Spin Structure and Dynamics in a Spin 1/2 One Dimensional Antiferromagnet, $[NiBr(chxn)_2]Br_2$ (chxn: 1*R*, 2*R*-cyclohexanediamine)

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The ^{1}H NMR spin-lattice relaxation time T_1 in a spin 1/2 1-D antiferromagnetic complex $[NiBr(chxn)_2]Br_2$ was observed down to 1.8 K. The observed T_1 temperature dependence was well reproduced by the Sachdev's treatment giving an exchange interaction energy (J) of ca. 2500 K. 1-D spin migration assignable to paramagnetic electrons in impurity amounts of Ni^{II} sites was observed at low temperatures.

Halogen-bridged one-dimensional (1-D) metal complexes with a chain structure of -X-M^{II}-X-M^{IV}-X- (M: Pt, Pd; X: Cl, Br, I) have been shown to form an almost isolated 1-D structure in which mixed valence states of metals M(II) and M(IV) are formed owing to strong electron phonon interactions characteristic in this system. Recently, new halogen-bridged 1-D complexes $[NiX(chxn)_2]X_2$ (chxn: 1*R*, 2*R*-cyclohexanediamine; X: Cl, Br) were prepared[1] and shown that bridging halogen atoms are located at the center between two neighboring Ni atoms suggesting the formation of an averaged valence structure (Mott-Hubbard system) consisting of 1-D chains of paramagnetic Ni(III) expressed as -X-Ni^{III}-X-Ni^{III}-X-. To reveal its magnetic structure, the magnetic susceptibility measurement on the Br complex has been performed[2] and obtained results were tried to explain with the Bonner-Fisher model[3] of an antiferromagnetically coupled 1-D system. It is noteworthy that the analyzed result suggested a quite large exchange interaction energy (J) amounting to ca. 3600 K.[2] However, this result is not clear because such a large J value is difficult to be determined from data observed in the low-temperature range up to 300 K. If this reported J value is acceptable, this system would be the 1-D system having the strongest antiferromagnetic interaction so far reported.

It has been shown that 1-D systems consisting of $S = 1/2$ paramagnetic spins with antiferromagnetic interactions cannot form an ordered state at low temperatures, but it has a fluctuated spin state of quantum mechanical origin. From this effect, we can anticipate the non-vanishing NMR spin-lattice relaxation rate in the limit of the low temperature. By assuming the Heisenberg-type interaction, Sachdev proposed[4] that the spin-lattice relaxation time T_1 in the range of $T/J < 0.5$ is expressed as

$$T_1^{-1} \propto \ln^{1/2}(2J/T) \quad (1)$$

where J is defined by $H_{ex} = 2J\Sigma \boldsymbol{S}_i \cdot \boldsymbol{S}_{i+1}$ giving finite T_1 at low temperatures. We confirmed this prediction in the low-temperature range by measuring ^{1}H T_1 in $[CuBr_2(AdH^+)_2]Br_2$ (Ad: adenine)[5] which has been shown to be an antiferromagnetically coupled $S = 1/2$ 1-D system with $J = 52.6$ K.[6]

In the present study, we intend to reveal the magnetic structure and dynamic electron-spin behavior of 1-D chains in $[NiBr(chxn)_2]Br_2$ and obtain the information of magnetic interactions expected to be quite strong by measuring the temperature dependence of the ^{1}H NMR spin-lattice relaxation time at low temperature range and discussing the obtained data in connection with the above relaxation theory.

We prepared crystalline samples of $[NiBr(chxn)_2]Br_2$ for the NMR measurement by two methods which gave quite different results. Starting from a monomer complex $[Ni(chxn)_2]Br_2$ containing Ni^{II} prepared according to literature,[1] the polymer complex $[NiBr(chxn)_2]Br_2$ was obtained in the first method by the oxidation of the monomer complex dissolved in methoxyethanol by slowly diffusing Br_2 gas. Fine plate like crystals were obtained in a week. The second method was performed by the recently developed electrochemical oxidation technique.[7] Using a methanol solution of the monomer complex containing tetra-*n*-butylammonium salt as a supporting electrolyte, several mm size single crystals were appeared on the Pt electrode in 2–3 months with a current of ca. 10 μA. The crystals obtained by 1st and 2nd methods are hereafter named Sample **1** and **2**, respectively. We confirmed that both Sample **1** and **2** have the same crystal structure.

The ^{1}H NMR spin-lattice relaxation time T_1 was measured by a Bruker SXP100 pulsed NMR spectrometer using the inversion recovery method with a homemade temperature controller in a range 100–300 K. A home made pulsed spectrometer applying the same pulse sequence was used in a range 4.2–100 K using an Oxford CF1200 cryostat. For the measurement below 4.2 K, an NMR spectrometer and a cryostat made in Hokkaido University was used. The sample temperature was controlled and determined within $\pm$1 and $\pm$0.1 K, above and below 100 K, respectively. For detecting possible phase transitions taking place at low temperatures, we carried out single crystal X-ray diffraction measurements on Sample **1** using a low-temperature X-ray imaging-plate (IP) system (DIP320V, Mac Science Co., Ltd.) with a graphite monochromated Mo Kα radiation and a continuous He gas-flow cryostat. The crystal structure determined at ca. 20 K ($I222$, $a = 23.469(3)$, $b = 5.138(1)$, $c = 7.071(2)$ Å, $Z = 2$) showed the same isomorphous nondistorted 1-D chains as determined at room temperature[1] and no diffused scattering pattern was observed. These results imply that no spin Peierls type transition is expected down to ca. 20 K.

In the NMR relaxation measurement, the ^{1}H magnetization observed after a $\pi/2$ pulse plotted against the pulse interval τ showed a nonexponential decay in both samples. We roughly evaluated T_1 from the initial linear part of the decay. This short T_1 component was ca. 90% of the ^{1}H magnetization in the whole temperature range studied. At first, we measured ^{1}H T_1 in Sample **1** and obtained data shown in Figure 1 exhibiting a T_1 expansion upon cooling to 1.8 K. This result was inconsistent with the above theoretical prediction by Sachdev.[4] The recently prepared Sample

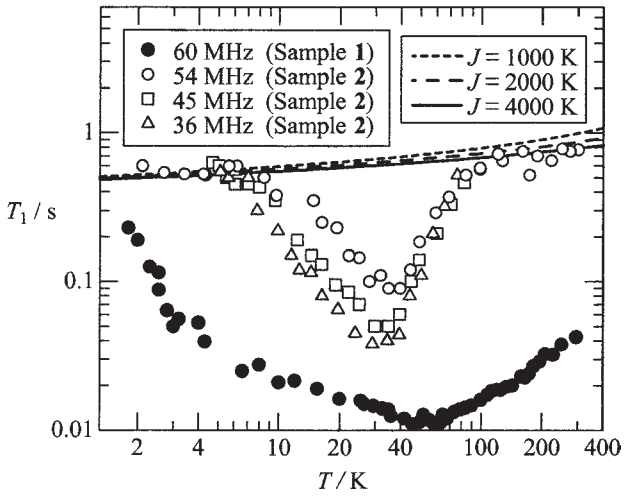

Figure 1. ^{1}H NMR spin-lattice relaxation time T_1 observed in $[NiBr(chxn)_2]Br_2$ prepared by Br_2 diffusion method (Sample **1**) and electrochemical oxidation (Sample **2**). Solid and broken lines are theoretically calculated by Sachdev's treatment.

2, however, showed a quite different relaxation from in Sample **1** as given in Figure 1, where no T_1 expansion was observed below 4.2 K. The observed T_1 in **2** was ca. 10 times longer than in **1** and gave almost temperature independent values in both high- and low-temperature ranges except for a minimum observed ca. 30 K. Quite different relaxation behavior observed in Sample **1** and **2** suggests marked influences from chain ends, impurities and other lattice imperfections being expected more in Sample **1**. The T_1 temperature dependence observed in Sample **2** can be divided into two components: the almost temperature-independent flat part and the minimum at ca. 30 K affording a marked Larmor frequency dependency as shown in Figure 2. The temperature independent part of T_1 tending to a finite value in the low-temperature limit is now consistent with the theoretical expectation and its temperature dependency could be fitted by Equation (1) and fitted curves are shown in Figure 1. From the fitting, we could evaluate the exchange interaction energy $J = 2500 \pm 1,000$ K. This value is comparable to 2700 ± 500 K estimated from the spin susceptibility data obtained by ESR measurements[8] and also a recently reported value of 1700 K derived from the Bonner-Fisher fitting of the magnetic susceptibility.[9] It is noteworthy that these J values are almost the same as 2200 K in Sr_2CuO_3[10] that has been reported to be the antiferromagnetically coupled 1-D system having the highest J value so far reported.

Figure 2 shows Arrhenius plots of T_1 having a marked Larmor frequency (ω) dependence. This indicates the presence of time-dependent relaxation mechanisms different from the fluctuation of antiferromagnetically coupled 1-D electron spins in Ni^{III} sites that gives the flat part of T_1. The fact that a T_1 minimum was observed at ca. 30 K indicates the presence of another relaxation with a fluctuation rate close to the Larmor frequency at ca. 30 K by considering the T_1 minimum condition of $\omega\tau \approx 1.0$ where τ is the correlation time given by the reciprocal of the jumping rate. We assigned the origin of this mechanism to some spin motions associated with impurities formed along 1-D chains, because Sample **1** containing more impurities gave a more remarkable relaxation than in **2**. The most probable impurity expected in the present system is paramagnetic Ni^{II} sites having

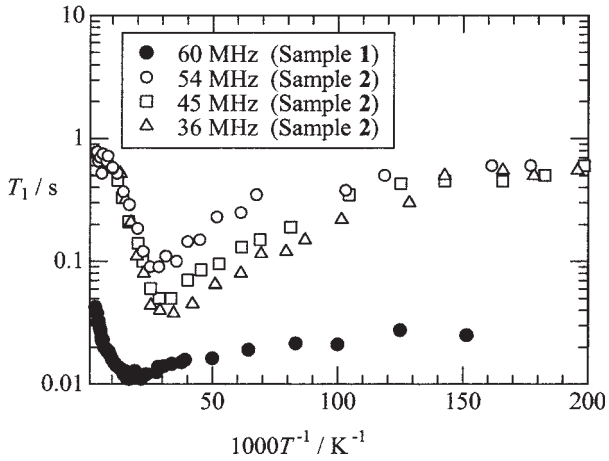

Figure 2. Arrhenius plots of temperature and Larmor frequency dependences of ^{1}H NMR T_1 in $[NiBr(chxn)_2]Br_2$.

an extra electron movable to neighboring normal Ni^{III} sites through Br $4p_z$ orbitals. This model can be supported by the reported high electrical conductivity of 7×10^{-2} S m^{-1} at room temperature,[9] which was also explained by the effect of Ni^{II} impurities.[2] From the present NMR results, we could determine the rate of random jumping of electrons in Ni^{II} sites along the chain to be 10^8/s at ca. 30 K.

The observed temperature and Larmor frequency dependences of T_1 given in Figure 2 were both unexplainable by the conventional BPP theory.[11] Since expected Ni^{II} impurities could be formed not only near cationic impurities, but at chain ends, several kinds of Ni^{II} sites with various concentrations and jumping activation energies seem to be possible. The observed asymmetric T_1 data are attributable to the superimposed effects from these impurities on the relaxation.

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