Leipzig University - Faculty of Physics and Earth Sciences

EPR Lab
Report

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Abstract

An activated (dehydrated) and a hydrated Cu^{2+} chabazite zeolite sample is investigated with a X-band electron paramagnetic resonance (EPR) spectrometer. The measurements recorded are used to infer geometry around Cu^{2+} ions which in turn informs about the location of Cu^{2+} ions in the crystal lattice.

1   Introduction

Electron paramagnetic resonance (EPR) or electron spin resonance (ESR) is a spectroscopic technique used to study materials with unpaired electrons. First EPR experiments were noticed by Yevgeny Zavoisky in 1944 and the technique has been improved greatly since [1].

Cu^{2+} being a transition metal ion with unpaired electrons is very suitable for this analysis. Copper has two isotopes Cu^{63} and Cu^{65}, both with nuclear spin $I = 3/2$ and a g-factor that differs only very slightly. Cu^{2+} compounds generally tend to be tetragonally symmetric hence they poses g- and A-tensors with axial symmetry. Also, with a total spin of $S = 1/2$ in d^9 configuration coupled with the sufficiently long relaxation time means that a distinctly observable spectrum can be observed even at room temperature. This is also the reason why a great amount of EPR analysis on Cu, studying its various features, already exists [2].

This report summarises EPR measurements performed on hydrated and dehydrated copper containing chabazite zeolite samples (hereafter called activated). Cu^{2+} shows variation in its speciation based on its local chemical environment and, by analysing and simulating the spectrum, its spatial characteristics can be inferred.

A chabazite zeolite has a crystal lattice framework with the basic primary building block of TO_4 (Primary block) where "T" could stand for Si or Al, see figure 1. The central globular region is known as 8-member ring and the each of the four smaller globular regions (labeled a, b, c and d) forming the protrusions to the central frame is known as 6-member ring. Due to substitution of some of the tetra-valent silicon by tri-valent aluminium ions, the framework has a net negative charge. In a particular sample preparation, this residual charge is counterbalanced by Cu^{2+} ions that like to sit comfortably near aluminium inside the 8-member ring position, constituting an extra-framework. However the exact spatial positioning of the Cu^{2+} depends on the distribution of aluminium on the surrounding 8-member ring.
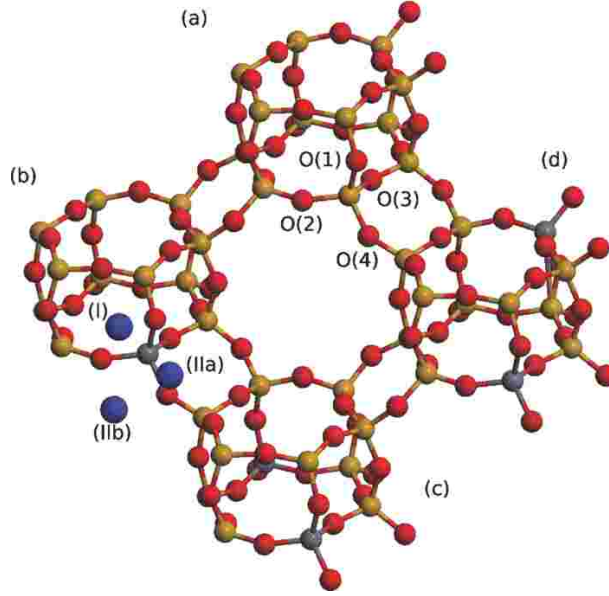
Figure 1: Chabazite zeolite lattice framework. Features (I), (IIa) and (IIb) represent migrating extra-framework metal ions. Red lattice points are oxygen, gold are silicon and grey represent aluminium displacing silicon. Note that the aluminium displacement is a stochastic process and displaced lattice sites would vary from unit cell to unit cell. [3]

In a hydrated chabazite sample the Cu^{2+} ion is not "naked" and forms a hexa-aqua-complex in being hydrated by 6 H_2O molecules ($Cu^{2+}(H_2O)_6$). This complex has an octahedral geometry, albeit distorted (elongation). The octahedral geometry of Cu^2 in the hydrated state typically experiences Jahn-Teller distortion, resulting in elongation along one axis. This distortion is significant as it influences the electronic properties and the EPR spectrum observed. The elongated octahedral geometry affects the splitting of d-orbitals, thereby impacting the magnetic resonance signals and providing insights into the local environment of the Cu^2 ions within the zeolite framework. Apart from Cu^{2+} our sample also contains Cs^{1+} ions that are obviously fairly large. Cs^{1+} ion is only accommodated inside the 8-member ring position.
On calcinating (activating) the sample, it is thought due to thermal excitation the $Cu^{2+}(H_2O)_6$ loses the hydrating water molecules and Cu^{2+} migrates inside the 6-member ring position, however, literature on the subject suggests that it could be that on activation the $Cu^{2+}(H_2O)_6$ reduces to $Cu^{2+}(H_2O)_5$ trigonal bi-pyramidal structure which can co-inhabit the 8-member ring space along with the Cs^{1+} ion.

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The goal of this report is to measure and discuss EPR spetra of such a chabazite sample that could allow inference into the environment of the Cu^{2+} ions.

2   Experimental Methods and Materials

Sample preparation

To prepare hydrated chabazite sample a portion of starting zeolite is soaked in a 1M solution of salt (depending on the type of cation that is intended to be exchanged). In this case the hydrated Cu-CHA sample was prepared by simultaneous ion exchange of the chabazite zeolite with 1M $Cu(acetate)_2$ and CsCl solutions under reflux condition at 70^oC for 24 h. After that the ion exchange, the sample was washed and dried in an oven set to $95^{\circ}C$ overnight.
Some Cs^{1+} (Cesium) ions were introduced by repeating the procedure except using a cesium salt (E.g. CsCl) this time. To activate the sample, a 20 mg portion was put into a 3.8 mm quartz tube purchased from QSIL. The sample tube was connected to the evacuation cell and heated to 400^oC for 2 h under vacuum (10-5 mbar) with the heating rate of $5^oC/min$.

Spectrometer

The spectrometer used is EMX micro from BRUKER BioSpin GmbH configured in continuous wave mode (cw) in the X band. For measurements at low temperatures ESR 900 helium cryostat from Oxford Instruments is used to get to the required level. The temperature drop is achieved using the circulation of liquid helium, while a heating coil is used to maintain the temperature at the required target temperature.
In general, a modulation frequency of 100 kHz is used. All measurements at temperature of 8K are performed at a microwave power of 1.002×10^{-1}mW and measurements at 77K are performed at 2.00mW. A common set of all other parameters is used for all measurements such as the modulation amplitude at 5G (Gauss), the microwave frequency at 9.416GHz.

Software

The spectra measurements are performed using software WinEPR Acquisition. For preliminary analysis of the results, software WinEPR is used. This is also the software used to infer g-values and other spectrum characteristics such as line width.

The recorded spectra are further analysed in MatLab using Easyspin [4]. Out of the various simulation functions available in Easyspin, our experimental features align with the use of the function Pepper. In order to compare the recorded spectra with simulated spectra, some baseline corrections are also made.

3   Results

EPR spectra were recorded at temperatures of 8K and 77K.

Notice that in the spectrum of dehydrated chabazite zeolite, we have a sharp signal peak at around 3350G. No such peak is visible in the case of the hydrated sample. This peak is a result of free radicals created in the calcination process used to activate the sample. This feature is therefore irrelevant for our investigation and ergo is wilfully ignored.

For the dehydrated case three species were discovered whereas for hydrated case there were two.

Tables 1 and 2 summarise the spin hamiltonian parameters of various species for both anhydrous and hydrous cases respectively. A, B and C enumerate different Cu-spectral species that are also used in simulations.

Species	$g_\parallel$	$g_\perp$	$A_\parallel$(in MHz)	$A_\perp$(in MHz)	Share
A	2.343	2.0615	470	50	62.5%
B	2.375	2.0687	420	50	31.25%
C	1.987	2.35 & 2.26	270	50 & 100	6.25%

Table 1: Speciation of Copper and Spin Hamiltonian Parameters of Species in Experiment of Cu-CHA Dehydrated

Species	$g_\parallel$	$g_\perp$	$A_\parallel$(in MHz)	$A_\perp$(in MHz)	Share
α	1.993	2.31	266	130	70%
β	2.385	2.07	440	45	30%

Table 2: Speciation of Copper and Spin Hamiltonian Parameters of Species in Experiment of Cu-CHA Hydrated
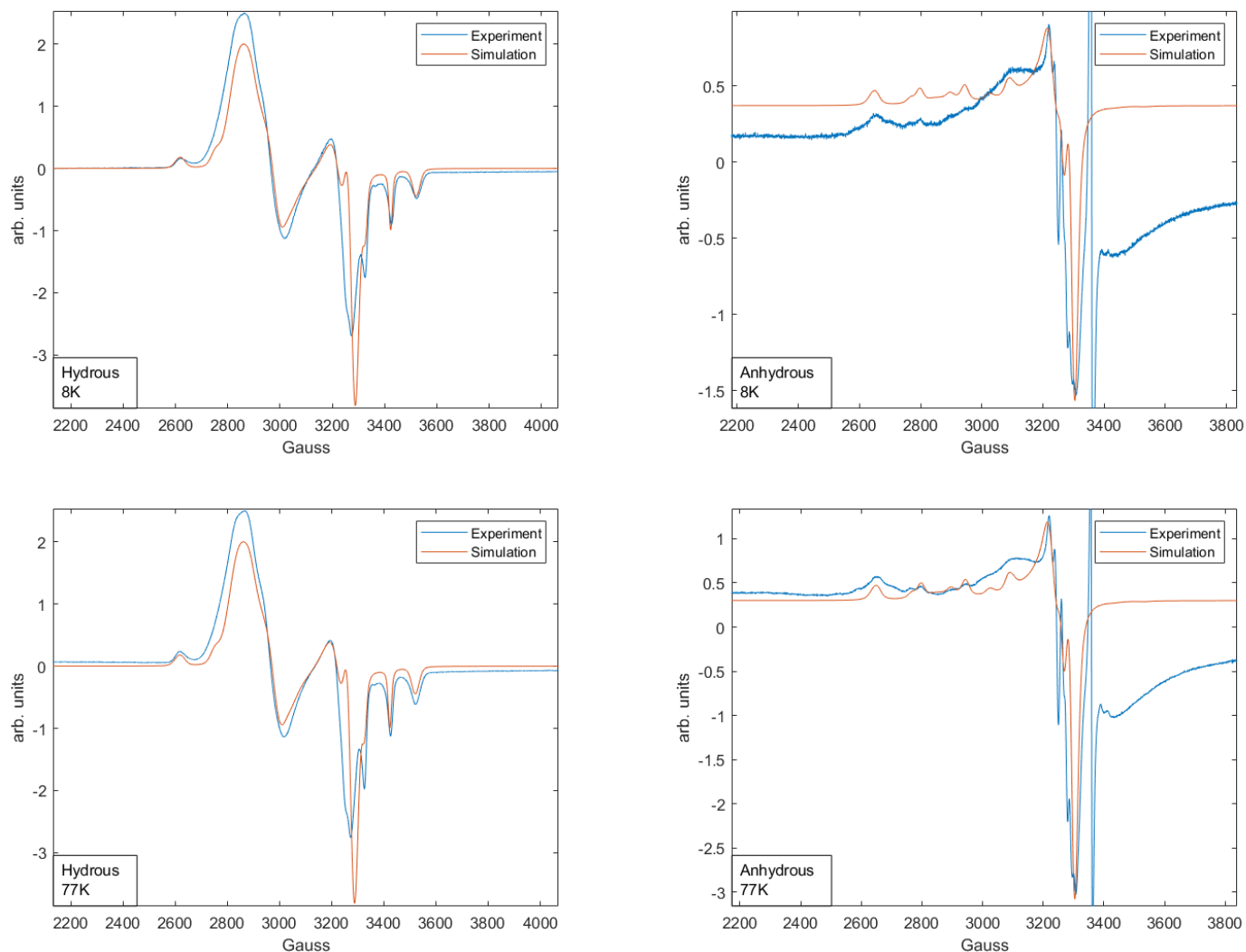
Figure 2: Measured and simulated spectra. On x-axis we have the magnetic field in units of Gauss. The information about different cases — Hydrated or Dehydrated and different temperatures — 8K or 77K is provided by the on figure labels.

4 Discussion

Table 3 lists reported spin hamiltonian parameters from a similar sample [5].

Species	$g_\parallel$	$g_\perp$	$A_\parallel$(in MHz)
A	2.325	2.07	487
B	2.358	2.07	464
C	2.388	2.07	530
D	$\sim$2.17	$\sim$2.17	not resolved

Table 3: [5] Speciation of Copper and Spin Hamiltonian Parameters of Species in Experiment of Cu-CHA Dehydrated

A reasonably close correspondence between parameters of species A and B listed in table 2 and those cited from the paper (Table 3) is observed. The difference in agreement can be a result of slightly different chemical environment of Cu^{2+} ions due to differences in sample. It could however also be due to imperfect experimental conditions or limitations in equipment precision.

In the experiment with anhydrous Cu-CHA, species A and B have $g_\parallel > g_\perp > g_e$ where g_e ($= 2.0023$) is the g factor for a free electron. This implies a tetragonal Cu(II) environment, elongated with a d_xy ground state [6]. Species C has $g_\perp > g_\parallel$, this species forms the inverse spectrum that captures the inverted hump towards the right of the spectrum. This species hints towards two possible geometric environments — square pyramidal or trigonal bi-pyramidal. In such a case if $g_\parallel$ (the one with higher symmetry axis) is practically equal to g_e, this indicates a d_{z^2} ground state which may be provided by a compressed octahedral geometry or a penta-coordinated geometry strongly shifted towards trigonal bi-pyramidal [6]. In this experiment a reasonable closeness to this case is observed in the spin hamiltonian parameters. Moreover, what is interesting is we have a split in perpendicular g-factor for species C. When this transition occurs, axial symmetry is lost, leading to a rhombic symmetry at the Cu(II) site. This transformation is driven by the crystal field effect, which is influenced by the surrounding ions and/or ligands, altering the local electronic environment of the Cu(II) ions.

In the experiment with hydrated Cu-CHA, species α gives an inverse spectrum and with the discussion in above paragraph the reasonable closeness of $g_\parallel$ with g_e is again noticed. This again would hint towards a trigonal bi-pyramidal environment. Similar to the discussion in above paragraph, species β has $g_\parallel > g_\perp > g_e$ which hints towards a tetragonal Cu(II) environment. However, to establish any of this in

a reasonably convincing manner more investigation is required which is outside the scope of this report.

5   Conclusion

For the dehydrated Cu-CHA, three spectral species have been identified enumerated by A, B and C. Species A and B have $g_\parallel > g_\perp > g_e$ and can be assigned to a tetragonal Cu(II) environment. Species C provides an inverted spectrum and g factor tensor hints towards a trigonal bi-pyramidal Cu(II) environment for this species.

In the hydrated case two spectral species have been identified, enumerated by α and β. From the g factor tensor of α, a trigonal bi-pyramidal environment is suggested, whereas the g factor tensor of β hints towards a tetragonal environment of the Cu(II) ions constituting the respective species.

In conclusion it is recognised that to establish any of these suggestions with a reasonable degree of confidence more investigation is needed which is outside the scope if this report.

References

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