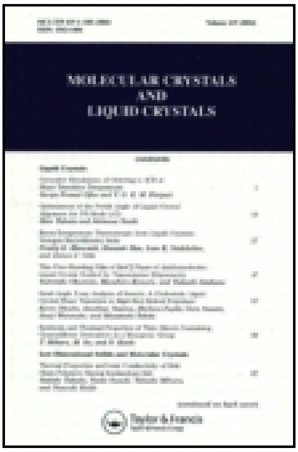

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Anomalous Pressure Dependence of the Magnetic Susceptibility of a Spin-Peierls Substance: MEM-[TCNQ] 2

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Static-pressure dependence of the susceptibility and the magnetization of an organic spin-Peierls substance, MEM-$[TCNQ]_2$, was measured by using a SQUID susceptometer with a hand-made pressure cell in the temperature range of 2-150K and at the pressure up to 8kbar. We have found that the susceptibility of the substance changes significantly with increasing static-pressure. As the pressure increases, the susceptibility at low temperatures increases as if free magnetic spins are produced and it overwhelms the spin-Peierls transition. Above 1kbar, there are no marks of spin-Peierls transition and the susceptibility at low temperatures follows the Curie-Weiss law.

Keywords: organic ion-radical salt; MEM-$[TCNQ]_2$; spin-Peierls; magnetic susceptibility; pressure dependence

INTRODUCTION

An organic ion-radical salt, N-methyl-N-ethylmorphorinium-[7,7',8,8'-tetracyanoquinodimethane]$_2$ (hereafter, MEM-$[TCNQ]_2$) is a one-dimensional(1D) spin system and shows a spin-Peierls (SP) transition[1] at a SP transition temperature(T_{SP}) of 18K[2]. The SP transition occurs in the salt because of an intrinsic magnetoelastic instability. Above T_{SP}, the salt is a uniform magnetic chain with a single exchange constant J acting between adjacent spins and its magnetic properties are well described by the Bonner-Fisher model[3]. Below T_{SP}, the salt changes into an alternating magnetic chain with two alternating, unequal exchange constants where the difference between the exchange constants increases with decreasing temperature. This makes a gap in the magnetic excitation spectrum, which separates a singlet, nonmagnetic ground state from a band of triplet magnon excitations.

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 is expected to be affected by magnetic field(H) and static-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.* determined the P-T phase diagram for MEM-[TCNQ]$_2$[5] and showed that T_{SP} increased linearly with pressure when the pressure was increased. Such experimental results were explained theoretically by a mean field theory[6].

In this paper the static-pressure dependence of the magnetic susceptibility and magnetization of MEM-[TCNQ]$_2$ is reported. We have obtained peculiar pressure dependence of magnetic properties, which are rather different from the results reported by Bloch *et al.*[5] We have found that many free spins are reversibly produced in MEM-[TCNQ]$_2$ under high pressures.

EXPERIMENTAL PROCEDURES

The salt, MEM-[TCNQ]$_2$, was synthesized by the standard method and crystallized by slow cooling of an acetonitrile solution. The crystals were crushed into powder and the powder specimen was used for the measurement of magnetic susceptibility and magnetization. The susceptibility was measured 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 pressure cell was a standard clamping-type one and made after a report by Koyama *et al.*[7] with non-magnetic Cu-Be alloy. The sample pressure at low temperatures was estimated by measuring the pressure dependence of the superconducting transition temperature of Pb. Below 1kbar the pressure was estimated assuming that the pressure is directly proportional to the contraction of the volume of the specimen.

EXPERIMENTAL RESULTS AND DISCUSSION

The paramagnetic susceptibility of the salt at various pressures is shown in Fig. 1 as a function of temperature. The low temperature and small susceptibility region of the susceptibility is enlarged and inset in the Fig. 1. The diamagnetic susceptibility of each component has been corrected.

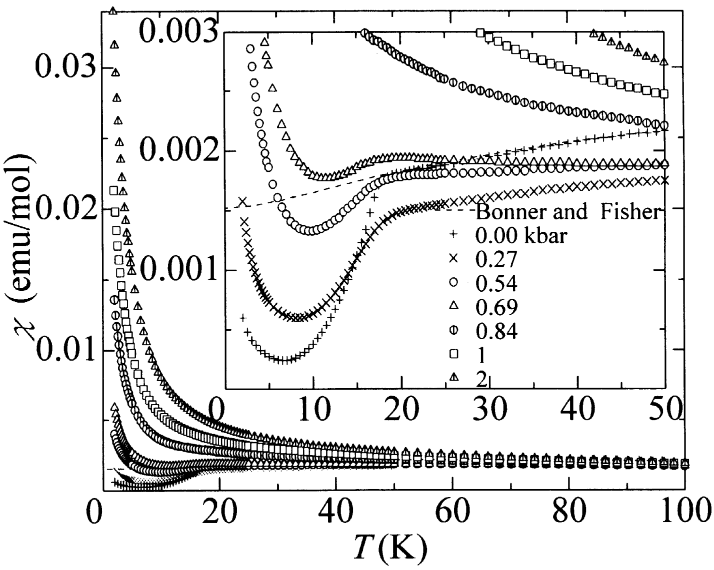

FIGURE 1. Temperature dependence of the magnetic susceptibility at various pressures.

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.

The susceptibility at 0.27kbar is smaller than that at ambient pressure above 15K and the spin-Peierls transition becomes vague and the transition temperature T_{SP} is higher than 18K. On the other hand, the susceptibility at 0.27kbar is larger than that at ambient pressure below 15K and significantly increases below 8K as the temperature decreases.

As the pressure is increased up to 4kbar, the susceptibility at low temperatures becomes large. The susceptibility at above 0.84kbar monotonically increases with decreasing temperature and does no longer show any minimum.

The temperature dependence of the inverse susceptibility at low temperatures and at high pressures is shown in Fig. 2. The inverse susceptibility at low temperatures is well proportional to the temperature, obeying the Curie-Weiss law. The Curie constant at 8kbar corresponds to S=1/2 free spins of 0.25mol. Furthermore, the magnetization at 2K as a function of magnetic field can be fitted by the Brillouin function.

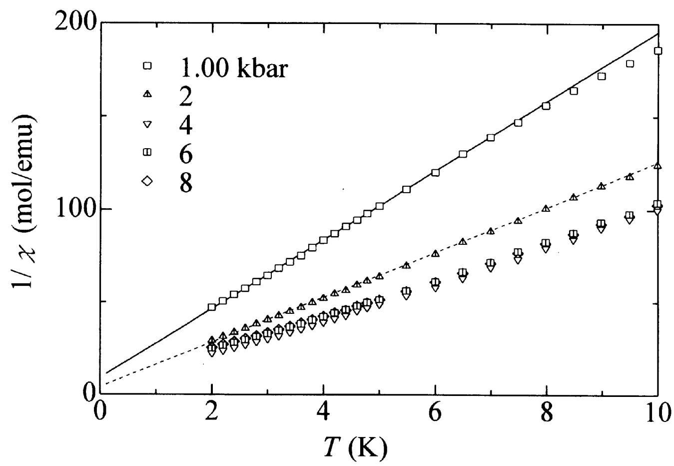

FIGURE 2. Temperature dependence of the inverse susceptibility at high pressures.

By subtracting the susceptibility obeying the Curie-Weiss law from the measured susceptibility shown in Fig. 1, we obtained residual susceptibility. The temperature dependence of the residual susceptibility is shown in Fig. 3.

As the pressure is increased, the residual susceptibility decreases and the temperature dependence of the susceptibility changes gradually. The spin-Peierls transition becomes vague with increasing pressure, though the spin-Peierls transition temperature, T_{SP}, seems to increase. The residual susceptibility at higher pressures decreases to zero at low temperatures and its temperature dependence is qualitatively described by a spin-pair model, which is significantly different from the results reported by Bloch *et al.*[5]. The calculated curves based on the spin-pair model to fit the experimental plots are shown in Fig. 4, where J/k=-65K at 4kbar and J/k=-72K at 8kbar.

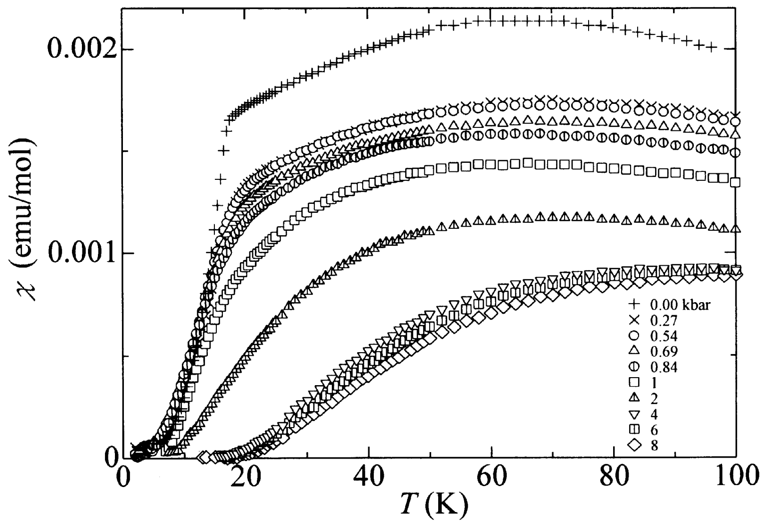

FIGURE 3. Temperature dependence of the residual susceptibility at various pressures.

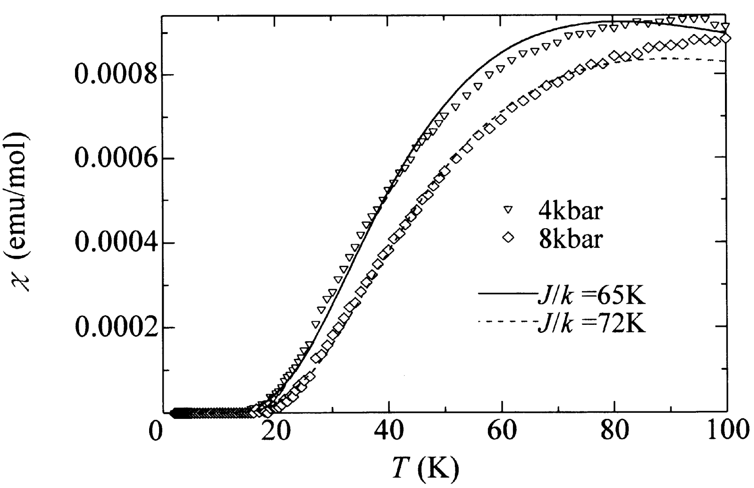

FIGURE 4. Calculated curves based on the spin-pair model to fit the experimental plots at higher pressures.

CONCLUSIONS

In conclusion, the magnetic properties of the organic spin-Peierls substance, MEM-[TCNQ]$_2$, show significant pressure dependence. The increase of the susceptibility at low temperatures and higher pressures is attributable to the free spins which are produced by separating spin–pairs. The residual susceptibility, which is obtained by subtracting the contribution of the free spins from the measured susceptibility, still shows the spin-Peierls transition at lower pressures. However, at higher pressures no critical phenomena were observed in the temperature dependence of the residual susceptibility. The residual susceptibility at higher pressures seems to be explained by a spin-pair model.

Acknowledgments
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