights $T:T' = 5.5:1$. It has been shown by spin-echo double resonance (SEDOR) that T' is a modified T site. Since this result challenges the basic understanding of the structure of A_3C_{60} compounds, it has attracted much interest [Alloul *et al.*, 1994; Yoshinari *et al.*, 1994; Zimmer *et al.*, 1996; Pennington *et al.*, 1996; Gorny *et al.*, 1997; Kraus *et al.*, 1999].

Later this phenomenon was demonstrated in the whole family of A_3C_{60} fullerides with merohedrally disordered fcc structure. Moreover, the splitting of the NMR line of the octahedral site (O–O' splitting) has also been observed [Zimmer *et al.*, 1996] by magic angle spinning (MAS).

Several possible explanations have been put forward for the T–T' splitting, including a

deviation from the regular orientational configuration, displacement of the alkali ions, Jahn–Teller distortion of the C_{60}^{3-} ion, etc. However, all attempts to distinguish unambiguously between these possibilities failed. This makes the so-called T' problem one of the oldest unresolved problems related to the structure of fulleride salts.

Our aim was to contribute to the resolution of this longstanding problem by examining the T site NMR properties in $A_2A'C_{60}$ compounds of sc symmetry, where A and A' denote different alkali metal.

Methods

Orientalional defects and short-scale orientational correlations are difficult if not impossible to investigate with diffraction techniques. Local probes such as NMR, on the other hand, are ideally suited to the problem. In this work we put a broad arsenal of NMR techniques into action to investigate molecular motion, orientational order, and orientational correlation in a class of A_3C_{60} superconductors with sc ground state. In the experiments a 7.5-T home built homodyne NMR spectrometer was used. Moreover, a two-dimensional NMR method, the spin-echo double resonance is applied to exclude the possibility of phase segregation of the sample. The SEDOR spectrometer was constructed and assembled and the computer software code was extended by the author of this thesis.

The samples were synthesized according to the alkali intercalation protocol conventionally applied to prepare fulleride compounds [Prassides *et al.*, 1994]. The samples were characterized by x-ray diffraction, SQUID magnetometry and ESR spectroscopy, as well as by NMR measurements. For the NMR measurements about 50-100 mg powder was sealed in a quartz tube under He atmosphere.

New results

1. I have observed in an alkali-fulleride superconductor of simple cubic structure that the NMR line associated with the alkali nucleus of tetrahedral C_{60} coordination splits into two at low temperature.^{1,2} I have demonstrated this phenomenon in three different materials:³ Na_2CsC_{60} , Na_2RbC_{60} , and Na_2KC_{60} . Using a two-dimensional NMR technique, spin-echo double resonance (SEDOR), I have proven that the two lines originate from the same phase⁴ (*i.e.*, the second line does not result from phase segregation).
2. By measuring the temperature dependence of the ^{23}Na NMR spectrum, spin-lattice and spin-spin relaxation times in Na_2CsC_{60} , I have found that the origin of the splitting of the NMR line is a dynamic two-site exchange.⁴ The exchange rate is temperature activated in the temperature range 125 to 299 K with a single activation energy 3300 ± 240 K. This finding rules out the existence of a phase transition in the above temperature range. I have proposed that the two sites differ in the fullerene orientational environment^{1,2} reflecting the large concentration of orientational defects observed by neutron diffraction [Prassides *et al.*, 1994] in the same material. The mechanism of the site exchange is the reorientation of the C_{60} molecule. Assuming no correlation between the defects, I have obtained the same defect concentration³ as found in neutron diffraction experiments.
3. I have shown that the temperature dependence of both the ^{23}Na Knight shift and the spin-lattice relaxation differ from rigid-lattice expectations for a metal: At low temperature the Knight shift is temperature dependent and the spin-lattice relaxation time violates the Korringa law. I have successfully interpreted this phenomenon as arising from modes involving the librational motion of the C_{60} molecules.³

4. In alkali-fulleride superconductors of face centered cubic ground state (such as K_3C_{60} and Rb_3C_{60}) I have revisited the problem of the line splitting of the alkali nuclei with tetrahedral C_{60} coordination. I have re-analyzed the result of SEDOR experiments in the literature and I confirmed that, just as in the simple cubic structure, the line splitting in the face centered cubic structure can be interpreted as due to site exchange between different fullerene orientational environments. The result of this analysis is a unified description of the alkali line splitting in trivalent fulleride superconductors.

References

- ALLOUL H, HOLCZER K, YOSHINARI Y, AND KLEIN O
³⁹K NMR study of phase transitions and electronic properties in K₃C₆₀
Physica C **235–240**:2509–2510 (1994)
- FABRIZIO M AND TOSATTI E
Nonmagnetic molecular Jahn-Teller Mott insulators
Physical Review B **55**:13465–13472 (1997)
- GORNY K, HAHM C, MARTINDALE JA, YU S, PENNINGTON CH, BUFFINGER DR, AND ZIEBARTH RP
Is “Rb₃C₆₀” really Rb₃C₆₀? The NMR T, T' problem
Physical Review Letters **79**:5118–5121 (1997)
- GUNNARSSON O
Superconductivity in fullerenes
Reviews of Modern Physics **69**:575–606 (1997)
- HEBARD AF, ROSSEINSKY MJ, HADDON RC, MURPHY DW, GLARUM SH, PALSTRA TTM, RAMIREZ AP, AND KORTAN AR
Superconductivity at 18 K in potassium doped C₆₀
Nature **350**:600–601 (1991)
- KRÄTSCHMER W, LAMB LD, FORISTOPOULOS K, AND HUFFMAN DR
Solid C₆₀: a new form of carbon
Nature **347**:354–358 (1990)
- KRAUS M, KLEIN O, BUNTKOWSKY G, AND LÜDERS K
New aspects in the interpretation of the T' and T ⁸⁷Rb NMR lines in Rb₃C₆₀
Physica B **271**:7–14 (1999)
- KROTO HW, HEATH JR, O'BRIEN SC, CURL RF, AND SMALLEY RE
C₆₀: Buckminsterfullerene
Nature **318**:162–163 (1985)
- PENNINGTON CH, HAHM C, STENGER VA, GORNY K, RECCHIA CH, AND MARTINDALE JA
Double-resonance NMR probes of structural distortions in alkali-metal-fulleride superconductors
Physical Review B **54**:R6853–6856 (1996)

PRASSIDES K, CHRISTIDES C, THOMAS IM, MIZUKI J, TANIGAKI K, HIROSAWA I, AND EBBESEN TW

Crystal structure, bonding, and phase transition of the superconducting Na₂CsC₆₀ fulleride
Science **263**:950–954 (1994)

STEPHENS PW, MIHÁLY L, LEE PL, WHETTEN RL, HUANG SM, KANER R, DIEDERICH F, AND HOLCZER K

Structure of single-phase superconducting K₃C₆₀
Nature **351**:632–634 (1991)

WALSTEDT RE, MURPHY DW, AND ROSSEINSKY M

Structural distortion in Rb₃C₆₀ revealed by ⁸⁷Rb NMR
Nature **362**:611–613 (1993)

YOSHINARI Y, ALLOUL H, HOLCZER K, AND FORRÓ L

NMR study on Rb₃C₆₀
Physica C **235–240**:2479–2480 (1994)

ZIMMER G, THIER KF, MEHRING M, RACHDI F, AND FISCHER JE

⁸⁷Rb NMR and the T' problem in Rb₃C₆₀
Physical Review B **53**:5620–5625 (1996)

Publications related to Ph.D. thesis

1. MATUS P, ALLOUL H, SINGER PM, BROUET V, KRIZA G, GARAJ S, AND FORRÓ L
Fullerene local order in Na₂CsC₆₀ by ²³Na NMR
Applied Magnetic Resonance **27**(1–2):133–138 (2004)
2. MATUS P, ALLOUL H, AND KRIZA G
Fullerénmolekulák lokális orientációjának vizsgálata mágneses magrezonancia (NMR) spektroszkópiával Na₂CsC₆₀-on
Magyar Kémiai Folyóirat **109–110**(4):112–115 (2004)
3. MATUS P, ALLOUL H, KRIZA G, BROUET V, SINGER PM, GARAJ S, AND FORRÓ L
Influence of local fullerene orientation on the electronic properties of A₃C₆₀
cond-mat/0608715, submitted to Physical Review B

4. MATUS P, ALLOUL H, KRIZA G, BROUET V, SINGER PM, GARAJ S, AND FORRÓ L
Configurational fluctuations around tetrahedrally coordinated sodium sites in Na₂CsC₆₀ by NMR
Journal of Superconductivity and Novel Magnetism, accepted for publication in vol. 19(3) (2006)

Other publications

5. KLUPP G, MATUS P, QUINTAVALLE D, KISS LF, KOVÁTS É, NEMES NM, KAMARÁS K, PEKKER S, AND JÁNOSSY A
Phase segregation on the nanoscale in Na₂C₆₀
cond-mat/0607245, submitted to Physical Review B
6. KLUPP G, KAMARÁS K, NEMES NM, MATUS P, QUINTAVALLE D, KISS LF, KOVÁTS É, PEKKER S, AND JÁNOSSY A
Nanosegregation in Na₂C₆₀
AIP Conference Proceedings 786:17–20 (2005)
7. NÉMETH L, KRIZA G, MATUS P, AND ALAVI B
NMR evidence of hidden order in the high-temperature phase of (TaSe₄)₂I
Journal de Physique IV 131:357–358 (2005)
8. BORONDICS F, BOKOR M, MATUS P, TOMPA K, PEKKER S, AND JAKAB E
Reductive functionalization of carbon nanotubes
Fullerenes Nanotubes and Carbon Nanostructures 13:375–382 (2005)
9. NÉMETH L, MATUS P, KRIZA G, AND ALAVI B
NMR in the pseudogap- and charge-density-wave states of (TaSe₄)₂I
Synthetic Metals 120:1007–1008 (2001)
10. MATUS P, BÁNKI P, AND KRIZA G
⁸⁷Rb NMR spin-lattice relaxation in the charge-density wave phase of Rb_{0.3}MoO₃
Journal de Physique IV 9:267–268 (1999)