

Further Electron Spin Resonance Studies of Cu(II) in Linde Y Zeolite*

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As a continuation of previous work carried out on the electron spin resonance characteristic of Cu(II) Linde Y zeolite, measurements were made in both X- (9.5 GHz) band and in Q- (35 GHz) band at room, liquid-nitrogen and liquid-helium temperatures. Deuterated samples were measured to cut down the influence of dipole-dipole broadening of the Cu(II) signal by the protons of the ligand water molecules. Solid state effect measurements at low temperatures were used to supplement the resolution of the Cu(II) complex spectrum. Evidence for the existence of two sites for Cu(II) in the lattice was examined critically. The presence of copper(II) clusters in more concentrated Cu(II) samples, particularly after heat treatment, was substantiated. The influence of gases adsorbed or reacting with the Cu(II) zeolite was investigated.

INTRODUCTION

In a previous communication (1) from this laboratory the electron spin resonance characteristics of Cu(II) zeolite were presented, using the X-band radiation (9.5 GHz). The variation of the ESR parameters g_{\perp} , g_{\parallel} , A and B with temperature of dehydration and Cu concentration allowed the calculation of molecular orbital crystal field parameters. Evidence was presented that in the hydrated state the hydrated copper(II) ions tumbled freely in the large cavities of the zeolite. When the water was removed from the zeolite, this motion was restricted and the partially hydrated copper(II) ions was bonded to the surface of the cavity. It was shown that during this process the trend was a change in the covalency characteristic of the bonding.

Since our publication several authors

have studied ESR characteristics of Cu(II) zeolites. Richardson (2) measured both hydrated and dehydrated (at 400°C) 2% Cu(II) zeolites in which the other exchanged ions were Na, K, Li, Ba, Ca, and Mg. The g_{\parallel} and g_{\perp} and A and B were found to be similar to those found by Nicula, Stamires and Turkevich (1), with a deviation in the case of the Mg(II) ion Cu(II) zeolite which may be within experimental error. A simplified theory was used to interpret the results. It is not clear from the paper why in the dehydrated Cu(II) zeolite the Cu(II) is assigned a square planar configuration. Kruerke and Jung (3) showed that a sample dehydrated at 150°C gave evidence of two types of Cu(II). They gave indications that only part of the Cu(II) ions was detected by ESR technique, that this varied with heat treatment. The minimum signal was obtained after dehydration at 150°C. No evidence was presented to show how well the electronic integrator used to determine the intensities followed the ESR bands which had long tails or bands that had sharp hyperfine lines superimposed on broad bands. Slot and Verbeck (4) con-

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firmed the existence of two sets of Cu(II) ions in Y zeolites whose other component was either Mg(II), Zn(II), or La(III). No difference was found in ESR characteristics in these different samples except in the relative intensity of the Cu(II) lines. These differed from sample to sample and from heat treatment. It was concluded by the authors that the migration of the majority cations, Mg(II), Zn(II), La(III) to "favorable" yet "unidentified" sites influenced the position that was taken by Cu(II).

Mikheikin, Shvetz and Kazanski (5) confirmed the results obtained by Nicula, Stamires and Turkevich (1) at room temperature on the symmetrical line at $g = 2.16$ for the hydrate form and its conversion to an asymmetric signal with g'_{\perp} equal to 2.08 and $g'_{\parallel} = 2.38$ ($A = 126$ gauss) at liquid-nitrogen temperature. On dehydration they obtained an asymmetric signal similar to the previous one and another with $g''_{\perp} = 2.05$ ($B = 22$), $g''_{\parallel} = 2.32$ ($A = 162$ gauss). The details of this resolution are not given. The g_{\perp} in their figure shows four hyperfine lines and a shoulder. The g_{\parallel} shows five lines and three shoulders. The second peak was assigned to a Cu(II) in a square pyramid or square planar configuration on the basis of theoretical deduction from a very simplified crystal field theory. An increase in Δg_{\perp} with a constant Δg_{\parallel} was taken to indicate a decrease in coordination. The observed change was 37.5% and 15% for Δg_{\perp} and Δg_{\parallel} , respectively.

Tikhomirova and Nikolaeva (6) showed in Cu(II) zeolite A, dehydrated at 400°C and measured at -196°C, an asymmetric spectrum with $g_{\perp} = 2.038$ and 2.049, $g_{\parallel} = 2.347$ and 2.305, B_{\perp} of 30 and A_{\parallel} of 110 gauss. They found another line at $g = 2.156$ with a width of 120 gauss and of Lorentzian shape. It increased with Cu²⁺ concentrations.

This investigation is an extension of the work previously reported. A comparison is made of the results obtained with X-band (9.5 GHz) with those obtained with Q-band (35 GHz). A deuterated sample is used to obtain sharper resolution. Measurements

were made not only at liquid-nitrogen temperature but also at those of liquid helium. Furthermore double resonance techniques studying the interaction of protons in the zeolite with the Cu(II) ions at liquid-helium temperature were used to elucidate the nature of the Cu(II) ions in the zeolite.

EXPERIMENTAL

Sample Preparation

The samples were prepared by treating sodium faujasite (Linde Y) with aqueous solutions of copper(II) nitrate of different concentrations. The extent of exchange was determined by gravimetric analysis of the sodium eluted. The samples were washed with distilled water and then dried at 100°C. They were then exposed overnight to water vapor at room temperature. Eight samples were prepared containing 19.5 Cu(II) per unit cell (70% exchanged), 13.8 Cu(II) (53% exchanged), 10.8 (42% exchanged), 10.4 Cu(II) (37% exchanged), 7.8 Cu(II) (29% exchanged), 1.6 Cu(II) (5.2% exchanged), 0.5 Cu(II) (2% exchanged), and 0.01 Cu(II) (0.2% exchanged).

The deuterated Cu(II) sample was prepared by evacuation of the ordinary hydrated copper(II) zeolite at 200°C and subsequent equilibration at room temperature with heavy water vapor.

We wish to thank Dr. Pickert of the Linde Division of Union Carbide Corporation for the "ultra pure" sample of sodium Linde Y sample which was the basis of our preparation.

Measurement Techniques

The ESR measurements were performed in the X-band or 9.5 GHz Varian spectrometer, Model V-4500, and in the Q-band with a 35 GHz Varian spectrometer, Model V-4561.

The double resonance technique is described in a forthcoming publication (7). NMR detection was by the Pound single-coil method, using a Precision Gaussmeter, Nuclear Magnetic Corporation, Model M-2 as oscillator and Pound bridge. The output

of the bridge is connected to a PAR Model 170 lock-in amplifier with a modulation frequency of 80 Hz.

Examination of Hydrated Samples

Examination of the 5% exchanged Cu(II) zeolites (which had been in equilibrium with H₂O) in the X-band at room temperature gives an asymmetric line with an apparent g value of 2.16 as determined by the crossing of the base line (Fig. 1). A shoulder is observed on the high field peak and a hyperfine structure on the low field peak. The separation of the low field peak from the high field peak is 190 gauss. Mikheikin, Shvetz, and Kazanski (5) report $g = 2.16$ with line-width 170 gauss. Using the DuPont curve resolver this ESR spectrum was resolved into a symmetric and unsymmetric spectra as indicated in Fig. 1. The symmetric peak has a g value of 2.17 and a peak to peak width of 160 gauss. The asymmetric peak consists of two components with $g_{\perp} = 2.10$ and $g_{\parallel} = 2.38$. The separation from the bottom to the top of the $g_{\perp} = 80$ gauss.

Examined at room temperature in the Q-band, the asymmetry of the overall peak becomes more marked (Fig. 1). (The six-line hyperfine structure complex seen in the high field side is due to a slight manganese(II) contamination and will not be discussed.) The curve again has an apparent g value of 2.17, however, neither the shoulder nor the hyperfine structure are detected in the Q-band. This curve was resolved into a symmetric and unsymmetric component by the DuPont curve resolver. The symmetric curve had a g value of 2.17 and a peak-to-peak width of 650 gauss (four times that of the X-band) indicating that it was composed of a number of Cu(II) ions with different g values. The asymmetric peak has again a g value of 2.10. The value for g_{\parallel} is difficult to determine. The peak-to-peak width of the g_{\perp} component is 240 gauss, slightly less than the 320 which would be predicted from X-band of 80 gauss. However, the latter value certainly has an uncertainty of at least 20 gauss. The ratio of intensities of the symmetric band to the asymmetric

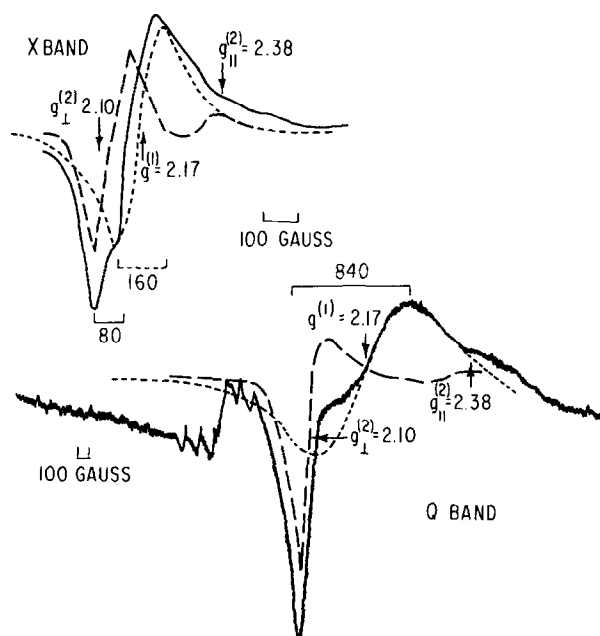


FIG. 1. The ESR spectrum of 5% Cu(II) in Linde Y zeolite as measured in the X-band (9.5 GHz) and in the Q-band (35 GHz) at 293°K. The solid line represents the experimental curve; the dotted and dashed line the component curves.

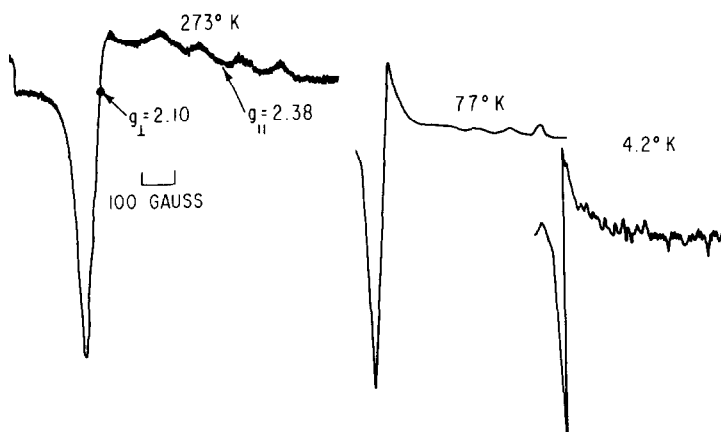


FIG. 2. The ESR spectrum of 5% Cu(II) Linde Y zeolite at 273, 77, and 4.2°K in the X-band.

band is the same in the X-band and Q-band.

The symmetric band disappears when the measurement is carried out at zero degrees in the X-band (Fig. 2). The asymmetric curve is clearly delineated with $g_{\perp} = 2.10$ and $g_{\parallel} = 2.38$. The peak-to-peak in the g_{\perp} component is 80 gauss and the width of the hyperfine structure in g_{\parallel} is 125 gauss. This confirms the details of the asymmetric curve as determined at room temperature. The ESR curve at liquid-nitrogen temperature is similar to that at 0°C. The g_{\perp} is 2.10 and g_{\parallel} 2.38. The peak-to-peak distance of the g_{\perp} is 80 gauss. The upper part of the g_{\perp} curve is sharper than that measured at 0°C. The hyperfine structure in the g_{\parallel} section is still observed but with a different sequence of intensities. Measurement at 4.2°K shows an asymmetric signal with g_{\perp} well defined, and having a slightly smaller 60 gauss peak-to-peak separation. The upper part of the g_{\perp} is much sharper, the g_{\parallel} part cannot be observed. The signal saturates readily giving a T_1T_2 value of 2.2×10^{-12} sec using the progressive saturation method (Fig. 3).

Samples with 2% copper concentration showed similar characteristics; the intensities, however, were lower, being approximately proportional to the copper concentration.

Samples with copper concentration of 29% and higher show at room temperature in the X-band a symmetrical curve with a

g value of 2.175 and a peak-to-peak width of 190 gauss (Fig. 4). However, examination in the Q-band shows a shoulder on the high field side of the low field peak. This can be again resolved into an asymmetric peak with $g = 2.10$, with a peak-to-peak width of 340 gauss and a symmetric peak at $g = 2.17$ with width of 650 gauss, and of much higher intensity than the asymmetric peak. Thus we are dealing with the same two peaks that were observed at lower concentration with the symmetric peak increasing in intensity as the copper concentration increases.

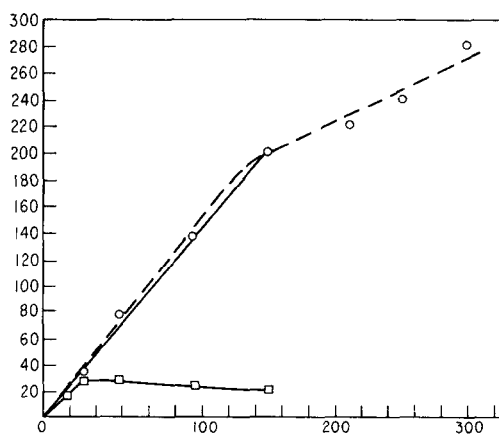


FIG. 3. Saturation curve of Cu(II) Linde Y zeolite at room temperature. Variation of signal intensity with microwave power. Abscissa—microwave power in milliwatts. Ordinate—signal intensity in arbitrary units. \square 5% Cu(II); \circ 29% Cu(II).

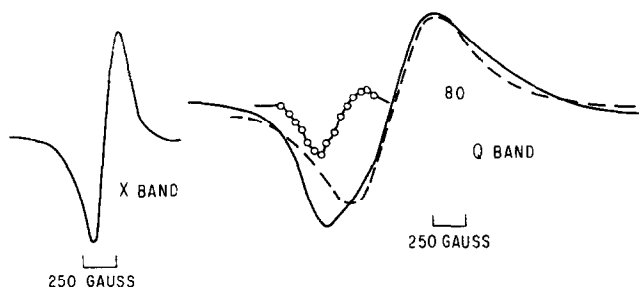


Fig. 4. ESR signal of 29% Cu(II) faujasite in the X-band (9.5 GHz) and the Q-band (35 GHz).

When the temperature is lowered to liquid nitrogen, the ESR spectrum becomes asymmetric in the X-band and more so in the Q-band. A resolution into asymmetric and symmetric bands can be affected with the characteristics presented previously.

At liquid-helium temperatures both the 29% and 70% Cu(II) zeolite give an asymmetric curve with a peak-to-peak separation of 280 ± 20 gauss, much wider than the 60 gauss width observed at these temperatures for the 5% and 2% Cu(II) samples. The upper portion of the asymmetric curve is much broader. Furthermore the intensity of the 70% Cu(II) sample is lower than that of the 29% sample. Both of these samples did not saturate readily with microwave power (Fig. 3). The difficulty is saturating this peak with available microwave power accounts for the difficulty in observing the solid state effect for samples with high copper(II) concentration.

Proton Resonance

The proton resonance line was observed at liquid-helium temperature in the 10–15 megacycle region at a magnetic field appropriate to the free proton. The width is 17 gauss. Its intensity decreases with increase in copper concentration being (in arbitrary units) 7.2 for the 2%, 7.5 for the 5%, 6.5 for the 29% and 5.6 for the 70% Cu(II). This supports the point of view that with increase in copper ion concentration, more and more protons are affected by the local magnetic field of the Cu(II) ions and their magnetic resonances are not only shifted to frequencies different from those of the free proton but are also broadened.

Double Resonance

The enhancement of the proton resonance line on saturation of the ESR line of Cu(II) was measured at liquid-helium temperature of 4.2°K for 2% and 5% Cu(II) zeolite. The enhancement is expressed as the intensity difference of the proton line before and after switching on of the microwave power divided by the intensity before switching (8, 9). An asymmetric solid-state curve was obtained (Figs. 5 and 6) with the positive side having a gaussian shape. These asymmetric solid-state curves were resolved into two components, A and B. The high field component A has a g value of 2.10 (and 2.11), and maxima shifted from g value of 50 (and 60) gauss for the 2% (and 5% Cu(II)) zeolites. The width at half height is 70 (and 88 gauss) while the maximum enhancement height is 9.7 (and 8.3, respectively). However, the total intensity under the high field component is the same for both concentrations.

The low field component of the solid-state curve B has a g value of 2.17 (and 2.18) and a maximum shifted from the g value by 45 (and 65) gauss for the 2% (and 5%) Cu(II) zeolites. The width at half-height is smaller than for the high field component A, being 60 (and 45) gauss. The maximum enhancement is also smaller, being 4.3 (and 3.6).

Measurements at 1.9°K produce the same type of curve with the maximum in the component increasing from 9.7 to 12.7, while the minimum remains the same as at 4.2°K undoubtedly due to the compensation of the minimum in A by the maximum in B.

No solid-state effect was observed at

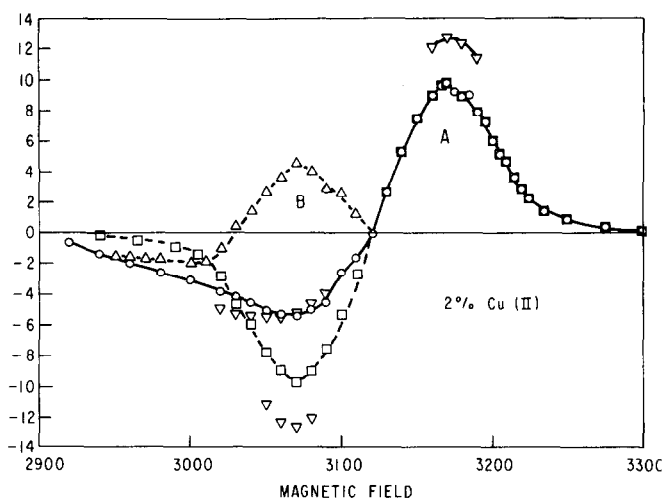


Fig. 5. Solid-state effect produced in 2% Cu(II) Linde Y zeolite at 4°K: ○—experimental curve; □—high field component; △—low field component. (The partial data points indicated by triangles indicate solid-state effect at 1.9°K.) Ordinate: enhancement of proton signal expressed as difference between proton signal after switching on microwave frequency and the proton signal before switching divided by the signal intensity before switching. Abscissa: intensity of magnetic field in gauss.

liquid nitrogen or at room temperatures for the 2% and 5% Cu(II) zeolites. No solid-state effect was observed at liquid-helium temperatures of 1.8°K for the 26%, 29% and 40% exchanged Cu(II) zeolite. The solid-state effect indicates that there

are two types of Cu(II) present with $g = 2.10$ and $g = 2.17$.

Examination of Deuterated Samples

In order to obtain a sharper resolution of the hyperfine structure, deuterated sam-

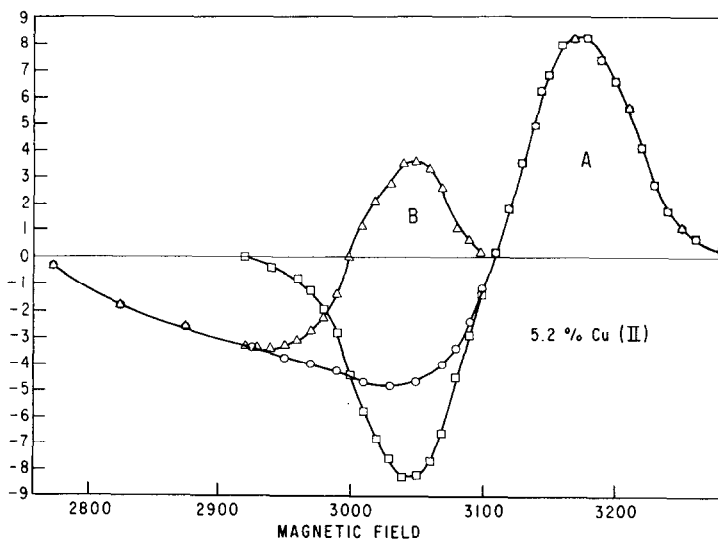


Fig. 6. Solid-state effect produced in 5% Cu(II) Linde Y zeolite at 4°K: ○—experimental curve; □—high field component; △—low field component. Ordinate: enhancement of the proton signal expressed as the difference between proton signal after switching on the microwave frequency and the proton signal before switching divided by the signal intensity before switching. Abscissa: intensity of magnetic in field gauss.

ples were prepared. The replacement of the protons by deuterium should reduce the dipole-dipole coupling between the Cu(II) ion and the hydrogen of the water since the magnetic moment of the deuteron (0.85741) is smaller than that of the proton (2.79277). The deuterated 5% Cu(II) zeolite was subjected to various degrees of dedeuterization by evacuating overnight at various temperatures 20, 50, 70, 125, 200, 400°C. The best results were obtained with 50 and 70°C samples measured at liquid-nitrogen temperature.

The X-band ESR signal could be decomposed into a low field g_{\perp} and a high field g_{\parallel} band (Fig. 7).

The low field band shows five lines at 50°C and six in the 70°C evacuated sample. These can be resolved into two sets with $g'_{\perp} = 2.084$ and $B' = 0.0016 \text{ cm}^{-1}$ and another $g''_{\perp} = 2.048$ with B'' equal to 0.0024 cm^{-1} . The average $\langle g_{\perp} \rangle = 2.061$ and $\langle B \rangle = 0.00021 \text{ cm}^{-1}$. Kruerke and Jung (3) also report one value for $g_{\perp} = 2.058$ and no B value. Slot and Verbeck (4) also report only one value for g_{\perp} which varies from 2.056 to 2.067, depending on the sample and its heat treatment giving an average value of 2.062 and a B value of 0.0018 cm^{-1} . Mikheikin, Shvetz and Kazanski (5) report two g_{\perp} values of $g'_{\perp} = 2.08$ and $g''_{\perp} = 2.05$ and only one B value of 0.021 cm^{-1}

consistent with our data. We did obtain two B values.

The high field component can also be decomposed into two sets of hyperfine lines. The basis for this decomposition is the measurement of four equidistant peaks by one set. The other set may be discerned from direct observation of two distinct peaks, a presumed overlap of one peak with a peak of the first set and a presumption of the fourth peak hidden in the background noise. If this type of resolution is valid, we obtain a g'_{\parallel} equal to 2.323 and an A' of 0.0176 cm^{-1} and a g''_{\parallel} of 2.386 and an A'' of 0.013 cm^{-1} . These average out to $\langle g_{\parallel} \rangle$ of 2.355 and $\langle A \rangle$ of 0.0153 cm^{-1} . Kruerke and Jung (3) report g'_{\parallel} of 2.310 and A' of 175 ± 5 gauss and a g''_{\parallel} of 2.350 with a A'' of 120 gauss. Slot and Verbeck (4) obtain for various samples a g'_{\parallel} of 2.326–2.333 and a g''_{\parallel} of 2.375–2.383 while their value of A' is 0.0150 and A'' is 0.107 cm^{-1} , slightly lower than the value we find. Mikheikin, Shvetz and Kazanski (5) report g'_{\parallel} of 2.32 and A' of 0.0118 cm^{-1} and a g''_{\parallel} of 2.38 and A'' of 0.0092 cm^{-1} . Thus our measurements are consistent with those of previous workers but we feel are based on clearer resolution of the complex Cu(II) zeolite spectrum. There is also evidence on the basis of two extra lines of a third set of peaks in the

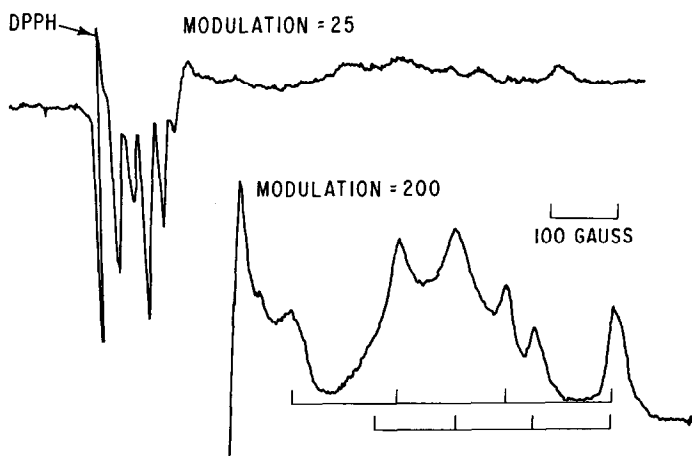


FIG. 7. The ESR signal from deuterated 5% Cu(II) faujasite pumped at 50°C and measured at liquid nitrogen. Upper spectrum overall spectrum showing the hyperfine structure of low field component. The insert, expansion of the high field component showing hyperfine structure.

spectrum of the sample evacuated at 70°C with a g_{\perp} (3) of 2.20 and A (3) of 0.0074 cm^{-1} . This third set of peaks seems to increase as the temperature of the dehydration increases. Samples evacuated at high temperature give ESR spectra which are not as clearly defined. They can be interpreted in a consistent way in terms of the values of g_{\perp} , g_{\parallel} , A and B just presented. The data presented support the idea that there are two or possibly three sites for the Cu(II) ions in the zeolite structure. However, it should be pointed out that the validity of such a resolution and the identification of the sites rests on the assumption that observed hyperfine structure is not complicated by the presence of a third g , by the possibility of the hyperfine constant A being a tensor with principal values A and B , with the occurrence of quadruple effects due to the strong electric field gradients in the dehydrated zeolites and finally by an overlap of another symmetrical band which we will ascribe to clustering of Cu(II) ions.

Q-band studies were made in an attempt to resolve more clearly the lines in the low and high field bands. The results were discouraging. The hyperfine components of the spectra taken at room temperature and at liquid nitrogen were present more as points of inflection rather than clear-cut hyperfine spectral lines. The reason for this was the presence of still another band whose effect became more and more apparent as the temperature of evacuation was raised from 200 to 250, 300 and 400°C. This band becomes apparent even in the X-band spectrum taken at room temperature. The usually sharp g_{\perp} band splits and assumes a more symmetrical form. It decreases in width with increase in temperature of evacuation, being 167 gauss for 250°C evacuation and 130 gauss for 400°C evacuation.

These effects become more striking when the ESR measurements are carried out in the Q microwave region of 35 GHz. There the separation between ESR bands of different g values is greater permitting much higher resolution than in the X-band since the dipole-dipole interaction which may

determine the width of the line is not affected. The perpendicular asymmetric band at $g_{\perp} = 2.070$ is shown to have a symmetrical component at $g = 2.169$. The symmetrical component increases in intensity with increase in evacuation temperature at the expense of the unsymmetrical peak at g_{\perp} . The width of the symmetrical peak decreases with increase in temperature of evacuation, being 319 gauss at 250°C evacuation, 300 gauss for 300°C, 240 gauss at 350°C and 264 gauss at 400°C (Fig. 8). It does not appear in the spectrum of the sample containing 1.6 Cu(II) per unit cell. It is observed in the sample containing 7.8 Cu(II), and the ratio of the intensity of the symmetric to the asymmetric signal increases with increase in copper concentration while the width of the symmetric signal decreases, being 290 gauss for the 7.8 Cu(II) per unit cell, 240 gauss for the 10.4 Cu(II), 220 gauss for the 11.8 Cu(II) and 216 gauss for the 13.8 Cu(II) (Fig. 9). The signal must be due to redistribution of the Cu(II) in the zeolite to assume more symmetrical crystal field surroundings. There is also a possibility of clustering of

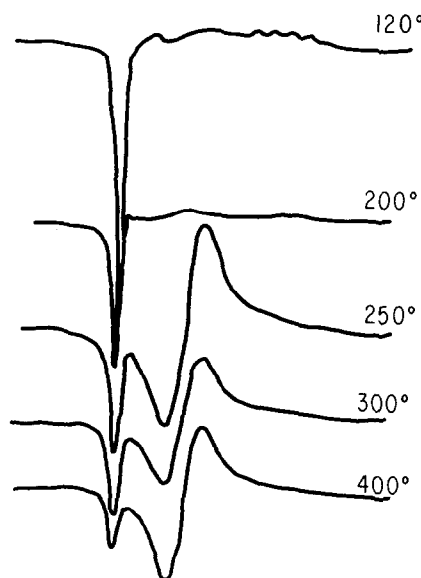


FIG. 8. ESR spectrum of 3% Cu(II) Linde Y zeolite on the Q-band (35.5 GHz) taken at room temperature as a function of temperature dehydration.

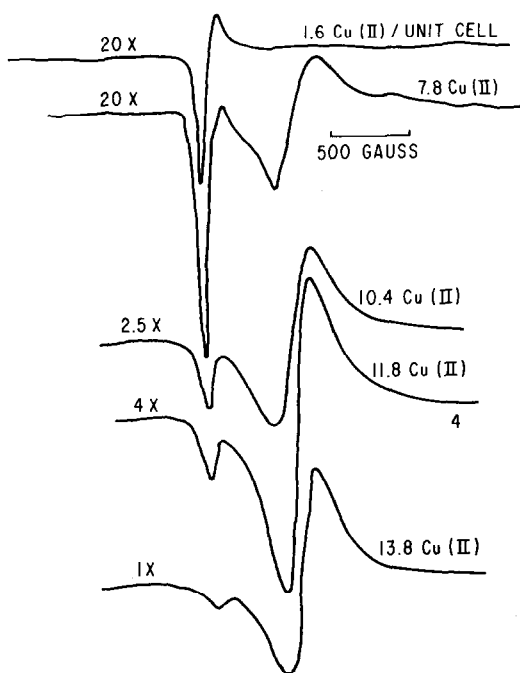


FIG. 9. ESR spectrum of Cu(II) Linde Y zeolite dehydrated at 200°C and taken at room temperature in the Q-band (35 GHz) as a function of Cu(II) concentration.

the Cu(II) with a concomitant destruction of the zeolite structure. This is being checked by X-ray investigation.

This series of measurements points up the necessity of thorough study of the ESR signals in order to determine under what conditions the data can be applied to the determination of crystal field parameters.

Reaction of Various Gases with Copper (II) Zeolites

The 5% Cu(II) zeolite sample was evacuated at 400°C and treated with the following gases and vapors.

Oxygen. Treatment of the sample at 400°C with 1 atm and subsequent evacuation at room temperature only slightly broadened the spectrum.

Hydrogen. The sample turned red in color and the signal disappeared on heating in hydrogen at 1 atm at 400°C.

Carbon monoxide. The intensity of the Cu(II) signal decreased on heating in carbon monoxide for 2 hr at 200°C. The signal disappeared and the sample developed a red color on heating in carbon monoxide overnight at 400°C.

Pyridine. Treatment with 20 mm Hg pressure of pyridine at room temperature did not alter the Cu(II) zeolite spectrum. Heating to 120°C for 1 hr produced an ESR spectrum (Fig. 10) with additional hyperfine structure of at least seven lines. This did not change on heating for an additional hour at 120°C nor evacuation for 1 hr at 200 or 300°C. This spectrum is similar to that reported for the Cu(II)-(pyridine) complex in frozen aqueous solution (10). The Cu(II) on the surface of the zeolite must be coordinated with four pyridine molecules. This should give nine lines but the first and the last may not be observed. The ESR characteristics are $g_{\perp} = 2.007$, $g_{\parallel} = 2.249$, A_{\parallel} of 0.0185 cm^{-1}

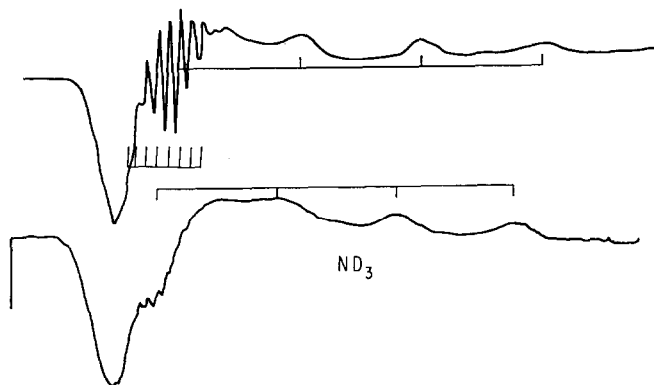


FIG. 10. ESR spectrum at room temperature of the X-band of Cu(II)-pyridine complex and Cu(II)-ammonia complex.

and the superhyperfine constant due to the four nitrogens of the pyridine A_N is equal to 0.016 cm^{-1} . Schneider and Zelevsky (11) report for $\text{Pt}(\text{Pyridine})_4(\text{NO}_3)_2$ single crystals an A_{NH} of 0.00125 cm^{-1} . It would be of interest to investigate the catalytic properties of this complex since the Cu(II)-pyridine system has been reported to be a good catalyst for homogeneous oxidation (12).

Ammonia. Treatment of the sample at room temperature with 300 mm Hg of ammonia changed the spectrum considerably. The structure in the spectrum becomes more pronounced if ND_3 is used (Fig. 10). Its ESR characteristics are a g_{\perp} of 2.002, g_{\parallel} of 2.228 and an A of 0.0178 cm^{-1} and A_N of 0.014 cm^{-1} . The resemblance of the spectrum of the ammonia complex to that of pyridine complex suggests the formation of $\text{Cu}(\text{NH}_3)_4^{2+}$ on the surface. Evacuation of the system at room temperature destroyed the superhyperfine structure. The ESR characteristics become g_{\perp} of 2.055, g_{\parallel} of 2.254, and A' of 0.0173 cm^{-1} , and A_N of 0.0150 cm^{-1} . The low field side of the spectrum suggests the presence of two kinds of copper species. Heating at 100 and 200°C for 2 hr destroyed the hyperfine structure. This may be due to a transformation of the Cu(II) species from a tetragonal or square planar to a tetrahedral crystal field environment since the tetrahedral complex has a small Cu(II) hyperfine coupling constant. When the system was evacuated at 300°C (13, 14), and spectra observed were almost identical to those of the original Cu(II) zeolite before ammonia treatment. Venuto and Landis (15) report transition metal-containing zeolites which catalyze ammonia decomposition and the amination of toluene to produce benzonitrile. These reactions might conceivably take place via a copper-ammonia or amine complex which is detectable by the ESR signal.

DISCUSSION

The discussion of the complicated situation that the ESR examination of Cu(II) zeolite discloses can best be made using the 5% Cu(II) sample as the starting point.

The hydrated form, originally thought by Nicula, Stamires and Turkevich (1) to be a single signal, has now been shown to consist of a symmetrical signal at $g = 2.17$ and an asymmetric signal with $g_{\perp} = 2.10$ and $g_{\parallel} = 2.38$. The first is associated with $\text{Cu}(\text{II}) (\text{H}_2\text{O})_6^{2+}$ distorted octahedral complexes tumbling in the large cavity. It may also be ascribed to clusters of the Cu(II) ions. The asymmetric signal is interpreted to be Cu(II) ions localized on the walls of the cavity. The fact that two signals are evident in the ESR measurements indicates that there is little exchange between the Cu(II) localized in the zeolite and the freely tumbling copper ion. Lowering the temperature increases the number of Cu(II) which are localized and the symmetric signal disappears. It is interesting to note that double resonance technique reveals the existence of two different paramagnetic species at exactly the same position, i.e. at $g = 2.17$ and 2.38 .

The dehydrated forms present three peaks, two asymmetric peaks at $g_{\perp} = 2.048$ and $g_{\parallel} = 2.323$ and $g_{\perp} = 2.084$ and $g_{\parallel} = 2.386$ and a symmetric peak at $g = 2.17$. The latter is similar to the peak found in the hydrated form but which in the dehydrated samples cannot be associated with freely moving Cu(II). It must be ascribed to clusters of Cu(II) which exchange electrons with each other. This is supported by the increase in intensity of the signal with Cu(II) concentration.

The identity of the two asymmetric lines is more difficult to interpret. In the first communication (1) we did not report the existence of two sets of peaks. The "hyperfine" structure of Cu(II) has complications inherent to the nuclear characteristics of the copper nuclei. First of all there are two isotopes of copper, of mass 63 and 65, with an abundance ratio of 61% and 39% and differing magnetic moments, 2.2206 and 2.3790 nuclear magnetons. This will produce two different A' and A'' which in our case will differ by 7%. While this will not produce extra lines in the ESR spectrum, it will certainly broaden the lines. Both copper nuclei have an electric quadrupole moment of -0.45 and -0.14 units.

This will interact with any gradient in the electric force field surrounding the nucleus and lead to extra lines. Such extra lines have been observed in Cu(II) Tutton salts (16). Since the existence of the second set of A's and B's is based on the presence of at most two lines, it is quite possible that these "extra" lines are not necessarily due to an additional site but due to transitions induced by the electrical quadrupole interaction. Inability to obtain better resolution of the hyperfine structure in the Q-band (where we were successful for other cases of resolving curves into component signals of different g) raises serious question as to whether there are really two different Cu(II) sites in dehydrated Cu(II) zeolite. Another complication is in postulating that the g tensor can be represented by the values g_{\perp} and g_{\parallel} . This is only valid if the symmetry is tetragonal. Actually the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex in crystals is not tetragonal but orthorhombic characterized by three g values: g_{xx} , g_{yy} and g_{zz} which only in the tetragonal case become $g_{xx} = g_{yy} = g_{\perp}$ and $g_{zz} = g_{\parallel}$. Thus on the basis of single crystal examination of Tutton salt $\text{K}_2^{2+}(\text{Cu}^{2+})(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, Clarkson and Turkevich (7) found $g_x = 2.300$, $g_y = 2.207$ and $g_z = 2.105$ while in a variety of copper tungstates the g_x and g_y values are very similar, being 2.334 and 2.343, respectively, while the $g_z = 2.013$ (17). Thus, having both a g_x and a g_y in the ESR spectrum of Cu(II) in zeolites with their accompanying set of hyperfine constants will certainly complicate the identification of the presence of more than one site. In addition there is the complication that the Cu(II) ions may cluster producing extra lines. This clustering in the extreme cases produces the exchange narrowed line at $g = 2.17$. Finally, there is the possibility that the hyperfine constant A is not a scalar but a tensor with at least two different values, A and B . This will produce extra peaks, distorted widths and deviations from theoretically expected intensities of the hyperfine component peaks.

While there is no question that the ESR measurements have disclosed at least two different sites in the zeolites, an unequivocal identification of these sites and their characterization must await the study of Cu(II) in single crystal zeolites. Then the contributions of secondary complications just enumerated can be evaluated.

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