Electrons of alkali metals in regular nanospaces of zeolites

Takehito Nakano and Yasuo Nozue
Graduate School of Science, Department of Physics, Osaka University, Toyonaka, Japan

ABSTRACT
The s-electrons of alkali metals loaded into regular nanospaces (nanocages) of zeolite crystals display novel electronic properties, such as a ferrimagnetism, a ferromagnetism, an antiferromagnetism, an insulator-to-metal transition, etc., depending on the kind of alkali metals, their loading density, and the structure type of zeolite frameworks. These properties are entirely different from those in bulk alkali metals of free-electrons. Alkali-metal clusters are stabilized in cages of zeolites, and new quantum states of s-electrons, such as 1s, 1p, and 1d states in the spherical quantum-well model, are formed. An electron correlation, a polaron effect, and an orbital degeneracy in the quantum states of s-electrons play critical roles in taking on the novel electronic properties. Electronic properties can be overviewed systematically by a coarse-grained model of localized s-electron states in cages based on the tight-binding approximation, followed by the t-U-S-n diagram of the correlated polaron system given by the so-called Holstein–Hubbard Hamiltonian: an electron transfer energy through windows of cages (t), a Coulomb repulsion energy between two s-electrons in the same cage (U), a short-range electron-phonon interaction energy due to the cation displacements (S), and an average number of s-electrons per cage (n). Beyond the jellium background model of alkali-metal clusters, a huge spin-orbit interaction has been observed in the 1p degenerate orbitals of clusters, similarly to the Rashba mechanism.

ARTICLE HISTORY
Received 14 December 2015
Accepted 3 January 2017

KEYWORDS
Nano clusters; alkali metals; ferromagnetism; insulator-to-metal transition; spin-orbit interaction; zeolites

PACS
73.22.-f Electronic structure of nanoscale materials and related systems; 75.75.-c magnetic properties of nanostructures; 71.38.-k polarons and electron-phonon interactions; 71.30.+h metal-insulator transitions and other electronic transitions

CONTACT
Yasuo Nozue nozue@phys.sci.osaka-u.ac.jp

© 2017 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group. This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
1. Introduction

Alkali metals loaded into regular nanospaces (nanocages) of zeolite crystals acquire novel electronic properties which are significantly different from those observed in the bulk form of alkali metals. Alkali metals in bulk form are well-known as simple metals consisting of free electrons. New quantum states of \( s \)-electrons are created in zeolite cages. These \( s \)-electrons can be transferred to adjacent cages through windows. These \( s \)-electrons have effects of different interactions, such as an electron correlation by the Coulomb repulsion between them and a deformation by an electron-phonon interaction, etc. The loading of alkali metals into zeolites are ideal for the material design, because the wide range control of electron density is available without the change of the basic structure of regular nanospaces. The \( s \)-electron density can be increased up to about ten per cage. Electronic interactions play essential roles in novel properties of \( s \)-electrons, such as a ferrimagnetism, a ferromagnetism, an antiferromagnetism, an insulator-to-metal transition (IMT), etc. A new paradigm of electronic system can be provided by the alkali-metal loading into zeolites. Up to now, comprehensive researches have been carried out [1–53], especially on magnetic properties [1,2,9,11,13–18,23–31,34–37,39,41,43–46,48,50,51], optical properties [1,3,7,24,38,49,53], electrical properties [42,43,49,50,52,53], structural analyses [8,12,22,47] and theoretical calculations [4–6,10,19–21,32,33,40]. These materials are consisting of abundant elements, such as O, Si, Al, Na, K, but possess new exotic properties not found in the elements themselves. Recently, this kind of nanostructured hybrid materials have attracted much attention as new functional materials of a ubiquitous element strategy [54].

In original aluminosilicate zeolites, many alkali cations (positive ions) are distributed in the nanospaces inside the negatively charged framework. Regular free nanospaces can be provided for guest alkali metals by the complete dehydration of zeolites without structural change of framework, because of the stable aluminosilicate frameworks of zeolites. The \( s \)-electrons of guest alkali atoms are shared with zeolite cations, and are repelled by the framework. Cation-rich clusters with common \( s \)-electrons are stabilized in cages. The electronic potential of alkali cations is so shallow that the jellium background model [55] which ignores the local potential of cations is applicable to the quantum confinement of \( s \)-electrons as the simplest model. The transfer of \( s \)-electrons to adjoining cages occurs through the windows.

In Figure 1(a), a schematic image is illustrated for the \( s \)-electron wave function of the 1s quantum state (a large blue sphere) confined in an \( \alpha \)-cage (or \( \alpha \)-cavity) of aluminosilicate zeolite with \( M \)-cations, where the effective inside diameter is \( \approx 11 \) Å. As stated later in Figure 9(a) of Section 5, \( \alpha \)-cages appear in zeolite A which has the framework structure type of LTA (IUPAC nomenclature [56]). \( \alpha \)-cages are arrayed in a simple cubic structure by the sharing of eight-membered rings (8Rs) in zeolite A. The chemical formula of zeolite A with monovalent
Figure 1. Schematic illustrations of (a) the s-electron wave function (a large blue sphere for the 1s quantum state) confined in an α-cage of aluminosilicate zeolite with M cations, and (b) 1s, 1p, and 1d quantum states in the spherical quantum-well with a diameter ≈11 Å at a finite confinement potential. Numbers in parentheses indicate degeneracies including spins.

M-cations is given by $M_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$ per α-cage. The framework is negatively charged by the number of Al atoms. For the charge neutrality, $12M$ cations per α-cage are distributed in the spaces of framework. The effective confinement size for s-electrons is basically given by that of the α-cage, $≈11$ Å [3,24]. As the interior of α-cage is nearly spherical, a confinement of an s-electron is simplified by a free electron in the spherical quantum-well potential. The respective kinetic energies of the 1s, 1p and 1d states in the infinite spherical potential are given by

$$
\frac{\hbar^2}{2m_0} \left( \frac{\pi}{a} \right)^2, \quad \frac{\hbar^2}{2m_0} \left( \frac{4.493}{a} \right)^2, \quad \frac{\hbar^2}{2m_0} \left( \frac{5.763}{a} \right)^2,
$$

(1)

where $m_0$ and $a$ are the mass of the electron and the radius of the spherical potential, respectively. In the real system, the confinement potential $V_0$ is finite. In order to find the bound state for the 1s state, for example, $V_0$ must satisfy the condition

$$
V_0 > \frac{\hbar^2}{8m_0} \left( \frac{\pi}{a} \right)^2.
$$

(2)

In Figure 1(b), a schematic illustration is given for some lower quantum states of spherical-well potential with a diameter $2a ≈ 11$ Å. Numbers in parentheses indicate degeneracies including spin. Optical excitations from 1s to 1p and from 1p to 1d quantum states have been observed [3]. Successive occupations of s-electrons at 1s and 1p quantum states configure a shell model of clusters with the increase in the number of guest alkali atoms, where the first two and the next six s-electrons are for 1s and 1p states, respectively. s-electrons of clusters in adjoining α-cages have mutual interaction through 8Rs as well as within a cluster. These aspects of alkali-metal clusters in zeolites are compared to superatoms [19,20,44] with the electronic shell structure of metal clusters [57] and their regular arrays to cluster crystals [1,26,58]. New promising material designs have been proposed based on the regular nanostructures of porous crystals.
Differently from ordinary materials, the s-electron wave function is distributed not only near alkali cations but also at the free space of the cage center where no cation is distributed. This leads to a low atomic character of cluster [59], where the s-electron wave function consists of orbital at the free central space of cage as well as atomic s-orbitals near respective alkali cations. The decrease in the hyperfine splitting of electron spin resonance spectrum has been observed in Na$_4^{+4}$ paramagnetic clusters stabilized in $\beta$-cages of zeolite Y (the framework structure type of FAU), and the mechanism is assigned to the low atomic character [59].

In channel type zeolites, the one-dimensional wave functions can be expected for s-electrons, such as potassium metals in the bundle of cylindrical channels of zeolite L (the framework structure type of LTL) [4,8,53]. Other guest materials are also loaded into porous materials. Quantum liquids of $^4$He [60–64] and $^3$He [65] are introduced into porous materials, and novel properties of superfluidity have been observed. Clusters of semiconducting materials and other metal elements, such as Se, PbI$_2$, HgI$_2$, BiI$_3$, InP, etc., are also incorporated into zeolites and mesoporous materials, and novel properties related to the quantum confinement of electrons in nanoscale have been observed [58,66–69]. The more than two-hundred types of framework structures in zeolite crystals are know up to now [56]. Zeolites are widely used as microporous (nanoporous) crystals for industrial applications [70,71].

In the present review article, we will systematically overview the properties of alkali metals loaded into typical zeolites based on the following t-U-S-n diagram with the coarse-grained model of localized s-electron states in these materials.

### 2. t-U-S-n diagram

Generally, electrons have an interaction with phonons and form polarons. The polaron effect plays an important role in solids [72,73]. Long- and short-range electron-phonon interactions are provided, respectively, by the Fröhlich interaction with optical phonons and the deformation potential interaction with acoustic phonons. According to the theory of electron self-trapping in the deformable lattice, unbound large polaron (free) and self-trapped small polaron (immobile) states are formed separately, and they have a barrier in the adiabatic potential [74]. The discontinuity between large and small polaron ground states can occur with the increase in the deformation potential interaction, not by the increase in the Fröhlich interaction [74–76]. The system in which small polarons are stabilized by the short-range interaction becomes insulating [77,78]. At intermediate electron-densities, large and small polarons coexist in the metallic state near the boundary between metallic and insulating regions [79]. If the deformation potential interaction is large enough to bind two polarons against the Coulomb repulsion between them, small bipolarons with a very heavy mass are stabilized in the singlet state [80].
The tight-binding approximation can be applied to $s$-electrons of alkali-metals loaded into zeolites, when $s$-electrons are well-localized in cages with narrow windows. A narrow energy band of $s$-electrons with a strong electron correlation is expected [19,20]. Theoretical models based on the tight-binding approximation can deal with an electron correlation and an electron-phonon interaction [81–84]. Taking an overview of the electronic properties of alkali-metals loaded into zeolites, it is effective to introduce simplified coarse-grained parameters. A transfer energy $t$ of $s$-electron is introduced for the overlapping of wave function between nearest-neighbor cages through windows. Two $s$-electrons in the same cage have a Coulomb repulsion energy $U$ (the Hubbard $U$). The lattice relaxation energy by the short-range electron-phonon interaction $S$ is provided by the on-site interaction between $s$-electron and cation-displacement in a cage (the Holstein model [85]). The Hamiltonian of the correlated polaron system with $t$, $U$ and $S$ is given by the so-called Holstein–Hubbard Hamiltonian [84,86]

$$
H = -\sum_{i,j,\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} + U \sum_i n_i^\uparrow n_i^\downarrow + \sum_i \left( \frac{p_i^2}{2m} + \frac{1}{2} m \omega_i^2 Q_i^2 \right) - \lambda \sum_i Q_i \left( n_i^\uparrow + n_i^\downarrow \right),
$$

(3)

where $a_{i\sigma}$ ($a_{i\sigma}^\dagger$) is the annihilation (creation) operator of the electron with the spin $\sigma$ at the $i$th site, and $n_{i\sigma} = a_{i\sigma}^\dagger a_{i\sigma}$. $t_{ij}$ is the electron transfer energy between the $i$th and the $j$th sites. The localized phonons (Einstein phonons) with the mass $m$ and the frequency $\omega$ are assumed in the third term. $Q_i$ and $P_i$ are the lattice distortion and the conjugated momentum at the $i$th site, respectively. In the last term, the on-site electron-phonon interaction is introduced by the assumption of the site diagonal coupling constant $\lambda$. Here, we define the lattice relaxation energy $S$ as [84]

$$
S = \frac{\lambda^2}{m \omega^2}.
$$

(4)

If we consider the electron transfer between the nearest neighbor sites $\langle i, j \rangle$ only, the first term of the right-hand side of Equation (3) can be written as

$$
-t \sum_{\langle i,j \rangle, \sigma} a_{i\sigma}^\dagger a_{j\sigma}.
$$

(5)

If we assume one electron system, we consider the problem of the large polaron continuum in the energy band and a small polaron localized at a site [77], as shown in Figure 2. The large polaron has many parabolic curves as a function of the lattice distortion $Q$ for different wave vectors in the Brillouin zone, and form the continuum state with the energy band width $2B$. If $B < S/2$, a small polaron will be stabilized, as shown by the adiabatic potential curve in the figure.
Figure 2. Schematic illustration of the large polaron continuum with the band width $2B$ and a small polaron for the case $B < S/2$ as a function of the lattice distortion $Q$. Note: An adiabatic potential curve is drawn for a small polaron and the lowest state of a large polaron.

Figure 3. Schematic illustrations of the Holstein–Hubbard model. Notes: (a) The nearest neighbor electron transfer energy $-t$, the Coulomb repulsion energy $U$ between two electrons in the same site, the energy of small polaron $-S/2$ and that of small bipolaron $U - 2S$ are illustrated, where the one-electron quantum state is assumed in respective sites. (b) The diagram of $t-U-S$ triangle is symbolically illustrated at the average electron concentration per site, $n$.

As schematically shown in Figure 3(a), the electron has the energy $-t$ by the transfer to the nearest neighbor site with the same energy and the same phase. If we assume the transfer between nearest neighbor sites only, $B$ is given by $zt$, where $z$ is the number of nearest neighbor sites. The electron with the successive transfer into all sites with the same phase (namely at the $\Gamma$ point of the Brillouin zone) has the energy $-B$. The electron with the successive transfer into all sites with the alternate phases (namely at the Brillouin zone boundary) has the energy $B$. The delocalized electron has a very weak lattice distortion, and becomes a large polaron which is mobile over many sites. If an electron is localized completely at one site as a small polaron, it has the energy $-S/2$ by the interaction with the local phonons. If we assume many electrons, they have mutual interactions. Two electrons in the same site has the Coulomb repulsion energy $U$. If two electrons are localized completely at the same site as a small bipolaron, they have the total energy $U - 2S$ by the interaction with the local phonons. The energy of a small bipolaron is $U - S$ higher than that of two independent small polarons.
This means that small polarons are stable at $U > S$ and $B < S/2$, namely at $2B < S < U$.

The stable electronic phase can be illustrated on the $t$-$U$-$S$ triangle [81–84] depending on the average electron concentration per site, $n$, as shown symbolically in Figure 3(b). The fruitful phase diagram of the $t$-$U$-$S$-$n$ system has been calculated in the mean field theory [84]. If $U > S$ and $B < S/2$ (the lower-left area of the $t$-$U$-$S$ triangle in Figure 3(b)), each electron will be self-trapped at each site for $n \leq 1$ as the small polaron (magnetic). If $U < S$ and $2B < 2S − U$ (the lower-right area of the $t$-$U$-$S$ triangle), small bipolarons (non-magnetic) are stable. If $U > 2B$ at $S = 0$ (the lower-left side of the $t$-$U$-$S$ triangle), the system has a finite Hubbard gap at the just half-filled condition ($n = 1$) and becomes a Mott insulator (magnetic), because of the avoidance of Coulomb repulsion energy $U$. If $U > 2B$ and $U > S > 0$, a magnetic insulator phase appears not only at $n = 1$, because the additional gain of the electron-phonon interaction ($S/2$) stabilizes the localized magnetic states. This means that the Mott insulator phase is robust against the deviation from the just half-filled condition in the presence of the finite electron-phonon interaction. Fruitful results at $U \approx S$ with rather small $t$ (the lower-central area of the $t$-$U$-$S$ triangle) have been expected near the half-filled condition [81–83], and more reliable calculations have been given by the dynamical mean-field theory [72,73,87–92]. Large bipolarons at $U \approx S$ may play an important role in superconductivities [72,73,87–90,92].

In the present materials, however, real situations are not so simple. In dehydrated zeolites without the loading of alkali metals, many alkali cations are distributed at preferred sites near the negatively-charged framework, under keeping finite distances between cations. With the loading of guest alkali atoms, $s$-electrons are introduced into the space of zeolite, and are shared with cations for the formation of clusters. These $s$-electrons are repulsed from the framework, because the energy of unoccupied states of negatively-charged framework is very high. The framework of zeolites is very hard and stable, because of the strong covalent bond. Cations, however, can move easily in the space of framework. The quantum confinement of $s$-electrons is provided by the repulsive force of the framework of cages and the attractive force of cations, where the cages have windows shared with adjoining cages. The confinement in cages with windows is somewhat different from the muffin-tin spherical potential used in the augmented plane wave method of the energy band calculation, where spheres of the muffin-tin potential have no overlap. The localized nature of $s$-electrons leads to a strong electron correlation and also the interaction with the displacements of cations, the latter of which forms polarons. On the whole, the correlated polaron system will be formed. When we look at the system in detail, however, we can add many extensions in cation displacements, confinement potentials, etc. In some quantum states, such as the 1p state, the orbital degeneracy may have an important contribution to the magnetism. In some zeolites, two or more types of cages are nested. In the cases of wide windows and/or shallow confinement
potential, it may exceed the limitation of the tight-binding approximation. Nevertheless, we overview the properties of the present materials based on the $t-U-S-n$ model for the simplicity.

The $s$-electron transfer energy $t$ between zeolite cages depends on the following effective parameters: (a) the potential depth of $s$-electron in cage, (b) the kinetic energy of $s$-electron with the quantum confinement, (c) the framework potential at windows between cages. They depend on the kind of alkali metals, the cation configurations, the interior sizes of cages, the interior sizes of windows, the framework structures, the loading densities, etc. The effective value of $U$ is inversely proportional to the size of the cluster (cage), and is not so small compared with values in atoms because the Coulomb repulsion operates at long range. For example, the unscreened Coulomb repulsion energy between two electrons in the 1s quantum state of the spherical-well potential with a radius $a$, $U_{1s}$, is given by [93,94]

$$U_{1s} = 1.786 \frac{e^2}{a}. \quad (6)$$

This value becomes 5.1 eV at $a = 5 \, \text{Å}$. The value of $t$ becomes large for wide windows, because of the larger overlapping through wider windows, where the inside diameters of 6R, 8R, and 12R are roughly estimated to be 3, 5, and 8 \, \text{Å}, respectively. The four-membered ring (4R) has effectively no space for the $s$-electron overlapping. The value of $t$ becomes large for heavier alkali metals, because the shallower cluster potential is provided by the low ionization energy of heavy atoms, where the ionization energies of Na, K, Rb, and Cs atoms are 5.14, 4.34, 4.18, and 3.87 eV, respectively. The value of $S$ becomes small for heavier alkali atoms, because of smaller ionization energies (namely shallower electronic potentials). As a large $t$ and a small $S$ contribute to the stability of metallic phase, a metallic phase is expected in heavier alkali metals.

The average $s$-electron density per cage, $n$, can be controlled by the loading density of alkali atoms up to about ten in large cages. This is because there is a large loading capacity for guest materials, where about half volume of zeolite crystals is empty. Pressure loading is also available for further loading [28,39]. With the increase in the loading density of alkali atoms, the number of cations increases as well as the number of $s$-electrons. The increase in the number of cations deepens the electronic potential of cluster and the lowest 1s quantum state has a deeper energy. The energy of the highest occupied quantum state, however, increases with the increase in the number of $s$-electrons. Qualitatively, the effective value of $t$ for the highest occupied state increases with $n$, and a metallic phase appears with the increase in $n$. Overall, a rich diversity of electronic properties in alkali metals loaded into different framework structure types of zeolites is expected in the diagram of $t-U-S-n$.

An $s$-electron at a quantum state with the orbital degeneracy, such as the 1p state for $n > 2$, can have an orbital angular momentum. They can have a strong spin–orbit interaction (SOI) in the presence of many cations within the 1p wave
function, even though original atomic orbitals are mainly \( s \)-like [26], as discussed later in Section 5. This effect is neglected in the jellium model [55], but is quite large because of the asymmetric potential at cation sites, similarly to the Rashba effect [98,99]. The SOI leads to novel magnetic properties.

In the case of large windows, we start from the extended \( s \)-electron wave functions not based on the tight-binding approximation. A typical case is the one-dimensional electrons in the cylindrical potential at the main-channel of zeolite L [4,53]. The tight-binding approximation is applied to the inter-channel electron transfer among the bundle of main-channels.

3. Ferrimagnetism and ferromagnetism in Na-K alloy system in zeolite LSX

In Figure 4(a), a framework structure of zeolite low-silica X (LSX) is illustrated together with typical sites of exchangeable cation \( M \). The framework structure type of zeolite LSX is FAU (IUPAC nomenclature). The chemical formula of zeolite LSX with monovalent cation \( M \) is given by \( M_{12}Al_{12}Si_{12}O_{48} \) per \( \beta \)-cage (or supercage). This zeolite is abbreviated as \( M_{12}\)-LSX in the present paper. \( M_{12}\)-LSX loaded with \( nM \) alkali atoms is described by \( M_n/M_{12}\)-LSX. The average number of \( s \)-electrons is \( n \) per \( \beta \)-cage (or supercage). In order to acquire an intuitive understanding of electronic properties of alkali-metal loaded zeolite LSX, coarse-grained images of framework polyhedra and spheres of \( s \)-electron wave functions of clusters in cages are illustrated in Figure 4(b). Each \( \beta \)-cage is connected to four neighboring \( \beta \)-cages by the sharing of hexagonal prisms (double 6-rings, D6Rs), and arrayed in a diamond structure. The inside diameter of \( \beta \)-cage is \( \approx 7 \) Å. Among \( \beta \)-cages, supercages (cavities) with the inside diameter of \( \approx 13 \) Å appear, and are arrayed in a diamond structure by the sharing of twelve-membered rings (12Rs). The inside diameter of 12R, \( \approx 8 \) Å, is so large that a large \( t \) system can be expected in the supercage network of zeolite LSX. Each supercage shares 6-membered rings (6Rs) with four adjacent \( \beta \)-cages, and \textit{vice versa}. A finite interaction is expected between supercage clusters and \( \beta \)-cage clusters. The direct interaction between \( \beta \)-cage clusters is scarcely expected, because of the long separation by D6Rs.

Na-K alloy clusters can be generated by the loading of guest \( nK \) atoms into \( \text{Na}_x\text{K}_{12−x}\)-LSX in which \( x\text{Na} \) and \( (12−x)\text{K} \) cations are contained per \( \beta \)-cage (or supercage). One of the most striking results in this system is the Néel’s N-type ferrimagnetism at \( x = 4 \) for \( 6.7 \leq n \leq 8 \) [23,37,44]. A typical temperature dependence of spontaneous magnetization at \( n = 7.8 \) is shown by red curve in Figure 5(a). A magnetization increases below the Curie temperature \( \approx 16 \) K, and has a zero-minimum at \( \approx 5 \) K under the low magnetic field of 10 Oe. Generally, the N-type ferrimagnetism is explained by the antiferromagnetic (AF) interaction between two non-equivalent magnetic sub-lattices, one of which has a very weak intra-sublattice interaction and a large saturated magnetization. A rough simulation of the Néel’s N-type ferrimagnetism is shown in Figure 5(b). With the
Figure 4. Schematic illustrations of (a) framework structure of zeolite low-silica X (LSX) and M cations, and (b) coarse-grained images of framework polyhedra and spheres of s-electrons of clusters in cages for alkali-metal loaded zeolite LSX.

decrease in the temperature just below the Curie temperature, a magnetization $M_1$ with a strong intra-sublattice interaction grows, and a magnetization $-M_2$ without an intra-sublattice interaction grows behind $M_1$ by the AF interaction. At the compensation temperature $T\text{\textsubscript{comp}}$, the absolute value of the total magnetization of two magnetic sublattices has a zero-minimum as $|M_1 - M_2| = 0$. The sign of magnetization is always positive, because of a very weak coercivity. A model of magnetic sublattices in $K_n/Na_4K_8$-LSX is given by the double diamond structure of supercages and $\beta$-cages, where localized magnetic moments at $\beta$-cages do not have a mutual interaction directly because of the large separation by D6Rs as illustrated in Figure 4(b). The s-electrons in supercage clusters form sp$^3$-orbitals by the hybridization of 1s and 1p states in the T$_d$ symmetry. They have a large overlapping with those in the nearest neighbor supercages through large 12R windows. They form a ferromagnetic narrow energy band of the diamond structure at low temperatures, and construct a magnetic sub-lattice $M_1$ in Figure 5(b). Each $\beta$-cage cluster has an AF interaction with four adjacent supercage clusters through 6Rs. The magnetization of the magnetic sub-lattice of $\beta$-cage clusters, $M_2$, grows with the decrease in temperature and exceeds $M_1$ below $T\text{\textsubscript{comp}}$.

The ferrimagnetic electronic state at low temperatures is schematically illustrated in Figure 6(a). Itinerant s-electrons below the Fermi energy $E_F$ at the narrow energy band of the supercage network have an AF interaction with s-electrons at $\beta$-cages. A singly occupied s-electron at $\beta$-cage has the energy $E_F - \Delta E - S/2$, where $E_F - \Delta E$ is the energy of an s-electron at $\beta$-cage without the lattice relaxation, and $S/2$ is the lattice relaxation energy at $\beta$-cage. The energy of the second s-electron at the $\beta$-cage increases by $U - S$ and becomes $E_F - \Delta E + U - 3S/2$, where $U$ is the Coulomb repulsion energy between two s-electrons at the same $\beta$-cage. The total energy of two s-electrons at the $\beta$-cage is $2E_F - 2\Delta E + U - 2S$. The value of $U$ at $\beta$-cage is so large that the energy of second s-electron can be higher than $E_F$, namely $E_F - \Delta E + U - 3S/2 > E_F$. In this
configuration, major spins of supercage $s$-electrons can have an AF interaction with $s$-electrons at $\beta$-cages. A small gap in the density of states (DOS) is expected at the Fermi energy at low temperatures, if the AF interaction is large enough to stabilize the ferromagnetic state of narrow band at supercages, as stated later. For the stability of an itinerant-electron ferromagnetism, a model of flat-band ferromagnetism [100,101] is quite suggestive. The degeneracy of sp$^3$-orbitals of supercage clusters may contribute to the stability of ferromagnetic sublattice as well, because a Hund’s rule coupling favors an itinerant-electron ferromagnetism [102].

In the present Na-K alloy system, Na cations are preferably distributed at $\beta$-cages because an attractive interaction of Na cations with the negatively charged framework is stronger than that of K cations, and Na-rich clusters are generated there. By the control of $x$, the potential balance between $\beta$-cage and supercage can be changed, where Na-rich clusters have a deeper electronic potential. A systematic $x$-dependence in magnetic properties have been observed for $0 \leq x \leq 4$ [37].

In pure K-system at $x = 0$ (namely $K_n/K_{12}$-LSX), a ferrimagnetism has been observed at higher K-loading densities ($n \approx 9$) [37], and a typical temperature dependence of magnetization is shown for $n = 8.9$ by green curve in Figure 5(a). The Curie and Weiss temperatures are 3.5 and $-12$ K, respectively. Differently from the Néel’s N-type ferrimagnetism at $x = 4$, there appears no zero-minimum at $x = 0$, because $M_2$ shown in Figure 5(b) may be smaller than $M_1$ at any temperatures. A negative Weiss temperature indicates an existence of the AF interaction between two magnetic sub-lattices of supercages and $\beta$-cages. The IMT has been observed at $n \approx 6$, and metallic low resistivities have been observed at $n \geq 6$ at higher temperatures, as shown in Figure 6(b) [43]. Resistivities
Figure 6. (a) A schematic representation of ferrimagnetic state of s-electrons in zeolite LSX at low temperatures. Electrons in the ferromagnetic narrow energy band of supercage network have an antiferromagnetic (AF) interaction with singly-occupied localized electrons at β-cages. A singly-occupied s-electron in β-cage has the energy $E_F - \Delta E - S/2$, where $E_F - \Delta E$ is the energy of an s-electron at β-cage without the lattice relaxation, and $S/2$ is the lattice relaxation energy at β-cage. The energy of the second s-electron at the β-cage increases by $U - S$ and becomes $E_F - \Delta E + U - 3S/2$, where $U$ is the Coulomb repulsion energy between two s-electrons at the β-cage. See text in detail. (b) Temperature dependences of electrical resistivity in $K_n/K_{12}$-LSX for $n = 6.0, 6.2, 8.4$ and $9.0$. Resistivity decreases remarkably with $n$ at higher temperatures ($\gtrsim 50$ K), but increases with $n$ at low temperatures for ferrimagnetic samples at $n = 8.4$ and 9.0.

at higher temperatures ($\gtrsim 50$ K) decrease remarkably with $n$. A remarkable increase in the resistivity, however, is seen with the decrease in temperature for ferrimagnetic samples at $n = 8.4$ and 9.0. The increase in the resistivity at low temperatures is assigned to the decrease in the DOS at the Fermi energy based on the model shown in Figure 6(a). This increase is likely as a Kondo insulator, because of the correlation interaction between itinerant electrons in supercage network and localized electrons at β-cages [43]. The metallic band of supercage network, however, is narrow and ferromagnetic, and this situation is different from the ordinary Kondo insulator [103].

At much higher values of $x$ ($x > 4$), some Na cations are distributed in supercages as well as β-cages. In Na-rich system at $x = 7.3$ (namely $K_n/Na_{7.3}K_{4.7}$-LSX), nearly pure ferromagnetism has been observed at $8.4 < n < 9.7$ [50]. A typical result at $n = 8.9$ is shown by blue curve in Figure 5(a). A spontaneous magnetization increases below the Curie temperature $\approx 11$ K. The Weiss temperature is almost same as the Curie temperature, indicating that the ferromagnetic interaction is dominant. An electrical resistivity is basically insulating at any values of $n$. A clear coincidence has been observed between the growth of localized magnetic moments and the appearance of new optical reflection band of β-cage clusters at $n > 8$, indicating that the origin of magnetic moments are β-cage clusters. The direct magnetic interaction between β-cage clusters, however, is impossible (bipartite lattice), because of the large separation by D6Rs, as shown in Figure 4(b). A ferromagnetic superexchange coupling between


\[266\]

\[T.NAKANOANDY.NOZUE\]

Figure 7. Temperature dependences of (a) magnetic susceptibility \[42\] and (b) \(^{23}\)Na-NMR spectra \[46\] in \(\text{Na}_{n}/\text{Na}_{12}\)-LSX at \(n = 10\) and \(\approx 16\). (c) Illustration of average distributions of Na cations in \(\text{Na}_{n}/\text{Na}_{12}\)-LSX at \(n = 9.4\) and 16.7 extracted from the data in \[47\]. The radius of each Na atom is drawn in proportion to the square root of the site occupancy. The aluminosilicate framework is simplified by connected grey lines. See text in detail.

\[\beta\]-cage clusters is proposed via the sp\(^3\)-like closed-shell clusters at supercages \[50\]. The superexchange coupling between magnetic ions via ligand oxygen orbitals is known to be essential in the magnetism of transition metal oxides. According to the Goodenough-Kanamori-Anderson rules \[104–107\], no kinetic exchange interaction takes place, if \(d\)-electrons hybridize with orthogonalized \(p\)-orbitals of oxygen at the 90° bonding. In this case, the potential exchange interaction gives rise to a ferromagnetic interaction \[107\]. A similar ferromagnetic superexchange interaction can be assumed between \(\beta\)-cage clusters via the 109.5° orthogonalized sp\(^3\) orbitals with the \(T_d\) symmetry of supercage clusters in the ferromagnetism of \(\text{K}_{n}/\text{Na}_{7.3}\text{K}_{4.7}\)-LSX. A similar electron correlation in the sp\(^3\) hybridized state has been calculated in CH\(_4\) molecule \[108,109\].
4. IMT and thermally excited paramagnetism in Na-loaded zeolite LSX

In $\text{Na}_n/\text{Na}_{12}$-LSX, insulating and non-magnetic states have been observed at $n \lesssim 11$. A sudden change to the metallic state, however, has been observed in the optical reflection spectra with the increase in $n$, and a Drude-type optical reflection spectrum has been observed at IR-region for $n \approx 16$ [38] (the value $n \approx 12$ in [38] is revised here). A paramagnetic susceptibility is found to increase with temperature at $n \approx 16$, as shown in Figure 7(a), where the temperature-independent susceptibility $\chi_0$ is subtracted [42]. An increase below $\approx 50$ K is caused by impurity spins ($\approx 1\%$ of supercages). In an insulating phase at $n = 10$, no increase in susceptibility is observed at higher temperatures. The value of $\chi_0$ for $n \approx 16$ involves a spin susceptibility of $\approx 3 \times 10^{-6}$ emu/cm$^3$ which corresponds to the Pauli paramagnetism of free electrons. An increase of paramagnetic susceptibility at room temperature amounts to $3 \times 10^{-7}$ emu/cm$^3$ for $n \approx 16$. This large value is comparable to the distribution of spin-$1/2$ paramagnetic moments at $\approx 30\%$ of supercages. The thermally excited paramagnetic susceptibility has also been observed in the shift of $^{23}\text{Na}$ NMR spectra [46], as shown in Figure 7(b). A shifted component (SC) is clearly seen at higher temperatures at $n \approx 16$ (the value $n \approx 12$ in [46] is revised here). With the decrease in temperature, the SC peak has a decrease in the NMR shift and an increase in the spectral width. A spin-lattice relaxation rate $T_1^{-1}$ resembles the Bloembergen-Purcell-Pound (BPP)-type mechanism [111] with the activation energy $\approx 0.11$ eV. A structure analysis of $\text{Na}_n/\text{Na}_{12}$-LSX has been performed at $n = 9.4$ and $16.7$ [47]. Average distributions of Na cations are illustrated in Figure 7(c), where the radius of each atom is drawn in proportion to the square root of the site occupancy, namely a cross section of each Na sphere is graphically proportional to the site occupancy. The aluminosilicate framework is simplified by connected grey lines. Cation sites are classified to three types: near framework (light blue), inside supercage (red) and at center of 12R-window (yellow). At $n = 9.4$, most of the Na cations are distributed near the framework, and their site-occupancies are almost unity. At $n = 16.7$, occupancies of Na sites increase inside supercages and at the centers of 12R-windows. The temperature dependence of electrical resistivity is measured at various values of $n$ [42], and revised $n$-dependences at 300 and 200 K are indicated in Figure 8(a). The resistivity suddenly decreases with $n$ around $n \approx 11.5$ by several orders of magnitude, and a metallic phase has been observed at $n \approx 12$ in accordance with the optical spectra in [38].

According to above results, Na cations inside supercages and those at the centers of 12R-windows in Figure 7(c) are assigned to the main origin of metallic phase. There are many Na cation sites which contribute to metallic phase. In the case of static distribution of Na cations, many NMR peaks must appear. In $^{23}\text{Na}$-NMR spectra in Figure 7(b), however, observed SC is a single line. This result indicates that Na cations are hopping thermally over many Na sites at
higher temperatures during the NMR time window of 106 MHz, and nuclei of relevant Na cations feel average paramagnetic field. With the decrease in temperature, the hopping is put down, and nuclei feel inhomogeneous field as well as the decrease in the paramagnetic field. Recently, a Korringa-like behavior has been observed in metallic samples at low temperatures in NMR signal [52].

In order to explain both the IMT with the increase in \(n\) and the thermal excitation of paramagnetic susceptibility in metallic samples, a polaron model is introduced [42]. Electronic states of small polarons and bipolarons are strongly dependent on local structures of real materials. In the present materials, the aluminosilicate framework is very hard but the locations of alkali cations are very soft. A small polaron can be formed in cage as the cluster with a large cation-displacement. As the deformation potential interaction in Na system is expected to be larger than that in K system, small bipolarons and successive small multiple-bipolarons can be stabilized up to higher electron densities. An insulating and non-magnetic phase in Na\(_{n}/Na_{12}\)-LSX at \(n \lesssim 11\) is explained by small multiple-bipolarons stabilized in supercages [38,42]. The stability of multiple-bipolaronic states is assigned to the strong electron-phonon interaction conditions \(U < S\) and \(2B < 2S - U\) in the \(t-U-S\) triangle. A metallic phase at \(n \gtrsim 12\) is explained by the full occupation of small multiple-bipolaron states followed by the formation of large polarons delocalized over many supercages, because the highest state of s-electrons has a larger \(t\) with the increase in \(n\). According to the theoretical calculation [79], small polarons can coexist with large polarons at the metallic phase near the IMT. In Figure 8(b), the energy change of the total electron-phonon system in a metallic phase is illustrated schematically as a function of the lattice distortion, where small polarons are metastable. Small polarons are paramagnetic and can be thermally excited [42].
A thermally excited paramagnetic susceptibility at $n \approx 16$ in Figure 7(a) and (b) can be explained by these metastable paramagnetic small polarons in this adiabatic potential. Na cations are dynamically moving between large and small polaron states at temperatures higher than $\approx 100$ K. Paramagnetic moments of small polarons lead to the thermal excitation of paramagnetic susceptibility and the temperature shift of narrow SC line in $^{23}$Na-NMR spectra as well.

5. **Mott insulator and canted antiferromagnetism in K-loaded zeolite A**

In Figure 9(a), a framework structure of zeolite A with the space group Fm$\bar{3}$c is illustrated together with typical sites of exchangeable alkali-cation $M$. The framework structure type of zeolite A is LTA, and equivalent $\alpha$-cages are arrayed in a simple cubic structure by the sharing of 8Rs. An inside diameter of 8R is $\approx 5$ Å. K clusters are generated in $\alpha$-cages in K-loaded K-form zeolite A ($M = K$). The chemical formula is given by $K_n/K_{12}Al_{12}Si_{12}O_{48}$ per $\alpha$-cage (abbreviated as $K_n/K_{12}$-$A$). At higher K-loading densities ($n > 2$), superlattice reflections have been observed in diffraction experiments [12,22]. According to the structure analysis, adjoining clusters become nonequivalent in the space group F23 [22]. The alternate ordering of clusters is schematically illustrated in Figure 9(b), where two types of $s$-electron wave functions are indicated by large spheres in respective $\alpha$-cages. The size of 8Rs is so middle that an intermediate $t$ system can be expected. A ferromagnetic property has been observed at low temperatures [1], and changes systematically with $n$ [2]. At $n \ll 1$, an optical absorption band assigned to the 1s-1p optical transition in Figure 1(b) has been observed at the expected energy 1.2 eV [3]. Optical reflection spectra show a successive change with $n$ [3], as shown in Figure 10(a) [44]. The 1s-1p band at 1.2 eV grows with $n$ at $n < 2$, and shrinks with $n$ at $n > 2$. A new reflection band at 2 eV assigned to the 1p-1d transition appears at $n > 2$, and grows with $n$ to the dominant reflection band by the enhancement effect of the surface plasmon which is the collective excitation of confined $s$-electrons. These behaviors are basically explained by the successive occupation of $s$-electrons at 1s and 1p states shown in Figure 1(b). A spontaneous magnetization appears suddenly for $n > 2$, and attributed to $s$-electrons at 1p states [15]. Negative Weiss temperatures have been observed [7,11]. The Curie and Weiss temperatures change with $n$ [13,26,44], as shown in Figure 10(b). A finite optical gap has been observed in IR absorption tails [7,11], and ferromagnetic samples are assigned to Mott insulators. Based on the magnetization curve [18] and the $\mu$SR study [30], a spin-cant model of antiferromagnet is proposed for spontaneous magnetization. The spin canting can be caused by the Dzyaloshinsky-Moriya (DM) antisymmetric exchange interaction, where the orientations of up- and down-spins deviates from the antiparallel configuration of the ordinary antiferromagnetic exchange interaction. The DM interaction requires the lack of the inversion symmetry between structures at adjacent magnetic moments. According to the above
mentioned structure analysis [22], a new space group at $n > 2$ is proposed as F23, and the inversion symmetry between adjacent clusters is absent, as illustrated in Figure 9(b). Furthermore, the DM interaction is strongly enhanced by the degeneracy of 1p state [111]. Generally, the DM interaction is closely related to the SOI. A huge SOI has been observed at the 1p state [26]. Any way, the degeneracy of 1p state and the lack of the inversion symmetry play essential roles in the enhancement of the DM interaction. The canting angle is estimated to be $\approx 30^\circ$ which is extremely larger than the value in the ordinary DM interaction [18]. The arrangement of spin ordering is not well known yet [29].
Figure 11. (a) Schematic illustration of a huge SOI of K-cluster at the 1p state. The orthogonalized s-electron wave function contains 3p ion core wave functions of K cations, and has a large SOI in the 1p state. See text in detail. (b) Magnetic moment per $\alpha$-cage (magnetization) up to $5.2 \times 10^5$ Oe (52 T) for $K_{4.5}/K_{12}$-A at 1.3, 4, and 10 K, where the Curie temperature is $\approx 6$ K. The maximum value 0.96 $\mu_B$ estimated from the Curie constant is indicated by horizontal dotted line. Magnetic moment per $\alpha$-cage (magnetization) for for $K_{7.2}/K_{12}$-A (the Curie temperature is $\approx 0$ K) at 4 K is also shown.

The huge SOI at the 1p state is explained by the orthogonality between s-electron in the 1p state and core electrons of K cations located at the asymmetric potential of the cluster [26], as illustrated in Figure 11(a), where a counterclockwise rotation of a 1p state s-electron induces clockwise rotations of core electrons of K cations at the equator. This enhancement mechanism is quite similar to that in the 2p state of F-center [112,113], as follows. The $\mu$th Schmidt orthogonalized wave function $\phi_{\mu}$ for s-electron in cluster is given by [112]

$$\phi_{\mu} = \frac{1}{\sqrt{1 - \sum_{\alpha} S_{\mu\alpha}^2}} \left( u_{\mu} - \sum_{\alpha} S_{\mu\alpha} \varphi_{\alpha} \right), \quad (7)$$

where the overlap integral $S_{\mu\alpha}$ between the $\mu$th unorthogonalized s-electron wave function $u_{\mu}$ and an occupied cation core wave function $\varphi_{\alpha}$ is defined by $S_{\mu\alpha} = \langle u_{\mu} | \varphi_{\alpha} \rangle$. Then, the s-electron wave function $\phi_{\mu}$ can be orthogonal to the occupied cation wave function as $\langle \phi_{\mu} | \varphi_{\alpha} \rangle = 0$.

The SOI may be written approximately as [112]

$$H_{SO} = \frac{1}{2m_0^2c^2} \sum_I \frac{1}{r - \mathbf{R}_I} \frac{\partial V_I}{\partial (r - \mathbf{R}_I)} \mathbf{L}_I \cdot \mathbf{S}, \quad (8)$$

where $m_0$ and $c$ are the mass of the electron and the velocity of light, respectively. $\mathbf{S}$ and $\mathbf{R}_I$ are the electron spin operator and the center position of the $I$th ion, respectively. $V_I$ is the potential of the $I$th ion. $\mathbf{L}_I$ is the orbital angular
momentum operator with respect to the center of the $I$th ion. The expectation value of the SOI in $1p$ orthogonalized $s$-electron wave functions of $\frac{1}{\sqrt{2}} (\phi_x \pm i\phi_y)$ is given by $\langle \phi_x | H_{SO} | \phi_y \rangle$ which consists of three terms: (1) the cluster orbital term $\langle u_x | H_{SO} | u_y \rangle$, (2) the cluster orbital vs. ion core term $\langle u_x | H_{SO} | \varphi_y \rangle$ and (3) the ion core term $\langle \varphi_x | H_{SO} | \varphi_y \rangle$. The first and second terms are very small, because the wave functions of cluster orbital, $u_x$ and $u_y$, are so smooth that the derivative of the ionic potential scarcely contributes to the SOI in the form of Equation (8). The main contribution comes from the last term [112]. In the present clusters, the 3p ion core term of K cations contributes to the SOI for the $1p$ quantum state.

In crystals, Equation (8) can be rewritten to the form proportional to the wave vector of electron, and has a finite value in the crystals with no inversion symmetry [95–97]. The SOI in the crystals with the inversion symmetry is enhanced at the surface at finite wave vector along the surface by the Rashba mechanism, because the asymmetric potential is induced at surface atoms [98,99]. A potassium cluster in $\alpha$-cage contains a lot of K cations, $\approx 20$, and a large spin-orbit splitting is expected in the $1p$ state of cluster [26], where the wavelength along the equator is $2\pi a$ which corresponds to a large wave vector. In the $1s$ state, however, the contributions to the SOI are cancelled, because the wavelength along the equator has an infinite length which corresponds to the zero wave vector (namely the $\Gamma$ point of the Brillouin zone). Hence, the enhancement mechanism of SOI in clusters is equivalent microscopically to the Rashba mechanism at finite wave vectors.

The $g$-value estimated from ESR spectra at 10 K clearly decreases for $n > 2$ in $K_n/K_{12}$-A. The decrease is assigned to the contribution from the orbital angular momentum at the $1p$ state [15]. At $n \gtrsim 6$, the $g$-value does not decrease at 10 K, but decreases at 300 K. The $1p$ orbital is formally triply degenerate in the average structure, but the local structure may split into doubly- and singly-degenerate states at 10 K at $6 > n > 2$. At $n \gtrsim 6$, the structure at 10 K has no degeneracy statically. The structure at 300 K, however, may change in the degeneracy dynamically, and the large spin damping is induced by the dynamical mixing among $1p$ states.

The ESR spectrum in $\text{Rb}_3\text{C}_{60}$ is known to be much broader than that in $K_3\text{C}_{60}$ [114,115]. The origin of the broadening may be assigned to the similar enhancement model of the SOI by surrounding Rb atoms which have the very large SOI of core electrons [26,113]. The conduction electrons mainly occupy the degenerate $t_{1u}$ orbital of $\text{C}_{60}$. The SOI for the $t_{1u}$ orbital can be enhanced by electron wave function partly extended to Rb atoms. The main part of the wave function on the Rb atom is 5s, but the 4p core orbital on Rb atom is induced by the asymmetric potential on the surface of $\text{C}_{60}$. According to the model presented here, the rotational motion of 4p electron on Rb atom is expected to enhance the SOI in the $t_{1u}$ orbital of $\text{C}_{60}$ in $\text{Rb}_3\text{C}_{60}$. Then, the spectral width of ESR can be broadened by the spin relaxation by the SOI. This is a kind of the external heavy atom effect at the degenerate orbitals. The present enhancement in $K_n/K_{12}$-A
is classified into the internal heavy atom effect, but the mechanisms are similar with each other.

In nuclei, the shell structure of a single particle state of neutrons or protons has been well understood as the basic model of nuclear structure [116]. The single particle states, such as 1s, 1p, 1d states, are often calculated by the Woods-Saxon potential which is a quite smooth function. The SOI in nuclei plays an important role in the explanation of the magic number, 28, 50, 82, which are different from the regular magic number in the shell model, 20, 40, 70 for 1s-1d, 1s-2p and 1s-3s closed shell states, respectively. The strong SOI in nuclei is explained by the short-range nucleonic two-body-interaction. This SOI has a large contribution near the nuclear surface. The SOI in alkali metal clusters has a similar analogy with that in nuclei [26]. The single particle potential derived from the jellium model is quite insufficient for the explanation of the large SOI observed in experiments. The short-range two-body interaction between cluster s-electron and cation core electrons plays an important role in the enhancement of the SOI, when the cluster electron has an orbital angular momentum at the 1p state.

At high magnetic fields up to $5.2 \times 10^5$ Oe (which corresponds to 52 T), an extraordinary magnetization has been observed for $n = 4.5$ [26,27], as shown in Figure 11(b), where the Curie temperature is $\approx 6$ K for $n = 4.5$. The magnetic moment per $\alpha$-cage at 1.3 K for $n = 4.5$ exceeds the value 0.96 $\mu_B$ (horizontal dotted line) estimated from the Curie constant at higher temperatures. At 4 and 10 K, the magnetic moment per $\alpha$-cage is less than 0.96 $\mu_B$ up to $52 \times 10^4$ Oe. The extraordinary magnetic moment at 1.3 K for $n = 4.5$ is explained by the crossover between $1p(E_u)$ states with $J_z = \pm 3/2$ and $\pm 1/2$ at high magnetic fields, and the spin-orbit splitting energy is estimated to be $\approx 1.5$ meV [27]. This value well corresponds to a roughly estimated value in the above mentioned SOI model [26]. At 4 and 10 K, the motion of K cations are thermally excited and the degeneracy of the 1p state is gradually lifted dynamically. Then, the magnetization at high magnetic fields may be suppressed. A large SOI can suppress the Jahn-Teller instability of degenerate orbitals [15]. Spin-triplet states have been not observed in experiments [15,17,44]. On the other hand, the magnetization for $n = 7.2$ in Figure 11(b) is clearly saturated at high magnetic fields and has the value estimated from the Curie constant. A Curie law has been observed although most $\alpha$-cages are occupied by spin-1/2 moments, indicating that adjacent clusters have no magnetic interaction [11]. This result is explained by the mutually orthogonalized orbitals of 1p-holes at $n = 7.2$ [11,15].

According to the first-principle band calculation in simplified structures at $n = 1$ and 3 in $K_n/K_{12}$-A, an energy band structure is very close to the tight-binding approximation based on 1s and 1p states [20]. A Mott insulator is expected because $U$ is calculated to be much larger than $t$, in accordance with the experimental evidence.
In Rb-loaded Rb-form zeolite A (Rb\textsubscript{n}/Rb\textsubscript{12}-A), a ferromagnetic property has been observed [24,25], but the \( n \)-dependence is essentially different from that in K\textsubscript{n}/K\textsubscript{12}-A. A nearly metallic phase has been observed. The magnetism in Rb\textsubscript{n}/Rb\textsubscript{12}-A is assigned to the ferrimagnetism, where two non-equivalent magnetic sublattices at \( \alpha \)-cages and \( \beta \)-cages have the AF interaction through 6Rs. In Cs\textsubscript{n}/Cs\textsubscript{12}-A, no ferromagnetic property has been observed [24]. These differences are assigned to the small ionization energies of Rb and Cs atoms, which will increase \( t \) but decrease \( S \) (towards the upper-left area of the \( t-U-S \) triangle in Figure 3(b)).

6. Alkali metals in other zeolites

In sodalite which has the framework structure type of SOD, \( \beta \)-cages are arrayed in a body centered cubic structure by the sharing of 6Rs. As shown in Figure 12(a), an \( M_4^{3+} \) magnetic cluster involving an \( s \)-electron can be stabilized in each \( \beta \)-cage by the loading of an \( M \) atom at \( n = 1 \), where the chemical formula is given by \( M/M_3\text{Al}_3\text{Si}_3\text{O}_{12} \) per \( \beta \)-cage (abbreviated as \( M/M_3\text{-SOD} \)). Shared 6Rs are rather narrow, but a large kinetic energy is expected for the \( s \)-electron, because of a narrow inside diameter of \( \beta \)-cage, \( \approx7\) Å. These lead to the system of a large \( U \) with a finite \( S \). According to the \( t-U-S-n \) model, a robust Mott-insulating phase is expected at \( n \approx 1 \) when \( U > 2B \) and \( U > S \). Actually, an antiferromagnetism has been clearly observed in Na/Na\textsubscript{3}-SOD below the Néel temperature \( \approx 50 \) K [9,16]. In K/K\textsubscript{3}-SOD and Rb/K\textsubscript{3}-SOD, much higher Néel temperatures have been observed at 70 and 80 K, respectively [14,34,35]. The increase in the Néel temperature is assigned to the increase in \( t \), because of the
decrease in the confinement potential in the heavy alkali atoms. The anisotropy field of this antiferromagnetism is estimated to be at 1–2 Oe by the ESR studies [31]. This field is significantly small, and this magnetism is assigned to an ideal Heisenberg antiferromagnet. A direct observation of $s$-electron spin ordering and the magnetic form factor of Na$_4^{3+}$ clusters in Na/Na$_3$-SOD have been made by the neutron diffraction experiment [41], as shown in Figure 12(b). The dependence on the scattering vector $q$ clearly elucidates the wide distribution of spin density expected from the spherical-well potential with an inside diameter of 7 Å (the dotted blue curve) and that calculated by using the maximally localized Wannier orbital [32] (the solid red curve). In K/K$_3$-SOD, the wider spread of spin density has been observed by the neutron diffraction experiment [51]. The hyperfine field in K/K$_3$-SOD is evaluated to be 9.2 ± 3.0 T at 8 K by the synchrotron-radiation-based Mössbauer spectroscopy of $^{40}$K [48]. These systems are in a Mott insulator in accordance with the theoretical calculations [10,32]. In Rb/Rb$_3$-SOD, a metallic phase is expected in the theoretical calculation [21].

Zeolite P has the framework structure type of GIS, and provides a quasi two-dimensional space for guest materials by the connection of GIS cages. A metallic phase has been observed at $n > 1$ in K-loaded zeolite P [49]. The insulating phase at $n < 1$ is assigned to the distribution of two-site type small bipolarons, where two adjoining clusters are paired in the bonding state. The two-site type small bipolarons, however, are not expected in the on-site electron-phonon interaction model of Equation (3). We need an additional electron-phonon interaction term to stabilize the pairing of $s$-electrons in the adjoining sites. Excess $s$-electrons at $n > 1$ occupy the anti-bonding states of small bipolarons. These $s$-electrons are not well localized in cages, and contribute the metallic conductivity as mobile carriers.

Zeolite L has the framework structure type of LTL, and is constructed of a bundle of cylindrical channels with an inside diameter of $\approx 1$ nm. Quasi one-dimensional electronic states have been expected theoretically in zeolite L [4], and observed experimentally in K-loaded zeolite L [53]. The kinetic energy of an electron in a quantum cylinder has two terms. 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 motion along the cylinder. At intermediate loading densities in K-loaded zeolite L ($n \gtrapprox 5$), the one-dimensional metallic properties have been observed in the increases both in the infra-red absorption and in the Pauli paramagnetism [53]. When cylinders have a finite potential depth, electrons are expected to have the band-type coherent motion in the bundle of regular cylinders and the hopping-type incoherent motion over cylinders. Two terms in the thermal activation of carriers have been observed in the temperature dependence of conductivity in K-loaded zeolite L [53]. One term with a higher thermal activation energy is dominant at lower loading densities, and is assigned to the inter-channel hopping motion of $s$-electrons in 1s and 1p quantum states. The other term with a lower thermal
activation energy is dominant at higher loading densities \((n \gtrsim 9)\), and is assigned to the band-type motion of carriers in the three-dimensional state of the 1d quantum states.

7. Summary

Alkali metals loaded into various zeolite crystals display novel magnetic, optical, electric properties. They vary widely depending on the kind of alkali metals, the loading density, and the structure type of zeolites. Electronic properties can be overviewed systematically by the \(t-U-S-n\) diagram of the correlated polaron system. The large \(t\) is expected in the large window size, the low ionization energy of heavy alkali atoms and the large quantum-confinement energy in the small cage. The \(t\) increases with \(n\) by the occupation of \(s\)-electrons at higher quantum states. The \(U\) is important in the nanoscale and becomes large in the small cage. The \(S\) increases in light alkali metals. The \(U\) and \(S\) work well in case of \(U \gg t\) and/or \(S \gg t\). A huge SOI has been observed beyond the jellium model of clusters in the degenerate orbitals. The further extension of materials design and new exotic properties are expected in the wide variety of guest material loading into different zeolite crystals.

Acknowledgements

We are deeply grateful to S. Araki, N.H. Nam, T.C. Duan, D.T. Hanh, P.T. Thi, L.M. Kien, G.P. Hettiarachchi, M. Igarashi, T. Ikeda, K. Kindo, A. Matsuo, M. Hagiwara, T. Kagayama, I. Watanabe, F.L. Pratt, Y. Ikemoto, T. Kodaira, Y. Sakamoto, and O. Terasaki for experimental studies and discussions. We are also grateful to R. Arita, Y. Nohara, K. Nakamura, and H. Aoki for theoretical studies and discussions.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

Relevant studies were supported by Grant-in-Aid for Scientific Research on Priority Areas [grant number JP19051009], Grant-in-Aid for Scientific Research (A) [grant number JP24244059] and [grant number JP13304027] and (C) [grant number JP26400334], Grant-in-Aid for Creative Scientific Research ‘New Phases of Matter in Multidisciplinary Approaches’ [grant number JP15GS0213], Global COE Program ‘Core Research and Engineering of Advanced Materials-Interdisciplinary Education Center for Materials Science’ [grant number G10], the 21st Century COE Program ‘Towards a new basic science: depth and synthesis’ [grant number G17], JSPS from MEXT Japan http://dx.doi.org/10.13039/501100001691 by Core Research for Evolutional Science and Technology (CREST) ‘New Arrayed Clusters in Microporous Materials: Syntheses, Structures and Physical Properties’ 7-6, JST http://dx.doi.org/10.13039/501100002241, and also by Osaka University [grant number 10.13039/501100004206].
References

[1] Y. Nozue, T. Kodaira and T. Goto, Phys. Rev. Lett. 68 (1992) p.3789.
[2] Y. Nozue, T. Kodaira, S. Ohwashi, T. Goto and O. Terasaki, Phys. Rev. B 48 (1993) p.12253.
[3] T. Kodaira, Y. Nozue, S. Ohwashi, T. Goto and O. Terasaki, Phys. Rev. B 48 (1993) p.12245.
[4] M.J. Kelly, J. Phys.: Condens. Matter 7 (1995) p.5507.
[5] C.P. Ursenbach, P.A. Madden, I. Stich and M.C. Payne, J. Phys. Chem. 99 (1995) p.6697.
[6] A.Z. Chowdhury and K. Nasu, J. Phys. Chem. Solids 56 (1995) p.1193.
[7] Y. Ikemoto, T. Nakano, Y. Nozue, O. Terasaki and S. Qiu, Mater. Sci. Eng. B 48 (1997) p.116.
[8] P.A. Anderson, A.R. Armstrong, A. Porch, P.P. Edwards and L.J. Woodall, J. Phys. Chem. B 101 (1997) p.9892.
[9] V.I. Srdanov, G.D. Stucky, E. Lippmaa and G. Engelhardt, Phys. Rev. Lett. 80 (1998) p.2449.
[10] O.F. Sankey, A.A. Demkov and T. Lenosky, Phys. Rev. B 57 (1998) p.15129.
[11] T. Nakano, Y. Ikemoto and Y. Nozue, Eur. Phys. J. D 9 (1999) p.505.
[12] Y. Maniwa, H. Kira, F. Shimizu and Y. Murakami, J. Phys. Soc. Jpn. 68 (1999) p.2902.
[13] T. Nakano, Y. Ikemoto and Y. Nozue, J. Magn. Magn. Mater. 226–230 (2001) p.238.
[14] H. Tou, Y. Maniwa, K. Mizoguchi, L. Damjanovic and V.I. Srdanov, J. Magn. Magn. Mater. 226–230 (2001) p.1098.
[15] T. Nakano, Y. Ikemoto and Y. Nozue, J. Phys. Soc. Jpn. 71 (2002) p.199.
[16] R. Scheuermann, E. Roduner, G. Engelhardt, H.-H. Klauss and D. Herlach, Phys. Rev. B 66 (2002) p.1444291.
[17] T. Nakano, D. Kiniwa, F.L. Pratt, I. Watanabe, Y. Ikemoto and Y. Nozue, Phys. B 326 (2003) p.550.
[18] T. Nakano, D. Kiniwa, Y. Ikemoto and Y. Nozue, J. Magn. Magn. Mater. 272–276 (2004) p.114.
[19] H. Aoki, Appl. Surf. Sci. 237 (2004) p.2.
[20] R. Arita, T. Miyake, T. Kotani, M. van Schilfgaarde, T. Oka, K. Kuroki, Y. Nozue and H. Aoki, Phys. Rev. B 69 (2004) p.195106.
[21] G.K.H. Madsen, Acta Cryst. A 60 (2004) p.450.
[22] T. Ikeda, T. Kodaira, F. Izumi, T. Ikeshoji and K. Oikawa, J. Phys. Chem. B 108 (2004) p.17709.
[23] T. Nakano, K. Goto, I. Watanabe, F.L. Pratt, Y. Ikemoto and Y. Nozue, Phys. B 374–375 (2006) p.21.
[24] T.C. Duan, T. Nakano and Y. Nozue, E-J. Surf. Sci. Nanotech. 5 (2007) p.6.
[25] T.C. Duan, T. Nakano and Y. Nozue, J. Magn. Magn. Mater. 310 (2007) p.1013.
[26] T. Nakano and Y. Nozue, J. Comput. Methods Sci. Eng. 7 (2007) p.443.
[27] T. Nakano, D. Kiniwa, A. Matsuo, K. Kindo and Y. Nozue, J. Magn. Magn. Mater. 310 (2007) p.e295.
[28] N.H. Nam, S. Araki, H. Shiraga, S. Kawasaki and Y. Nozue, J. Magn. Magn. Mater. 310 (2007) p.1016.
[29] T. Nakano, T. Takase, S. Araki, T. Kamiyama, Y. Nozue and S. Ikeda, Nucl. Instrum. Methods Phys. Res. A 600 (2009) p.240.
[30] T. Nakano, J. Matsumoto, T.C. Duan, I. Watanabe, T. Suzuki, T. Kawamata, A. Amato, F.L. Pratt and Y. Nozue, Phys. B 404 (2009) p.630.
[31] T. Nakano, T. Kashiwagi, A. Hanazawa, K. Watanabe, M. Hagiwara and Y. Nozue, J. Phys. Soc. Jpn. 78 (2009) p.084723.
[32] K. Nakamura, T. Koretsune and R. Arita, Phys. Rev. B 80 (2009) p.174420.
[33] Y. Nohara, K. Nakamura and R. Arita, Phys. Rev. B 80 (2009) p.220410.
[34] M. Igarashi, T. Nakano, A. Goto, K. Hashi, T. Shimizu, A. Hanazawa and Y. Nozue, J. Phys. Chem. Solids 71 (2010) p.638.
[35] T. Nakano, R. Suehiro, A. Hanazawa, K. Watanabe, I. Watanabe, A. Amato, F.L. Pratt and Y. Nozue, J. Phys. Soc. Jpn. 79 (2010) p.073707.
[36] T. Kashiwagi, T. Nakano, A. Hanazawa, Y. Nozue and M. Hagiwara, J. Phys. Chem. Solids 71 (2010) p.544.
[37] D.T. Hanh, T. Nakano and Y. Nozue, J. Phys. Chem. Solids 71 (2010) p.677.
[38] T. Nakano, T. Mizukane and Y. Nozue, J. Phys. Chem. Solids 71 (2010) p.650.
[39] N.H. Nam, T. Ohtsu, T. Araki, S. Araki and Y. Nozue, J. Phys.: Conf. Ser. 200 (2010) p.012062.
[40] Y. Nohara, K. Nakamura and R. Arita, J. Phys. Soc. Jpn. 80 (2011) p.124705.
[41] T. Nakano, M. Matsuura, A. Hanazawa, K. Hirota and Y. Nozue, Phys. Rev. Lett. 109 (2012) p.167208.
[42] Y. Nozue, Y. Amako, R. Kawano, T. Mizukane and T. Nakano, J. Phys. Chem. Solids 73 (2012) p.1538.
[43] T. Nakano, D.T. Hanh, A. Owaki, Y. Nozue, N.H. Nam and S. Araki, J. Korean Phys. Soc. 63 (2013) p.512.
[44] T. Nakano, D.T. Hanh, Y. Nozue, N.H. Nam, T.C. Duan and S. Araki, J. Korean Phys. Soc. 63 (2013) p.699.
[45] T. Nakano, H. Tsugeno, A. Hanazawa, T. Kashiwagi, Y. Nozue and M. Hagiwara, Phys. Rev. B 88 (2013) p.174401.
[46] M. Igarashi, T. Nakano, P.T. Thi, Y. Nozue, A. Goto, K. Hashi, S. Ohki, T. Shimizu, A. Krajnc, P. Jeglič and D. Arčon, Phys. Rev. B 87 (2013) p.075138.
[47] T. Ikeda, T. Nakano and Y. Nozue, J. Phys. Chem. C 118 (2014) p.23202.
[48] T. Nakano, N. Fukuda, M. Seto, Y. Kobayashi, R. Masuda, Y. Yoda, M. Mihara and Y. Nozue, Phys. Rev. B 91 (2015) p.140101(R).
[49] G.P. Hettiarachchi, T. Nakano, Y. Masaki, M.N.M. Muhid, H. Hamdan and Y. Nozue, J. Phys. Soc. Jpn. 84 (2015) p.014702.
[50] L.M. Kien, T. Goto, D.T. Hanh, T. Nakano and Y. Nozue, J. Phys. Soc. Jpn. 84 (2015) p.064718.
[51] T. Nakano, M. Matsuura, A. Hanazawa and Y. Nozue, JPS Conf. Proc. 8 (2015) p.034011.
[52] M. Igarashi, P. Jeglič, A. Krajnc, R. Žitko, T. Nakano, Y. Nozue and D. Arčon, Sci. Rep. 6 (2016) p.18682.
[53] P.T. Thi, T. Nakano, Y. Sakamoto and Y. Nozue, J. Phys. Soc. Jpn. 85 (2016) p.024703.
[54] H. Hosono, K. Hayashi, T. Kamiya, T. Atou and T. Susaki, Sci. Technol. Adv. Mater. 12 (2011) p.034303.
[55] M. Brack, Rev. Mod. Phys. 65 (1993) p.677.
[56] International Zeolite Association (IZA), Available at http://www.iza-online.org
[57] W.A. de Heer, W.D. Knight, M.Y. Chou and M.L. Cohen, Solid State Phys. 40 (1987) p.93.
[58] V.N. Bogomolov, Sov. Phys. Usp. 21 (1978) p.77, [Usp. Fiz. Nauk 124 (1978), p.171].
[59] M.R. Harrison, P.P. Edwards, J. Klinowski and J.M. Thomas, J. Solid State Chem. 54 (1984) p.330.
[60] N. Wada, T. Matsushita, M. Hieda and R. Toda, J. Low Temp. Phys. 157 (2009) p.324.
[61] K. Yamashita and D.S. Hirashima, Phys. Rev. B 79 (2009) p.014501.
ADVANCES IN PHYSICS: X

[62] T. Eggel, M.A. Cazalilla and M. Oshikawa, Phys. Rev. Lett. 107 (2011) p.275302.
[63] J. Taniguchi, K. Demura and M. Suzuki, Phys. Rev. B 88 (2013) p.014502.
[64] T. Matsushita, A. Shinohara, M. Hieda and N. Wada, J. Low Temp. Phys. 183 (2016) p.273.
[65] J. Taniguchi, A. Yamaguchi, H. Ishimoto, H. Ikekami, T. Matsushita, N. Wada, S.M. Gatica, M.W. Cole, F. Ancilotto, S. Inagaki and Y. Fukushima, Phys. Rev. Lett. 94 (2005) p.065301.
[66] Y. Nozue, T. Kodaira, O. Terasaki, K. Yamazaki, T. Goto, D. Watanabe and J.M. Thomas, J. Phys.: Condens. Matter 2 (1990) p.5209.
[67] Z.K. Tang, Y. Nozue and T. Goto, J. Phys. Soc. Jpn. 60 (1991) p.2090.
[68] Z.K. Tang, Y. Nozue and T. Goto, J. Phys. Soc. Jpn. 61 (1992) p.2943.
[69] J.R. Agger, M.W. Anderson, M.E. PEMble, O. Terasaki and Y. Nozue, J. Phys. Chem. B (1998) p.3345.
[70] R. Xu, W. Pang, J. Yu, Q. Huo and J. Chen, Chemistry of Zeolites and Related Porous Materials, John Wiley & Sons, Singapore, 2007.
[71] P.A. Wright, Microporous Framework Solids, RSC Materials Monographs, The Royal Society of Chemistry, RSC Publishing, Fife, UK, 2008.
[72] Polaron in Bulk Materials and Systems With Reduced Dimensionality (Proc. Intern. School Phys. ‘Enrico Fermi’ (Course CLXI)), G. Iadonisi, J. Ranninger and G. De Filippis, eds., IOS Press, Amsterdam, 2006.
[73] Polaron in Advanced Materials, in Springer Series in Materials Science 103, A.S. Alexandrov, ed., Springer, Dordrecht, 2007.
[74] Y. Toyozawa, Prog. Theor. Phys. 26 (1961) p.29.
[75] A. Sumi and Y. Toyozawa, J. Phys. Soc. Jpn. 35 (1973) p.137.
[76] Y. Toyozawa and Y. Shinozuka, J. Phys. Soc. Jpn. 48 (1980) p.472.
[77] H. Sumi, J. Phys. Soc. Jpn. 33 (1972) p.327.
[78] B. Gerlach and H. Löwen, Rev. Mod. Phys. 63 (1991) p.63.
[79] S. Suzuki and Y. Toyozawa, J. Phys. Soc. Jpn. 59 (1990) p.2841.
[80] H. Hiramoto and Y. Toyozawa, J. Phys. Soc. Jpn. 54 (1985) p.245.
[81] Y. Toyozawa, J. Phys. Soc. Jpn. 50 (1981) p.1861.
[82] K. Nasu and Y. Toyozawa, J. Phys. Soc. Jpn. 51 (1982) p.2098.
[83] K. Nasu and Y. Toyozawa, J. Phys. Soc. Jpn. 51 (1982) p.3111.
[84] Y. Shinozuka, J. Phys. Soc. Jpn. 56 (1987) p.4477.
[85] T. Holstein, Ann. Phys. 8 (1959) p.325, [Reprint: Ann. Phys. 281 (2000) p.706].
[86] P.W. Anderson, Phys. Rev. Lett. 34 (1975) p.953.
[87] G. Sangiovanni, M. Capone, C. Castellani and M. Grilli, Phys. Rev. Lett. 94 (2005) p.026401.
[88] W. Koller, A.C. Hewson and D.M. Edwards, Phys. Rev. Lett. 95 (2005) p.256401.
[89] P. Werner and A.J. Millis, Phys. Rev. Lett. 99 (2007) p.146404.
[90] J. Bauer and A.C. Hewson, Phys. Rev. B 81 (2010) p.235113.
[91] E.A. Nowadnick, S. Johnston, B. Moritz, R.T. Scalettar and T.P. Devereaux, Phys. Rev. Lett. 109 (2012) p.246404.
[92] Y. Murakami, P. Werner, N. Tsuji and H. Aoki, Phys. Rev. B 88 (2013) p.125126.
[93] Y. Kyanuma, Solid State Commun. 59 (1986) p.405.
[94] Y. Kyanuma, Phys. Rev. B 38 (1988) p.9797.
[95] G. Dresselhaus, Phys. Rev. 100 (1955) p.580.
[96] Y. Nozue, M. Itoh and K. Cho, J. Phys. Soc. Jpn. 50 (1981) p.889.
[97] Y. Nozue, J. Phys. Soc. Jpn. 51 (1982) p.1840.
[98] E.I. Rashba, Fiz. Tverd. Tela 2 (1960) p.1224, [Sov. Phys. Solid State 2 (1960) p.1109].
[99] Y.A. Bychkov and E.I. Rashba, Pis’ma Zh. Eksp. Teor. Fiz. 39 (1984) p.66, [JETP Lett. 39 (1984), p.78].
[100] S. Sakai, R. Arita and H. Aoki, Phys. Rev. Lett. 99 (2007) p.216402.
[101] Y. Li, E.H. Lieb and C. Wu, Phys. Rev. Lett. 112 (2014) p.217201.
[102] L.M. Roth, Phys. Rev. 149 (1966) p.306.
[103] H. Tsunetsugu, M. Sigrist and K. Ueda, Rev. Mod. Phys. 69 (1997) p.809.
[104] J.B. Goodenough, J. Phys. Chem. Solids 6 (1958) p.287.
[105] J. Kanamori, J. Phys. Chem. Solids 10 (1959) p.87.
[106] P.W. Anderson, Phys. Rev. 79 (1950) p.350.
[107] P.W. Anderson, Phys. Rev. 115 (1959) p.2.
[108] G. Stollhoff and P. Fulde, J. Chem. Phys. 73 (1980) p.4548.
[109] P. Fulde, Correlated Electrons in Quantum Matter, World Scientific Publishing, Singapore, 2012.
[110] N. Bloembergen, E.M. Purcell and R.V. Pound, Phys. Rev. 73 (1948) p.679.
[111] M. Tachiki, J. Phys. Soc. Jpn. 25 (1968) p.686.
[112] D.Y. Smith, Phys. Rev. 137 (1965) p.A574.
[113] H. Pick, Structure of Trapped Electron and Trapped Hole Centers in Alkali Halides “Color Centers”, in Optical Properties of Solids, F. Abelés, ed., North–Holland Publishing, Amsterdam, Chapter 9, 1972, p.653.
[114] A. Jánossy, O. Chauvet, S. Pekker, J.R. Cooper and L. Forró, Phys. Rev. Lett. 71 (1993) p.1091.
[115] K. Tanigaki, M. Kosaka, T. Manako, Y. Kubo, I. Hirosawa, K. Uchida and K. Prassides, Chem. Phys. Lett. 240 (1995) p.627.
[116] A. Bohr and B.R. Mottelson, Nuclear Structure, in Single-Particle Motion, (Benjamin, 1969), New ed., World Scientific, Singapore, 1998.