Pressure effect on the charge ordering in \( \theta-(\text{BEDT-TTF})_2M\text{Zn(SCN)}_4 \) \([M=Rb, Cs]\)

Ryo Chiba a, Ko-ichi Hiraki a, Toshihiro Takahashi a, Hiroshi M. Yamamoto b and Toshikazu Nakamura c

a Department of Physics, Gakushuin University, Mejiro, Tokyo 171-8588, Japan
b The Institute of Physical and Chemical Research, 2-1 hirosawa, Wakou 351-0198, Japan
c Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

Abstract

To clarify the role of charge ordering at the MI transitions in \( \theta \)-phase compounds, we performed \( ^{13}\text{C-NMR} \) measurements in \( \theta-(\text{BEDT-TTF})_2\text{CsZn(SCN)}_4 \) and \( \theta-(\text{BEDT-TTF})_2\text{RbZn(SCN)}_4 \) under pressure. We found that charge ordering is strongly affected by pressure. No long-range static charge ordering is stabilized in Cs salt. Moreover, we found a region where charge disproportionation already develops but no long-range static charge ordering is stabilized.

Key words: Nuclear magnetic resonance spectroscopy, Metal-insulator phase transition, Organic conductors based on radical cation and/or anion salts

1. Introduction

Organic conductors, \( (\text{BEDT-TTF})_2X \) with two-dimensional closed Fermi surface undertake a metal-insulator (MI) transition at a finite temperature, \( T_{MI} \). Recently, it has been clarified that the MI transitions in \( \alpha-(\text{BEDT-TTF})_2I_3 \) and \( \theta-(\text{BEDT-TTF})_2\text{RbZn(SCN)}_4 \) (abbreviated as Rb salt) are accompanied by charge ordering. The charge ordering phenomenon is an important keyword to clarify the electronic state in the 2D electron system.

H. Mori pointed out that physical properties of \( \theta \)-phase compounds have close correlation with dihedral angle which may determine electronic correlation parameter, \( U/t \), where \( U \) is onsite Coulomb repulsion energy and \( t \) is transfer integral.\[1\] When hydrostatic pressure is applied to the Rb salt, MI transition temperature rises.\[2\] Dihedral angle is expected to increase by pressure. When uniaxial strain is applied along \( a \)-axis to reduce the dihedral angle, MI transition was actually suppressed.\[3\] MI transition temperature of \( \theta-(\text{BEDT-TTF})_2\text{CsZn(SCN)}_4 \) (abbreviated as Cs salt) falls down to 20 K. This salt is believed to be in a situation similar to that of the Rb salt with negative (chemical) pressure.

To clarify the pressure effect on charge ordering transition, we performed \( ^{13}\text{C-NMR} \) measurement for a single crystal under physical and chemical pressure.

2. Experimental

A single crystal, in which the central double-bonded carbon sites of BEDT-TTF were selectively labeled with \(^{13}\text{C} \) isotope (\( I = 1/2 \)), were prepared. The shift is measured with respect to the resonance position of tetramethylsilane(TMS). Measurements were performed at a resonance field of 8.2 T. NMR lineshape under hydrostatic pressure was measured using a clamp-type pressure cell with fluorocarbon oil (DENUM S-20) as pressure medium: we used stycast 1266 for uniaxial strain.
3. Results and discussions

Temperature dependence of NMR lineshape of the Rb salt at ambient pressure is shown in the central part of Fig. 1. External field is applied along a-axis. At room temperature NMR lineshape comprises four sharp peaks. As temperature decreases, line width remarkably increases. Then NMR lineshape drastically changes just at the transition temperature: Sharp lines are assigned to charge poor sites: Charge rich sites make a broad line due to the moments of localized spins.

Next, we applied a hydrostatic pressure of 7 kbar on the Rb salt and measured NMR lineshape for static field applied along a-axis. Results are shown in the left of Fig. 1. NMR lineshape at room temperature is already broad as observed at temperatures just above $T_{MI}$ at ambient pressure. Below 250 K sharp structures appear. This change in lineshape is quit similar to that observed at the MI transition at ambient pressure. With decreasing temperature, NMR shift gradually decreases, indicating a non-magnetic ground state just as at ambient pressure. The right of Fig. 1 shows NMR lineshape under uniaxial strain of 7 kbar applied along a-axis. Lineshape has sharp structures at room temperature. As temperature decreases, lineshape becomes broader. Below 91 K the sharp structures disappear and only a broad line is seen. $T_{MI}$ was clearly suppressed in this condition. These behaviors are consistent with the transport properties under pressure. The long range charge ordering appears below $T_{MI}$.

The anomalous broadening of resonance line just above $T_{MI}$ was not understood well. To address this question, we measured the angular dependence of linewidth when the external field is rotated in the ab-plane. We found that the angular dependence of the second moment scales well with the square of Knight shift. This is the evidence that the broadening is caused by the fluctuations of the Knight shift, indicating the existence of charge disproportionation with extremely slow fluctuations in space and/or time. Similar broadening is observed in Cs salt below 200 K. No static charge ordering was observed at low temperatures.

4. Conclusion

We performed $^{13}$C-NMR measurements for single crystals of $\theta$-(BEDT-TTF)$_2 MZn(SCN)$_4$ ($M$=Rb, Cs). It was confirmed that charge ordering was strongly affected by pressure. Moreover, we found a temperature region where charge disproportionation already develops but no long-range static charge ordering is stabilized.

5. Acknowledgements

One of the authors (R. C) thank K. Murata and K. Iwashita (Osaka City Univ.) for technical supports. This work was financially supported by Nomura foundation and "Research for the Future" Project, JSPS-REPTF97P00105, by Japan Society Promotion of Science.

References