

Electronic properties of alkali-metal loaded zeolites: Supercrystal Mott insulatorsRyotaro Arita,¹ Takashi Miyake,² Takao Kotani,³ Mark van Schilfgaarde,⁴ Takashi Oka,¹ Kazuhiko Kuroki,⁵ Yasuo Nozue,³ and Hideo Aoki¹¹*Department of Physics, University of Tokyo, Hongo, Tokyo 113-0033, Japan*²*Department of Physics, Tokyo Institute of Technology, Oh-okayama, Tokyo 152-8551, Japan*³*Department of Physics, Osaka University, Toyonaka, Osaka 560-0043, Japan*⁴*Department of Chemical and Materials Engineering, Arizona State University, Tempe, Arizona 85287-6006, USA*⁵*Department of Applied Physics and Chemistry, University of Electro-Communications, Chofu, Tokyo 182-8585, Japan*

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First-principles band calculations are performed for an open-structured zeolite with guest atoms (potassium) introduced in the cages. A surprisingly simple band structure emerges which indicates that this system may be regarded as a “supercrystal,” where each cluster of guest atoms with diameter $\sim 10 \text{ \AA}$ acts as a “superatom” with well-defined *s*- and *p*-like orbitals, which in turn form tight-binding bands around the Fermi energy. The calculated Coulomb energy for these states turns out to be in the strongly correlated regime. We show, with the dynamical mean-field theory, that the system resides in the Mott-insulator regime in accord with experimental results. We envisage that this class of systems can provide a new avenue for materials design.

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I. INTRODUCTION

Materials design is usually done by varying chemical elements and/or atomic crystal structures. As an alternative way, we may envisage to construct the system by introducing guest atoms or cluster of them into open-structured host (cages). In fact, doped zeolites are a typical class of such systems. They are unique in that (i) in these host-guest systems the host itself appears in a rich variety (crystal structure of cages, size of the intercage window, etc.), on top of rich possibilities for the species and the number of guest atoms;¹ (ii) the size of the cage is of the order of nanometers, where we can expect even more versatile possibilities for the design. In passing we can note that the doped zeolites are rather distinct from the doped solid fullerene: The latter, while a nanostructured supercrystal as well, has the relevant orbitals that are basically lowest unoccupied molecular orbitals/highest occupied molecular orbital of the cage (C_{60}) rather than those of dopants even after doping with alkali metals.² While (i) implies higher degrees of freedom for the design, (ii) implies that the Coulomb interaction energy for the cluster doped in the cage, which only decreases inversely with the size, can remain large (of the order of eV for nanometer dimensions). This is why we expect that these can provide a fascinating play ground for a *systematic control* of the electron correlation as a new avenue for materials design.

Indeed, experimental results by Nozue *et al.*^{3,4} have established that some zeolites (Fig. 1) loaded with clusters (\approx five atoms per cage) of potassium are ferromagnetic for $T < 8 \text{ K}$, which is unique in that magnetism occurs despite all the ingredients being nonmagnetic elements.⁵ Another puzzle is that an infrared analysis for the K-loaded zeolite shows clear absorption edges, indicative of insulating behavior, even when the average number of conduction electrons is odd per unit cell;⁶ Namely, a finite optical gap $\approx 1 \text{ eV}$ has been observed in doped zeolites, while the undoped one is an ordinary insulator with an optical gap of $\approx 7 \text{ eV}$.

Here we address the underlying electronic structure of the

doped zeolite, namely, the question we want to ask is: can we expect for such a host-guest system (where the number of atoms in a unit cell can be as large as 84) to have simple electronic structures. So we start by showing that the relevant states of K-doped zeolite can, in fact, be viewed as a “supercrystal.” Namely, the first-principles electronic structure as computed with the local-density approximation (LDA) for a typical zeolite is surprisingly accurately described as a tight-binding band of “superatoms” (i.e., the states in the clusters of dopants) with well-defined *s* and *p* orbitals. This explains why the experimentally obtained optical spectrum may be interpreted as transitions between *s* and *p* (or *p* and *d*) orbitals in a simple well.⁷ Although there has been an attempt at a band calculation for a zeolite, an unphysical situation was assumed there, while the present result reveals the above property with the correct numbers and positions of cations.⁸

Second, we question the electron-correlation effects, namely, we have estimated the Coulomb interaction for these superatom orbitals by plugging in the LDA wave functions. The calculated Coulomb energy for these states turns out to be in the strongly correlated regime. We have actually studied the effect of correlations on the spectral function in the spirit of the LDA+dynamical mean-field theory (DMFT) (Ref. 9) to show that the system can reside well on the Mott-insulator side. This resolves the puzzle that the band calculation predicts that the system is a metal, while experiments indicate an insulator.

II. FORMULATION AND THE RESULT FOR THE UNDOPED ZEOLITE

We start with the undoped zeolite with a typical structure having a simple-cubic array of cages (Fig. 1), where each cage (called α) is an Archimedes polyhedron. The region surrounded by eight α cages forms another cage called β . Aluminosilicate with this structure (zeolite A) has Si and Al atoms situated at the vertices of the cages and connected by

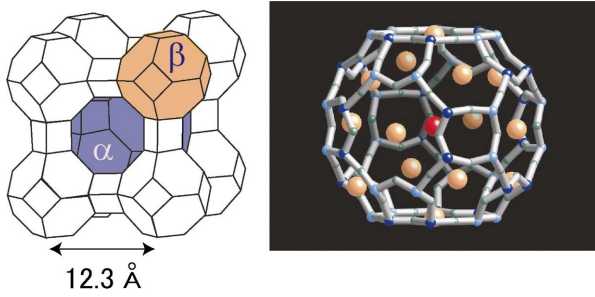


FIG. 1. (Color) Left: Geometry of the LTA structure. Right: Unit cell (i.e., α cage) of the undoped zeolite considered here, with dark blue: Si, light blue: Al, dark green: oxygen, orange and red: K.

O atoms with the inner diameter of an α cage ~ 10 Å. The material used in most experiments^{3,4} is K(potassium)-form zeolite A [abbreviated as LTA (Ref. 10) hereafter], whose chemical formula, $K_{12}Al_{12}Si_{12}O_{48}$ (with 84 atoms per unit cell), already contains some K atoms. Eleven out of the twelve K atoms are located on the centers of faces of the α cage (orange atoms in Fig. 1), while the remaining K (red), assumed to be at the cage center, changes its position as K's are added to change the doping as we shall describe. For the atomic positions of Al, Si, O within the unit cell, we have adopted the accurate crystal structure obtained from a recent neutron powder diffraction study by Ikeda *et al.*^{11,12} Hereafter we set the lattice constant as the unit of length.

For the LDA calculation we adopt here the all-electron full-potential linear muffin-tin (MT) orbitals (FP-LMTO).¹³ The result for the band structure for the undoped LTA is displayed in Fig. 2, which shows that the undoped zeolite is

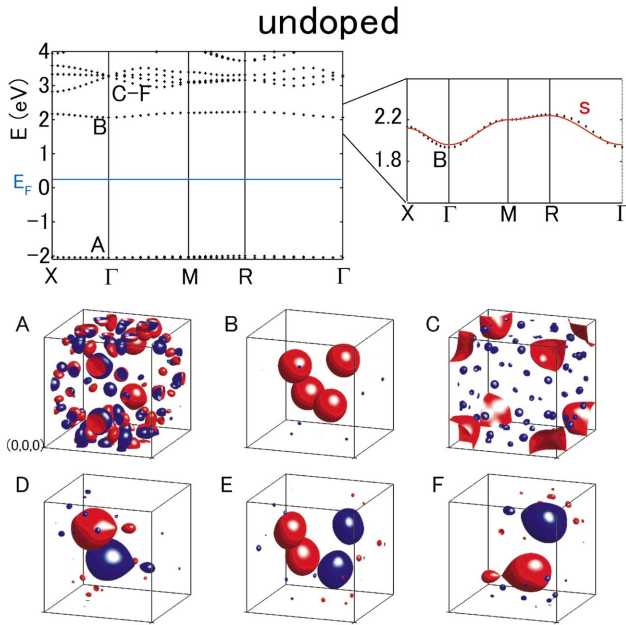


FIG. 2. (Color) The band structure of the undoped zeolite LTA. The top right panel is a blowup of the lowest conduction band, where the red line is a tight-binding fit. Bottom panels are wave functions (red contours: positive, blue: negative for $|\psi|^2=2.0$) at Γ in the bands A–F as labeled in the band structure.

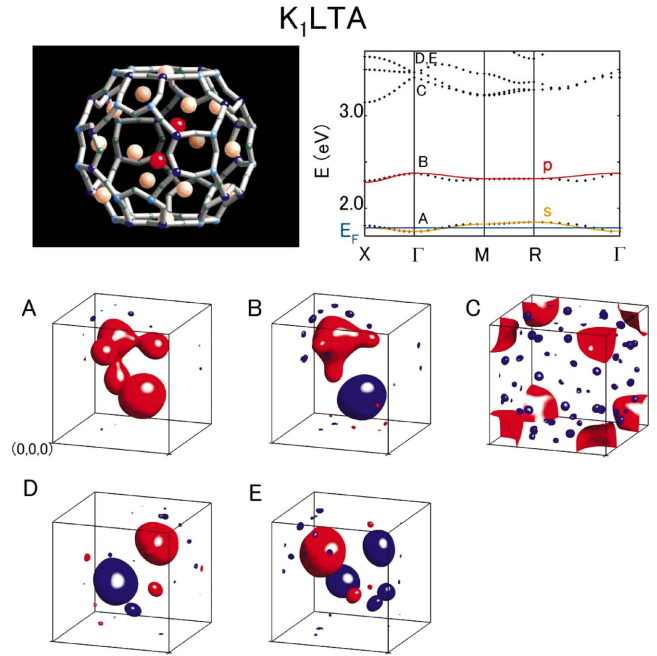


FIG. 3. (Color) Band structure of a K-doped zeolite K_1LTA . Colored curves are a tight-binding fit. Top left inset depicts the atomic configuration, where two red K's (the doped one and the red one in Fig. 2) form a cluster in the α cage. Bottom panels are wave functions at Γ in the bands A–E as labeled in the band structure.

an insulator with a gap ≈ 4 eV. If we look at the wave functions (the smoothed part of the eigenfunctions in the FP-LMTO scheme¹³) in Fig. 2, the conduction-band states (labeled as B–F) primarily reside within the α cage (for B, D, E, F) or within β (C) (while the valence-top state sits on the framework).

The dispersion of the lowest conduction band (B) can be fitted, as shown in the right panel of Fig. 2, by the dispersion of a tight-binding band on the simple cubic lattice,

$$\varepsilon(\mathbf{k}) = t_x \cos(k_x) + t_y \cos(k_y) + t_z \cos(k_z),$$

with $(t_x, t_y, t_z) \approx (-20, -10, -5)$ (meV). The fitting is excellent and, with all of $t_x, t_y, t_z < 0$ and the wave function being nodeless (Fig. 2, with its tetrahedral shape due to the configuration of surrounding K atoms), we may interpret the band as an “s band of the supercrystal.” Similarly, three (D, E, F) out of the four next-lowest conduction bands, with large amplitudes within the α cage, may be interpreted as p bands.¹⁴

III. RESULTS FOR THE DOPED ZEOLITES

For the doped zeolite let us first present the result for the case where one K atom per unit cell is doped, which we denote as K_1LTA . While experiments indicate that two (one already existing in the host shown in red in Fig. 1 and the doped one) K atoms form a cluster in the α cage, the precise atomic configuration has not been determined. Thus we have placed them diagonally at (x_1, x_1, x_1) and (x_2, x_2, x_2) , which are optimized to be $(x_1, x_2) = (-0.34, 0.39)$ (Fig. 3) to mini-

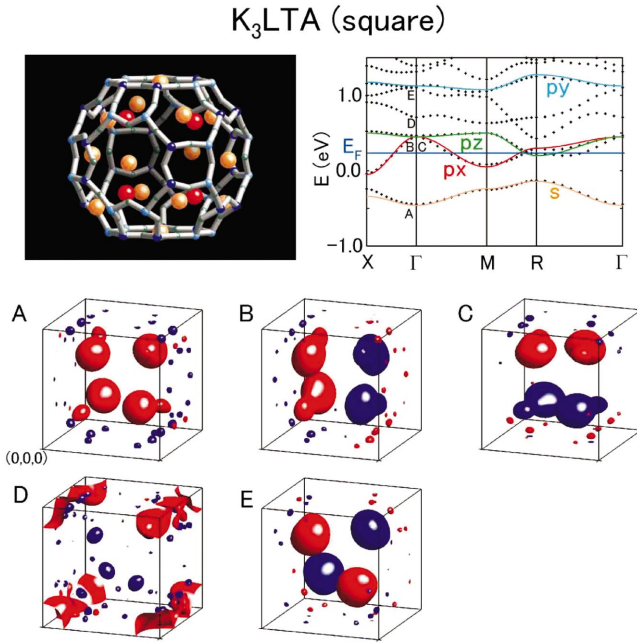


FIG. 4. (Color) A plot similar to Fig. 3 for K_3LTA , when the four red K's (three doped ones and the red one in Fig. 2) form a square in the α cage.

minimize the total energy.¹⁵

The obtained band structure in Fig. 3 has the Fermi energy shifted to the middle of the conduction (s) band, while the p band remains empty. A tight-binding fit to these bands is again excellent, where we have $(t_x, t_y, t_z) \approx (-10, -10, -5)$ in meV for the s band and $\approx (25, -10, -1)$ for the p . We have to stress that the good fit to a simple tight-binding model is highly nontrivial, since the framework, being an ionic compound $(K^+)_{12}(Al^{3+})_{12}(Si^{4+})_{12}(O^{2-})_{48}$ with nominal valence indicated, may at first seem to possess a wildly varying potential well. Chemically, however, the cage has a low electron affinity so that the electrons stay well away from the wall of the well. The wave function is indeed seen to do so, which we consider to be an intuitive reason why a simple well is effectively realized.

When we further dope the system to have K_3LTA (which is experimentally in the magnetic regime), we have now four K atoms (the doped three on top of a red ball in Fig. 1) which form a cluster in the α cage. The precise atomic configuration has not been experimentally determined, so we have focused here on the following two configurations: (i) a square with the four atoms at $(0.5 \pm x_1, 0.5, 0.5 \pm x_1)$, where $x_1 \approx 0.25$ minimizes the total energy (Fig. 4), and (ii) a tetrahedron with the four atoms at $(0.5 + x_2, 0.5, 0.5 \pm x_2)$, $(0.5 - x_2, 0.5 \pm x_2, 0.5)$, where $x_2 \approx 0.25$ is optimum (Fig. 5).

If we look at the band structure and the wave functions for case (i), we can see that three bands around E_F (located above the s band that has fallen below E_F) have amplitudes within the α cage. We identify these as p_x , p_y , and p_z bands, respectively, as confirmed by a fit of the dispersions to the tight-binding model, where the fit is again excellent. To be precise E_F intersects the p_x and p_z bands, which are degenerate, reflecting the symmetry of the cluster. The fitted

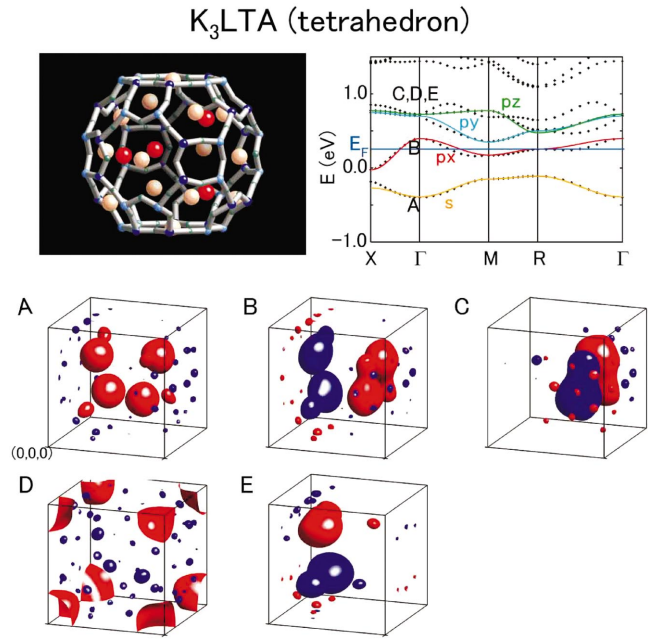


FIG. 5. (Color) A plot similar to Fig. 3 for K_3LTA , when the four red K's form a tetrahedron in the α cage.

hopping integrals for s , p_x , p_y , and p_z bands are, respectively, $(t_x, t_y, t_z) = (-30.0, -25.0, -0.5)$, $(125, -25.0, -62.5)$, $(-12.5, 25.0, -50.0)$, and $(-12.5, -0.5, 75.0)$ meV.

For the tetrahedral cluster (Fig. 5) the bands around E_F are fitted excellently by the tight-binding models with “ s ,” “ p_x ,” “ p_y ,” and “ p_z ” orbits as well. The p_y and p_z bands are degenerate at Γ , which reflect the symmetry of this cluster. The fitted hopping integrals for s, p_x, p_y , and p_z bands are, $(t_x, t_y, t_z) = (-30.0, -30.0, -10.0)$, $(105, -50.0, -20.0)$, $(-12.5, 100, -37.5)$, and $(-12.5, -0.5, 75.0)$ meV, respectively.

In both cases, the hopping integrals are almost an order of magnitude greater than those for K_1LTA , which is expected from the larger cluster size in K_3LTA . On the other hand, it is interesting to note that an electron spin resonance experiment shows that the g value decreases with $n > 2$ in K_nLTA .¹⁶ This may be understood as the degeneracy of the occupied p bands enhancing the spin-orbit interaction, thereby reducing the g value.

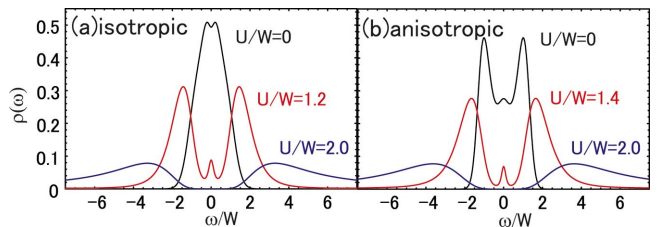


FIG. 6. (Color) Spectral function $\rho(\omega)$ for various values of U/W obtained with the dynamical mean-field theory for the Hubbard model on an anisotropic cubic lattice ($t_x : t_y : t_z = 5 : 1 : 1$) (b) as well as for the isotropic case (a) for comparison.

IV. ELECTRON-CORRELATION PROPERTIES

Now we come to a big question of whether the system is strongly correlated. As mentioned, experimentally K_1 LTA and K_3 LTA are insulators, while the LDA finds them to be metals. So we move on to estimate the Coulomb matrix elements. The largest one is the intraorbital Coulomb interaction U , which is $U = \int |\phi(\mathbf{x})|^2 V(\mathbf{x}-\mathbf{y}) |\phi(\mathbf{y})|^2 d\mathbf{x} d\mathbf{y}$, where ϕ 's are the wave functions at Γ . Regarding the electron-electron interaction V , it is assumed to be the bare Coulomb interaction as a first approximation. The value of U may be overestimated, for which methods such as the constrained LDA will be necessary.¹⁷

Since superatomic orbitals reside primarily in the interstitial region rather than on muffin tins (in the LMTO), in the calculation of the Coulomb integral, we have neglected the augmented part of the wave functions inside the MT sphere, and have used only the smoothed part in the FP-LMTO scheme.¹³ The integration is performed numerically, where we consider a $64 \times 64 \times 64$ grid for the primitive cell.¹⁸ Note that, with the Coulomb integral being inversely proportional to the linear dimension a of the orbit as mentioned in the Introduction, the atomic value of $U \geq 10$ eV with $a \sim 1$ Å becomes $U \geq 1$ eV with $a \sim 10$ Å for the superatom.

U is calculated to be $U \approx 4.5$ eV for the s band in K_1 LTA, and ≈ 4.0 eV for the p_x band in K_3 LTA. Given that $U/W \sim 10 \gg 1$, where $W \approx 0.4$ eV is the bandwidth, we can expect that these materials are Mott insulators.

However, since the relevant bands are p bands with significantly anisotropic dispersions, we have to be careful in estimating the critical U_c for the metal-insulator transition. Here we have employed the dynamical mean-field theory¹⁹ with the maximum entropy method²⁰ to estimate the transition point for a typically anisotropic ($t_x : t_y : t_z = 5 : 1 : 1$) Mott system by calculating the spectral function in the single-band Hubbard model.²¹ We have used the Quantum Monte Carlo method to solve the impurity problem in the DMFT, adopting the density of states for the three-dimensional tight-binding

model, where the charge density is set to be half filling.²² As for the temperature T , we have found that U_c does not sensitively depend on T for $T \leq 0.03$, and we set $T = 0.03$.

Figure 6 shows the result for various values of U/W , where we can see that the system becomes an insulator (as identified from a gap in the spectral function) for $U/W \geq 2$ in the anisotropic case.²³ So we conclude that this particular K-doped zeolite is well on the Mott-insulator side. In a broader context we expect that the metal-insulator transition can be controllable through control of U/W . For example, a zeolite called faujasite is known to be metallic when alkali-metal doped,²⁴ where this form of zeolite has a significantly wider (7 Å against 5 Å for LTA) window between the cages. A wider window should imply a larger transfer energy, hence a larger band width W , so faujasite, having the same cage as LTA, should have a smaller U/W .

V. DISCUSSION

Finally, we comment on the Mott transition, for which K_n LTA is experimentally²⁵ insulating even when the nominal doping level (averaged n) is fractional. This may possibly be related to the coexistence of differently doped regions with a domain structure.^{25,26} It would be interesting to investigate whether superconductivity as in the high- T_c cuprates can appear when we realize doped Mott insulators in the present system (by, e.g., destroying such a domain structure). Future work should also include an elaboration of the LDF + DMFT approach. These will enable us to systematically study electronic and magnetic effects in the “supercrystal,” for which some experimental and theoretical attempts are under way.

ACKNOWLEDGMENTS

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