Location of Cation Sites in a Hydrated Copper-exchanged Chabazite by Extended *X*-Ray Absorption Fine Structure†

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The local structure around copper ions in a hydrated copper-exchanged chabazite has been characterized by means of extended *X*-ray absorption fine structure spectroscopy. The model proposed on the basis of the experimental results indicates that copper ions occupy two sites, one with a distorted octahedral co-ordination, the other with a square-pyramidal geometry. The previously suggested hypothesis that copper ions are located in the large cavity of the chabazite is confirmed, although a different co-ordination for one site was detected.

Location of cations in hydrated zeolites is generally a hard task often because of fractional occupancies of cations and water molecules. As a consequence, *X*-ray analysis sometimes gives controversial results. A typical example is furnished by the crystal structure analysis of a hydrated Cu^{2+}-exchanged chabazite, reported some years ago by Smith and co-workers.[1] The interpretation of the electron density in the large cage of the chabazite was uncertain, showing however that all Cu^{2+} and H_2O molecules are present in those cages. These authors concluded that further speculation is futile, but the placement of Cu^{2+} in two sites of approximately equal occupancies, one in a near-octahedral environment, the other in a pentagonal bipyramid, is not crystal-chemically unreasonable.[1] More reliable information about the local co-ordination geometry of cation sites could be obtained by extended *X*-ray absorption fine structure (EXAFS) measurements. This technique provides a description of the short-range order of selected atomic species in terms of the number of neighbours, distances, and thermal and static disorder within a range of those distances without the need for long-range order.

Experimental

Sample Preparation.—A sample of a natural calcium-rich chabazite, of starting composition $Ca_{1.4}Sr_{0.3}Al_{3.8}Si_{8.3}O_{24}\cdot 13H_2O$ from N.E. Azerbaijan, Iran,[2] was ion exchanged in 1 mol dm^{-3} NaCl solution and then with 0.01 mol dm^{-3} $CuCl_2$ solution, following the procedure of ref. 1. Chemical analysis of the pale blue-green powder showed complete exchange by copper.

EXAFS Spectroscopy and Data Reduction.—The EXAFS experiment consisted in the measurement of the *X*-ray absorption coefficient as a function of the *X*-ray energy. Structural information was deduced by relating the experimental modulation of μx (where μ is the absorption co-efficient and x the thickness of the sample) above the absorption edge E_0, $\chi(k)$, to a theoretical description in the single-electron, single-scattering, plane-wave approximation (1),[3] where k is the wave

$$\chi(k) = \frac{1}{k}\sum_i \frac{N_i}{R_i^2} F_i(k) e^{-2\sigma_i^2 k^2} \sin[2R_i + \Phi_i(k)] \quad (1)$$

vector of the ejected photoelectron, N_i the number of neighbours at a distance R_i from the absorbing atomic species, $F_i(k)$ the amplitude of back scattering, σ_i a Debye–Waller-like term, and $\Phi_i(k)$ the total phase shift experienced by the photoelectron for each co-ordination shell i; $\Phi_i(k)$ is characteristic of a particular combination of absorbing atom and back-scattering shell, whereas $F_i(k)$ is almost entirely dependent on the back-scattering shell. The last two terms mentioned can be calculated theoretically[4] or derived experimentally from reference compounds of known crystal structure. The latter procedure was used here. Analysis of the EXAFS data was carried out according to a standard procedure of Fourier filtering and fitting described elsewhere.[5]

The EXAFS spectra of CuO, $CuSO_4\cdot 5H_2O$, and the chabazite were measured. Known amounts of finely powdered samples were deposited on nucleopore membranes in order to obtain a very homogeneous film of thickness x and to have $\mu x \approx 2$ after the photoelectron excitation. The measurements were performed at LURE (French synchrotron national facility, Orsay) at the station EXAFS-I, installed on the DCI storage ring, working at 1.85 GeV, a typical current being 200 mA, in the classic transmission mode. A Si 311 channel-cut monochromator was used in order to reject harmonics. All EXAFS spectra were collected in the energy range 8 700—9 800 eV, $\Delta E = 2$ eV. Each point was measured for 1.5 s. All spectra were measured three times, in air at room temperature.

Results and Discussion

Figure 1 shows the EXAFS spectra for the reference compound CuO, $CuSO_4\cdot 5H_2O$, and for the chabazite. The structure of CuO is characterized by a first shell of four oxygen atoms around each Cu^{2+} ion, nearly in a plane at the corners of a square at a distance of 1.95 Å.[6] The k^3 multiplied spectra were then Fourier-transformed in the range 48—650 eV after application of a Gaussian window. The moduli which represent the radial distribution function in R space are shown in Figure 2, where it should be noted that the peaks are shifted towards lower values of R than the real distances because of the k dependency of the function $\Phi(k)$. Only one peak appears in the Fourier transform of both $CuSO_4\cdot 5H_2O$ and the chabazite, which is easily attributed to Cu–O atom pairs. The amplitude and phase functions were calculated from the Fourier-filtered first peak of CuO.

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† *Non-S.I. unit employed:* eV ≈ 1.60 × 10^{-19} J.

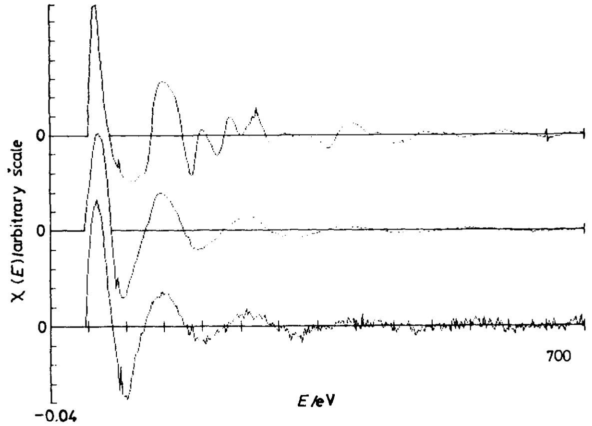

Figure 1. Experimental EXAFS signals for (top to bottom) CuO, $CuSO_4{\cdot}5H_2O$, and the chabazite as $\chi(E)$ *versus* E

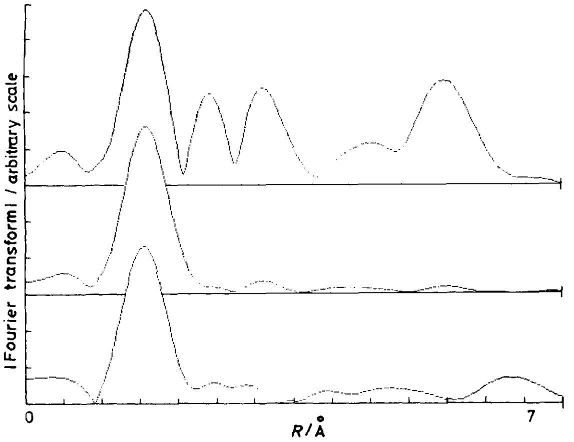

Figure 2. Moduli of the Fourier transforms for (top to bottom) CuO, $CuSO_4{\cdot}5H_2O$, and the chabazite

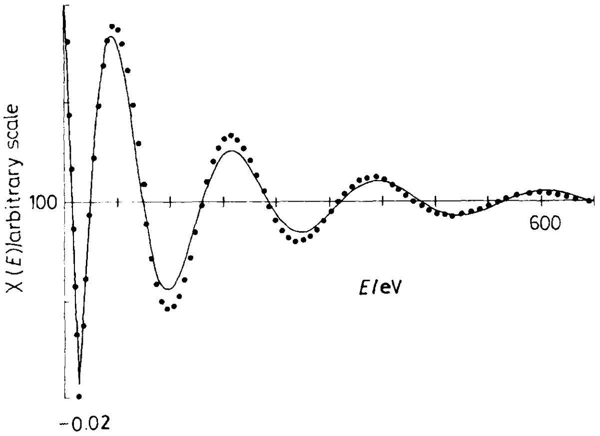

Figure 3. One-shell fit (continuous line) of the Fourier-filtered peak (dotted line) for $CuSO_4{\cdot}5H_2O$

Table. Results of the one- (*a*) and two-shells (*b*) fits for the three samples; *N* is the number of O atoms at a distance *R* from Cu

Sample	*N*	*R* (Å)	Δσ (Å)	E_0 (eV)	ΔE_0 (eV)
CuO	4	1.95	—	8 988	—
$CuSO_4{\cdot}5H_2O$	(*a*) 3.5	1.95	0.000	8 991	−3.0
	(*b*) 4.2	1.96	0.020	8 991	−2.5
	(*b*) 1.8	2.30	0.075		
Chabazite	(*a*) 3.2	1.95	0.002	8 988	−3.6
	(*b*) 3.9	1.96	0.002	8 988	−1.4
	(*b*) 1.5	2.25	0.080		

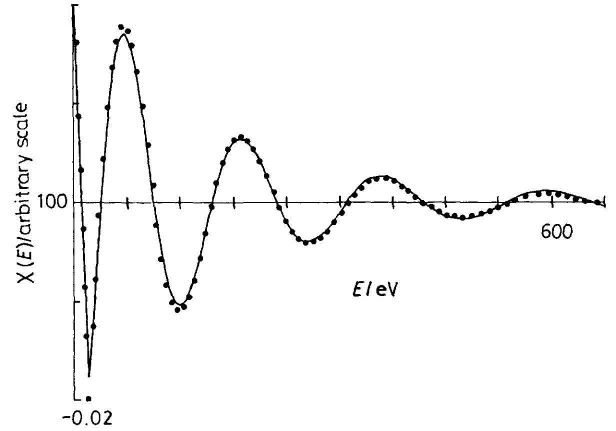

Figure 4. Two-shells fit (continuous line) of the Fourier-filtered peak (dotted line) for $CuSO_4{\cdot}5H_2O$

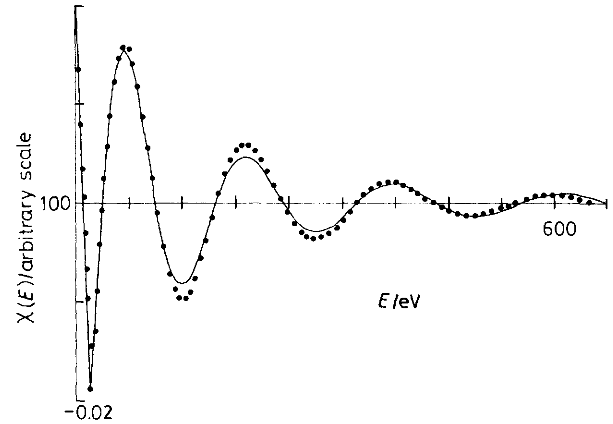

Figure 5. One-shell fit (continuous line) of the Fourier-filtered peak (dotted line) for the chabazite

The reliability of these functions was checked by transferring them to the Fourier-filtered peak of the $CuSO_4{\cdot}5H_2O$ sample, considered as a structural unknown. In this compound, copper is surrounded by a tetragonally distorted octahedron of oxygen atoms[7] from water molecules (four oxygens) and from sulphate ions (distances: 4 × 1.97 and 2 × 2.40 Å). Since Joyner,[8] studying the same sample, concluded that EXAFS is not able to reveal the longest distance, a least-squares fitting of the signal assuming only one detectable distance was carried out.

For the fit a variation of ΔE_0 was introduced, to take into account any approximation in the chemical transferability of amplitude and phase functions (E_0 was determined as the inflection point of the edge jump). Furthermore, σ has only a relative value Δσ, compared to that of the reference compound, where the term σ remains convoluted with the *F*(*k*) function during the extraction of the amplitude function. The fit is reported in Figure 3, and the values obtained are listed in the Table (*a*). As can be seen, the fit is of poor quality: the frequency is reproduced, but not the amplitude. At this point, a second shell was introduced in the calculation. The results are summarized in the Table (*b*) and the fit is shown in Figure 4. A significant improvement is apparent and the numerical values

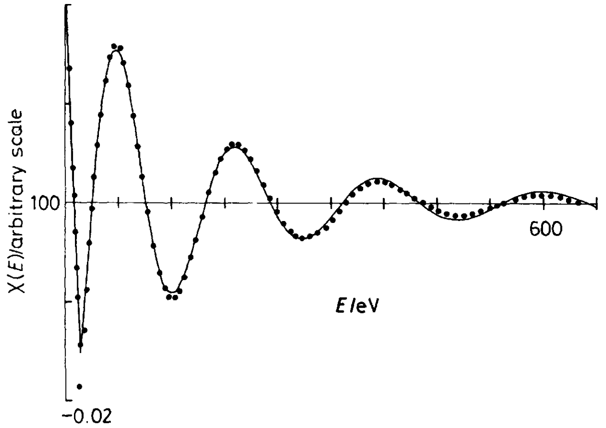

Figure 6. Two-shells fit (continuous line) of the Fourier-filtered peak (dotted line) for the chabazite

are very consistent with known crystallographic data. A shortening of the second distance (about 0.1 Å) deduced by EXAFS, as compared with the crystallographic one, is observed. This is in line with the observations of Crozier and Seary[9] about the shortening of distances seen by EXAFS with respect to crystallographic ones when the parameter σ is high, as in our case ($\Delta\sigma$ = 0.075 Å).

Similar calculations were performed on the zeolite signals. The one-shell fit is reported in Figure 5, while a two-shell fit is shown in Figure 6. The values are summarized in the Table. The analysis clearly shows that the experimental results are in agreement with a model where the Cu^{2+} ions are placed in two different environments, one represented by a tetragonally distorted octahedron, the other by an axially elongated square pyramid. The ratio between these two environments is about 1 : 1. This model may be interpreted by assuming that Cu^{2+} ions occupy one site, half of them with a distorted octahedral geometry, the remainder with a pyramidal geometry. Alternatively, Cu^{2+} ions occupy two different sites each with one of the two observed co-ordination geometries. Comparison of these results with those of the X-ray crystal structure analysis[1] strongly support the latter hypothesis. The previously suggested[1] pentagonal bipyramidal co-ordination for one site should be dismissed in favour of a square-pyramidal one. However, the location of cation sites in the large cavity is definitely confirmed.

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