Pressure Effect on the Magnetism and Structure of a Spin-Peierls Substance:MEM-$[TCNQ]_2$

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Abstract

An anomalous pressure effect on the magnetic susceptibility of a spin-Peierls substance, MEM-$[TCNQ]_2$, is observed. As the pressure increases, the susceptibility at low temperatures increases as if free magnetic spins are produced and it overwhelms the spin-Peierls transition. In order to clarify the pressure effect, the crystal structure of the substance under pressure has been studied by using synchrotron radiation X-rays. The reflection resulting from the superlattice of the spin-Peierls state below 18K disappears under pressure and the crystal structure is significantly affected even at room temperature.

Key words: spin-Peierls; MEM-$[TCNQ]_2$; magnetic susceptibility; pressure effect; crystal structure

1. Introduction

An organic ion-radical salt, N-Methyl-N-ethyl-morphorinium- [7,7',8,8'-tetracyanoquinodimethane]$_2$ (MEM-$[TCNQ]_2$), is a one-dimensional(1D) spin system and shows a spin-Peierls(SP) transition at the SP transition temperature($T_{\rm SP}$) of 18K [1,2]. Above $T_{\rm SP}$, the salt is a uniform magnetic chain and its magnetic properties are well described by the Bonner-Fisher model [3]. To the contrary, below $T_{\rm SP}$, the salt changes into an alternating magnetic chain accompanying lattice deformation because of an intrinsic magnetoelastic instability. As a result, a spin gap which separates a singlet, nonmagnetic ground state from an excited triplet state occurs in the magnetic excitation spectrum.

As the SP transition is mainly caused by the spin-phonon coupling between the 1D spin system and the three-dimensional(3D) phonon system, the transition should be affected by magnetic field(H) and pressure(P). A H-T phase diagram for MEM-$[TCNQ]_2$ has been studied [1,4]. However, the pressure dependence of the magnetic properties for MEM-$[TCNQ]_2$ has not studied so much. Bloch *et al*. [5] determined the P-T phase diagram for MEM-$[TCNQ]_2$ and showed that $T_{\rm SP}$ increased linearly with pressure when the pressure was increased.

We report the significant pressure effects on the magnetic properties of MEM-$[TCNQ]_2$ [6], though they are rather different from the results reported by Bloch *et al*. [5]. The effects suggest that many free spins are produced in the salt under high pressures [6]. In order to clarify such anomalous pressure effects on the magnetism, we have carried out the crystal structure analysis of the substance under pressure by using synchrotron radiation(SR) X-rays.

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2. Experimental procedures

The salt, MEM-[TCNQ]$_2$Cwas synthesized by the standard method and crystallized by slow cooling of an acetonitrile solution. The susceptibility was measured by using a SQUID susceptometer (Quantum Design MPMS-5) with a hand-made pressure cell in the temperature range of 2-300K and at the pressure up to 8kbar.

The SR X-ray diffraction measurements of the single or powder crystals of the salt under ambient and high pressures have been carried out at the Photon Factory, KEK at Tsukuba in Japan by the same method used for NaV_2O_5 [7]. Instead of the alcohol mixture, a fluorocarbon oil was used as the pressure medium.

3. Results and Discussion

The paramagnetic susceptibility of the salt at various pressures is shown in Fig. 1 as a function of temperature [6]. The susceptibility at ambient pressure(1bar) clearly shows the spin-Peierls transition at 18K below which the susceptibility suddenly decreases with decreasing temperature. The slight increase of the susceptibility below 7K is attributable to the small amount of paramagnetic impurities. Above 18K, the susceptibility is quantitatively explained by the Bonner-Fisher curve(dashed-line in the Fig. 1) with $J/k =$ -52K.

As the pressure is increased up to 8kbar, the susceptibility at low temperatures becomes large. The susceptibility at above 0.84kbar monotonically increases with decreasing temperature and does no longer show a minimum. The susceptibility at low temperatures and higher pressures obeys the Curie-Weiss law with a very small Weiss temperature. Therefore, the increase of the susceptibility at low temperatures and higher pressures may result from the free spins, which must be produced by separating spin-pairs. By subtracting the susceptibility obeying the Curie-Weiss law from the measured susceptibility, we obtained residual susceptibility. As the pressure is increased, the residual susceptibility decreases and its temperature dependence changes gradually. The spin-Peierls transition becomes vague with increasing pressure, though the spin-Peierls transition temperature, T_{SP}, seems to increase [6]. The residual susceptibility at higher pressures decreases to zero at low temperatures and its temperature dependence is qualitatively described by a spin-pair model [6], which is apparently different from the results reported by Bloch *et al*. [5].

The X-ray reflection resulting from the superlattice in the spin-Peierls state below 18K was clearly observed for a single crystal at ambient pressure. The temperature dependence of the intensity of the reflection is

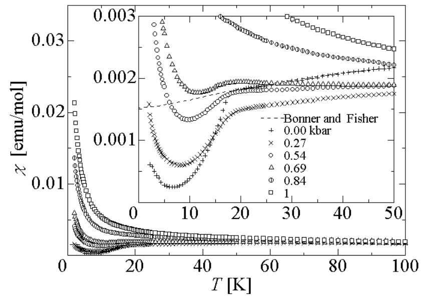

Fig. 1. Temperature dependence of the magnetic susceptibility at various pressures.

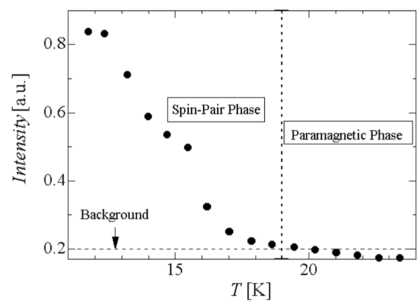

Fig. 2. Temperature dependence of the reflection intensity of superlattice in the SP state.

shown in Fig.2. However, the reflection was no longer observed under high pressures. It suggests that the spin-Peierls state is destroyed under pressure, which is consistent with the results of the magnetic measurements. The crystal structure of the salt is rather affected by the pressure even at room temperature.

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