High frequency ESR measurements of Co-delta chain

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Abstract. The ∆-chain, which consists of a sawtooth chain with frustrated spin trimers, is expected to have various ground state and low-lying excitations due to their geometrical spin network. The model substance of ∆-chain compound is [Co2(OH){1, 2, 3 – (O2C)3C6H3}3(H2O)] · (H2O), which consists of Co2+ ∆-chain. In this system Co2+ ion behaves like the Ising spin due to its magnetic anisotropy. To investigate the dynamical properties of this ∆-chain compound, high frequency ESR measurements have been performed using Gunn oscillators and BWO. Observed dynamical property of [Co2(OH){1, 2, 3 – (O2C)3C6H3}3(H2O)] · (H2O) will be discussed.

1. Introduction
Quantum spin chains have been studied extensively both experimentally and theoretically due to the rich variety of interesting magnetic properties. In the quantum spin systems, the ground state and the first excited state are affected by the quantum fluctuation, which is enhanced by the reduction of spin quantum number and the lattice dimensionality. Recently, there are many attempts to combine the frustration geometry with the low dimensionality in spin systems, such as the diamond chain[1], the zigzag chain[2], the ∆-chain (also called sawtooth chain)[3, 4]. There has been a great interest for such systems, in which both quantum and frustration effects are involved, that is, how quantum effects and/or spin frustration effects affect ground state properties as well as elementary excitations in the system[5, 6, 7, 8]. Among them, we focus on the simplest system, ∆-chain, which consists of the linear arrangement of triangles. Previously, we reported ESR study of S=1/2 Heisenberg ∆-chain system[4]. In this paper, we studied new S=1/2 Ising ∆-chain system. The model substance of ∆-chain compound [Co2(OH){1, 2, 3 – (O2C)3C6H3}3(H2O)] · (H2O) was synthesized by Gutschke et al. [9]. CoO6 octahedral (Co(1)) and CoO4 tetrahedral (Co(3)) sites alternate along the backbone of the chain, and pendant CoO5 trigonal-bipyramidal (Co(2)) sites are attached at each bridging hydroxide as shown in Figure 1(a). The Co ∆-chain is formed by corner sharing CoOx polyhedra. Therefore, three kinds of nearest-neighbor exchange interactions J1, J2 and J3 due to three different Co sites exist in a chain as shown in Figure 1(b). Co(1) octahedron and Co(3) tetrahedron have only minor deviations from the regular shape. On the other hand, Co(2) bipyramid is rather distorted. Co ∆-chains run along the crystallographic a and b axes, and no atoms are shared between

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The crystal structure of \([\text{Co}_2(\text{OH})\{1, 2, 3 – (\text{O}_2\text{C})_3\text{C}_6\text{H}_3\}\{\text{H}_2\text{O}\}] \cdot (\text{H}_2\text{O})\). (a) One-dimensional chain of CoO\_x polyhedra. Co(1), Co(2) and Co(3) show octahedron, bipyramid and tetrahedron, respectively. (b) Co\^{2+} spin network. (c) Co \(\Delta\)-chain configuration in the crystal.

Figure 2. Temperature dependence of ESR spectra observed at 260 GHz.

Orthogonal chains as shown in Figure 1(c). The magnetic susceptibility shows a simple Curie-Weiss dependence with the addition of a shoulder at approximately 4 K. Gutschke estimated the Weiss temperature to be \(\theta = -57\) K by fitting the magnetic susceptibility data in the temperature range from 50 to 300 K and it suggests that the dominant interaction is antiferromagnetic. No anomaly in the magnetic susceptibility down to 2 K suggests the existence of the spin frustration. To investigate spin dynamics and ground state properties of \(S=1/2\) Ising \(\Delta\)-chain, high frequency ESR measurements of \([\text{Co}_2(\text{OH})\{1, 2, 3 – (\text{O}_2\text{C})_3\text{C}_6\text{H}_3\}\{\text{H}_2\text{O}\}] \cdot (\text{H}_2\text{O})\) are performed.

2. Experimental

The powder samples of \([\text{Co}_2(\text{OH})\{1, 2, 3 – (\text{O}_2\text{C})_3\text{C}_6\text{H}_3\}\{\text{H}_2\text{O}\}] \cdot (\text{H}_2\text{O})\) are prepared by the hydrothermal synthesis from CoCl\(_2\)·6H\(_2\)O with 1,2,3-benzenetricarboxylic acid hydrate and NaOH. The detailed procedure of crystal growth is shown in the ref. [9]. The powder samples are confirmed to be in a single phase by the X-ray powder diffraction measurements. The submillimeter and millimeter wave ESR measurements have been performed using the pulsed magnetic field up to 16 T in the temeprature range from 80 K to 1.8 K. The frequency range is from 140 GHz to 550 GHz using Gunn oscillators and BWO (Backward traveling Wave Oscillator) as light sources. The details of our ESR system can be found in refs. [10].

3. Results and discussion

Figure 2 shows the temperature dependence of ESR spectra observed at 260 GHz. A sharp absorption line is a DPPH signal, which is the field marker of \(g = 2\). Arrow heads indicate the resonances A, B and C. A very broad absorption line at around 5 T is observed at 80 K. As the ESR spectra above 80 K is broaden, we could not estimate the resonance field at higher temperature. The valence of all Co ions in \([\text{Co}_2(\text{OH})\{1, 2, 3 – (\text{O}_2\text{C})_3\text{C}_6\text{H}_3\}\{\text{H}_2\text{O}\}] \cdot (\text{H}_2\text{O})\) is expected to be 2+, therefore, the electronic state of Co\^{2+} is \(3d^7\). A Co\^{2+} ion is known to take the fictitious spin \(S=1/2\) and is very anisotropic [11]. As we treat the powder sample, the powder pattern ESR spectra is expected due to anisotropic \(g\)-values of the Co ion in the paramagnetic state. However, a single broad absorption line is observed at 80 K. As three different Co sites interact each other by the super-exchange interactions, the anisotropic \(g\)-values average out to the isotropic \(g\)-value by the exchange narrowing. Below 40 K absorption...
resonances are observed in CoCl₂ · 2H₂O which shows two metamagnetic transitions for B // easy axis [12]. Considering the one-dimensional Ising chain with a uniform exchange interaction J as in the case of CoCl₂ · 2H₂O, the critical field B_{C1} of the metamagnetic transition is described...
as \( B_{C1} = zJ/\gamma gB \) using the molecular field approximation where \( z \) and \( \mu_B \) are the number of the nearest neighbor sites and the Bohr magneton, respectively. Then the exchange interaction \( J \) is estimated to be 3.3 K (70 GHz) using \( g_C = 2.21 \) and \( z = 2 \) in our case. On the other hand, as is well known, the spin cluster excitation shows a gap \( \Delta_{\text{gap}} \) which is twice the intrachain exchange coupling and is described by \( \Delta_{\text{gap}}/\gamma = zJ/\gamma gB \) where \( \gamma \) is the gyromagnetic ratio. Using this relation, the exchange interaction \( J \) is estimated to be 3.7 K (154 GHz) using the energy gap 139 GHz of mode C and B at \( B_{C1} \) and \( g_C \). Rough estimation of \( J \) from the gap shows a good agreement with that from \( B_{C1} \). Modes of the spin cluster resonances usually show linear dependence from the same gap \( \Delta_{\text{gap}} \) with different \( g \)-values \( n_g \), where \( n \) is the number of spins contained in the spin cluster. As the mode B has twice the \( g \)-value of C, and C starts the same frequency at \( B_{C2} \) in our case, the behaviors of modes B, C and the gap are very similar to the spin cluster resonance [12]. However, the spin configuration changes above the magnetic phase transition \( B_{C2} \), while modes B and C do not change above \( B_{C2} \). Moreover, the \( g \)-value of mode B do not coincide with the EPR \( g \)-value of 4.0 in the paramagnetic phase. Therefore, the simple spin cluster model is difficult to interpret ESR modes of Co \( \Delta \)-chain system completely. As the separation of resonances between B//easy axis and B//hard axis is difficult using the powder sample, further investigation using the single crystal, which is not possible at the moment, is required.

4. Conclusion
The submillimeter and millimeter wave ESR measurements of \( S=1/2 \) Ising \( \Delta \)-chain system \([\text{CO}_2(\text{OH})\{1, 2, 3 – (\text{O}_2\text{C})_3\text{C}_9\text{H}_2\}\cdot(\text{H}_2\text{O})]\) have been performed in the temperature range from 80 K to 1.8 K. Very broad single EPR absorption line is observed, and its \( g \)-value is estimated to be 4.0. From the frequency-field diagram at 1.8 K, two distinct mode changes suggest the magnetic phase transitions at \( B_{C1} = 4.5 \) T and \( B_{C2} = 7.5 \) T.

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