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μSR study of an antiferromagnetic insulator (BEDT-TTF)(TCNQ)

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Abstract

Zero-field μSR measurements for an antiferromagnetic Mott insulator (BEDT-TTF)(TCNQ) were performed for the first time in order to study the microscopic magnetic properties of this organics. Slight increase of the relaxation rate is observed below 20 K owing to the antiferromagnetic ordering of BEDT-TTF dimers, whereas clear muon precession signal is observed below 3 K owing to the antiferromagnetic ordering of TCNQ. Below 3 K, there exist at least two antiferromagnetic domains whose volume fractions changes with temperature.

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Keywords: (BEDT-TTF)(TCNQ); μSR; Antiferromagnetic state

1. Introduction

Recently, BEDT-TTF-based organic charge-transfer complexes with the β′-type crystal structure attract extensive interest due to our finding of superconductivity in β′-(BEDT-TTF)$_2$ICl$_2$ at 14.2 K under extremely high pressure of 8.2 GPa [1]. Origin of the superconductivity is not clear at present, but antiferromagnetic correlation is considered to play an important role for this pressure-induced superconductivity from the similarity of the temperature–pressure phase diagram to those of the κ-phase superconductors. It is therefore important to study magnetic properties of related materials with the β′-type crystal structure systematically.

Among β′-type charge transfer complexes (BEDT-TTF)(TCNQ) with the triclinic crystal structure shows interesting magnetic properties [2]. This salt consists of two-dimensional donor BEDT-TTF sheets and one-dimensional acceptor TCNQ chains. Each of BEDT-TTF and TCNQ molecules form of the dimer [3]. Although the band structure calculation predicts the metallic state, (BEDT-TTF)(TCNQ) shows a semi-conducting behaviour below 330 K at which metal–semiconductor transition occurs. From the magnitude of the Curie constant, the degree of charge transfer from a donor BEDT-TTF molecule to a acceptor TCNQ molecule is estimated to be about 0.5, and (BEDT-TTF)(TCNQ) can be recognized as the Mott–Hubbard insulator [2]. The magnetic susceptibility has a distinct kink at 3 K and starts to show anisotropy against field directions below this temperature, which suggest the antiferromagnetic transition. Since the Curie-like magnetic susceptibility of (BEDT-TTF)(TCNQ) is dominated by the contribution from TCNQ chains, the ordering at 3 K originates from the dimer of two TCNQ molecules [2]. The ^{1}H-NMR measurement also shows a distinct peak of $1/T_1$ at 3 K [4].

On the other hand, EPR measurements show that temperature dependence of the peak-to-peak line width shows a minimum around 30 K, suggesting another magnetic anomaly. The ^{13}C-NMR measurement of (BEDT-TTF)(TCNQ) using BEDT-TTF molecules whose the central double-bonded carbon sites and all hydrogen sites are simultaneously replaced by ^{13}C and deuterium shows that $1/T_1$ exhibits a sharp peak at 20 K [5]. It is concluded that the ordering at 20 K originates from the dimer of two BEDT-TTF molecules.

In this way (BEDT-TTF)(TCNQ) was suggested to have an interesting magnetic ground state with two kinds of

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magnetic orderings which originate from different molecular sites. In order to study the microscopic magnetic property of this interesting magnetic system, we performed the μSR measurement between 2 and 300 K. Small increase of the relaxation rate is observed below 20 K and a clear precession signal is observed below 3 K.

2. Experimental

The μSR measurements were performed at πA-port, Muon Science Laboratory, High Energy Accelerator Research Organization (KEK-MSL) down to 2 K. Most of measurements were performed under zero field. Powder-like single crystals of (BEDT-TTF)(TCNQ) were prepared by the direct reaction of BEDT-TTF and TCNQ which were dissolved in hot chlorobenzene and the solution was cooled down by a refrigerator for several days. Total amount of samples was 0.6 g. Samples were wrapped in aluminium foil which was fixed to a silver plate of the sample holder with kapton tapes. Crystals were randomly oriented. The sample holder was put in He exchange gas environment which is thermally attached to the heat bath whose temperature is controlled by the liquid He flow and the heater.

3. Results and discussion

Fig. 1 show zero-field μSR spectra at three typical temperatures, namely, a paramagnetic state (40 K), a intermediate state where only BEDT-TTF dimers order antiferromagnetically (7 K) and the ground state where both BEDT-TTF and TCNQ dimers order antiferromagnetically (2.3 K). Hereafter we refer to first transition temperature, 20 K, as T_{N1} and second one, 3 K, as T_{N2}. At the paramagnetic state above T_{N1}, μSR spectrum was fitted by the static Kubo–Toyabe function and does not show clear temperature dependence. Owing to the antiferromagnetic ordering of BEDT-TTF dimers, slight increase of the relaxation rate is observed below T_{N1}. Above T_{N1}, μSR spectrum can be decoupled by the longitudinal field of 50 G and the internal magnetic field is static. We try to fit μSR spectra between T_{N1} and T_{N2} by the simple product of the temperature-independent static Kubo–Toyabe function, $G_{KT}(t)$ and an exponential $\exp[-\lambda(T)t]$:

$$P(t) = A\,\exp(-\lambda t)G_{KT}(t). \quad (1)$$

Fig. 2 shows the temperature dependence of the relaxation rate $\lambda(T)$ above T_{N2}. Increase of $\lambda(T)$ is seen below T_{N1}. It is noted that the magnetic susceptibility [1] and ^{1}H-NMR [4] failed to detect an anomaly at T_{N1}. Additional internal magnetic field at the muon site between T_{N1} and T_{N2} is very small, say, 0.1 G.

Owing to another antiferromagnetic ordering of TCNQ dimers, a spontaneous muon spin-precession signal was observed below T_{N2}. Spectra were well fitted by the following function:

$$P(t) = A_1\,\exp(-\sqrt{\lambda_1 t})\,\cos(2\pi f t + \alpha) + A_2\,\exp(-\lambda_2 t). \quad (2)$$

Temperature dependence of the precession frequency is shown in Fig. 3. The precession frequency, f, at 2.3 K is 0.56 MHz and static magnetic field at a muon site is estimate to be 41 G. Compared to the internal magnetic

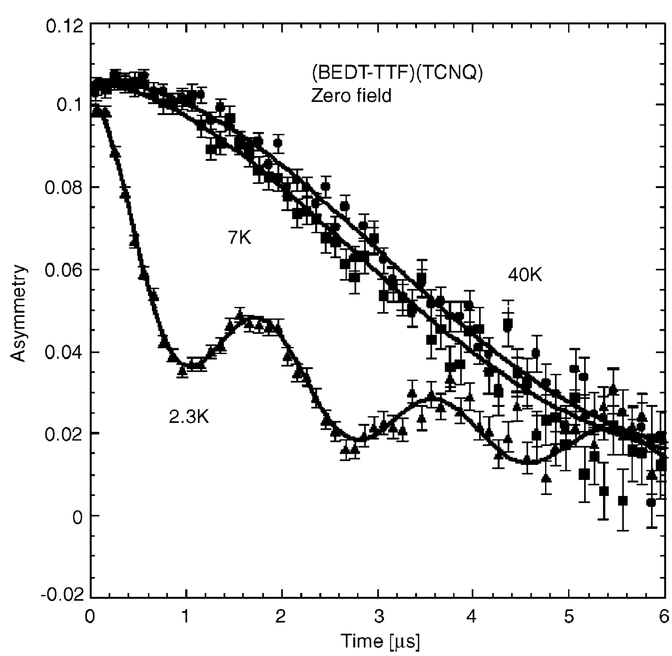

Fig. 1. Zero-field μSR spectra of (BEDT-TTF)(TCNQ) above T_{N1}, between T_{N1} and T_{N2}, and below T_{N2}. Relaxation rate becomes slightly faster below T_{N1} and clear precession signal is observed below T_{N2}. See text for fitting curves.

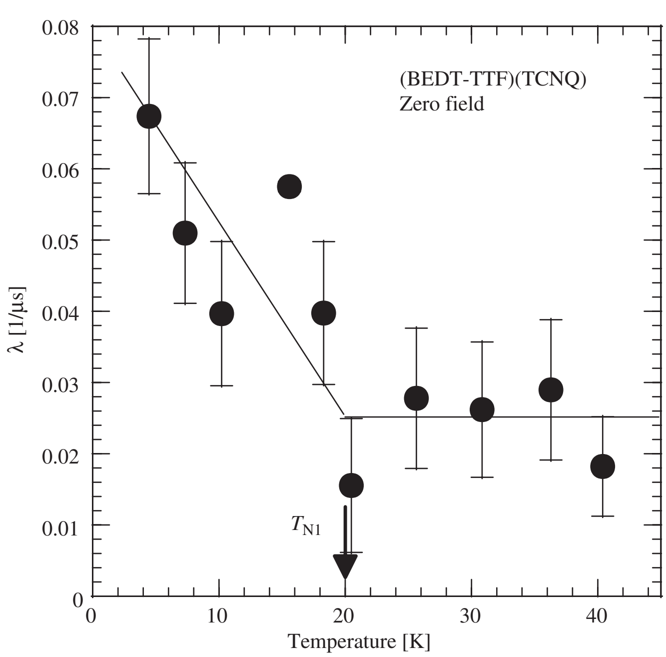

Fig. 2. Temperature dependence of the relaxation rate, λ, of (BEDT-TTF)(TCNQ) above 3 K. Solid lines are guides for readers' eyes. Small magnetic field at the muon site appears below T_{N1}.