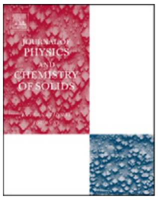
Journal of Physics and Chemistry of Solids 73 (2012) 1538–1541

Contents lists available at SciVerse ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs



Insulating state and metallic phase transition of heavily sodium-doped low-silica X (LSX) zeolites

Yasuo Nozue*, Yusaku Amako, Ryoko Kawano, Takahiro Mizukane, Takehito Nakano

Department of Physics, Graduate School of Science, Osaka University, 1-1 Machikaneyama-cho, Toyonaka, Osaka 560-0043, Japan

ARTICLE INFO

Available online 30 March 2012

Keywords:
A. Microporous materials
A. Nanostructures
D. Electrical conductivity
D. Magnetic properties
D. Phase transitions

ABSTRACT

Electrical resistivity was measured for Na-doped low-silica X (LSX) zeolite at various Na-loading densities. Many s-electrons are introduced into the regular array of zeolite nanocages by the loading of guest Na atoms. The average Na-loading density per unite cage, *n*, was changed from 0 to ≈ 12. Nonmagnetic and insulating properties are observed for $n \lesssim 11$. A drastic decrease in the resistivity is observed at $n \approx 12$, indicating that the insulating phase is changed to metallic one by the addition of less than one Na-atom per unite cage. At the same time, a remarkable increase in paramagnetic susceptibility is observed at room temperature. Insulating states are explained by spin-singlet clusters which are assigned to the self-trapped s-electron pairs (small bipolarons) due to the strong electron–phonon interaction against the Coulomb repulsive interaction between two s-electrons. Pairs of s-electrons occupy successively the quantum states of clusters in zeolite cages with increasing the Na-loading density. The metallic phase transition is explained by the formation of large polarons which are mobile over many cages through the zeolite windows. The increase in the paramagnetic susceptibility is explained by the thermal excitation of small polarons expected in the adiabatic potential.

1. Introduction

Different types of insulating states of materials are known, such as the band insulator, the Mott one, *etc*. In these insulators, the electrical resistivity remarkably decreases depending on the doping density or the deviation from the stoichiometric balance. Carriers in metallic states are usually in the large polaron state because of a rather weak electron–phonon interaction, and mobile over long distance. In some materials, however, electrons themselves make deep potentials by the strong electron–phonon interaction, and are trapped by those potentials, if the deformation potential is deep enough to bind an electron quantum-mechanically. They are called the small polaron, and immobile because of a very heavy mass. This process is called the self-trapping or self-localization [1]. The self-trapped state can be stabilized in case of both the strong electron–phonon interaction and the narrow energy band width. Small bipolarons are generated if the electron–phonon interaction overcomes the electron–electron Coulomb repulsive interaction in the bipolaron state. It is quite interesting to study the electronic properties of materials at heavy doping conditions, from the viewpoint of the competition between the strong electron correlation in the many polaron system and the electron–phonon interaction in the deformable lattice.

Aluminosilicate frameworks of zeolite crystals provide different types of regular array of nanocages, such as the double-diamond structure of β cages and supercages, the CsCl structure of α and β cages and the body centered cubic structure of β cages in zeolites X (or Y), A and sodalite, respectively. Aluminosilicate framework is negatively charged by the number of Al atoms. Exchangeable cations, such as Na^+, are distributing in the space of framework for the charge neutrality. Guest alkali metals can be loaded into these regular nanospace of zeolite crystals and s-electrons are shared with zeolite cations. Bulk alkali metals are of nonmagnetic elements having the simple s-electron system. These s-electrons, however, exhibit exotic magnetisms in zeolite crystals depending on the zeolite structures, alkali metals and the loading density, such as ferromagnetism in A [2–4], ferrimagnetism in X [5] and antiferromagnetism in sodalite [6,7].

Both of zeolites X and Y have the FAU framework structure, as shown in Fig. 1. In the FAU framework, β cages having the inside diameter of ≈ 7 Å are arrayed in the diamond structure by the sharing of double six-rings. Among them, the supercages of FAU with the inside diameter of ≈ 13 Å are formed and arrayed in the diamond structure by the sharing of 12-rings having the inside diameter of ≈ 8 Å. The chemical formula of zeolite X or Y with Na cations (so-called Na-X or Na-Y) is given as $Na_mAl_mSi_{24-m}O_{48}$ ($m \leqq 12$) per unit cage, where X and Y are zeolite names for the

---

* Corresponding author. Tel.: +81 6 6850 5373; fax: +81 668505376.
E-mail address: nozue@phys.sci.osaka-u.ac.jp (Y. Nozue).

0022-3697/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jpcs.2012.03.012

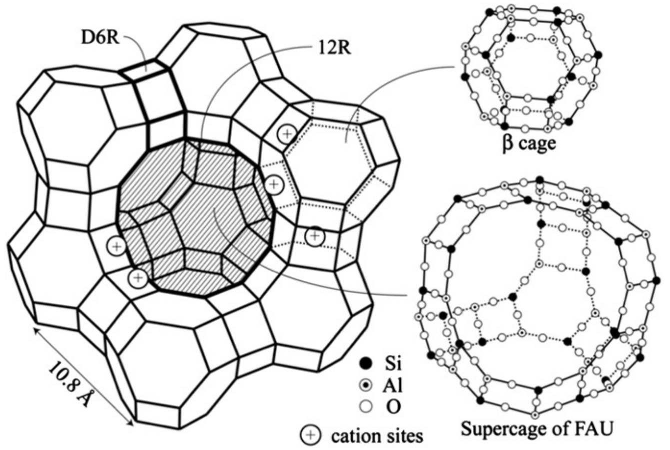


Fig. 1. Schematic illustration of FAU framework and typical cation sites in low-silica X (LSX) zeolite.

Si/Al ratio $(24-m)/m < 1.5$ and >1.5, respectively. Especially, X with Si/Al$=1$ ($m=12$) is called the low-silica X (LSX).

The first evidence of the small polaron state was afforded by the observation of an isolated paramagnetic cluster Na_4^{3+} stabilized in the β cage of zeolite Y, where Na metal is dilutely loaded into dehydrated Na-Y and one 3 s-electron of guest Na atom is shared with four Na cations [8]. With increasing the Na-loading density, the narrowing of the electron spin resonance (ESR) spectrum was observed [9]. This behavior was assigned to the motional narrowing. The theoretical calculation, however, concluded that the electron transfer energy between adjacent β cages through double six-rings is several orders of magnitude smaller than the Coulomb repulsion energy between two electrons in the common β cage, indicating that the system must be in the Mott insulator [10]. The observed ESR narrowing cannot be assigned to the motional narrowing in metallic state but to the exchange narrowing due to the magnetic interaction between clusters in the Mott insulating state. Actually, Na-loaded Na-Y and Na-X show ESR narrowing without metallic phase transition [11]. With increasing the Na-loading density, the stable structure of clusters are expected at supercages theoretically and the continuous electron distribution has been formed through the 12-membered rings [10], indicating that the metallic phase may be realized in NaY. In K-X (Si/Al$=$1.25), K_3^{2+} has been observed at supercage under the dilute loading of K metal [12]. An increase in the infrared absorption was observed with increasing the loading density, about 0.4 potassium atom per supercage, indicating that the metallic phase transition is easily realized in potassium clusters at supercages of K-X [12]. The metallic phase is slightly suppressed in K-LSX (Si/Al$=$1) at low loading densities [13].

In a previous study [14], we loaded nNa atoms into Na-LSX per β cage or supercage ($Na_{12}Al_{12}Si_{12}O_{48}$). The Na-loaded samples are abbreviated hereafter as Na_n/Na_{12}-LSX. At lower loading densities, Na-clusters are stabilized in β cages and show the finite optical gap energy of insulating phases. At higher loading densities, clusters are stabilized in supercages, but they are still insulating. The insulating phase is observed up to $n \approx 11$ in the optical spectra. This is quite strange behavior, because a lot of Na atoms loaded into zeolite do not contribute to the metallic properties. At $n \approx 12$, we have observed a sudden change in the optical reflection spectra. A clear Drude-type reflection appears suddenly in the IR spectral region. This change is assigned to the insulator-to-metal transition.

In the present study, we measured the electrical resistivity and magnetic properties of Na_n/Na_{12}-LSX. With increasing the loading density up to $n \approx 12$, we observed a sudden decrease in the electrical resistivity by several orders of magnitude. At the same time, we observed a sudden increase in the paramagnetic susceptibility around room temperature. The drastic change is assigned to the new type of metallic phase transition in the deformable lattice of the regular nanospace, based on the strong electron–phonon interaction accompanied with the strong electron correlation.

2. Experimental procedures

We used synthetic zeolite powder of Na-LSX checked by the chemical analysis for Si/Al ratio and the X-ray analysis for structural quality and purity. The complete dehydration of zeolite was made by the heating at 500 °C for one day under high vacuum. The complete dehydration was checked by the disappearance of resonant IR absorption of H_2O. Distilled sodium metal was sealed together with dehydrated zeolite powder in glass tube and adsorbed into zeolite powder at 160 °C by the vapor phase as well as the direct contact with the zeolite. The loading of guest Na metal is quite smooth within a zeolite crystal particle. In order to improve the homogeneity of loading density in different zeolite crystals of powder, the heat treatment was made for 2 weeks. Finally, we obtained the homogeneous Na-loading. The average loading density of nNa atoms per unit cage was adjusted by the weight ratio of Na metal and zeolite, and changed from $n=0$ to ≈ 12. The final chemical formula is given as $Na_{12+n}Al_{12}Si_{12}O_{48}$ (abbreviated as Na_n/Na_{12}-LSX). Na metal loaded into zeolites shows optical spectra which are clearly different from that of bulk Na-metal. No residual Na metal was seen in the optical spectrum as well as the image of optical microscope.

For the electrical resistivity measurements, sample powder was put between two gold electrodes, and an adequate compression force ≈ 1 MPa was applied during the measurements. Just after the application of pressure, the resistivity decreases, because of the increase in the contact area between powder particles. The value of electrical resistivity was obtained by multiplying the dimensional factor (area/thickness) of compressed powder. Due to the constriction resistance, the observed electrical resistivity is about one-order of magnitude larger than the true value. The relative value, however, can be compared with each other, because of the constant compression force. Because of the extreme air-sensitivity of sample, sample powder was kept in a handmade airproof cell. These procedures were completed in a glovebox filled with pure He gas containing less than 1 ppm O_2 and H_2O, and then, the cell was set in the sample chamber of Physical Property Measurement System (PPMS, Quantum Design). The sample temperature was controlled between 300 and 2 K. Impedance measurements of the cell were carried out by the 4-terminal measurement with Agilent 4824A LCR meter at the frequency range from 20 Hz to 2 MHz and DC. We analyzed the frequency dependence of complex impedance by the Cole–Cole plot, and checked the reliability of resistivity at $<10^9\ \Omega$ cm. In the present paper, we simply plotted the DC resistivity at $<10^9\ \Omega$ cm. A very small background resistivity is included at the order of $0.1\ \Omega$ cm originating from the electric circuit inside the cell. This contribution can be neglected in the present study, because the background is much smaller than present resistivity. Samples for magnetic measurement were sealed in quartz glass tubes. The DC magnetization was measured by using a SQUID magnetometer (MPMS-XL, Quantum Design) at the temperature range 1.8–300 K.

3. Experimental results

The temperature dependence of electrical resistivity in Na_n/Na_{12}-LSX is plotted for n=7.9, 10.1, 11.3, 11.6 and ≈ 12 in