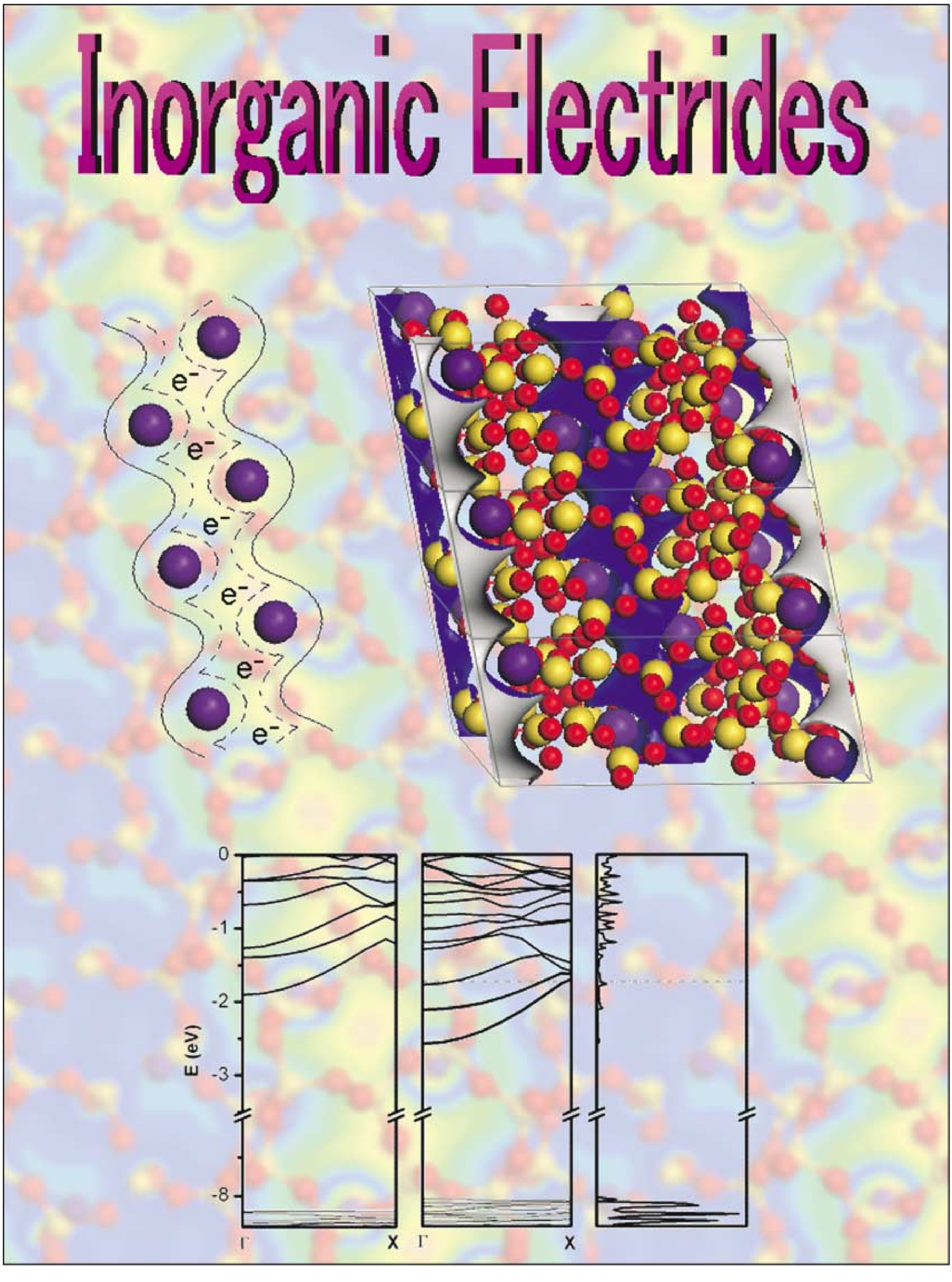

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Inorganic Electrides

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Abstract: Inorganic electrides are a novel kind of ionic compounds in which the anions are electrons confined in a complex array of cavities or channels and the cations are nanoscale arrays of alkali metal ions that provide charge balance. In electrides the donated electron behaves like a low-density correlated electron gas, whereby the dimensionality of the electron gas and its electronic and magnetic properties are determined by the topology of the cavities in the host matrix. Unlike traditional electrides, in which alkali cations are encapsulated within an organic cage, inorganic electrides are thermally stable. The current inorganic electrides based on alkali metal loaded zeolites can be designed as useful reduced-dimensionality materials. Inorganic electrides are powerful reducing agents, and they are able to reduce small aromatic molecules to the radical anions within the channels of the zeolite.

Keywords: alkali metals · electrides · reduction · zeolites

Introduction

How simple can an anion be? The appearance of electrides[1,2] shows that it can merely a stoichiometrically trapped or itinerant electron. In electrides, the electron density is spread over a cavity or channel rather than being confined to a particular atom or molecule. Analogues of these anionic electrons are solvated electrons in ammonia or electrons trapped at anion vacancies in alkali halide salts (F centers). The mechanism of electron trapping in electrides is suggested so as to minimize the kinetic energy by spreading the electron density throughout a large empty space despite the possible existence of a maximum in the potential energy in that region.[3] With such a unique structure, electrides provide a rich area for theoretical investigations and promise broad applications in chemical synthesis, catalysis, nanodevices, and functional materials.

Traditionally, the counterpart cations of electrides are alkali metals sequestered within organic molecular cages or sandwiched between two organic ligands. Because the trapped electrons are powerful reducing agents, they tend to destroy the organic ligands. Therfore, the organic electrides must be kept at temperatures below −40°C, which hampers the research and their potential application. Many efforts have been devoted to the search for thermally stable electrides.

Alkali metal loaded porous zeolites have been extensively studied.[4–6] The alkali metals are found dissolved and ionized in the zeolite host, which make this kind of systems a good candidate for an inorganic electride.[4] Recently room-temperature stable inorganic electrides with cation-to-electron ratios of 1:1, as found in organic electrides, have been synthesized by intercalating alkali metals to all-silica zeolites.[7,8] The aim of this article is to introduce the interesting concept of inorganic electrides based on alkali metal loaded zeolites.

Synthesis and Structure

In 1960s, Kasai and co-workers have found that electrons could be trapped in aluminosilicate zeolites by either ionizing radiation or exposure to sodium vapor.[9] To obtain stoichiometic inorganic electride, Dye et al. chose pure silica zeolites ITQ-4, ITQ-7, and β, which are free of pre-existing cations, to add alkali metals.[7,8] They have tested various alkali metals and zeolites, but we will only concern the typical cesium-loaded zeoite ITQ-4 example here. ITQ-4 has a unit cell with formula $Si_{32}O_{64}$ and has sinusoidal open channels with diameters of about 6.4 Å.[10] ITQ-4 with low defect concentrations was calcined by using fluoride as mineralizer. Then the dehydrated zeolite and a weighed amount of cesium are sealed under vacuum in a borosilicate flask, and the whole system is heated with frequent mechanical agitation or occasional brief exposure to an ultrasonic bath to ac-

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celerate the adsorption of cesium vapor. The surface of the powdered zeolite sample turned blue within a few hours; this is an indication of the generation of an electride. The reaction was completed overnight. After complete absorption of the cesium, the samples have overall uniform Cs concentrations between and within crystals, as indicated by energy dispersive spectroscopy. The overall amount of absorbed metal per unit cell of the zeolites was determined by collection of hydrogen gas produced by reduction of water, and by titration of the CsOH formed.

Based on the well-prepared sample, the pair distribution function (PDF) technique was used by Petkov et al. to determine the ionzation and atomic ordering of the cesium intercalated inside the pseudo-1D nansize pores of the zeolite ITQ-4.[11] In powder XRD, the added cesium atoms smear out the peaks into a diffuse pattern and no new Bragg peaks due to Cs appear; therefore, the location of the cesium species could not be directly determined. PDF analysis is a way to extract disorder information from an XRD pattern and can be applied to materials that exhibit any degree of structural coherence, ranging from perfect crystals to nanocrystalline particles and liquids. From the overall PDF patterns for 3.6 and 4.6 Cs per unit cell in ITQ-4, they found that the local Si–O structure is not significantly disturbed by the incorporation of Cs, but that the long-range order is disrupted. The Cs differential PDFs, which have the advantage of being chemically specific and reflect only the atomic correlations between Cs atomic or ionic species and their immediate environment, were best fit by a model of zigzag Cs^+ chains within the 1D sinusoidal channels of ITQ-4. Hence, the structural model established by PDF analysis is that the Cs^+ ions form continuous zigzag chains along the narrow pore channels as shown in Figure 1; this makes them distinct from the previously studied ionized large clusters of cesium in zeolite-X[5] and the body-centered cubic array of Na_4^{+3} ions in sodalite.[6]

This PDF structure model has been validated by our first-principles calculations.[12] We relaxed the geometry from the optimized zeolite unit cell ($Cs_4Si_{32}O_{64}$) together with randomly located cesium atoms in the zeolite channels. After the geometry relaxation, we found the zeolite framework was little affected and the doped cesium atoms formed zigzag cesium chains within the channels. The optimized positions of cesium atoms agree well with the PDF-fitting results, except for some deviations in the coordinates along the channel direction. We obtain variable Cs–Cs distances (5.42 and 5.65 Å alternately), which match the channel shape better than the PDF-fitting results and is consistent with the spin-paring model proposed on the which basis of magnetic susceptibilities and EPR spectra.[7] In the optimized geometry, each cesium atom is bound by several Si–O–Si units.

Abstract in Chinese: 无机电子阴离子化合物是一种新奇的化学材料。在这种材料中阴离子是限制在复杂的腔体或者通道阵列中的电子。而提供电荷平衡的阳离子是碱金属离子阵列。电子阴离子化合物中的离域电子作为低密度关联电子气，其电磁性质由所受空间限制的拓扑结构决定。与传统的有机电子阴离子化合物不同的是，无机电子阴离子化合物是热力学稳定的。目前基于沸石碱金属掺杂的无机电子阴离子化合物可以被用来设计各种低维电子结构。另外，无机电子阴离子化合物还可以被应用为一种强还原剂。

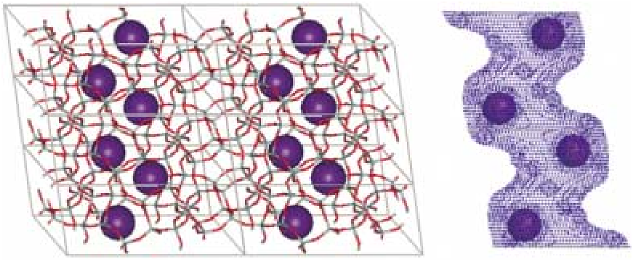

Figure 1. Schematic atomic structure of cesium loaded zeolite ITQ-4. Left: Perspective view of the unit cell. Alkali metal atoms (purple circles) are in the nanopores. Oxygen atoms are in red and silicon is in gray. Right: Channel model of zeolite ITQ-4. Within the sinusoidal zeolite channel, cesium forms zigzag chains.

Evidence for Ionization of Cs and Delocalization of Electrons

In organic electrides, the strongest experimental argument in favor of electron trapping comes from their structural similarity to alkalides, which are crystalline compounds with the same type of complexed cations and with alkali-metal anions occupy the anionic sites.[13] Here, structure analysis also gives a strong clue for the electride model of Cs loaded ITQ-4. By comparing their results of Cs differential PDF with models of ITQ-4 containing either neutral or charged cesium atoms, Petkov et al. found that only positively charged cesium fits the data.[11]

The optical spectra of thin organic electride films always show a distinct absorption peak in the near-IR region which is similar to that of solvated electrons in ammonia and is a characteristic of electron localization. Diffuse optical reflectance spectra were collected by the Dye group for the alkali metal loaded zeolite samples and converted to apparent absorbance with the Kubelka–Munk function.[7,8] The characteristic near-IR peak at 1400 nm for Cs loaded ITQ-4 sample has been observed. Our first-principles calculation shows that this peak may contribute to the transition between bands that mainly originate from the occupied and unoccupied Cs 6s orbitals.

Ichimura et al. have found additional experimental evidence from ^{133}Cs and ^{29}Si NMR spectra, obtained over wide scan regions,[7] for delocalization of the electrons following ionization of Cs in cesium loaded ITQ-4. No detectible signal was found in the ^{133}Cs spectrum and there was significant reduction in signal in the ^{29}Si spectrum. It is known that alkali metals in aluminosilicate zeolites often give observable signals in alkali metal, silicon, and aluminum NMR spectra, even at high loadings. However, in this case the electron density is spread out enough so as to broaden the NMR lines substantially. Air oxidation restores the NMR spectra.

Theoretical evidence comes from band structure calculations. Fictitious stand alone Cs^+ zig-zag chains with the same geometry as those of within the zeolite channel give prefect 6s band structure, which is coincident with the corresponding bands of cesium loaded zeolite ITQ-4. However, a band structure calculation for fictitious Cs atomic chains gives much higher energy for the 6s bands. This result strongly suggests the ionization of cesium with the channels. The delocalization of the excess electrons can be directly observed from our first-principles calculations. We plot the charge density in Figure 2 for one of the bands of those excess electrons. We can clearly see that the charge density distributes mainly within the zeolite channel and is delocalized from the cesium cations. In the iso-surface image, with the iso-value being a little larger than the mean value, we can find chains of connected charge density maxima that are very similar to those of organic electrides.

A simple but clear picture for ionization to form Cs^+ and itinerent electrons was proposed by Ichimura et al.[7] As shown in Figure 1 (left), the smaller Cs^+ can be strongly bound with the sinusoidal channel wall, whereas the large neutral cesium atom would be only weakly bound. The released electron could then occupy the remaining free space. Although the electron density is attracted to the cation through Coulombic forces, it is polarized away from the cation by the interaction of Cs^+ with the oxygen lone pairs.

Properties and Applications

Magnetic susceptibilities and EPR spectra for cesium added ITQ-4 show only a minor "Curie Tail", corresponding to paramagnetism from less than 1% of the total cesium. Despite the difficulties in the interpretation of the detailed magnetic behavior of the paramagnetic species in undoped zeolites, these experiments have indicated that most of the electrons in this inorganic electride are spin-paired; this suggests that loose dimmers or chains of ions and electrons are favored over separate Cs^+-e^- species. Electron spin-pairing is ubiquitous in open channel electrides such as $K^+(C222)e^-$[14] and in metal–ammonia solutions.

Besides Heisenberg antiferromagnetism, most confined electron gases in organic electrides exhibit Mott insulating behavior. However, our calculations give a metallic band structure for the cesium-loaded zeolite ITQ-4. When doped with cesium, two interstitial electride energy bands, which mainly originate from the Cs 6s electrons, appear in the energy gap of zeolite ITQ-4 near the bottom of conduction band. As well as the two electride bands, there are three energy bands crossing the Fermi level. The density of states at the Fermi level is 7.09 states per eV per cell. A simple estimation shows that the electron correlation should not be so strong in this inorganic electride, and the DFT description is valid. Calculations with various doping rates of Cs all predict metallic behavior. The metallic properties promise a broad application of this material in areas such as nanodevices. An example of metallic organic electride is $Li(NH_3)_4$.[15]

This material is a powerful reducing agent. In addition to their quantitative formation of hydrogen by reduction of water as mentioned above, the included cesium can reduce aromatic molecules such as benzene, which is difficult to reduce in solution, to radical anions within the pores of the zeolite, as shown by both EPR and optical spectra. The high reducing power of this material

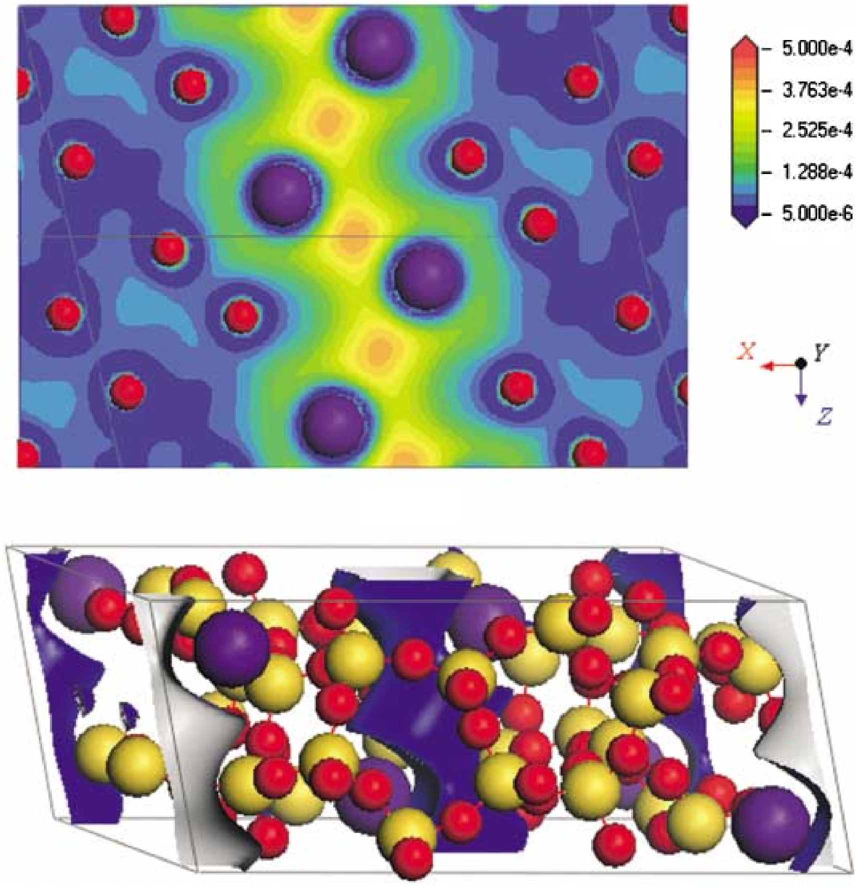

Figure 2. Charge density of an electride state at the Γ point in Brillouin zone (taken from reference [12]). Top: Contour map of the charge density within a slice parallel to the *a* and *c* axis. The purple and red circles are Cs and O atoms, respectively. Bottom: Isosurface of the charge density with the iso-value of 2.0×10^{-4} e Å^{-3}. The mean value of the charge density is 8.0×10^{-5} e Å^{-3}.

may originate from its relatively high Fermi energy and the delocalization of the donated electron density.

Conclusion

Inorganic electrides are room-temperature stable electrides. Within the channels of zeolites, the alkali metals are ionized and release nearly-free electrons. The inorganic electride based on cesium-loaded zeolite ITQ-4 has been predicted to have metallic behaviour. Given the advances in both synthesis and characterization of the room-temperature stable inorganic eletrides highlighted here, it may be possible to develop applications for electrides, such as detectors, catalysts, and electro-optics for communication. By careful control of the alkali metal content and the host structure, this material offers the possibility of a high degree of chemical control over important electronic properties.

Note Added in Proof

After the submission of this work, a new kind of inorganic electride was synthesized through the removal of clathrated oxygen ions from the crystallographic cages in a single crystal of $12\,CaO{\cdot}7\,Al_2O_3$.[16,17]

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