The ^{51}V-NMR study of Vanadium Hollandite

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Abstract

Several vanadium compounds $A_xV_8O_{16}$ are known to belong to the Hollandite family. We have investigated the temperature variations of the resistivity and magnetic susceptibility for some of them (A=Bi, Ba, Pb), which show non-stoichiometry in composition x ($1.60< x <1.80$ for Bi, $1.35< x <1.8$ for Pb and x=1.09, $1.2< x <1.36$ for Ba), resulting in a wide variety of their physical properties depending on x. For example, Bi-Hollandites with $1.6< x <1.71$ are metallic in the whole temperature range, while those with $1.72< x <1.80$ exhibit a temperature-induced metal-insulator transition. In order to elucidate their microscopic electronic states we have further performed ^{51}V-NMR experiments and will report their results.

Key words: Metal-Insulator transition; NMR; Hollandite; Vanadium oxide

Recently, low dimensional systems have attracted much attention in the field of solid state physics and chemistry, since they show various interesting quantum phenomena associated with spin frustrations, spin singlet formation, Peierls instability, etc. We have investigated vanadium-hollandite $A_xV_8O_{16}$. The most characteristic aspect in the hollandite structure is the [V_8O_{16}] 1D tunnel framework constructed by four V-O zigzag chain. In the zigzag chain V cations form triangles so that we can expect the spin frustration effect when antiferromagnetic interactions are dominant. In this compound we can control the valence of vanadium cation by changing the A concentration x. Therefore, we may expect the observation of the changing of physical properties depending on the valence of V atom. For example, in the case with A=Bi, the system has the A cation range of $1.60< x <1.80$, and occurs temperature-induced metal-insulator transition (MIT) with $1.72< x <1.80$[2]. Using NMR measurements, we have revealed the existence of antiferromagnetic interaction in the metallic phase with MIT samples. Thus, we concluded that the mechanism of MIT in this system is due to the relaxation of spin frustration in the metallic phase[3]. Furthermore, both of charge and orbital orderings may occur simultaneously at MIT[4]. For A=Pb, the system has $1.35< x <1.80$ range and occurs MIT around 150K. We also observed the transition in susceptibility at the MIT temperature[5].

$Ba_xV_8O_{16}$ similarly has the hollandite structure[6,7]. We can obtain the different vanadium valence state from those in Bi-hollandite because Ba has +2 valence. To elucidate how the vanadium valence state affects the physical properties in the vanadium hollandite system, we have measured the electric resistibility and the magnetic susceptibility of $Ba_{1.09}V_8O_{16}$. Moreover, we have performed ^{51}V NMR experiments in order to clarify the microscopic vanadium state. Hereafter we represent $A_xV_8O_{16}$ as $A(x)$. We synthesized the powder sample of Ba(1.09) as follows. BaV_2O_6,V_2O_3 and V_2O_5 were mixed in an appropriate molar ratio and heated in an evacuated silica tube at 1173K. The resistivity measurement was carried out using a conversional four-prove method. The magnetic susceptibility was measured by using a SQUID magnetometer. We measured ^{51}V NMR spectrum by the spin-echo technique using a standard

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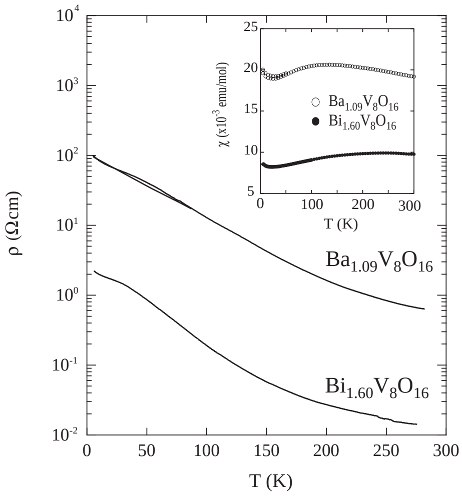

Fig. 1. Temperature dependence of magnetic susceptibility(inset) and electric resistibly.

phase coherent-type pulsed NMR spectrometer.

Figure 1 shows the temperature dependence of resistibility and susceptibility for Ba(1.09) compound. For a comparison, we also show the data of Bi(1.60), which indicates no transition down to 4.2K. Bi(1.60) shows metallic conductivity in the whole temperatures. The increase of the resistibility with decreasing temperature is possibly caused by the effect of grain boundary. The susceptibility of Bi(1.60) is almost temperature independent, indicating Pauli paramagnetic behavior. The resistibility and susceptibility of Ba(1.09) show similar temperature dependences to those of Bi(1.60), although the value of them are larger that of Bi(1.60). In order to reveal the physical properties of Ba(1.09) from a microscopic viewpoint, we performed ^{51}V NMR experiment. The spectra of Ba(1.09)and Bi(1.60) are shown in Fig.2. In the case of Bi(1.60), we observed a single broad line in the whole temperature range. In Ba(1.09), on the other hand, we observed several satellite lines at 4.2K, although a single broad line was observed at 75K. This spectrum can be explained in the term of quadra pole interaction with I=7/2. It seems that Ba(1.09) and Bi(1.60) have different electronic states at low temperatures.

In order to obtain further information such as spin dynamics, measurements of the nuclear spin-lattice relaxation time T_1 are now in progress.

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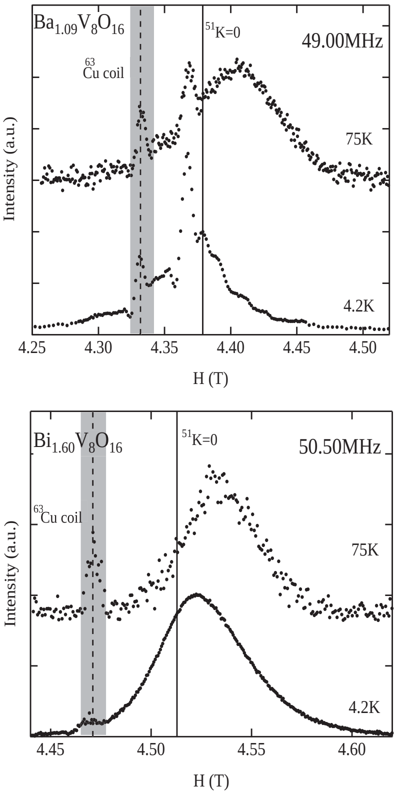

Fig. 2. ^{51}V NMR spectra of $Ba_{1.09}V_8O_{16}$ and $Bi_{1.60}V_8O_{16}$. The dashed lines and hatch parts stand for ^{63}Cu metal in a pick-up coil and the solid line for ^{51}K=0.

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