Electronic Properties of Alkali Metals Loaded into Channel-Type Zeolite L

P T Thi[1,2], T Nakano[2], Y Sakamoto[2,3] and Y Nozue[2]

[1]Center for Innovative Materials & Architectures (INOMAR), Vietnam National University, Ho Chi Minh City (VNU-HCM), Quart 6, Linh Trung Ward, Thu Duc District, Ho Chi Minh City, Vietnam
[2]Department of Physics, Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan
[3]Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), Kawaguchi, Saitama 332-0012, Japan

E-mail : nozue@phys.sci.osaka-u.ac.jp

Abstract. Rb metal was loaded into dehydrated Rb-form zeolite L. The loading density of Rb atoms per unit cell, n, was changed up to 7.1. A resonant optical absorption-reflection band is observed at ≈1.0 eV in all samples. A new reflection band appears at ≈1.7 eV for $n > 5$. The 1.0 and 1.7 eV bands are assigned to the respective excitations from 1s to 1p and from 1p to 1d quantum states of s-electrons one-dimensionally confined in main-channels with an inside diameter of ≈ 1 nm. A temperature-dependent semiconducting resistivity is observed at $n > 2$, and is assigned to the inter-channel polaron hopping between metallic 1s and 1p states. Besides, a nearly metallic resistivity with the low thermal activation energy is observed at $n > 5$. The metallic conductivity is assigned to three-dimensional s-electrons in the 1d state. The metallic property in Rb-loaded zeolite L is more remarkable than those in K-loaded zeolite L. The difference is explained by the smaller ionization energy of Rb atom, which leads to a shallower one-dimensional confinement potential of main-channel and a smaller polaron effect.

1. Introduction

Alkali metals loaded into zeolite crystals display novel properties of s-electrons, such as a ferromagnetism and an insulator-to-metal transition, depending on the kind of alkali metals, the loading density and the structure type of zeolites [1,2]. The quantum confinement of electrons in the bundle of cylindrical potentials has attracted deep interest in their novel electronic states [3,4]. An electron in a quantum cylinder has the two terms in the kinetic energy [3,4]. The first term is given by the radial confinement, and forms 1s, 1p and 1d quantum states in the increasing order of energy. The second term is given by the free motion along the cylinder. When a cylinders has a finite potential depth, the wave function of an electron spills out [5]. The hopping-type incoherent motion of polarons increases with the increase in temperature [6,7]. If the mutual overlap of wave function increases furthermore, the band-type coherent motion occurs as the three-dimensional (3D) metallic phase [3,4].

Aluminosilicate zeolite L has the LTL framework structure (IUPAC nomenclature), as shown in Figure 1. The one-dimensional (1D) main-channels with an inside diameter of ≈1 nm are bundled along the *c*-axis. The framework is negatively charged, and cations are distributed at the space of framework. K metal can be loaded into K-form zeolite L [4,8,9]. The loading density of K atoms per unit cell, *n*, was changed up to 9.6, and a resonant optical absorption-reflection band has been observed at ≈1.1 eV in all K-loaded samples [4,9]. Another reflection band appears at ≈1.8 eV for $n > 5$. These 1.1 and 1.8 eV bands are assigned to the respective excitations from 1s to 1p and from 1p to 1d quantum states of s-electrons confined in main-channels of zeolite L. An increase in the mid-infrared absorption coefficient at 0.3 eV has been observed at $n > 3$. This absorption is assigned to a tail part of the Drude term of the 1D metallic state of s-electrons confined in main-channels. A temperature-dependent semiconductive electrical conductivity has been observed at $n > 3$. A nearly metallic conductivity is observed at $n > 9$. The total conductivity is given by the sum of two terms with the high and the low thermal activation energies [4]. The semiconductive conductivity is assigned to the polaron hopping between main-channels in 1s and 1p quantum states. The metallic conductivity is assigned to the 3D state of s-electrons in 1d quantum states. A temperature independent spin-susceptibility extracted from the integrated intensity of ESR signal increases at $n > 5$. This term is assigned to the Pauli paramagnetism of metallic states. These properties are interpreted systematically in terms of an insulating states of 1s and 1p states at $n < 5$, 1D metallic states of 1s and 1p states at $n > 5$, and a 3D metallic state of 1d state at $n > 9$.

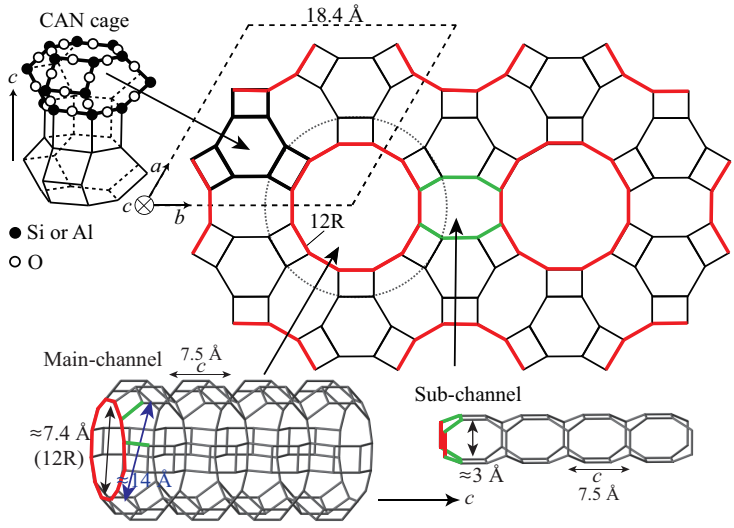

Figure 1. Schematic illustration of the LTL framework structure of zeolite L. Main-channels have the inside diameters of ≈14Å at the widest part and ≈7.4Å at 12-membered ring (12R). Sub-channels are located between main-channels, and share elliptic 8-membered rings with main-channels. Each CAN cages are surrounded by sub-channels and main-channels. Cations are not shown here.

The metallic property in Rb-system is expected to be more remarkable than those in K, because of the smaller ionization energy of Rb atom, which leads to a shallower 1D confinement potential and a smaller polaron effect. In the present study, we prepared Rb-loaded zeolite L at various Rb-loading densities, and measured their optical and electrical properties.

2. Experimental Procedures

K cations of synthetic zeolite L powder (Tosoh Corporation) were exchanged to Rb cations, and Rb-rich zeolite L with the chemical formula $K_2Rb_7Al_9Si_{27}O_{72}$ per unit cell was prepared. Rb metal was loaded into dehydrated Rb-rich zeolite at the loading density of *n*Rb atoms per unit cell. Hereafter, the samples are denoted by Rb_n/K_2Rb_7-L. We performed optical and electrical properties. Sample preparations and characterizations are detailed in Ref. 4.

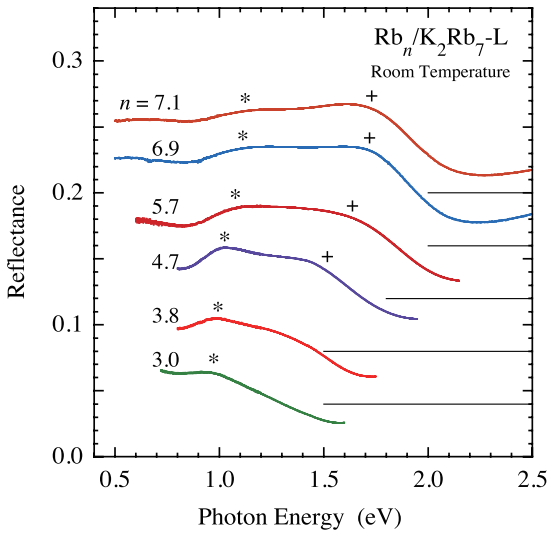

Figure 2. Reflection spectra of Rb_n/K_2Rb_7-L at room temperature.

3. Experimental Results and Discussions

In dilutely Rb-loaded Rb_n/K_2Rb_7-L, an absorption band clearly appears at ≈1.0 eV [9]. Figure 2 shows the reflection spectra of Rb_n/K_2Rb_7-L at room temperature. A reflection band at ≈1.0 eV with asterisk is seen all samples. New band at ≈1.7 eV with plus sign appears around $n > 5$ and grows with n. Similar reflection bands have been observed in K-loaded K-form L (K_n/K_9-L) [4]. These reflection bands can be assigned to the excitations from 1s to 1p and from 1p to 1d quantum states of s-electrons in the main-channel of zeolite L. Differently from the localized states in clusters (zero-dimensional), the excitation from 1s to 1p states appears together with that from 1p to 1d states, reflecting the continuous 1D energy band [4]. An increase in the mid-infrared absorption coefficient at 0.3 eV is observed at $n > 2$ in Rb_n/K_2Rb_7-L [9]. This absorption is assigned to a tail part of the Drude term in 1D metallic s-electrons in main-channels. At $n < 2$, s-electrons may become small bipolarons by the interaction with the cation displacement, and insulating properties with a finite optical gap are observed.

The temperature dependence of electrical resistivity ρ in Rb_n/K_2Rb_7-L is shown in Figure 3. The resistivity increases with the decrease in temperature at lower loading densities. The resistivity remarkably decreases with the loading density, and the increase at low temperatures becomes weak. These temperature dependence is explained by the following conductivity σ with two terms [4],

$$\sigma = \sigma_{\mathrm{H}} \exp\left(-\frac{E_{\mathrm{H}}}{k_{\mathrm{B}}T}\right) + \sigma_{\mathrm{L}} \exp\left(-\frac{E_{\mathrm{L}}}{k_{\mathrm{B}}T}\right), \quad (1)$$

where E_{H} and E_{L} are high and low thermal activation energies, respectively, and σ_{H} and σ_{L} the respective conductivities at the infinite temperature. k_{B} and T are the Boltzmann constant and the temperature, respectively. ρ is given by $1/\sigma$. The fitting results are indicated by solid curves in Figure 3, where the data at $n \leq 3.8$ and $n = 7.1$ are fitted by one term with the high and the low activation energies in Eq. 1, respectively. Estimated values of E_{H}, E_{L}, σ_{H} and σ_{L} are plotted in Figure 4 by closed squares, together with those in K_n/K_9-L [4] by open circles. Data of Rb_n/K_2Rb_7-L is clearly shifted to lower values of n compared with those of K_n/K_9-L.

The electrical conductivity is usually given by

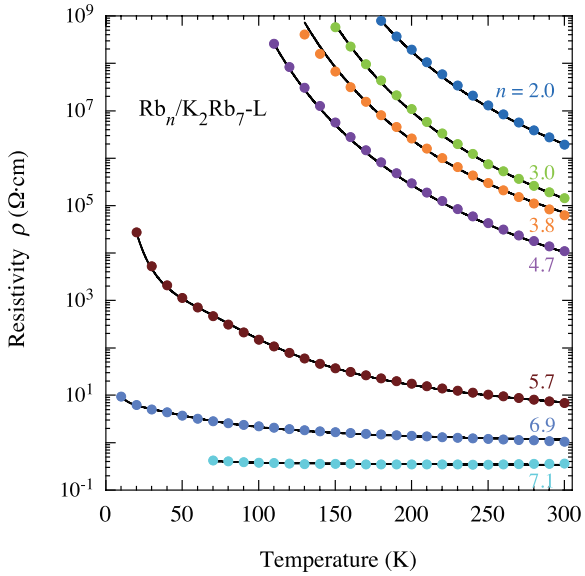

Figure 3. Temperature dependence of electrical resistivity in Rb_n/K_2Rb_7-L (closed circles). Solid curves are fitting results.

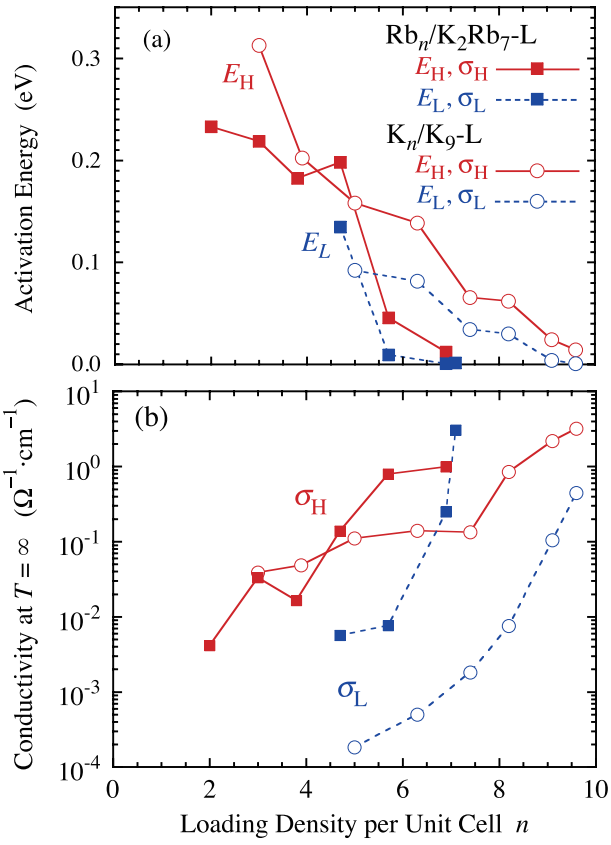

Figure 4. Parameters of conductivity in Eq. 1, E_{H}, E_{L}, σ_{H} and σ_{L}, estimated in Rb_n/K_2Rb_7-L (closed squares) and K_n/K_9-L (open circles).

$$\sigma = e\mu N , \qquad (2)$$

where e, μ and N are the elementary electric charge, the carrier mobility and the number density of carriers, respectively. The temperature dependence of conductivities are given by μ and/or N. In the bundle of channels, s-electrons in 1D quantum states can move to other channels by the hopping process with the increase in temperature. This mechanism contributes to the thermal excitation of mobility with the constant carrier density. The high thermal excitation term in Figure 4 can be assigned to the hopping of s-electrons in the 1s and 1p states. With the increase in n, low thermal activation term dominates the conductivity in Figure 4. This n-dependence is assigned to the thermal excitation of carriers with the band-type conduction in the 1d state, because a larger overlap of 1d wave function can be expected to form the 3D energy band.

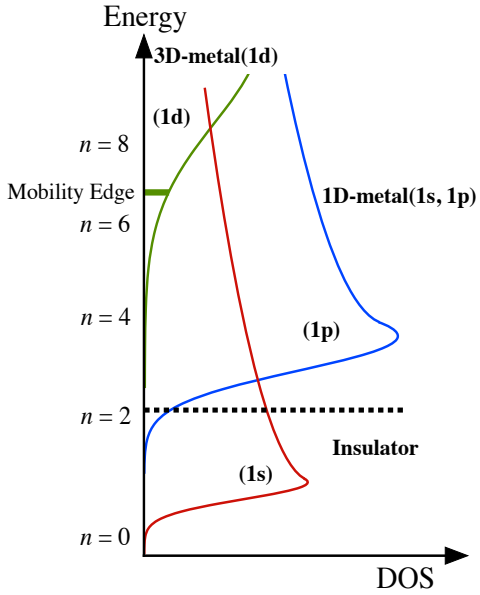

Figure 5. The density of states (DOS) of s-electrons in the bundle of main-channels in Rb_n/K_2Rb_7-L.

In order to overview, the electronic state in Rb_n/K_2Rb_7-L as the function of the Rb loading density, the density of states (DOS) is illustrated schematically in Figure 5. At $n < 2$, most of s-electrons in main-channels are localized as small bipolarons, and an insulating properties are observed. At $n > 2$, electrons in main-channels become 1D-metallic, and the hopping motion of them provides the conductivity with the high thermal activation energy. At $n > 6$, some electrons are distributed in the 1d state, and the band-type 3D-conduction with low thermal activation energy is observed below the mobility edge of the Anderson localization. At $n > 7$, the 3D metallic state is realized above the mobility edge. In K_n/K_9-L, the 1D-metallic state is assigned at $n > 5$, and the 3D-conduction is assigned at $n > 9$. The mechanism in Rb_n/K_2Rb_7-L is similar but the corresponding values of n is effectively smaller than those in K_n/K_9-L, as clearly indicated in Figure 4. This difference can be explained by the smaller ionization energy of Rb atom.

4. Summary

Rb metal was loaded into Rb-rich zeolite L at various loading densities. Optical and electrical properties vary systematically with n. Observed results are explained by the quantum confinement of s-electrons in 1s, 1p and 1d states of main-channels bundled in zeolite L. Results are compared with those in K_n/K_9-L.

References

[1] Nakano T and Nozue Y 2017 *Adv. Phys. X* **2** 254
[2] Nakano T, Hanh D T, Nozue Y, Nam N H, Duan T C and Araki S 2013 *J. Korean Phys. Soc.* **63** 699
[3] Kelly M J 1995 *J. Phys.: Condens. Matter* **7** 5507
[4] Thi P T, Nakano T, Sakamoto Y, Nozue Y 2016 *J. Phys. Soc. Jpn.* **85** 024703-1
[5] Van den Broek M and Peeters F M 2001 *Physica E* **11** 345
[6] Holstein T, 1959 *Ann. Phys. (Leipzig)* **8** 343 [Reprint **281** (2000) 725-773]
[7] Sumi H 1972 *J. Phys. Soc. Jpn.* **33** 327
[8] Anderson P A, Armstrong A R, Porch A, Edwards P P and Woodall L J 1997 *J. Phys. Chem. B* **101** 9892
[9] Thi P T 2016 *Doctor Thesis* Osaka University