Electronic properties of alkali-metal loaded zeolites — a “supercrystal” Mott insulator

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First-principles band calculations are performed for the first time for an open-structured zeolite (LTA) with guest atoms (potassium) introduced in their 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 \(\sim10\) \(\text{Å}\) acts as a “superatom” with well-defined \(s\) and \(p\)-like orbitals, which in turn form the bands around the Fermi energy. The calculated Coulomb and exchange energies for these states turn out to be in the strongly-correlated regime. With the dynamical mean-field theory we show the system should be on the Mott-insulator side, and, on a magnetic phase diagram for degenerate-orbital systems, around the ferromagnetic regime, in accord with experimental results. We envisage this class of systems can provide a new avenue for materials design.

Materials design is usually done by varying chemical elements and/or atomic crystal structures. Here we consider doped zeolites, which are unique in that (i) they are host-guest systems, where the host itself appears in a rich variety (crystal structure of cages, size of the inter-cage window, etc), on top of rich possibilities for the species and the number of guest atoms \cite{1}. (ii) the size of the cage is \(\sim\) nanometer. We can note the distinction of the zeolites from the solid fullerenes: The latter are also nanostructured supercrystals, but the relevant orbitals, even when doped with alkali metals, are LUMO/HOMO of the cage (buckeyball) rather than those of dopants \cite{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 (\(\sim\) eV for nanometer dimensions). Here we envisage that these can provide a fascinating playing ground for systemically control the electron correlation as a new avenue for materials design.

Indeed, experimental results by Nozue et al showed some zeolites (Fig.1) loaded with clusters (\(\sim\) five atoms per cage) of potassium is ferromagnetic for \(T < 8\) K \cite{3,4}, which is unique in that magnetism occurs even though all the ingredients are non-magnetic elements \cite{5}. At the same time, an infrared analysis for the K-loaded zeolite shows clear absorption edges, indicative of insulating behavior \cite{6}.

Here we address both phenomena, and show they can be explained in terms of strong electron correlations in a surprisingly simple electronic structure. We start by showing that the relevant states of K-doped zeolite can be viewed from a “supercrystal” point of view. Namely, the single-particle electronic structure as computed within the local-density approximation (LDA) for a typical zeolite having a cubic array of cages is very accurately described as a tight-binding band of “superatoms” (i.e., the states in the clusters of dopants) with simple \(s\) and \(p\) orbitals. This explains why the optical spectrum can be interpreted as transitions between \(s\) and \(p\) (or \(p\) and \(d\)) orbitals in a simplified well \cite{7}. For the LDA calculation we adopt the all-electron full-potential linear muffin-tin orbitals (FP-LMTO) \cite{8}. In fact ours is the first reliable band structure calculation for zeolites \cite{9}.

Next we estimate the Coulomb and exchange interactions for these orbitals by plugging in the LDA wave functions, and show that the interactions are large compared with the single-particle bandwidth, indicating strong electron correlations. Last, we study the effect of correlations on the spectral function in the spirit of the LDA+dynamical mean-field theory \cite{10}, and show the system resides well on the Mott-insulator side. This resolves a puzzle that the band calculation predicts that the system is a metal, while experiments indicate an insulator; moreover we show the calculated exchange energy (Hund’s coupling in superatoms) indicates ferromagnetism in the multi-orbital magnetic phase diagram, in accord with experiments.

We start with the undoped zeolite with a typical structure having a simple-cubic array of cages (Fig.1), where each cage (called \(\alpha\)) is an Archimedes polyhedron. The region surrounded by eight \(\alpha\) cages forms another cage called \(\beta\). Aluminosilicate with this structure (zeolite A) has Si and Al atoms situated at the vertices of the cages and connected by O atoms with the inner di-
ameter of α cage \(\sim 10 \text{ Å}\). The material used in most experiments \([3,4]\) is K(potassium)-form zeolite A (abbreviated as LTA hereafter), whose chemical formula, \(\text{K}_{12}\text{Al}_{12}\text{Si}_{2}\text{O}_{48}\) (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 \([11,12]\).

The result for the band structure for the undoped LTA is displayed in Fig.2, which shows that the undoped zeolite is an insulator with a gap \(\gtrsim 4\text{ eV}\), where the wave functions indicate that, while the valence-top state sits near the Fermi level, the conduction-band states (labeled as B-F) primarily reside within the α cage (for B,D,E,F) or within β (C).

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, \(\varepsilon(k) = t_x \cos(k_x) + t_y \cos(k_y) + t_z \cos(k_z)\), with \((t_x, t_y, t_z) \simeq (-20, -10, -5)\) (meV). The fitting is excellent, and, with all of \(t_x, t_y, t_z < 0\) and the wave function being nodeless (Fig.2(B), 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.

Now we come to the doped case. When one K atom is doped per unit cell (denoted as K$_1$LTA), the Fermi level shifts to the middle of the conduction (s) band (not shown), while the p band remains empty. Tight-binding fits to these bands are again excellent, with \((t_x, t_y, t_z) \simeq (-10, -10, -5)\) in meV for the s band and \(\simeq (25, -10, -1)\) for the p.

The good fit to the simple tight-binding model is highly nontrivial, since the framework, \((\text{K}^+)_{12}\text{Al}^{3+}_{12}\text{Si}^{4+}_{12}\text{O}_{48}^-\) with nominal valence indicated, is an ionic compound. Chemically, the cage has a low electron affinity so that the electrons stay well away from the wall. This is reflected in the localization of the wave function, and provides an intuitive reason why a simple well is effectively realized.

If we further dope the system to have K$_3$LTA (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(b)), which form a cluster in the α cage. The precise atomic configuration has not been experimentally determined, so we have focused here on the configuration where the four atoms (at \((0.5 \pm x_1, 0.5 \pm x_1, 0.5)\)) form a square, with \(x_1 \simeq 0.25\) minimizing the total energy, although we have calculated for other possibilities such as a tetrahedral configuration.

If we look at the band structure and the wave functions for the K$_3$LTA in Fig.3, 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 hopping integrals for \(s, p_x, p_y\) and \(p_z\) are, respectively, \((t_x, t_y, t_z) \simeq (-30.0, -25.0, -0.5), (125, -25.0, -62.5), (-12.5, 25.0, -50.0)\) and \((-12.5, -0.5, 75.0)\) in meV. The hopping integrals are almost an order of magnitude greater than those for K$_1$LTA, as expected from the larger cluster size. An ESR experiment shows that the g value decreases for K$_3$LTA with \(n > 2\) \([13]\). This may be understood as the degeneracy of the p bands enhancing the spin-orbit interaction and reducing the g value.

Now we come to a big question of whether the system is strongly correlated. As mentioned, a puzzle is that experimentally K$_1$LTA and K$_3$LTA are insulators, while the LDA finds them to be metals. So we first estimate the Coulomb matrix elements. The largest one is the intra-orbital Coulomb interaction \(U\), which is \(U = \int |\phi_1(x)|^2 V(x - y) |\phi_1(y)|^2 dx \, dy\), where \(\phi_1\)'s are the wave functions at \(\Gamma\). Here \(V\) is assumed to be the bare Coulomb interaction as a first approximation, since the s and p wave functions are well localized in the interior of each cage \([14]\). \(U\) is calculated to be \(U \approx 4.5\text{ eV}\) for the s band in K$_1$LTA, and \(\approx 4.0\text{ eV}\) for the \(p_x\) band in K$_3$LTA.

Given that \(U/W \sim 10 \gg 1\), where \(W\) is the band width, we can expect that these materials are Mott insulators.

However, since the relevant bands are p bands with very 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 theory \([15]\) with the maximum entropy method \([16]\) to estimate the transition point by calculating the spectral function in the single-band Hubbard model \([17]\) for a typically anisotropic \((t_x : t_y : t_z = 5:1:1)\) case as well as the isotropic \((1:1:1)\) one.

Fig. 4 shows the spectra for various values of Hubbard \(U/W\), where we can see that the system becomes an insulator (as identified from a gap in the spectral function) for \(U/W\) larger than \(\sim 2\) \([18]\) in the anisotropic case.

So we conclude that this particular K-doped zeolite is on the Mott-insulator side. In more general terms 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 [19], where this form of zeolite has a significantly wider (7Å against 5Å for LTA) window between the cages, which should result in a smaller \(U/W\).

We finally come to the magnetic property. To discuss this we require the inter-orbital \(U'\) and exchange integrals.
$J$ as well, where $U' = \int |\phi_1(x)|^2 V(x - y)|\phi_2(y)|^2 dx dy$, $J = \int \phi_1^*(x)\phi_2^*(y)V(x - y)\phi_1(y)\phi_2(x) dx dy$. For the $p_z-p_z$ pair in $K_3LTA$, we find $U' \simeq 3.7$ eV, and $J \simeq 0.7$ eV, which are similar to those roughly estimated by Nozue et al. [4]. Multi-orbital systems are in general favorable for ferromagnetism, since the inter-orbital kinetic-exchange coupling, $J_{\text{inter}}^{\text{kinetic-exchange}} = -2t^2/(U' - J)$, is ferromagnetic (accompanied by an orbital superlattice structure). $J_{\text{inter}}^{\text{kinetic-exchange}}$ is estimated here to be $(40 - 100)$ K for $p_z$ and $p_z$ bands in $K_3LTA$. This coupling competes with the intra-orbital kinetic-exchange coupling, $J_{\text{intra}}^{\text{AF}} \simeq 4Ut^2/(U^2 - J^2)$, which is antiferromagnetic. These exchange energies are $(60 \sim 160)$ K for $K_3LTA$, which are two orders of magnitude greater than the exchange energy, $4t^2/U \simeq O(1)$ K, for the (single-band case of) $K_1LTA$, where the difference is mainly due to an order of magnitude difference in $t$. If we look at the magnetic phase diagram in the literature [20,21], $K_3LTA$ is, as indicated in the inset of Fig.4, right around the ferromagnetic phase boundary.

Experimentally, ferromagnetism with finite magnetization has been observed for $K_nLTA$ with $2 < n < 7$ [3,4], where the Curie temperature $\sim 10$ K for $n \sim 3$ while the spin susceptibility for $T > 30$ K exhibits a Curie-Weiss law, $1/(T - \Theta)$, with the Weiss temperature $\Theta \simeq 0$ K for $K_1LTA$, while $(-40 \sim -30)$ K for $K_3LTA$ [3,4]. The doping dependence as well as the energy scale are consistent with the exchange interactions estimated here.

Finally we comment on the Mott transition, for which $K_nLTA$ is experimentally [22] insulating even when the nominal doping level (averaged with the exchange interactions estimated here. This may possibly be related to a coexistence of differently doped regions with a domain structure [22,23]. It would be interesting to know whether superconductivity as in the high-$T_c$ cuprates can appear when we realize doped Mott insulators in the present system (by, e.g., degrading 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.

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[18] For an infinite-dimensional system the metal-insulator transition point has been estimated to be $U/W = 1 \sim 2$. 

\[ \begin{align*}
J &= \int \phi_1^*(x)\phi_2^*(y)V(x - y)\phi_1(y)\phi_2(x) dx dy, \\
J &= \int |\phi_1(x)|^2 V(x - y)|\phi_2(y)|^2 dx dy,
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FIG. 1. Left: Geometry of the LTA structure. Right: Unit cell (i.e., \( \alpha \) cage) of the undoped zeolite considered here, with dark blue: Si, light blue: Al, dark green: oxygen, orange and red: K.

FIG. 2. 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) at \( \Gamma \) in the bands A-F as labeled in the band structure.

FIG. 3. Band structure of a K-doped zeolite \( K_3 \)LTA. Colored curves are a tight-binding fit. Top left inset depicts the atomic configuration, where four red K’s (the doped K + the red K in Fig.1) form a square in the \( \alpha \) cage. Bottom panels are wave functions at \( \Gamma \) in the bands A-E as labeled in the band structure.

FIG. 4. Spectral function, \( \rho(\omega) \), obtained with the dynamical mean-field theory for the Hubbard model on the cubic lattice with the isotropic(a) or an anisotropic(b) dispersions for various values of \( U/W \). The bottom inset shows the magnetic phase diagram for the degenerate Hubbard model against the inter-orbital Coulomb \( (U') \) and the Hund coupling \( (J) \) interactions after Ref. [21], where the parameter region for the doped zeolite is indicated by blue hatch with its widths representing the dependence on the atomic configuration of the cluster and on the assumption of \( U = U' + 2J \) on which the diagram is drawn. \( W \) is here defined as the width of the gaussian density of states.