

The NQR Observation of Spin-Peierls Transition in an Antiferromagnetic MX-Chain Complex $[\text{NiBr}(\text{chxn})_2]\text{Br}_2$

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In the field of solid-state chemistry and physics, there is much interest in one-dimensional (1-D) electron systems because pronounced phenomena characteristic of 1-D systems have been observed such as the Haldane gap in integer spin antiferromagnetic (AF) compounds,^{1,2} solitons and polarons observed in π -conjugated polymers,^{3,4} slow relaxation of magnetization in several ferromagnetic and ferrimagnetic compounds known as single-chain-magnets (SCMs),^{5–7} etc. Halogen-bridged 1-D metal complexes (MX-chains) also have been attractive targets because of the highly isolated 1-D chain structure and the variety of the electronic states which can be tuned by substituting those components, e.g., central metal (M), in-plane ligand (L), bridging halogen (X), and counteranion (Y).

MX-chain complexes with a mixed-valence structure $-\text{X}\cdots\text{M}^{2+}\cdots\text{X}-\text{M}^{4+}-\text{X}\cdots$ (M = Pd, Pt; X = Cl, Br, I) have been widely studied as 1-D materials with strong electron–lattice interactions. Their Peierls distorted 1-D structure was noted as a charge-density-wave (CDW) state, and unique optical and dynamical properties such as overtone progressions in resonant Raman spectra⁸ and luminescence with a large Stokes shift⁹ as well as the long-range migration of spin-solitons and polarons along 1-D chains¹⁰ have been reported. A recently prepared MX-chain complex $[\text{NiBr}(\text{chxn})_2]\text{Br}_2$ (chxn: 1*R*,2*R*-diaminocyclohexane) has been reported to be quite different from the CDW complexes, and it crystallizes in a Mott–Hubbard insulator expressed as $-\text{Br}-\text{Ni}^{3+}-\text{Br}-\text{Ni}^{3+}-\text{Br}-$.¹¹ In this complex, an unpaired electron ($S = 1/2$) in the $\text{Ni}^{3+} 3d_z^2$ orbital is strongly localized on the Ni atom owing to the strong electron correlation ($U \approx 5$ eV).¹² Quite a strong AF interaction ($J = 3600$ K) acts between neighboring Ni atoms through the Br 4p_z orbitals owing to the superexchange interaction.¹³ Such an electronic state is quite analogous to that of Sr_2CuO_3 having a 1-D chain expressed as $-\text{O}-\text{Cu}^{2+}-\text{O}-\text{Cu}^{2+}-\text{O}-$, which is a representative of the strongly correlated 1-D electron systems.^{14–16} Recently, this Ni complex has also been interested from the viewpoint of applied science because of the largest third-order nonlinear optical susceptibilities thus far reported, amounting to 10^{-4} esu.¹⁷

Despite many experimental and theoretical studies for revealing the electronic structure in the present complex, no information of the ground state has been obtained. Generally, an $S = 1/2$ 1-D AF system can be expected to form two types of ground states. Most of the compounds studied have been shown to have a Néel state as a ground state due to a weak interchain magnetic interaction, while several other systems (mostly organic conductors^{18–20} in which π electrons contribute to the magnetism and CuGeO_3)²¹ form a Peierls distorted ground singlet state.

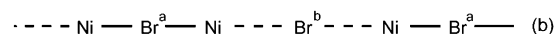
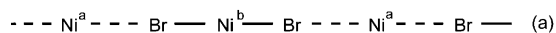


Figure 1. Schematic possible chain structures in (a) CDW and (b) spin-Peierls states in $[\text{NiBr}(\text{chxn})_2]\text{Br}_2$. In CDW and spin-Peierls states, nonequivalent Ni and Br sites are formed, respectively.

Quite recently, the magnetic susceptibility (χ) of this Ni complex was measured using a single crystal with few Curie impurities, and a rapid and isotropic decrease in susceptibility was observed below ca. 100 K,²² indicating the occurrence of some transition to a nonmagnetic ground state. This decrease has not been previously observed because of a large amount of Curie impurities.^{13,23} Furthermore, Bragg spots corresponding to the two-fold periodicity have been observed below 40 K in an X-ray analysis.²⁴ We also measured the temperature dependence of χ using single crystals. These data are shown in the Supporting Information. Observed χ data exhibited a clear decrease below 100 K upon cooling under a static magnetic field (1 T) parallel and perpendicular to the 1-D chain direction in good agreement with the reported data.²² Although these data are enough evidence of spin-Peierls transition in usual compounds, two different nonmagnetic states with two-fold periodicity are possible in the present Ni complex, namely CDW and spin-Peierls states (Figure 1).

To clarify this transition, we measured the temperature dependence of the nuclear quadrupole resonance (NQR) frequency of bridging Br atoms because the NQR is quite a sensitive probe for detecting subtle changes in the electron distribution around NQR nuclei.

Single crystals of $[\text{NiBr}(\text{chxn})_2]\text{Br}_2$ were prepared by the electrochemical oxidation method reported in the literature.²⁵ The Br NQR measurement was performed between 3.8 and 300 K using a homemade pulsed spectrometer constructed in National Institute for Materials Science (NIMS). The resonance signal was detected by observing free induction decay signals (FID) after a $\pi/2$ pulse. The resonance frequency was determined from the shape of the FID signal. The sample temperature was controlled with an Oxford CF1200 cryostat and an ITC 503 temperature controller. Measured single crystals were aligned so as that the pulsed rf field is perpendicular to the 1-D chain direction which is nearly parallel to the principal axis of the electric field gradient at Br nuclei.

We observed a single resonance line for ^{81}Br at 300 K (137.079 ± 0.005 MHz) and a pair of lines 130.874 ± 0.01 and 147.786 ± 0.01 MHz at 3.8 K. We assigned these resonance signals to ^{81}Br nuclei by observing corresponding ^{79}Br lines at 164.091 ± 0.005 MHz (300 K), and 156.656 ± 0.01 and 176.904 ± 0.01 MHz (3.8 K) in good agreement with the reported isotope frequency ratio ($^{79}\text{Br}/^{81}\text{Br}$: 1.1969).²⁶ These resonance frequencies could be assigned to bridging Br atoms and not to counter Br ions, because ^{79}Br

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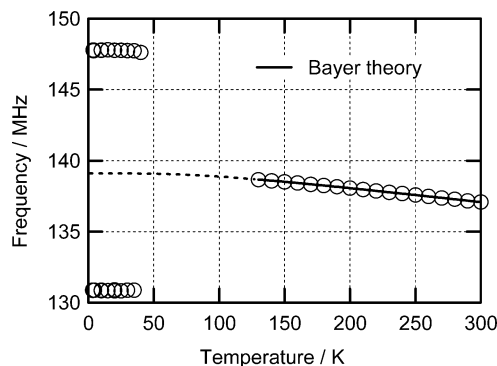


Figure 2. Temperature dependences of ^{81}Br NQR frequencies observed in $[\text{NiBr}(\text{chxn})_2]\text{Br}_2$. Dotted line is an extrapolation to 0 K according to the Bayer theory.

NQR frequencies in compounds with Ni–Br covalent bonds were observed in nearly the same frequency range, i.e., 126.26 MHz in $\text{NiBr}_2[\text{P}(\text{C}_3\text{H}_7)_3]_2$ ²⁷ and 126.53 MHz in $\text{NiBr}_2[\text{P}(\text{C}_4\text{H}_9)_3]_2$ ²⁷ at room temperature, whereas ionic Br ions mostly exhibit resonance lines²⁸ at frequencies of an order of magnitude lower than those in the present complex.

Figure 2 shows a temperature dependence of ^{81}Br NQR frequencies of the bridging Br in $[\text{NiBr}(\text{chxn})_2]\text{Br}_2$. A single ^{81}Br NQR line was observed at room temperature, consistent with the X-ray diffraction work¹¹ that all bridging Br sites are equivalent at room temperature, i.e., $[\text{NiBr}(\text{chxn})_2]\text{Br}_2$ is in the Mott–Hubbard state. The fact that the resonance frequency was gradually decreased with increasing temperature above 130 K can be explained by the averaged electric field gradient (EFG) at Br nuclei by lattice vibrations. This temperature dependence of the NQR frequency ($\nu(T)$) can be described by the harmonic oscillator model for lattice vibrations²⁹ and can be expressed as

$$\nu(T) = \nu_0 \left[1 - A \coth\left(\frac{\hbar\omega}{2kT}\right) \right] \quad (1)$$

where ν_0 , A , and ω are the resonance frequency for the static lattice, a coefficient depending on modes of lattice vibrations, and the averaged vibration frequency, respectively. The observed data were well fitted by eq 1, and the extrapolated frequency to 0 K was determined to be $\nu(0) = 139.1 \pm 0.2$ MHz.

Upon cooling, the NQR signal disappeared around 130 K, and two lines at 130.7 and 147.8 MHz appeared below ca. 40 K. The loss of resonance signals between 40 and 130 K is considered to be spectrum broadening attributable to the fluctuation of EFG by a phase transition. Since the averaged frequency of these two lines is almost the same as the frequency extrapolated from the high-temperature side, the NQR signals below 40 K are explained by the splitting of the high-temperature signal. Two resonance lines with a large frequency separation of 16.9 MHz at low temperatures indicate the presence of two nonequivalent Br sites, suggesting that some phase transition takes place between 40 and 130 K in $[\text{NiBr}(\text{chxn})_2]\text{Br}_2$.

We showed two possible schematic chain structures as nonmagnetic states in this complex in Figure 1. In the CDW state (Figure 1a) well-known in Pt- and Pd-halogen-bridged complexes, bridging Br sites locate at an off-centered position between neighboring metal sites so as to stabilize the mixed-valence structure. Since all Br sites in the chain are equivalent in this structure despite the formation of two nonequivalent Ni sites, this state affords a single Br NQR line. In the spin-Peierls state (Figure 1b) characterized by the displacement of Ni sites, however, two nonequivalent bridging

Br sites are formed, which is in good agreement with the two Br NQR lines. The splitting of the NQR signal indicates that a spin-Peierls transition occurs in $[\text{NiBr}(\text{chxn})_2]\text{Br}_2$ in the range 40–130 K. This explanation is consistent with the decrease in the magnetic susceptibility²² observed below 100 K.

In summary, we observed clear evidence of the spin-Peierls transition in an $S = 1/2$ 1-D Heisenberg AF complex $[\text{NiBr}(\text{chxn})_2]\text{Br}_2$ with an enormously large J value by the NQR method. This is the first report of spin-Peierls transition in the transition metal complexes in which only d electrons without π electrons contribute to the magnetism. In addition, we demonstrated a new experimental method for studying the spin-Peierls system.

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Supporting Information Available: Magnetic susceptibility of the present complex (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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