μSR study on antiferromagnetism in K-Rb alloy and Rb clusters in sodalite

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Porous crystals of zeolites make it possible to generate periodically arrayed alkali-metal nanoclusters. Various kinds of magnetically ordered states have been observed in these systems, although they do not contain any magnetic elements. Sodalite is a kind of aluminosilicate zeolites where the β cages with an inner diameter of $\simeq$ 7 Å are arrayed in a bcc structure as shown in Fig. 1 (a). The chemical formula is given by $A_3Al_3Si_3O_{12}$ per β cage where A indicates an alkali cation. By the loading of guest alkali atoms into dehydrated sodalite, an A_4^{3+} cluster is formed in the β cage as schematically shown in Fig. 1 (b), where an s-electron is shared by four A^+ ions and is confined in the cage. When Na_4^{3+} clusters are formed in all the β cages, antiferromagnetic (AFM) ordering occurs below the Néel temperature of $T_N = 48$ K[1–3] because of the exchange coupling between the adjacent clusters. The material is assigned to a Mott insulator. When heavier alkali cations are substituted for Na^+, T_N systematically increases: 72, 80, and 90-100 K for clusters with average chemical compositions of K_4^{3+}, $(K_3Rb)^{3+}$, and $(K_{1.5}Rb_{2.5})^{3+}$, respectively.[4,5] However, a recent work has revealed that Rb_4^{3+} does not show AFM ordering and shows metallic behavior. In the present work, we investigate in detail the magnetic properties of this system in the vicinity of the insulator-to-metal (I-M) transition by utilizing μSR. The experiments were performed at the RIKEN-RAL Muon Facility using the CHRONUS spectrometer.

Figure 2 (a) shows the zero-field μSR spectra of K-Rb alloy clusters ($(K_{1.7}Rb_{2.3})^{3+}$). At 5 K, a muon-spin precession signal with a large amplitude is clearly observed. This result indicates that the AFM order is robust in the major volume of the sample even just before the I-M transition. The internal field at the muon site is estimated to be 166 Oe. This is stronger than that in Na_4^{3+} (92 Oe)[2], K_4^{3+} (142 Oe), and $(K_3Rb)^{3+}$ (155 Oe)[4]. A systematic increase in the size of the s-electron wave function in the heavier alkali metals, which is the origin of the enhancement of AFM exchange interaction, is expected to provide a stronger Fermi contact between muon and s-electron. T_N is estimated to be $\simeq$ 90 K from the temperature dependence of the internal field. In contrast, the pure Rb clusters (Rb_4^{3+}) only show very slow relaxation even at 2 K as shown in Fig. 2 (b). This result confirms that a non-magnetic state is realized in the metallic phase after the I-M transition.

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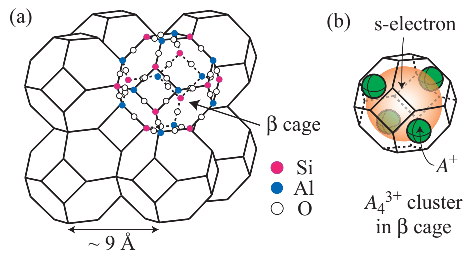

Fig. 1. Schematic illustrations of (a) the crystal structure of sodalite and (b) the A_4^{3+} cluster formed in the β cage, where A indicates an alkali element.

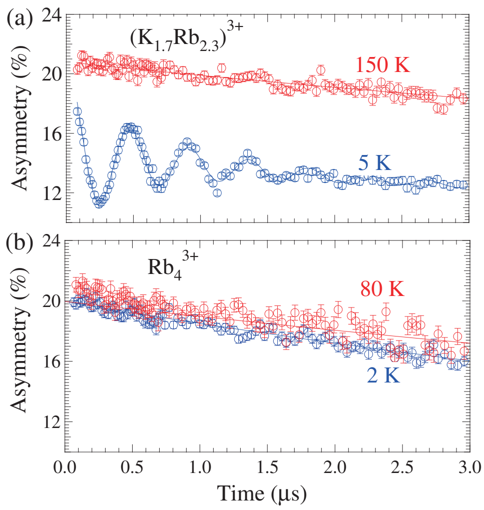

Fig. 2. Zero-field μSR spectra of (a) K-Rb alloy clusters and (b) Rb clusters in sodalite.

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