Metallic State in Rubidium-Loaded Low-Silica X zeolite

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We demonstrate that the metallic nature of rubidium clusters confined and arrayed in the framework of insulating low-silica X zeolite is preserved. The 87Rb NMR spin-lattice relaxation assigned to rubidium clusters shows a Korringa behavior from 190 K down to 10 K, which is compatible with a macroscopic observation of low electrical resistivity. The density of states at the Fermi level is found to be enhanced compared to the sodium case.

Alkali metals at ambient conditions crystallize in body centered cubic structure. They are described as a textbook example of simple metals with nearly-free electron model. In the bulk, the interatomic electron interactions remove the degeneracy of atomic states and form a conduction band, where the density of states (DOS) plays a crucial role in determining the properties of metals. However, for small nanosized particles and atomic clusters of alkali atoms their properties are determined by the statistics of the s-electron-level distribution. Therefore, when alkali clusters are formed in periodic nanospaces, quantum effects become important and new electronic states emerge, such as 1s, 1p and 1d states, which are the solutions of spherical quantum-well model. These states may be also influenced by electron correlations due to Coulomb repulsion and electron-phonon interactions. As a result the pristine metallic nature of alkali clusters can be suppressed.

Zeolites5) with periodic empty voids called cages possess a framework, which is strongly negatively charged and its cages can confine alkali clusters. In sodalite and zeolite A with relatively small cage sizes (∼7 Å and ∼11 Å for β-cage and α-cage, respectively) and small sizes of windows between the adjacent cages (∼3 Å and ∼5 Å), the metallic nature of alkali clusters is strongly suppressed, leading to Mott insulator ground state, where different magnetic transitions were reported5–7). On the contrary, larger cage and window sizes (∼13 Å and ∼8 Å for a supercage) found in low-silica X (LSX) zeolite seem to preserve the metallic nature of alkali clusters when the cages are loaded with sodium. However, the behavior of this sodium loaded LSX zeolite is not fully compatible with a simple metal. Although the Drude term is observed in optical spectra, resistivity remains relatively high, which is typical for bad metals. The 23Na spin-lattice relaxation rate divided by temperature, 1/T1T, shows a Korringa-like temperature independent behavior only at temperatures below 30 K, where a metallic ground state is concluded to exist on a microscopic scale with the small DOS at the Fermi level.10)

To gain a better understanding of how the metallic state of alkali clusters is influenced by the confinement in LSX zeolite, it would be desirable to exchange sodium with heavier alkali atoms. In the framework of the Holstein-Hubbard Hamiltonian (t-U-S-n model), which captures all the essential ingredients of s-electrons of alkali clusters confined in zeolite cages, heavier alkali metals have lower ionization energies resulting in shallower cluster potential. This increases s-electron transfer energy t, reduces the electron-phonon interaction energy S and promotes the metallic state at otherwise comparable values of Coulomb repulsion energy U and electron concentration n.

Here we report the first study of rubidium-loaded LSX zeolite employing complementary macroscopic and microscopic probes, and comparing it to the sodium-loaded LSX. Rb-form low-silica X zeolite (Rb12Al12Si12O48 per supercage), hereafter abbreviated as Rb12-LSX, was obtained by ion exchange method from K-form LSX powder soaked in a RbCl aqueous solution. Rub metal was adsorbed into fully dehydrated Rb12-LSX at a high loading density. The average number of guest Rb atoms per supercage, n ≃ 7.6, was estimated from the weight ratio of the metal to Rb12-LSX. The Rb-loaded sample is abbreviated as Rb9/Rb12-LSX. Similarly, Na-loaded Na-form LSX is abbreviated as Na9/Na12-LSX.11)

The detailed experimental procedure for dc resistivity, ρ(T), measurement is explained elsewhere.11) Optical spectra were measured with conventional optical spectrometer. Frequency-swept nuclear magnetic resonance (NMR) spectra were taken in a magnetic field of 9.4 T corresponding to the 87Rb Larmor frequency of νref = 130.895 MHz, determined with a frequency standard aqueous solution of RbCl. The Fast-Fourier-transform spectra were measured by a solid echo pulse sequence with a pulse length of 2.4 μs. The NMR spectra were taken at the frequency steps of 50 kHz and combined to obtain the full spectrum.

Optical reflectance spectra of Rb7.6/Rb12-LSX (not shown) exhibit clear peaks at ≃ 0.6 and ≃ 2.3 eV. These peaks are attributed to optical excitations of the s-electrons and confirm11) that guest Rb atoms are indeed confined in the supercage network and β-cages, respectively. Fig. 1 shows that ρ(T) of a pressed powder sample of Rb7.6/Rb12-LSX has more than one order of magnitude smaller value compared to Na16.5/Na12-LSX in the whole temperature range. It is important to note that ρ(T) of Na16.5/Na12-LSX does not diverge and stays limited below 5 × 105 Ω cm at 4 K, whereas Na9/Na12-LSX sample

Fig. 1. Temperature dependences of dc electrical resistivity of Rb7.6/Rb12-LSX and Na16.5/Na12-LSX zeolites.

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amples with moderate loading of guest sodium atoms show divergent behavior with orders of magnitude higher resistivity, e.g. for $n = 7.9$ the resistivity is above $10^7 \Omega \text{cm}$ already at room temperature.\(^9\) This is a clear indication of the insulator-to-metal transition in sodium loaded LSX zeolite at large $n$, which got further experimental support from NMR spin-lattice relaxation data.\(^10\) Therefore, based on ρ($T$) it is reasonable to conclude that Rb$_{7.6}$/Rb$_{12}$-LSX also has a metallic ground state. However, the observation of low and almost temperature independent ρ($T$) is reminiscent of bad metal behavior, where several possible transport mechanisms may become relevant, including the scattering by impurities,\(^12\) the variable range hopping,\(^13, 14\) and the thermally activated motion of cations already observed in insulating parent Na-form LSX zeolite.\(^15\)

The $^8$Rb NMR spectrum of Rb$_{7.6}$/Rb$_{12}$-LSX measured at 10 K is shown in Fig. 2(a). It is composed of three components, all of which have characteristic lineshapes and NMR shifts, and also exhibit different temperature dependences of spin-lattice relaxation time $T_1$ displayed in Fig. 2(b). The first component has a characteristic quadrupolarly-perturbed lineshape extending from −1600 ppm to 1600 ppm and its center is not shifted with respect to $ν_{\text{ref}}$. It corresponds to the so-called residual component (RC) previously also observed in the $^{23}$Na NMR study of Na-loaded Na-form LSX.\(^10, 16\) The narrow component at 6400 ppm has an NMR shift corresponding to the metallic rubidium.\(^17\) It is natural to assume that this component originates from the small amount of residual metallic rubidium at the surface of LSX crystals. In this work we assign it as the rubidium component (RbC). The broad component with by far the largest spectral weight, which is at 10 K moderately shifted (2400 ppm), has all the features of the so-called shifted component (SC) previously observed in Na$_{16.5}$/Na$_{12}$-LSX.\(^10, 16\) In the Na-loaded Na-form LSX the SC overlapped with the RC at low temperatures, which prevented the independent measurements of $T_1$ at the position of the Na clusters confined in supercages. This is clearly not a problem in Rb$_{7.6}$/Rb$_{12}$-LSX sample.

In Fig. 2(b) we show $^8$Rb $1/T_1T$ measured at the RC, SC and RbC peak positions. Magnetisation recovery curves were fitted with a stretched exponential model\(^10\) to account for the distribution of $T_1$ due to multiple rubidium sites contributing to RC and SC signals.\(^19\) $1/T_1T$ of the RC shows a strong temperature dependence, which can be attributed to the thermal motion of rubidium cations sitting in the LSX framework as already demonstrated in Na-form LSX.\(^15\) As anticipated for a metallic rubidium, the RbC component shows a Korringa behavior in the whole temperature range. Similarly, the SC shows an almost identical Korringa behavior from 190 K down to 10 K, which is a firm evidence of metallic ground state of rubidium clusters confined in the supercages of Rb$_{7.6}$/Rb$_{12}$-LSX. Compared to Na$_{16.5}$/Na$_{12}$-LSX, the DOS at the Fermi level is estimated\(^10\) to be enhanced by a factor of $\sqrt{8^7 T_1(\text{RbC})/8^7 T_1(\text{SC})} : \sqrt{23 T_1(\text{NaC})/23 T_1(\text{SC})} \sim 2.5$.

In this work, we have investigated the maximally Rb-loaded Rb-form LSX, which has been successfully synthesized for the first time. The resistivity is by an order of magnitude lower compared to the Na case. The $1/T_1T$ of SC is temperature independent in the investigated temperature range, confirming the metallic ground state in Rb$_{7.6}$/Rb$_{12}$-LSX. Whereas the maximally Na-loaded Na-form LSX zeolite shows that the DOS at the Fermi level is rather small compared to bulk sodium, the maximally Rb-loaded Rb-form LSX has a value comparable to bulk rubidium. This corroborates with the $t$-$U$-$S$-$n$ model, which predicts that the metallic ground state becomes more stable for zeolites with heavier alkali clusters.\(^3\)

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