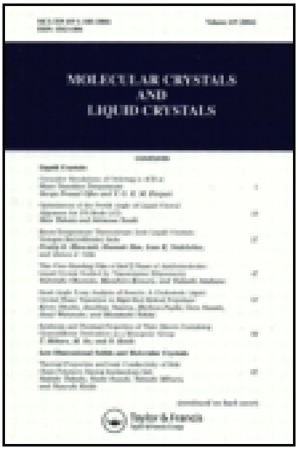

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Structural Influence on the Intensitiy Ratio of the T′ and T ^{87}Rb NMR Lines and the Superconductivity in Rb_3C_{60}

M. Kraus [a], O. Klein [a] & K. Lüders [a]

[a] Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, D-14195, Berlin, Germany

Version of record first published: 24 Sep 2006

Mol. Cryst. and Liq. Cryst., 2000, Vol. 340, pp. 593-598
Reprints available directly from the publisher
Photocopying permitted by license only

Structural Influence on the Intensitiy Ratio of the T′ and T ^{87}Rb NMR Lines and the Superconductivity in Rb_3C_{60}

M. KRAUS, O. KLEIN and K. LÜDERS

Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

(Received May 30, 1999; In final form June 21, 1999)

The intensity ratio of the T′/T ^{87}Rb NMR lines in Rb_3C_{60} could be changed by different cooling rates after annealing at 380 °C. The results are discussed with respect to magnetically different surroundings of the Rb ions through the two standard orientations of the C_{60}^{3-} ions. Additionally, the superconducting volume fraction is influenced by the different cooling procedures.

Keywords: Rb_3C_{60}; ^{87}Rb NMR; superconductivity

INTRODUCTION

The discovery of superconductivity in fullerene intercalation compounds [1] has stimulated intense research activities to investigate this new material. Particularly nuclear magnetic resonance (NMR) experiments contributed detailed information to the dynamics and the structure of fullerenes and their compounds. In A_3C_{60} with an ideal face centered cubic array of C_{60} ions, one octahedral (O) and two equivalent tetrahedral (T) interstitial sites per C_{60} molecule exist. Accordingly, one should expect two different NMR lines (O and T) for the intercalated alkali-metal ions with an O : T intensity ratio of 1 : 2. In Rb_3C_{60} this is indeed the case for temperatures above 370 K [2]. However, at room temperature, a third ^{87}Rb line clearly separated from the two others is observed [2 - 5]. The origin of the T line is still under discussion. Since up to now, no systematic influence on this intensity ratio is observed (e.g. by different preparation methods), the appearance of the T' line is regarded as an intrinsic effect of A_3C_{60} fullerides.

In several NMR spectra published the T line itself seems to consist of two lines (T^a and T^b). This is observable by a clear shoulder [5] and more pronounced in MAS NMR spectroscopy [6]. But yet the origin of the T^a and

T^b lines has not been discussed. The idea of this work is to influence the local structure (orientation of the C_{60}^{3-} ions with respect to each other) of a Rb_3C_{60} sample by different cooling times from the preparation temperature (380 °C) to ambient temperatures. It is shown that the ^{87}Rb NMR line intensity ratios as well as the superconducting volume fraction can be influenced by these different cooling rates.

RESULTS AND DISCUSSION

The Rb_3C_{60} sample was prepared earlier [7] and sealed in a glass tube since then. First NMR results of the sample were published previously [5]. Now, we reexamined this sample by ^{87}Rb NMR (Fig. 1(a)). Afterwards the sample was heated to the temperature used for the intercalation (380 °C) for about one hour and cooled very fast to room temperature (within 2-3 minutes). Hereafter the sample was heated again to 380 °C and slowly cooled down to room temperature within three weeks. After characterization by NMR and susceptibility measurements, it was heated again to 380 °C and cooled rapidly (within 2-3 minutes) for a second time.

^{87}Rb NMR measurements were performed in a 7.049 T magnetic field using RbCl (aq. solution) as a reference. The spectra show three clearly distinct lines: T', T, and O (Fig. 1a - c). The intensity ratio T': T after a 'normal' cooling rate (within the oven) is 0.22 (Fig. 1a). After the first warming and *rapid* cooling procedure, the intensity ratio of the three easily resolvable ^{87}Rb NMR lines (O, T', and T) was changed (Fig. 1b). The T'/T intensity ratio was now decreased to 0.15. After the following *slow* cooling rate (from 380 °C to room tempera-ture within three weeks), the T' intensity increased to a T'/T ratio of 0.39 (Fig. 1c), the highest relative T' intensity published until now. Finally, after a renewed warming (1 h at 380 °C) and a *rapid* cooling procedure, the T'/T intensity ratio was reduced again to 0.28.

The well-defined splitting as is observed for the T resonance line necessarily requires a definite origin. The existence of two standard orientations of the fullerene ions [8] could be such a well-defined origin. As a consequence,

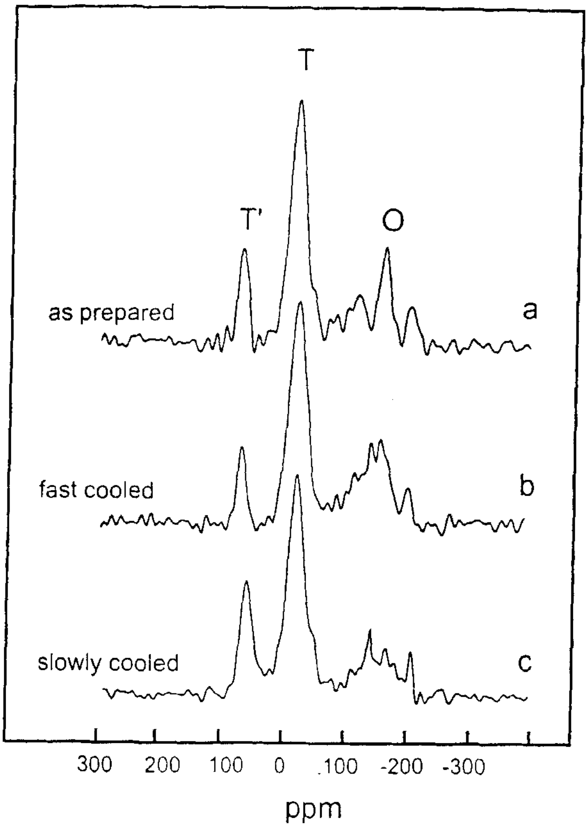

FIGURE 1 ^{87}Rb NMR spectra of Rb_3C_{60} after different cooling rates. (a) as prepared, (b) after rapid cooling (2-3 minutes), (c) after slow cooling (3 weeks).

three different surroundings of the Rb ion can be distinguished: First case: all of the four fullerene ions forming the tetrahedral surrounding are oriented in the same direction. Second case: three fullerenes are oriented in the same direction, while the fourth C_{60}^{3-} is in the other standard orientation, and the third case possible: two of the four C_{60}^{3-} ions are in the same orientation, respectively.

On a first view, there should be no difference concerning the surrounding of Rb nuclei placed at these different T sites since all Rb ions face four carbon hexagons as nearest neighbors. But in fact, there is an electronic difference between these constellations [9]. Furthermore, there are weak orientational forces between neighboring C_{60}^{3-} ions tending to orient them towards the same orientation [10]. Therefore, different cooling rates should influence the relative intensities of the NMR T lines. After a slow cooling procedure, there should exist more perfectly ordered T surroundings than after rapid cooling, where the C_{60} ions should be completely random disordered between the two standard orientations. This, in fact, can explain the results observed experimentally.

Ac susceptibility measurements after the slow cooling procedure and after the renewed rapid cooling process show clear differences in the sample's diamagnetic signal below the transition temperature to superconductivity (T_c). After the slow cooling process, the diamagnetic signal below T_c which is responsible to the sample's superconducting volume, is up to 15 % larger than after the rapid cooling pro- cedure (Fig. 2). The imaginary part of the ac susceptibility differs only slightly with respect to different cooling procedures. In static magnetic fields up to 7 T, we observe a tendency to smaller dissipation signals after the rapid cooling process. In all measurements there exists one sharp dissipation peak near T_c and a broad signal at lower temperatures. There is almost no influence of the cooling rate on T_c and only a slight one on the upper critical field B_{c2}. For example, at a temperature of 28.3 K after the fast cooling rate B_{c2} is 3.5 T while after slow cooling B_{c2} is 5 T. In the same external magnetic fields the transition temperature T_c tends to higher values after slow cooling compared to measurements after fast cooling (0.5 K at 5 T). These differences, however, might be caused by different internal stresses after the different cooling procedures.

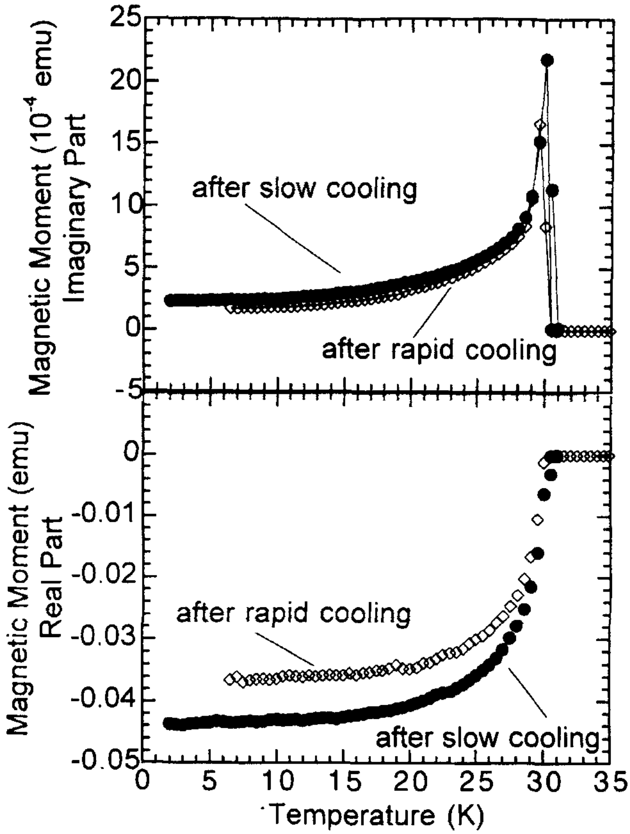

FIGURE 2 Imaginary and real parts of the ac susceptibility of Rb_3C_{60} after two different heat treatments. The curvature of the real parts corresponds to a pene-tration depth of $\lambda \approx 0.15$ a (a = average radius of the grains).

References

[1] A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Kortan, *Nature* (London), **350,** 600 (1991).

[2] R. E. Walstedt, D. W. Murphy, and M. Rosseinsky, *Nature* (London), **362**, 611 (1993).

[3] G. Zimmer, M. Helmle, M. Mehring, F. Rachdi, J. Reichenbach, L. Firlej, and P. Bernier, *Europhys. Lett.*, **24,** 59 (1993).

[4] C. H. Pennington and V. A. Stenger, *Rev. Mod. Phys.*, **68,** 855 (1996).

[5] M. Kanowski, H. Werner, R. Schlögl, H.-M. Vieth and K. Lüders, *Appl. Magn. Res.*, **11,** 285 (1996).
[6] G. Zimmer, K.-F. Thier, and M. Mehring, F. Rachdi, and J. E. Fischer, *Phys. Rev. B*, **53,** 5620 (1996).
[7] M. Kraus, H. Sindlinger, H. Werner, R. Schlögl, V. Thommen, H. P. Lang, H.-J. Güntherodt, and K. Lüders, *J. Phys. Chem. Solids*, **57,** 999 (1996).
[8] P. W. Stephens, L. Mihaly, P. L. Lee, R. L. Whetten, S.-M. Huang, R. Kaner, F. Deiderich, and K. Holczer, *Nature*, **351,** 632 (1991).
[9] M. Kraus, O. Klein, G. Buntkowsky, and K. Lüders, to be published.
[10] M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press Inc., San Diego, 1996.