Structure of Intercalated Cs in Zeolite ITQ-4: An Array of Metal Ions and Correlated Electrons Confined in a Pseudo-1D Nanoporous Host

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The presence of Cs^+ ions in the pseudo-1D nanopores of zeolite ITQ-4, $Si_{32}O_{64}$, is confirmed by x-ray diffraction and atomic pair distribution function analysis. Inside the nanopores the Cs^+ ions are found to assemble in zigzag chains and thus form an extended, positively charged sublattice providing charge balance for a low-density electron gas also confined to the nanopores.

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Nanoscale arrays of metal atoms are being extensively studied because they often exhibit interesting and useful properties not occurring in bulk metals. Examples include nanomagnets [1], nanocatalysts [2], composites with improved optical properties [3], and nanodevices [4]. The subject of this Letter is the class of novel, and poorly understood, low-dimensional electron systems known as ''electrides'' [5,6]. In these materials a low-density gas of correlated electrons is confined in the cavities of an inert nanoporous host coexisting with nanoscale arrays of alkali metal ions that provide charge balance [6]. The confined electron gases exhibit Mott insulating behavior and Heisenberg antiferromagnetism [6].

Understanding and predicting the novel electronic and magnetic properties of all these nanostructured materials require a detailed knowledge of the atomic ordering at the nanoscale. Usually the structure of materials is obtained from the Bragg peaks in their diffraction patterns. However, materials constructed at the nanoscale often do not possess the translational symmetry and long-range order of conventional crystals. Instead they assume structures of reduced dimensionality and/or accommodate a large number of defects and local disorder [1–6]. The diffraction patterns of such materials show a pronounced diffuse component and few Bragg peaks, if any. This poses a real challenge to the traditional techniques for structure determination. In this Letter we use the atomic pair distribution function (PDF) technique [7,8] to determine the ionization and atomic ordering of the cesium *intercalated inside the pseudo-1D nanosize pores* of the zeolite ITQ-4, $Si_{32}O_{64}$. The direct observation of regular zigzag chains of Cs^+ ions clearly demonstrates that the material is the first example of an inorganic electride [9]. The discovery of a room-temperature stable inorganic electride will facilitate more extensive research in these low-dimensional correlated electron materials.

Ionic solids such as CsCl have a lattice of Cs^+ ions with Cl^- as counterions. Cs^+ can also be stabilized in solution when solvated by polarizable molecules. Electrides are at the interface of these extremes, where an ionic lattice forms from solvated alkali cations such as Cs^+ and the counterions are simply the donated electrons. In electrides the donated-electron density has been shown to be confined within cavities and channels in the matrix [6,10]. It behaves like a low-density correlated electron gas where the dimensionality of the electron gas and its electronic and magnetic properties are determined by the *topology* of the cavities in the host matrix [6].

The first known electrides relied on organic molecules as cation-encapsulating agents, which rendered them extremely reactive and unstable at room temperature and hampered research. Recently, a likely candidate for an inorganic electride that is stable at room temperature has been synthesized by intercalating cesium in zeolite ITQ-4 [9]. Optical and NMR spectra suggest that cesium ionizes to yield Cs^+ cations and trapped electrons, but no unequivocal structural evidence has been advanced to date. Here we use the PDF technique to demonstrate the presence of Cs^+ ions and to determine their arrangement inside the nanopores. The PDF method has been used widely to study the structure of bulk amorphous [7] and nanocrystalline materials [8], as well as to find local structural distortions in crystals [11]. Here we use it to determine the structure of species intercalated inside nanoporous materials as has been demonstrated previously [12]. The Cs^+ ions form continuous zigzag chains along the narrow pore channels, making them distinct from the previously studied ionized large clusters of cesium in zeolite-X [13] and the bcc array of Na_4^{+3} ions in sodalite [14].

The atomic PDF is a function that gives the number of atoms in a spherical shell of unit thickness at a distance r from a reference atom and thus reflects the structure of materials. The PDF, $G(r) = 4\pi r[\rho(r) - \rho_o]$, is defined as

$$G(r) = (2/\pi) \int_{Q=o}^{Q_{max}} Q[S(Q) - 1]\sin(Qr)dQ, \quad (1)$$

where ρ_o is the average atomic number density, $\rho(r)$ is the

atomic pair density, Q is the magnitude of the wave vector, and the so-called structure function $S(Q)$ is the corrected and properly normalized powder diffraction pattern of the material [7]. By using the PDF approach, materials that exhibit any degree of structural coherence, ranging from perfect crystals [11] to nanocrystalline particles [8] and liquids [7], can be quantitatively studied.

Three samples were investigated: pristine $Si_{32}O_{64}$ and the electrides $Cs_xSi_{32}O_{64}$ ($x = 3.6, 4.6$). The all-silica zeolite $Si_{32}O_{64}$ is an ordered framework of corner-shared SiO_4 units with a high density of pores and channels of nanometer size [15]. Most noticeable is the system of pseudo-1D sinusoidal channels with diameter ~7 Å running parallel to the c axis of the monoclinic unit cell. To prepare the electrides, dehydrated zeolite and a weighted amount of cesium metal were sealed under vacuum in borosilicate flasks and heated to 60 °C. The reaction was completed overnight. The amount of absorbed Cs was determined by collection of hydrogen evolved upon reaction with water, and by titration of the CsOH formed. As prepared electrides and pristine ITQ-4, all in sealed capillaries, were used for powder diffraction experiments with 29.09 keV ($\lambda = 0.425$) x rays at the beam line X7A of the National Synchrotron Light Source, Brookhaven National Laboratory. Scattered radiation was collected with an intrinsic germanium detector connected to a multi-channel analyzer. The raw diffraction data were corrected for flux, background, Compton scattering, and sample absorption. The intensities were normalized in absolute electron units, reduced to structure functions $S(Q)$, and Fourier transformed to the corresponding PDFs, $G(r)$. All data processing was done using the program RAD [16]. Experimental powder diffraction patterns are shown in Fig. 1(a) and the corresponding PDFs $G(r)$ in Fig. 2. Sharp Bragg peaks are present in the diffraction pattern of pristine $Si_{32}O_{64}$ [Fig. 1(a)]. The corresponding $G(r)$ (Fig. 2) also features sharp peaks reflecting the presence of an ordered network of SiO_4 units in this crystalline material. A model PDF calculated on the basis of the well-known 96-atom unit cell [15] of $Si_{32}O_{64}$ is also shown in Fig. 2. Model calculations were done with the program PDFFIT [17] within the constraints of the monoclinic $Im/2$ space group. As expected the model and experimental data agree quite well. Bragg peaks in the diffraction patterns of the samples loaded with Cs are significantly attenuated [see the inset in Fig. 1(a)] and already at ~2 Å^{-1} merge into a slowly oscillating diffuse component. This reflects the tendency of the zeolite host to become structurally disordered upon absorbing alkali metals. The significant diffuse scattering present in the $Cs_xSi_{32}O_{64}$ diffraction patterns contains important information about the structure of the intercalants that is lost in a usual crystallographic analysis relying on the Bragg scattering only. In the total structure functions extracted from the diffraction patterns [see Fig. 1(b)] all components of the diffraction data, including the weak but equally important features at higher
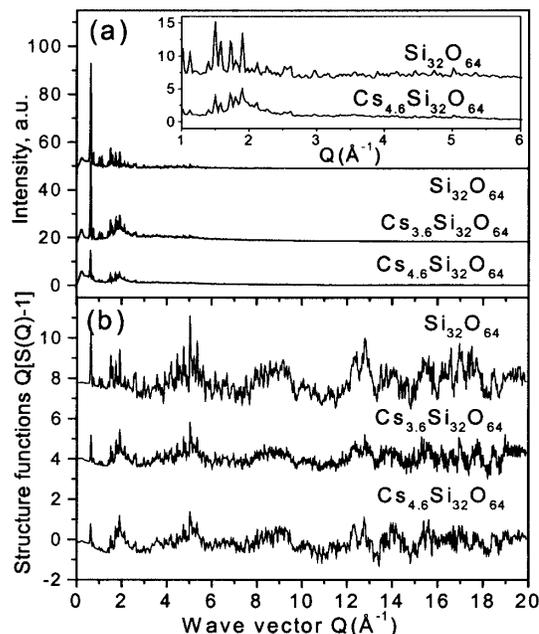
FIG. 1. Powder diffraction patterns (a) and the corresponding structure functions (b) of pristine $Si_{32}O_{64}$ and electrides $Cs_xSi_{32}O_{64}$. A portion of the diffraction patterns is given on an expanded scale in the inset.

wave vectors Q, are taken into account. This enhances the sensitivity to local atomic ordering and makes the Fourier couple $Q[S(Q) - 1]$/PDF an experimental quantity well suited to study materials of limited structural coherence such as Cs intercalated ITQ-4. As can be seen in Fig. 2 the PDFs of the electrides are rich in distinct, structure-related features. Evidently, although the silicate framework in $Cs_xSi_{32}O_{64}$ electrides is distorted, its topology is
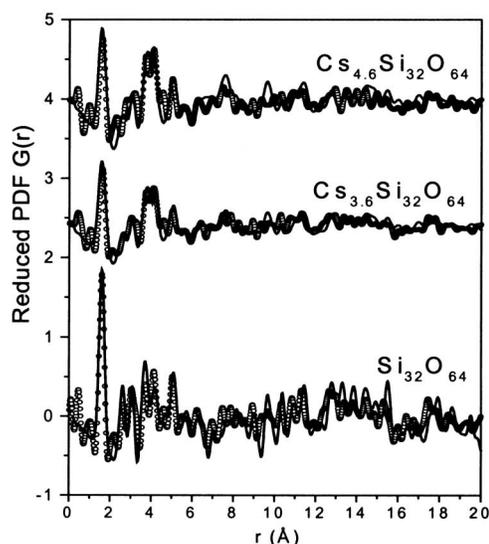
FIG. 2. Experimental (circles) and model (line) PDFs for $Cs_xSi_{32}O_{64}$ ($x = 0, 3.6, 4.6$).

preserved, and locally they remain well-ordered materials. In particular, the building SiO_4 units, seen as a sharp peak at 1.61 Å in all three PDFs, remain intact. This is supported by the fact that treatment with water and subsequent neutralization and washing restores the Bragg peaks in the diffraction pattern [9].

Careful inspection of Fig. 2 reveals a new feature at approximately 4 Å in the experimental PDFs of the Cs-doped samples. This feature grows in line with the number of Cs atoms absorbed in the nanopores and thus can be unambiguously ascribed to atomic correlations involving Cs atoms/ions. Cesium differential PDFs, properly weighed differences of the total PDFs of Fig. 2, are shown in Fig. 3. They reflect only the atomic correlations between the Cs atomic or ionic species and their immediate environment (Cs-Cs and Cs-silicate framework), while the total PDFs of Fig. 2 reflect all atomic correlations in $Cs_xSi_{32}O_{64}$. Differential PDFs have the advantage of being chemically specific and are frequently used in structure studies of complex materials [12,18]. They are usually obtained by extra experiments involving isotope substitution or resonant scattering. We followed a simpler and equally efficient approach by taking the difference of experimental PDFs for samples with different Cs contents; this approach works well in our case since the local structure of the underlying silicate framework survives in the electrides.

As can be seen in Fig. 3 the experimental differential PDFs exhibit physical oscillations up to interatomic distances of 13 Å and possibly beyond. This shows that Cs atoms/ions assume a particular atomic ordering inside the nanopores of $Si_{32}O_{64}$. To identify the atomic ordering in the assembly of Cs atoms/ions we considered several structural models and tested them against the experimental PDFs. The models were constructed by placing cesium

atoms and/or ions inside the nanopores in $Si_{32}O_{64}$. Care was taken that no atoms/ions came closer than the sum of the corresponding atomic/ionic radii: $Cs^+ \sim 1.8$ Å; $Cs^0 \sim 2.67$ Å; $Cs^- \sim 3.5$ Å; $O^{2-} \sim 1.2$ Å; $Si^{4+} \sim 0.4$ Å. No model involving neutral Cs atoms, Cs^0, or negatively charged cesium ions, Cs^-, was found to come even close to reproducing the experimental PDF data. The modeling rules out the presence of significant atomic Cs and Cs^- ions inside the nanopores and supports the finding of optical and NMR experiments [9] that Cs atoms ionize to Cs^+ when absorbed in $Si_{32}O_{64}$.

Models that involve Cs^+ ions sitting inside the sinusoidal channels in $Si_{32}O_{64}$ did a much better job in reproducing the experimental PDF data. Several models of that type were attempted and the one with Cs^+ ions occupying positions $4h$ (1/2, y, 0) and $4g$ (0, y, 0) (space group $I2/m$) performed best. Total and Cs differential PDFs calculated with Cs^+ ions alternating on the $4h$ [$y = 0.870(5)$] and $4g$ [$y = 0.370(5)$] sites with occupancies reflecting the particular chemical compositions are shown in Figs. 2 and 3, respectively. The agreement with experimental data is very good.

According to the model, Cs^+ ions sit close to the walls of the sinusoidal channels in $Si_{32}O_{64}$. Since the free space inside the channels is limited, the intercalated alkali metal are forced to come as close together as possible with increasing doping. As expected, this trend is opposed by an increase in the Coulomb repulsion between the positively charged metal ions. Our model shows that with $Cs_xSi_{32}O_{64}$ the balance is achieved when most of Cs^+ ions occupy positions $4h$ and $4g$ alternatively and are separated by at least 5.2 Å. Thus, when x approaches four, Cs^+ ions in $Cs_xSi_{32}O_{64}$ alternate on $4h$ and $4g$ sites, resulting in exactly half of them being occupied
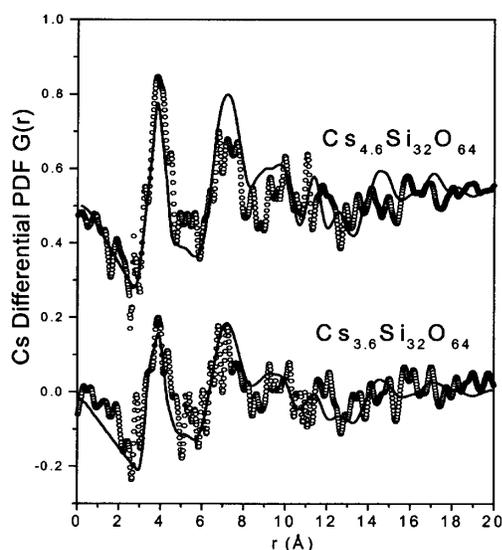
FIG. 3. Cs differential PDFs for $Cs_xSi_{32}O_{64}$ electrides. Experimental data (circles) and model data (line).
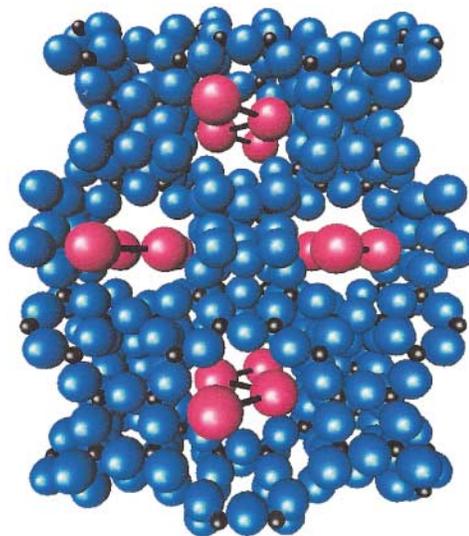
FIG. 4 (color). Fragment of the atomic structure of $Cs_xSi_{32}O_{64}$ with Cs^+ ions (red circles) in the nanopores assembled in zigzag chains. Oxygen atoms are in blue and silicon is in black.

and forming an assembly of zigzag chains inside the silicate framework as shown in Fig. 4. The similarity between the total and Cs differential PDFs for $x = 3.6$ and $x = 4.6$ (see Figs. 2 and 3) suggests that such zigzag chains (although shorter) are very likely to exist even at light levels of doping. This scenario also naturally explains the empirical observation that $Cs_xSi_{32}O_{64}$ electrides become increasingly difficult to synthesize as x exceeds 4. More than four alkali metals per unit cell requires that more than half of the $4h$ and $4g$ sites are occupied necessitating a short (~ 4 Å) Cs^+-Cs^+ contact. This strongly increases Coulomb repulsion and is the likely limit to the cesium loading observed to be $x = 4.6$ at which point the number of Cs^+ ions on the shorter segments is one per two unit cells of ITQ-4. It may be added that an extended cationic sublattice of the type shown in Fig. 4 will necessitate that its counterpart, the confined electron gas, spreads out along the encapsulating sinusoidal channels. This is fully consistent with the observed broadening of the NMR lines and antiferromagnetic properties of $Cs_xSi_{32}O_{64}$ [9].

In conclusion, using the atomic PDF technique we have provided direct structural evidence that cesium intercalated in zeolite ITQ-4 is in the form of Cs^+ ions arranged in short-range ordered zigzag chains. This verifies that $Cs_xSi_{32}O_{64}$ is a room-temperature stable inorganic electride. The PDF technique yields that atomic ordering of the intercalated cesium in terms of quantitative parameters such as atomic coordinates even when the structural coherence of the intercalated species is only on the nanometer length scale. The PDF technique probes the bulk and is an essential complement to scanning probe microscopy and other imaging techniques that are useful only when nano-arrays are exposed on an open surface. The structural coordinates published here could be used in electronic structure calculations of this new inorganic electride revealing new insight into novel low-dimensional correlated electron materials.

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