Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 17 Oct 2011.

To cite this article: Toshihiro Takahashi (1985): NMR-Analysis of Magnetic Properties of TTF-TCNQ, Molecular Crystals and Liquid Crystals, 120:1, 97-100

To link to this article: http://dx.doi.org/10.1080/00268948508075767

Mol. Cryst. Liq. Cryst. 1985, Vol. 120, pp. 97-100
0026-8941/85/1204-0097/$10.00/0

Printed in the United States of America

NMR-ANALYSIS OF MAGNETIC PROPERTIES OF TTF-TCNQ

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Abstract ^{13}C-NMR Knight shift data for the organic conductor TTF-TCNQ are used to decompose the total spin susceptibility into contributions coming from individual TTF and TCNQ bands. The difference in electronic characteristics between the TTF and TCNQ bands is discussed.

INTRODUCTION

The one dimensional organic conductor TTF-TCNQ contains two types of conducting stacks; the donor (TTF) and the acceptor (TCNQ) stacks, both of which have contributions different from each other to the observable quantities via different electronic characteristics.[1] In order to achieve full understandings of the physical properties of this material, it is very important to separate the individual contributions of the two stacks.[2-5]

RESULTS

^{13}C-NMR Knight shift K and relaxation time T_1 have been measured in TTF-TCNQ with ^{13}C-enriched TTF molecules. Experimental details were described elsewhere,[2] so that we only summarize here the important features of the results. (See Figure 1.)

i) A real gap in the conduction band of TTF stacks opens only below 38 K, as indicated by a rapid decrease of the NMR Knight shift K (proportional to the local susceptibility χ_F) and the relaxation rate T_1^{-1}. No anomary is observed within experimental errors either at 54 K or at 48 K, as far as the NMR properties are

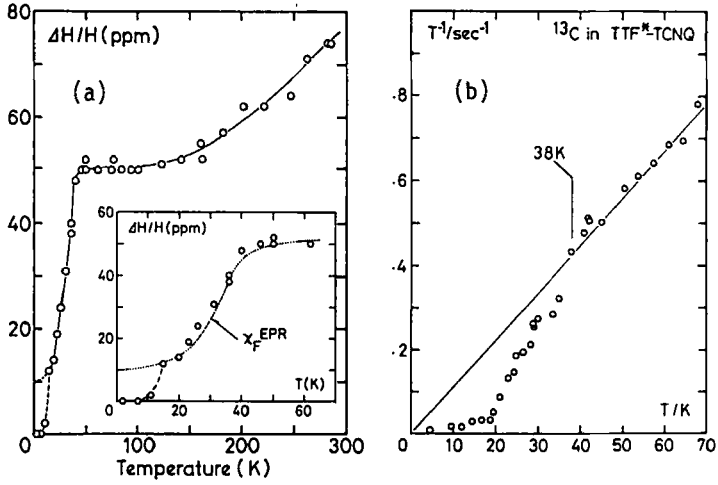

FIGURE 1 Temperature dependence of ^{13}C-NMR Knight shift (a) and relaxation rate T_1^{-1} (b) in TTF(^{13}C)-TCNQ.

concerned.

ii) Below 38 K, the observed temperature dependence can be described with an activation energy of $\sim$ 100 K.

iii) In the metallic region ($\sim$ 70 K), a large enhancement of the Korringa relation of a factor $\sim$ 30 was found, indicating the existence of large on-site Coulomb correlation.

iv) The temperature dependence of TTF susceptibility is very small compared with the previously determined TCNQ susceptibility.[3]

v) Below 15 K, small anomalies are observed both in K and T_1^{-1} suggesting another phase instability.

The features i) and ii) agree well with the published EPR results,[4] at least, below 60 K. iii) is also consistent with ^1H-NMR analysis.[5] These results were more quantitatively discussed in ref. 2.

DECOMPOSITION OF SPIN SUSCEPTIBILITY

The Knight shift is proportionsl to the local susceptibility of in-

dividual stacks, as $K = H_{hf}\chi_s$. The published Knight shift data of ^{13}C on TCNQ stacks[3] and the present results enables us to decompose the total susceptibility χ_T[6] into χ_F and χ_Q (the local susceptibility). We use the relation for the normalized values as;

$$\chi_T(T)/\chi_T(300K) = (1-x)\chi_Q(T)/\chi_Q(300K) + x\ \chi_F(T)/\chi_F(300K),$$

with a fitting parameter x. The best decomposition was obtained for x = 0.35, as shown in Figure 2(a). To show the different temperature dependence of χ_Q and χ_F, the ratio χ_Q/χ_F is plotted versus temperature in Figure 2(b).

DISCUSSIONS

The new decomposition of the spin susceptibility reveals several important features of the different roles of TTF and TCNQ stacks.

i) The TCNQ susceptibility is larger than the TTF susceptibility

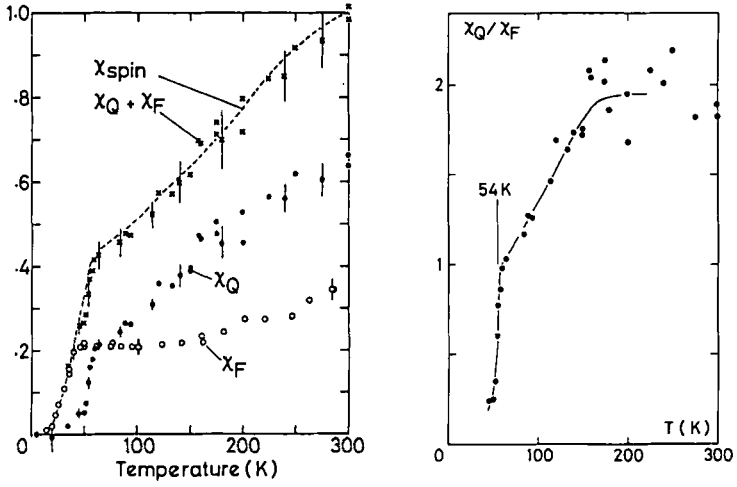

FIGURE 2 (a) Decomposition of total spin susceptibility (broken line) into the local susceptibility on TTF ( ) and TCNQ ( ) stacks. The crosses are the sum of both contributions. (b) The ratio χ_Q/χ_F vs. T, evaluated from (a).

above 60 K. χ_Q/χ_F amounts to $\sim$ 2 at room temperature. In ref. 2, we found the on-site Coulomb correlation energy U is of the order of the bandwidth for both stacks. The bandwidth was estimated as 0.65 eV and 0.40 eV for TTF and TCNQ stacks, respectively. The broader TTF bandwidth than TCNQ contradicts the previous expectation[1] but agrees with a band calculation.[7]

ii) The observed large temperature dependence of χ_T between 60K and 150 K must be attributed to χ_Q, since χ_F is nearly constant in this region. We suggest that this may indicate the gradual onset of pseudo-gap due to the fluctuating CDW's. In fact, 1D X-ray diffuse lines with the wave number of $2k_F$ becomes visible in this temperature domain. An important point is that the $2k_F$ pseudo-gap appears only on the TCNQ stacks. This is consistent with recent X-ray observations.[8]

iii) Above 150 K, χ_F and χ_Q have almost the same temperature dependence (χ_Q/χ_F is nearly constant), which may be partly because of the lattice contruction resulting in increasing bandwidth as lowering temperature. It is also possible that a change in the degree of charge transfer from 0.59 at low temperatures to 0.55 at room temperature[9] leads to an increase ($\sim$ 5% for the tight binding calculation) of the density of states at Fermi level.

Acknowledgments The author thanks D. Jerome, F. Masin, J. M. Fabre and L. Giral for their collabration and S. Barisic for his interest in this work.

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