JOURNAL OF SOLID STATE CHEMISTRY **56**, 101–115 (1985)

Migration and Structure of Aqueous Cu^{2+} Complexes in Faujasite

JANINA GOSLAR AND ANDRZEJ B. WIĘCKOWSKI

Institute of Molecular Physics, Polish Academy of Sciences,
Smoluchowskiego 17, 60-179 Poznań, Poland

Received March 28, 1984

EPR studies were performed for NaY zeolite samples of the faujasite type with an Si/Al ratio of 2.56 with a part of the Na^+ ions replaced by Cu^{2+}. A six-stops pathway of Cu^{2+} migration in the faujasite network was postulated and the sites of copper complexes localization were determined vs the dehydration temperature varied from 25 to 400°C. Six different kinds of Cu^{2+} complexes appear successively in the dehydration process: a hexahydrate copper complex rotating freely within the supercage and localized complexes of different water content. EPR parameter analysis in terms of MO-theory indicated four kinds of six-coordinated Cu^{2+} complexes with the symmetry of tetragonally elongated octahedron (D_{4h}) and two quasi-identical four-coordinated Cu^{2+} complexes of pseudotetrahedral symmetry (D_{2d}). © 1985 Academic Press, Inc.

1. Introduction

X,Y zeolites are crystalline aqueous aluminosilicates of alkali metals, chiefly Na, K, and Ca. They are characterized by a high sorptive ability due to the presence, in the framework, of large holes and channels between the cuboctahedra and hexagonal polyhedra (prisms) into which the $(Si,Al)O_4$ tetrahedra dispose themselves. X and Y zeolites have a crystal structure similar to that of natural faujasite. Their structure has been established by Smith (*1*). That of faujasite-type zeolite is shown in Fig. 1. The secondary building unit of faujasite is a cuboctahedron consisting of $(Si,Al)O_4$ tetrahedra; the diameter of the free space of this unit amounts to 6.6 Å, whereas that of the "window" in the six-membered ring to 2.5 Å. The tetrahedral linkage of the cuboctahedra by way of hexagonal prisms forms a supercage with a free space diameter of 11.6 Å. The free diameter of the "window" in the 12-membered ring ranges from 7.5 to 9 Å.

Structural studies (*1*) have shown the cations to occupy specific ion-exchange positions in the zeolite structure denoted, after Smith, as SI, SI′, SU, SII′, SII, SII*, and SV (Fig. 2). Also, the oxygen atoms in the lattices of faujasite type zeolites have been denoted conventionally, as shown in Fig. 3.

Since ion-exchanged zeolites are good catalysts for many chemical reactions, it is of relevance to determine the sites of the crystal lattice into which the cations direct themselves in the exchange process and to elucidate the influence of these cations on the catalytic properties. The localization and occupation of the various positions (the selectivity with regard to position) is dependent on the Si/Al ratio, the nature and charge of the cations, the content of water

0022-4596/85 $3.00

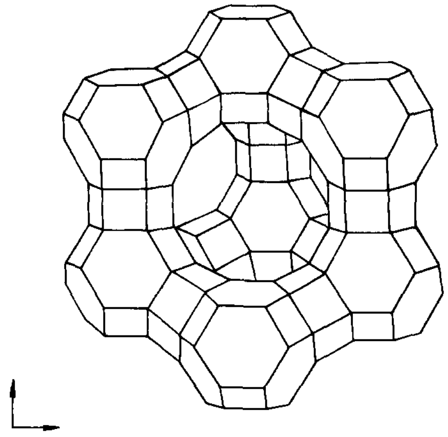

FIG. 1. *Structure of zeolites of the faujasite type.* The chemical composition of the unit cell is given by the general formula $Na_nAl_nSi_{192-n}O_{384} \cdot \sim 250\ H_2O$.

molecules, as well as on other ligands. In the case of paramagnetic cations all of these parameters can influence EPR spectra. The hyperfine structure and *g*-factors of an EPR spectrum are sensitive to changes in a paramagnetic complex geometry and can reflect changes in the surrounding of the paramagnetic ion during dehydration of a zeolite sample.

For many years, EPR has been successfully applied to studies of transition metal complexes in the lattice of zeolites. A number of papers have been devoted to the study of aqueous complexes of Cr^{3+} (*2*), Mn^{2+} (*3, 4*), Fe^{2+} (*5*), Co^{2+} (*6, 7*), Ni^{2+} (*8*), V^{4+} (*9*), and especially Cu^{2+} (*10–19*), in samples with different degrees of ion exchange and of zeolite hydration. Beside its aqueous complexes, Cu^{2+} has been studied in coordination with various molecules, e.g., ethylenediamine (en) and *N,N,N′,N′*-tetramethylenediamine (tmen) (*20*), 2,2′-bipyridine (bipy) (*21*), trimethylphosphine (*22*), and NH_3 (*23*).

The great amount of EPR work on Cu^{2+} complexes has shown that, with increasing dehydration of CuNaY zeolite, the Cu^{2+} ions migrate in the free spaces of the zeolite network toward specific positions (Fig. 2). This involves a change in symmetry of the nearest surroundings of the ion apparent as a change in the parameters of the EPR spectrum. It has been found that in the process of dehydration, the symmetry of a copper complex changes from that of a distorted octahedron to plane-square (*10, 12, 14*). Herman (*13*) has discovered a pentacoordinated copper complex having a

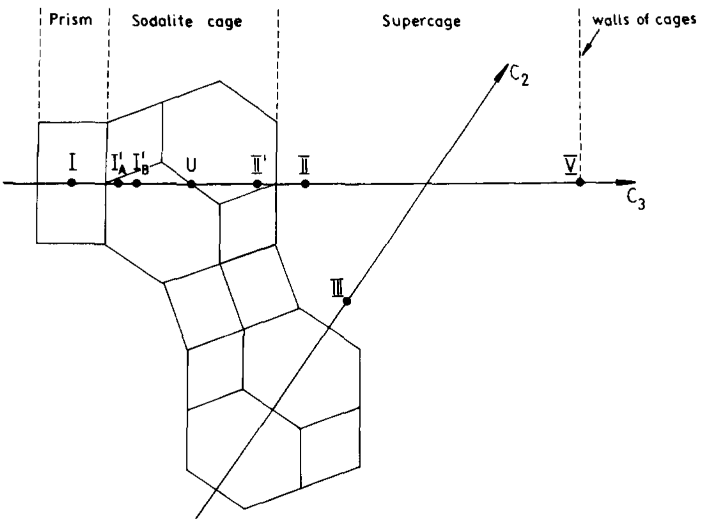

FIG. 2. Exchangeable positions of cations in the faujasite type network.

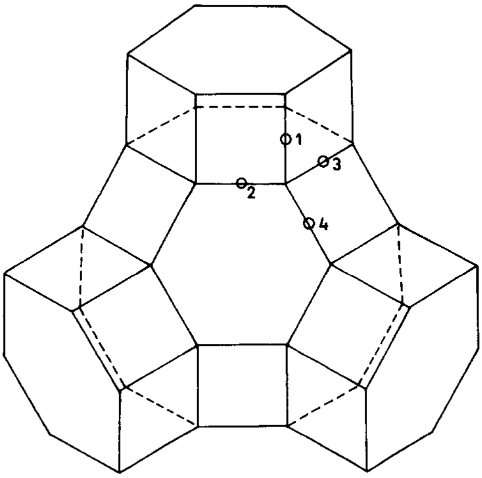

FIG. 3. Notation of the oxygens O^{2-} in the faujasite type network: O(1), O(2), O(3), O(4).

trigonal bipyramid symmetry ($g_{\parallel} < g_{\perp} \cong 2{,}3$) with Cu^{2+} in the center of the hexangular window. The complex is unstable at higher temperatures and converts into a complex with a different structure. Similar complexes were found by the electron spin echo method (*40, 41*).

The interpretation of X-ray results for the localization and occupation of ion-exchange sites in X and Y zeolites and in faujasite is difficult. Essential discrepancies exist with regard to hydrated zeolites, where localization of the cations is impeded by the mobility of water molecules. Differences in the localization and occupation of specific positions occur for zeolites subjected to exchange with mono- and polyvalent cations, as well as for bivalent cations in samples with a high degree of ion exchange (*24*). Ogawa (*24*) has drawn attention to the fact that the selectivity with regard to position should be defined in relation to cation size rather than to cation nature (small cations: Li^+, Na^+, Ca^{2+}, Sr^{2+} → SI; large cations: K^+, Cs^+, Ba^{2+} → SII). Structural studies of dehydrated CuNaY zeolite (*25*) as well as of hydrated and dehydrated copper-exchanged natural faujasite single crystal (*26*) have shown Cu^{2+} ions to prefer the position SI with D_{3h} symmetry. In the hydrated sample of Cu-faujasite only a part of the Cu^{2+} ions were found to be localized in SI′ position whereas the localization of the remainder was by no means established with certainty. The determination of localization of all the Cu^{2+} cations became possible only after dehydration of the sample, and the copper ions were found to occupy positions SI, SI′, SII, SII*, and SIII.

It should be emphasized that, whereas structural studies are usually carried out on samples with a high concentration of Cu^{2+} (this affects occupation of specific positions), EPR is performed on samples with a low Cu^{2+} concentration. Hence, one should be very cautious while interpreting results obtained by the two methods.

The above-cited results suffice for proving that the occupation of specific ion exchange sites is still an open question. Experimental as well as theoretical work on the subject is rapidly going on.

Our present paper is aimed at determining the path of Cu^{2+} migration, at a closer elucidating the structure of the complexes, and at determining the parameters describing the latter. From the experimental data, we have calculated the molecular orbital parameters for the complexes of symmetry D_{4h} and D_{2d}. Moreover, we propose models of the complexes arising during dehydration of ion-exchanged zeolites as well as their localization in the lattice.

2. Experimental

Zeolite samples of different copper content were obtained by ion exchange at room temperature of NaY zeolite in solution of copper nitrate $Cu(NO_3)_2$ in accordance with the reaction $Na_{54}Al_{54}Si_{138}O_{384} + n\ Cu^{2+} \rightarrow Cu_nNa_{54-2n}Al_{54}Si_{138}O_{384} + 2n\ Na^+$. The NaY zeolite was provided by the Institute of Industrial Chemistry, Warsaw. In order

TABLE I

Cu^{2+} AND WATER CONTENTS OF THE ZEOLITES INVESTIGATED[a]

Sample	Cu concentration in solution $c_{Cu^{2+}}$ [mole/liter]	Water content p_{H_2O} [wt%]	Cu^{2+} content in anhydrous zeolite $p_{Cu^{2+}}$ [wt%]	Exchange ratio η_{Cu} [%]	Number of Cu^{2+} ions $n_{Cu^{2+}}$
CuNaY-06	0.005	26.0	0.84	6.2	1.7
CuNaY-12	0.01	24.2	1.56	11.6	3.1
CuNaY-25	0.02	25.4	3.33	24.9	6.7
CuNaY-41	0.05	23.5	5.49	41.3	11.2
CuNaY-57	0.1	23.5	7.46	56.5	15.2
CuNaY-60	0.2	22.6	7.93	60.1	16.2
CuNaY-65	0.5	22.3	8.53	64.8	17.5

[a] When calculating the exchange ratio $\eta_{Cu^{2+}}$ we assumed the composition $Na_{54}(AlO_2)_{54}(SiO_2)_{138}$ for the unit cell (*32*).

to obtain samples differing as to their Cu^{2+} content, copper nitrate solutions with concentrations of 0.5, 0.2, 0.1, 0.05, 0.02, 0.01, and 0.005 *M* were prepared. To these, NaY zeolite was added in a manner to obtain a solution/solid ratio of 20 cm^3/g. The solutions were subjected to stirring for 4 hr, filtering and the residue was rinsed repeatedly with distilled water. The samples were then dried at room temperature. Copper content was determined by atomic absorption technique on a ASS-1 spectrometer made by Carl Zeiss, Jena. Degree of replacement of Na^+ by Cu^{2+} ions ranged from 6.2 to 64.8% (Table I, Fig. 4). The following relations were held between the number of Cu^{2+} ions per unit cell $n_{Cu^{2+}}$, the degree of ion exchange between Na^+ and Cu^{2+} ions $\eta_{Cu^{2+}}$, and the Cu^{2+} content in mass units, $p_{Cu^{2+}}$:

$$n_{Cu^{2+}} = \tfrac{1}{2}\eta_{Cu^{2+}} + n_{Na} \qquad (n_{Na} = 54)$$

$$\eta_{Cu^{2+}} = \frac{m_{NaAlO_2} + a_{Si/Al} \cdot m_{SiO_2}}{\tfrac{1}{2}m_{Cu}\left(\dfrac{1}{p_{Cu}} - 1\right) + m_{Na}}$$

$$a_{Si/Al} = \frac{192 - n_{Na}}{n_{Na}} \qquad (a_{Si/Al} = 2.56)$$

where n_{Na} number of Na^+ ions per unit cell prior to ion exchange, and m_{NaAlO_2}, m_{SiO_2}, m_{Cu}, m_{Na} are the respective molecular masses.

To achieve dehydration, the samples were heated under normal pressure at 70, 100, 150, 200, and 400°C. At each of these temperatures, heating lasted 24 hr, after which EPR spectra were recorded.

EPR measurements of the ion-exchanged CuNaY zeolite samples with different Cu^{2+} concentration were carried out at room

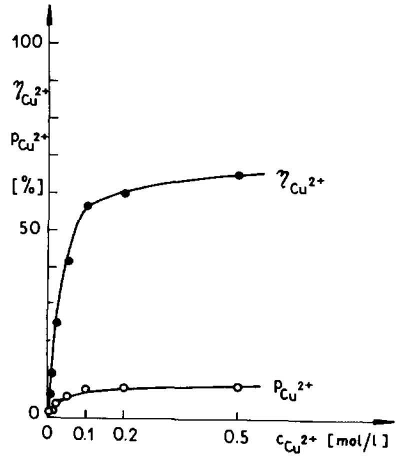

FIG. 4. Na^+/Cu^{2+} exchange ratio $\eta_{Cu^{2+}}$ and Cu^{2+} ion weight content $p_{Cu^{2+}}$ versus $Cu(NO_3)_2$ concentration in the aqueous solution used for the exchange process.

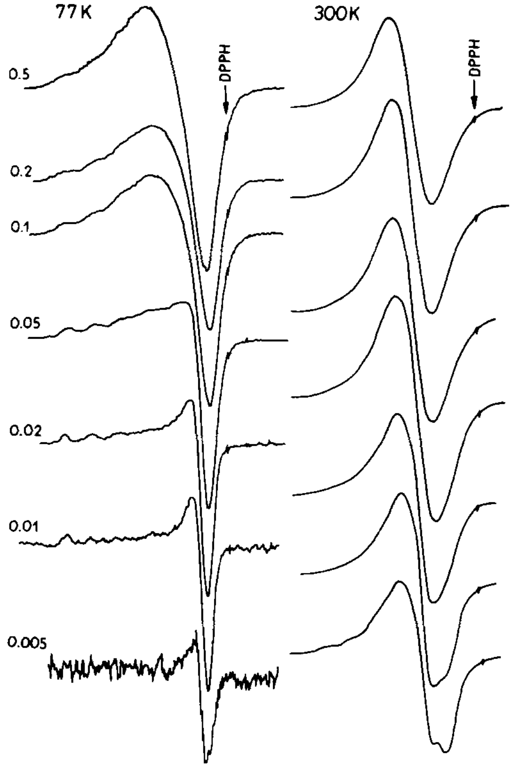

FIG. 5. EPR spectra of nondehydrated faujasite samples measured at 77 and 300 K versus Cu^{2+} concentration in the solution.

temperature as well as at 77 K with an X-band (9.4 GHz) spectrometer of type SE/X-200, made by "Radiopan," Poznań, and equipped with a TE_{102} cavity and 100 kHz modulation. The value of the spectroscopic splitting factor g was determined with respect to a DPPH standard ($g = 2.0036$). The magnetic field was monitored with an automatically tracing NMR magnetometer MJ-111, made by "Radiopan."

3. EPR Results

EPR spectra from powder samples of Cu NaY zeolite, dried at room temperature, and having different concentrations of copper ions Cu^{2+}, were recorded at 300 and 77 K (Fig. 5). The spectra of samples with high Cu^{2+} concentrations observed at 300 K consist of a single, symmetric line, but show growing asymmetry for decreasing Cu^{2+} concentrations. The isotropic g-factor amounts to $g_{iso} = 2.183$ for a symmetric line, and the linewidth is $2\Delta B_{1s} = 18.0$ mT. The shape of the spectra at low Cu^{2+} concentration points to the presence of yet another EPR line. For high Cu^{2+} concentrations, the spectrum is dominated by the isotropic component.

The same samples were measured at 77 K. Their EPR spectra are shown in Fig. 5. Each spectrum is seen to originate essentially from one type of copper complex with axially symmetric crystal field. Such a spectrum is characteristic of polycrystalline samples. The experimental spin Hamiltonian parameters amount to $g_{\parallel} = 2.408$, $g_{\perp} = 2.088$, $A_{\parallel} = 14.6 \times 10^{-3}$ cm^{-1} (since the hfs line at perpendicular orientation remained unresolved it was not possible to determine $A_{\perp}$ precisely; however, it is known that $A_{\perp} < 1.5 \times 10^{-3}$ cm^{-1}). For these spectra, the width of the individual line increases with a rise in Cu^{2+} concentration. Zeolite samples with different Cu^{2+} concentrations were subjected to dehydration at 70, 100, 150, 200, and 400°C. The EPR spectra of these samples are shown in Fig. 6. The spectra differ depending on Cu^{2+} concentration and on dehydration temperature. The hfs is more clearly resolved for lower Cu^{2+} concentrations. For a fixed dehydration temperature, the Cu^{2+} concentration dependence of the spectrum is rather weak, whereas at a given Cu^{2+} concentration the dependence of the spectra on the temperature of dehydration is much stronger. Especially, the spectra of the samples CuNaY-06 obtained from 0.005 M Cu^{2+} solution exhibit, for different temperatures of dehydration, lines which originate from different copper ion complexes in the zeolite. The shape of most of the spectra points to at least two copper complexes as their origin; however, in each of the spectra obtained

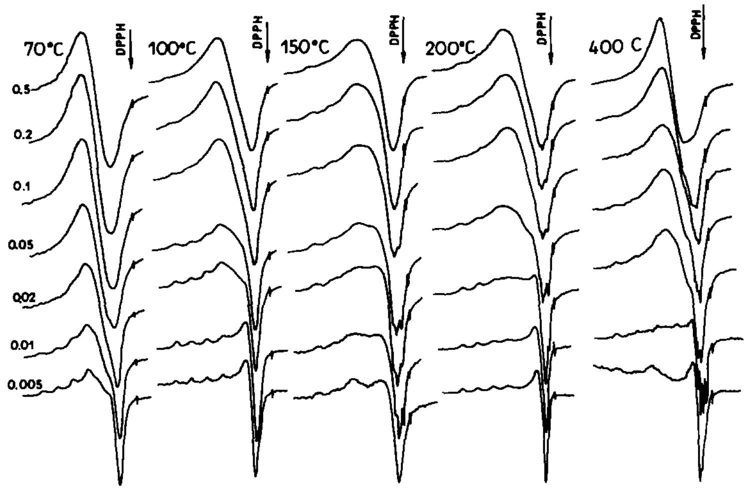

FIG. 6. EPR spectra of dehydrated faujasite samples measured at 300 K versus temperature of dehydration and Cu^{2+} concentration in the solution.

for the samples CuNaY-06 and CuNaY-12, one of the components predominates. From the shape of the EPR line characteristic of powder spectra of copper complexes, we easily determined the spin Hamiltonian parameters $g_{\parallel}$ and $A_{\parallel}$ on the assumption of axial symmetry of the complexes. However, in order to determine $g_{\perp}$ and $A_{\perp}$, we worked out a spectrum simulation program for digital computer SM-3 based on the position of the additional peak occurring in the powder spectra at the magnetic field strength corresponding to the extremum at the position of the hfs line for the transition with quantum number $m_I = -\frac{3}{2}$ (*30, 42*). We checked the thus calculated parameters $g_{\perp}$ and $A_{\perp}$ by simulation of the powder spectrum and by comparing the simulated and experimental spectra. In Table II we give the values of $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$, and $A_{\perp}$, vs the temperature of dehydration, for the aqueous copper complexes predominant in the samples CuNaY-06 or CuNaY-12. One notes that, for the samples dehydrated at

TABLE II

SPIN HAMILTONIAN PARAMETERS FOR AQUEOUS Cu^{2+} COMPLEXES IN SAMPLES CuNaY-06 OR CuNaY-12 AS A FUNCTION OF DEHYDRATION TEMPERATURE OF FAUJASITES

Measuring temperature (K)	Dehydration temperature (°C)	$g_{\parallel}$[a]	$g_{\perp}$	g_{av}	g_{iso}	$A_{\parallel}$[a]	$A_{\perp}$	A_{av}
						[$\times 10^{-3}$ cm^{-1}]		
77	25	2.408	2.088	2.194		14.6	<1.5	<5.8
300	25			2.183	2.183			
300	70	2.375	2.099	2.191		13.3	2.0	5.8
300	100	2.381	2.085	2.184		13.2	1.6	5.5
300	150	2.336	2.055	2.149		16.7	2.4	7.2
300	200	2.366	2.062	2.163		12.7	1.3	5.1
300	400	2.336	2.055	2.149		16.7	2.4	7.2

[a] Errors: $g \pm 0.004$, $A \pm 0.3$.

70, 100, and 200°C, the values of $g_\parallel$, $g_\perp$, $A_\parallel$, and $A_\perp$ are similar and originate from one group of complexes, whereas for samples dehydrated at 150 and 400°C the parameters are identical within the limits of experimental error and originate from another group of complexes (in a first approximation, the spectra differ only in individual linewidth). The EPR spectra of samples dehydrated at 400°C exhibit moreover an isotropic line with $g = 2.186$. Also samples dehydrated at 70°C—particularly those with a high Cu^{2+} concentration—show, in addition to the anisotropic line, an isotropic one, identical with that shown by the sample dried at room temperature.

A detailed analysis of the EPR spectra from samples with different Cu^{2+} concentrations dehydrated at 200°C points to a gradual change in relative concentration of two different complexes. At low Cu^{2+} content the spectrum is almost exclusively due to the complex with spin Hamiltonian parameters of the first (70, 100, 200°C) group, whereas at high Cu^{2+} concentrations the samples reveal the presence of the complex with parameters of the second group (150 and 400°C). In a CuNaY-06 sample dried at 150°C we have observed additionally a weak broad line with $g_\perp \cong 2.3$ presumably due to the five-coordinated Cu^{2+} complex of trigonal bipyramid symmetry found by Herman (*13*).

Dehydration of zeolite samples is a reversible process. Samples stored in air undergo rehydration. For instance, in the case of samples dried at 100°C, it is almost exclusively the isotropic line ($g = 2.183$) that disappears and the spectrum observed is that of the anisotropic complex. However, 10 days later, in the presence of air, the intensity of the isotropic line grows anew. After 10 months the isotropic line becomes stronger than the anisotropic line, the intensity of which decreases simultaneously. To some extent the same process takes place in samples dried at room temperature; here, too, one can observe similar changes, dependent on the time of storage (Fig. 7).

4. Discussion of the Results

Our studies, as well as those of other authors, show that depending on the temperature of dehydration, Cu^{2+}-exchanged zeolites contain different type hydrated copper complexes. In our opinion, these complexes fall essentially into two groups, characterized markedly by the values of their parameters $g_\parallel$ and $A_\parallel$ (Table III). A slight experimental dispersion of these EPR values is primarily due to differences in the methods of preparation of the NaY zeolites, their Si/Al ratios and Cu^{2+} concentrations, as well as the conditions of thermal and chemical treatments of the samples. The values of the spin Hamiltonian parameters obtained by us are in good agreement with those found by others (*10–20*) for hydrated Cu^{2+} complexes in NaY zeolites.

However, the very diversity of the interpretations put forward in those papers re-

TABLE III

COMPARISON OF $g_\parallel$ AND $A_\parallel$ VALUES FOUND BY OTHER AUTHORS AND BY US FOR THE COMPLEXES INVESTIGATED

Group of complexes	Other authors (*10–20*)	This work
I	$g_\parallel = 2.360$–2.389 $A_\parallel = (13.1$–$14.0) \times 10^{-3}\ cm^{-1}$	$g_\parallel = 2.366$–2.381 $A_\parallel = (12.7$–$13.3) \times 10^{-3}\ cm^{-1}$
II	$g_\parallel = 2.313$–2.347 $A_\parallel = (15.8$–$17.0) \times 10^{-3}\ cm^{-1}$	$g_\parallel = 2.336$ $A_\parallel = 16.7 \times 10^{-3}\ cm^{-1}$

garding positions of the complexes within the zeolite lattice as well as the symmetry of the complexes justifies our attempt to analyze the parameters anew. The presence of at least two sets of spin Hamiltonian parameters points, in a first approximation, to the existence of two types of complexes in faujasite, differing in their coordination number or in the type of symmetry of their surroundings.

As mentioned above, X-ray structural studies (*25, 26*) have shown the copper Cu^{2+} ions to occupy all the characteristic cation sites presented in Fig. 2. However, studies applying X-ray as well as EPR show that, for a given temperature of zeolite dehydration, one type of copper complex, occupying a well-defined position in the zeolite, is predominant. For example, in the case of samples of $Cu_{16}Na_{24}Al_{56}Si_{136}O_{384}$ dehydrated at 500°C, Gallezot *et al.* (*25*) have found the copper ions to occupy predominantly SI′ positions and some small numbers of Cu^{2+} to be in SI positions.

In samples with high concentrations of exchanged Cu^{2+} ions, presumably all types of the Cu^{2+} complexes observed are present in different positions. At low Cu^{2+} concentrations some of the complexes occupy well-determined positions, making possible their selective observation in the EPR spectra in function of the dehydration temperature. The change in EPR spectra of the complexes appearing in the course of dehydration of the zeolite samples leads to the conclusion that, as dehydration of the faujasite proceeds, the hydrated copper complexes migrate through the free spaces of the sodalite cells and, at well-defined temperatures of dehydration, occupy specific positions in the lattice.

According to the results obtained by various authors, in samples with low Cu^{2+} concentrations, not subjected to high-temperature treatment and dehydration, the copper complexes are present chiefly in supercages. With increasing dehydration at a high temperature, the copper ions traverse the "windows" of the six-membered rings and migrate in the direction of the cuboctahedral sodalite cell to finish up inside a hexangular prism on passing through the next window. Thus, the migration of Cu^{2+} can be expressed schematically as a sequence of the positions: SV → SIII → SII → SII′ → SI′ → SI.

The $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$, and $A_{\perp}$ values obtained for hydrated copper complexes observed in dehydrated samples have been used in order to determine the symmetry of the crystal field originating in the ligands and to calculate the bonding parameters by the method of LCAO MO.

5. The Symmetry of the Complexes

The majority of hexacoordinated copper Cu^{2+} complexes is known to possess the symmetry of a tetragonally elongated *trans*-octahedron D_{4h}. In the limiting case of infinitely extended *trans*-ligands, the symmetry becomes square four-coordinated D_{4h}. For the four-coordinated copper complexes also the symmetries D_{2d} and D_2 of a tetrahedrally distorted square, referred to as pseudotetrahedral, occur. The square can transform continuously into a tetrahedron, if the ligands lying on the diagonals of the square are shifted pairwise upward and, respectively, downward of the plane parallel to the C_4 axis. This leads to the transformation of the symmetry

$$D_{4h}(\text{square}) \rightarrow D_{2d}(\text{pseudotetrahedron}) \rightarrow T_d(\text{tetrahedron}) \quad \text{(a)}$$

The square can also transform into a pseudotetrahedron by a rotation of two ligands about C_2 axis of the square. The transition now is

$$D_{4h}(\text{square}) \rightarrow D_2(\text{pseudotetrahedron}) \rightarrow D_{2d}(90^\circ \text{ pseudotetrahedron}) \quad \text{(b)}$$

In the case (a), when the planar-square symmetry D_{4h} reduces to D_{2d} due to the tetrahedral perturbation, the bonding and spin Hamiltonian parameters are related mutually according to the Sharnoff formulae (*33*). We adduce them in the form proposed by Yokoi and Addison (*34*). For the symmetry D_{2d} the wave functions of the electron (in addition to the $3d$ orbitals) have to involve the contribution from $4p$ orbitals in the bond, and take the form

$$\begin{aligned}
\phi(b_2) &= \alpha d_{xy} + \eta p_z + \rho\phi_{\text{lig}}(xy)\\
\phi(e) &= \gamma d_{xz} + \xi p_y + \sigma\phi_{\text{lig}}(xz)\\
\phi(e) &= \gamma d_{yz} + \xi p_x + \sigma\phi_{\text{lig}}(yz)\\
\phi(b_1) &= \beta d_{x^2-y^2} + \mu\phi_{\text{lig}}(x^2 - y^2)\\
\phi(a_1) &= \delta d_{3z^2-r^2} + \varepsilon s + \nu\phi_{\text{lig}}(3z^2 - r^2)
\end{aligned}$$

The spin Hamiltonian parameters for $\phi(b_2)$ ground state are

$$\begin{aligned}
\Delta g_{\parallel} &= g_{\parallel} - g_e = -\frac{8\alpha\beta\lambda_d\kappa_{\alpha\beta}}{\Delta_{\parallel}}; \qquad g_e = 2.0023\\
\Delta g_{\perp} &= g_{\perp} - g_e = -\frac{2(\alpha\gamma\lambda_d - \eta\xi\lambda_p)(\kappa_{\alpha\gamma} - \eta\xi)}{\Delta_{\perp}};\\
A_{\parallel} &= \theta + P_d\left[-\tfrac{4}{7}\alpha^2 + \Delta g_{\parallel}\frac{\alpha\beta}{\kappa_{\alpha\beta}} + \tfrac{3}{7}\Delta g_{\perp}\frac{\alpha\gamma}{\kappa_{\alpha\gamma} - \eta\xi}\right] + P_p\left[\tfrac{4}{5}\eta^2 + \tfrac{3}{5}\Delta g_{\perp}\frac{\eta\xi}{\kappa_{\alpha\gamma} - \eta\xi}\right];\\
A_{\perp} &= \theta + P_d\left[\tfrac{2}{7}\alpha^2 + \tfrac{11}{14}\Delta g_{\perp}\frac{\alpha\gamma}{\kappa_{\alpha\gamma} - \eta\xi}\right] + P_p\left[\tfrac{2}{5}\eta^2 - \tfrac{13}{10}\Delta g_{\perp}\frac{\eta\xi}{\kappa_{\alpha\gamma} - \eta\xi}\right];\\
\kappa_{\alpha\beta} &= \alpha\beta + \beta\rho S_d + (1 - \beta^2)^{1/2}\rho[T(n)]C/2;\\
\kappa_{\alpha\gamma} &= \alpha\gamma + \gamma\rho S_d + (1 - \gamma^2)^{1/2}\rho[T(n)]C/2^{1/2};\\
\theta &= -\kappa_0(\alpha^2 P_d + \eta^2 P_p);\\
P_{d,p} &= 2\gamma_N\mu_0\mu_N\langle r^{-3}\rangle_{3d,4p}
\end{aligned}$$

with the normalization condition

$$\alpha^2 + \eta^2 + \rho^2 + 2\rho(\alpha S_d + \eta S_p) = 1$$

$$P_d = 36.0 \times 10^{-3}\ \text{cm}^{-1}; \qquad P_p = 40.2 \times 10^{-3}\ \text{cm}^{-1}$$

$\lambda_{d,p}$—the spin–orbit coupling constant for the $3d$ and $4p$ orbitals, respectively, of the free copper ion Cu^{2+}, $\lambda_d = -828\ \text{cm}^{-1}$, $\lambda_p = -925\ \text{cm}^{-1}$

$S_{d,p}$—the overlap integral for the orbital $\langle 3d$ or $4p|\phi_{\text{lig}}\rangle$ in the molecular orbital $\phi(b_2)$, $S_d \cong S_p \cong 0.1$

κ_0—Fermi's contact term for the free copper ion Cu^{2+} $\kappa_0 = 0.43$

C—factor accounting for the geometry 1 (for the square) $> C > \sqrt{2}/3 = 0.816$ (for the tetrahedron) $T(n) \cong 0.2$.

In the limiting cases of the symmetries D_{4h} and T_d the above formulae simplify because for symmetry of the elongated octahedron or that of the planar square D_{4h}: $\eta = \xi = 0$; for tetrahedron symmetry T_d: $\alpha = \gamma$, $\eta = \xi$.

The experimental results obtained by us allow to calculate principal bond parameters between the copper ion Cu^{2+} and the ligands. This is performed applying the preceding formulae, and the results are given in Table IV. In our calculations some simplifying assumptions had to be made, primarily for a lack of spectroscopic data concerning energy of the transitions between orbital levels in the visible band for the Cu^{2+} complexes in faujasite. Moreover, we assumed alternatively the parameters $A_{\parallel}$

TABLE IV

BINDING PARAMETERS CALCULATED BY LCAO MO THEORY FOR AQUEOUS Cu^{2+} COMPLEXES VS DEHYDRATION TEMPERATURE

Measuring temperature (K)	Dehydration temperature (°C)	Symmetry of the complex	α^2	β^2	γ^2	$\eta^2 = \xi^2$	κ_0	$\Delta_\parallel$ (cm^{-1})	$\Delta_\perp$ (cm^{-1})
300	25	D_{4h}	Rotating octahedron						
300	70	D_{4h}	0.76	0.79	0.94	0	0.45	10,700	12,300
300	100	D_{4h}	0.78	0.78	0.78	0	0.42	10,700	12,300
300	150	D_{2d}	0.90	0.90	0.90	0.10	0.40	16,100	19,800
300	200	D_{4h}	0.77	0.76	0.58	0	0.39	10,700	12,300
300	400	D_{2d}	0.90	0.90	0.90	0.10	0.40	16,100	19,800

and $A_\perp$ as both positive or both negative. Since calculations for the case $A_\parallel$, $A_\perp > 0$ led to $\alpha^2 < 0$, we finally assumed $A_\parallel$, $A_\perp < 0$.

The spin Hamiltonian parameters obtained for the complexes dehydrated at 70, 100, and 200°C can be interpreted by assuming that the complexes have the elongated octahedron symmetry D_{4h}. The transition energies $\Delta_\parallel = 10{,}700$ cm^{-1} and $\Delta_\perp = 12{,}300$ cm^{-1} were calculated as mean values, obtained on the assumption of $\alpha^2 \cong \beta^2 \cong \gamma^2$. The numerical values of the transition energies obtained by us are in agreement with those commonly observed (*35*) and corroborate our conclusion that the complexes have hexacoordinated symmetry of the elongated octahedron D_{4h}.

The interpretation of the EPR spectra, however, is quite different when we deal with the copper complexes of the faujasite samples dehydrated at 150 and 400°C (one should stress that the EPR spectrum of these complexes appears as well for higher Cu^{2+} concentrations). In this case, too, it was possible to calculate approximately the bonding parameters α^2, β^2, γ^2, $\eta^2 = \xi^2$ and κ_0; however, the high values of the hfs interaction constant $A_\parallel = -16.7 \times 10^{-3}$ cm^{-1} and transition energies $\Delta_\parallel = 16{,}100$ cm^{-1} and $\Delta_\perp = 19{,}800$ cm^{-1} bring evidence that, here, the symmetry and coordination number of the ligands are lower than for the complex with D_{4h} symmetry. Hence, a symmetry able to correspond to the complexes in question is to be found in the four-coordinated symmetry of the tetrahedrally distorted square or pseudotetrahedral D_{2d} or D_2, discussed above.

Pseudotetrahedral symmetries are obtained either by tetrahedral distortion of the squares (cases (a), (b)) or by a similar distortion of the tetrahedron.

In the latter case the transformations can be written as

$$T_d \text{ (tetrahedron)} \rightarrow D_{2d} \text{ (pseudotetrahedron)} \rightarrow D_{4h} \text{ (square)} \quad \text{(c)}$$

$$T_d \text{ (tetrahedron)} \rightarrow D_2 \text{ (pseudotetrahedron)} \rightarrow D_{2h} \text{ (rectangle)} \quad \text{(d)}$$

The transformations (a) and (c) are identical. However, so as to complete the picture, we still have to consider the case (d), i.e., the transformation from a tetrahedron to a rectangle. Formulae for $g_\parallel$, $g_\perp$, $A_\parallel$, and $A_\perp$ for the symmetry D_{2h} have been proposed by Bullugiu *et al.* (*36*). Their formulae are rather complicated, and the great number of unknowns make practical applications impossible. Nonetheless, after some slight simplifications, consisting in the omission of the role of the d_{z^2} orbital in

TABLE V

SYMMETRY AND LOCALIZATION SITE OF AQUEOUS COMPLEXES OF Cu^{2+} IN FAUJASITE

Dehydration temperature (°C)	Symmetry of the complex	Coordination number	Site	Composition of the complex	Structure of the complex
25	D_{4h}(tumbl.)	6	SV	$Cu(OH_2)_6^{2+}$	Elongated octahedron
70	D_{4h}	6	SIII	$Cu(OH_2)_4O_2(1)^{2+\,a}$	Elongated octahedron
100	D_{4h}	6	SII	$Cu(OH_2)_3O_3(2)^{2+}$	Elongated octahedron
150	D_{2d}	4	SII′	$Cu(OH_2)O_3(4)^{2+}$	Pseudotetrahedron
200	D_{4h}	6	SI'_B	$Cu(OH_2)_3O_3(3)^{2+}$	Elongated octahedron
400	D_{2d}	4	SI'_A	$Cu(OH_2)O_3(3)^{2+}$	Pseudotetrahedron

[a] The central copper ion Cu^{2+} can also be coordinated to two O(3) or two O(4) atoms.

the ground state, these formulae become formally identical with those given above for the symmetry D_{2d}.

Hoffmann and Goslar (*37*) have performed calculations of the spin Hamiltonian parameters by the method of crystal field theory for Cu^{2+} complexes of pseudotetrahedral symmetry D_{2d} and C_{2v}. For D_{2d} they defined the angle β between the bisectrix of the ligand-central ion-ligand angle and the central ion-ligand bond as 54.7° (for tetrahedron) $< \beta <$ 90° (for square). For C_{2v}, they defined an angle Φ (valid also for symmetry D_2) as that subtended by the plane containing the bonds: ligand 1–central ion–ligand 2 and the plane containing the bonds ligand 3–central ion–ligand 4, respectively, as 0° (for rectangle) $< \Phi <$ 90° (for tetrahedron). Calculations (*37*) show that for $\beta = 85°$ in D_{2d} and $\Phi = 35°$ in C_{2v} (or, in our case, D_2) the numerical values obtained are almost identical: $g_\parallel = 2.33$ and $A_\parallel = -17.0 \times 10^{-3}$ cm^{-1}, in excellent agreement with the values observed by us: $g_\parallel = 2.336$ and $A_\parallel = -16.7 \times 10^{-3}$ cm^{-1}. This provides no sufficient basis for deciding whether the copper complexes of faujasite samples dehydrated at 150 and 400°C have the symmetry D_{2d} or D_2. Nonetheless these results allow to draw the conclusion that the ligands of the central ion form a four-coordinated, tetrahedrally distorted square or pseudotetrahedral structure. Since the tetrahedral distortion of the square measured as the difference $90° - \beta = 90° - 85° = 5°$ for D_{2d} requires less energy than the distortion $\Phi = 35°$ for D_2, we are inclined to accept the symmetry D_{2d} as that of the four-coordinated Cu^{2+} complexes.

6. Localization of the Complexes

The calculations performed enable us to postulate, for the complexes in faujasite lattice, the symmetries and positions assembled in Table V.

The isotropic EPR line with $g = 2.183$ observed by us in undehydrated samples after ion exchange is assigned to the hexahydrate copper complex $Cu(OH_2)_6^{2+}$. Its anisotropic spin Hamiltonian parameters undergo averaging due to tumbling of the complex in the supercage and its interaction with the oxygen atoms of the 12-membered ring by means of hydrogen bonds. Thus, the complex occupies the position SV. Presumably, the emergence of hydrogen bonds is responsible for the anisotropic EPR spectrum of the complex apparent on freezing at 77 K.

As dehydration of the zeolite proceeds on heating, the degree of hydration of the complex is, in general, lower whereas the remaining coordination valences are saturated with lattice oxygens. In the position SIII, still within the supercage, the copper

TABLE VI

DEHYDRATION TEMPERATURES FOR WHICH DIFFERENT CATION SITES OF FAUJASITE ARE MAXIMALLY OCCUPIED BY CATIONS Na^+ (RUBIO *et al.* (*31*)) OR, ALTERNATIVELY, BY CATIONS Cu^{2+} (THIS WORK)[a]

Site of cation localization	Dehydration temperature (°C)			
		Na^+ cations		Cu^{2+} cations
SV		25	500	25
SIII		25		70
SII		130		100
SII′	25	150	500	150
SI'_B		200		200
SI'_A		500		400
SI		500		

[a] In all cases, the exchange process was carried out at room temperature.

ion is still able to form a bond with two oxygens O(1) of the zeolite lattice. The remaining ligands are provided by oxygens, supplied by four molecules of water. As dehydration of the zeolite proceeds further, the EPR parameters of the copper complexes change; hence we conclude that the complexes change their positions (and structure) in the zeolite lattice. The commonly accepted assumption is that the complexes, formed on hexangular internal and external walls of the sodalite cell, coordinate with three oxygens of the window, whereas the remaining ligands are oxygen atoms of water molecules. The number of these ligands and the symmetry of the complex have to be in agreement with the conclusions derived from the LCAO MO calculations of the bond parameters carried out on the basis of the available spin Hamiltonian parameters (Tables II, IV, V).

The four-coordinated complex with tetrahedrally distorted square symmetry is observed distinctly at 150 and 400°C, whereas at 200°C the normal six-coordinated complex, having the symmetry of a tetragonally elongated octahedron, is predominant. Similar observations have been performed by Conesa and Soria (*14*) who, transitorily, observed at 150°C the EPR spectrum of a copper complex with spin Hamiltonian parameters equal to $g_\parallel = 2.327$, $g_\perp = 2.054$, $A_\parallel = 16.8 \times 10^{-3}$ cm^{-1}, and $A_\perp = 2.2 \times 10^{-3}$ cm^{-1}, i.e., exhibiting good agreement with our measurements of $g_\parallel = 2.336$, $g_\perp = 2.055$, $A_\parallel = 16.7 \times 10^{-3}$ cm^{-1}, and $A_\perp = 2.4 \times 10^{-3}$ cm^{-1}. The transitory occurrence of a four-coordinated complex of low symmetry and a low degree of hydration can be explained by the requirement that, in order to pass through the hexangular ring from the supercage into the sodalite cell, the Cu^{2+} ions has to get rid of some water molecules, since a cation with an ionic radius exceeding 1.15 Å cannot go through the six-membered ring in question. The ionic radii of Na^+ and Cu^{2+} are known to amount to 0.95 and 0.72 Å, respectively, and their hydrated complexes have diameters that are several times larger. This justifies the postulate that the complex mentioned occupies positions SII′ inside the sodalite cell immediately after passing from supercage through a six-membered ring on reduction of the number of its water molecules.

Rubio *et al.* (*31*) have investigated NaY zeolite versus the temperature of dehydration by X-ray diffraction technique. They have found there exist two, slightly different possible positions SI'_A and SI'_B of the cations; of the two, SI'_A lies somewhat closer to six-membered ring neighboring on hexagonal prism. It is in these positions that we localize the copper complexes appearing in faujasite dehydrated at 200°C (SI'_B) and 400°C (SI'_A). In Table VI are listed those temperatures for which the individual sites in the zeolite network are maximally occupied by cations Na^+. It turns out that there is agreement with the temperatures for which a given site of the network is invested with cations Cu^{2+}. The general trend of the changes in occupation of the sites by cations Na^+ is thus seen to be in agreement

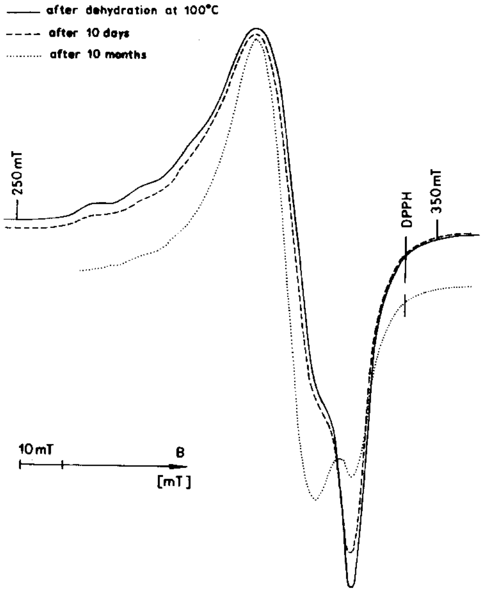

FIG. 7. Time-evolution of the EPR spectrum for sample CuNaY-06 dehydrated at 100°C.

with the postulated migration of the cations Cu^{2+} in the faujasite network according to the scheme $SV \rightarrow SIII \rightarrow SII \rightarrow SII' \rightarrow SI'_B \rightarrow SI'_A$ ($\rightarrow$ SI). Noteworthy is the fact that the investment of SII′ by Na^+ becomes minimal for the dehydration temperature of 200°C (*31*), providing a good interpretation of the analogous decrease in concentration of low-symmetry Cu^{2+} complexes in the samples dehydrated at 200°C.

It is well-known that, as the dehydration of NaY zeolites proceeds, cations (especially divalent ones) show a tendency to occupy positions SI in a hexagonal prism. Our studies do not permit an evaluation of whether any amount of Cu^{2+} cations occupy positions SI in the range of temperatures 25–400°C of our measurements. However, from the work of Gallezot *et al.* (*25*) the conclusion can be drawn that Cu^{2+} migration toward the hexagonal prism becomes considerable at dehydration temperatures of 500–600°C. We interpret the presence of the weak isotropic EPR line with $g = 2.186$ in samples dehydrated at 400°C as due to strong exchange interactions between two Cu^{2+} complexes localized within the same sodalite cell, as postulated by Chao (*18, 38*) and Lunsford (*39*), or lying close to each other inside and outside the cell, as proposed by Conesa and Soria (*14*).

Figure 8 shows the path of migration of Cu^{2+} in the faujasite network as a function of the dehydration temperature, as well as the cation sites successively occupied at given temperatures. We hence draw the conclusion that, for given temperatures of dehydration, well-defined cation sites in the framework achieve a high degree of activity, causing a fixation of the cations. Since, however, ageing in air of previously dehy-

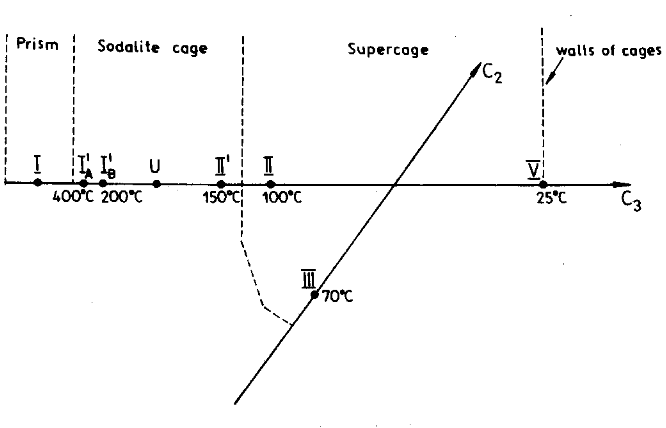

FIG. 8. Scheme showing the migration of Cu^{2+} in the faujasite network depending on dehydration temperature.

drated zeolite samples leads to the vanishing of anisotropic EPR spectra and to the appearance anew of the isotropic spectra, we come to the conclusion that rehydration of the zeolite leads to a deactivation of the sites, a reverse migration of the cations Cu^{2+}, and a reconstruction of the tumbling complex $Cu(OH_2)_6^{2+}$ in the supercage. Thus, Cu^{2+} diffusion occurs in the network in both of the directions shown schematically in Fig. 8; at a given temperature of dehydration, the complex "reaches" a well-defined equilibrium position, determined by the degree of its dehydration and the activity of the lattice site.

7. Conclusions

Depending on the temperature at which Cu^{2+} ion-exchanged faujasite is subjected to when placed under dehydration, copper complexes differing in their symmetry and in degree of dehydration arise. The differences in the EPR parameters observed for the complexes are related with the migration of the copper ions in the faujasite network which go from supercages via sodalite cells to hexagonal prisms. An interpretation of the EPR spectra of Cu^{2+} complexes in faujasite is first proposed on the basis of formulae expressing the spin Hamiltonian parameters in terms of bonding parameters of the LCAO MO approximation for the symmetry D_{2d}, and comprising by these formulae the limiting case of symmetry D_{4h} also. At given dehydration temperatures in the range from 25 to 400°C, well-defined positions available to the cation exhibit a cation-fixing activity. The changes in EPR spectrum accompanying dehydration are reversible, as confirmed by the process of rehydration of the complexes and their migration to supercages when a sample undergoes ageing in air. Hence, the activity of the sites available to cations is related with the degree of dehydration of the faujasite sample.

Acknowledgments

The authors express their appreciation to Professor Jan Stankowski and Dr. Stanisław K. Hoffmann for their valuable suggestions and interest in this work. Thanks are also due to Dr. Wiesław Wasiak for measurements of the copper concentration.

References

1. J. V. Smith, *Adv. Chem. Ser.* **101,** 171 (1971).
2. E. Trif, A. Nicula, and A. Bodi, *Proc. Congr. Ampere, 16th 1970.*
3. I. Ursu and A. Nicula, *Rev. Roum. Phys.* **9,** 343 (1964).
4. T. I. Barry and L. A. Lay, *J. Phys. Chem. Solids* **29,** 1395 (1968).
5. J. W. Jermyn, T. J. Johnson, E. F. Vansant, and J. H. Lunsford, *J. Phys. Chem.* **77,** 2964 (1973).
6. K. A. Windhorst and J. H. Lunsford, *J. Amer. Chem. Soc.* **94,** 1407 (1975).
7. R. F. Howe and J. H. Lunsford, *J. Amer. Chem. Soc.* **97,** 5156 (1975).
8. P. H. Kasai and R. J. Bishop, *J. Phys. Chem.* **77,** 2308 (1973).
9. G. Martini, M. F. Ottaviani, and G. L. Seravalli, *J. Phys. Chem.* **79,** 1716 (1975).
10. W. Mörke, F. Vogt, and H. Bremer, *Z. Anorg. Allg. Chem.* **422,** 273 (1976).
11. E. Trif, L. Cociu, and A. Nicula, *Rev. Roum. Phys.* **18,** 451 (1973).
12. R. G. Herman and B. R. Flentge, *J. Phys. Chem.* **82,** 720 (1978).
13. R. G. Herman, *Inorg. Chem.* **18,** 995 (1979).
14. J. C. Conesa and J. Soria, *J. Chem. Soc., Faraday Trans.* **75,** 406 (1979).
15. J. C. Conesa and J. Soria, *J. Magn. Res.* **33,** 295 (1979).
16. I. R. Leith and H. F. Leach, *Proc. Roy. Soc. London Ser. A* **330,** 247 (1972).
17. H. G. Maksimov and V. F. Anufrenko, *Zh. Strukt. Khim.* **13,** 1020 (1972).
18. Ch. Ch. Chao and J. H. Lunsford, *J. Chem. Phys.* **57,** 2890 (1972).
19. J. C. Conesa and J. Soria, *J. Phys. Chem.* **82,** 1575 (1973).
20. G. Martini and M. F. Ottaviani, *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **33,** 62 (1978).
21. W. Dewilde and J. H. Lunsford, *Inorg. Chim. Acta* **34,** L229 (1979).
22. R. G. Herman, *Inorg. Chim. Acta* **34,** 119 (1979).
23. E. F. Vansant and J. H. Lunsford, *J. Phys. Chem.* **76,** 2860 (1972).

24. K. Ogawa, *J. Phys. Chem.* **82,** 1655 (1978).
25. P. Gallezot, Y. Ben Taarit, and B. Imelik, *J. Catal.* **26,** 295 (1972).
26. I. E. Maxwell and J. J. deBoer, *J. Phys. Chem.* **79,** 1874 (1975).
27. D. H. Olson, G. T. Kokotailo, and J. F. Charnell, *Nature (London)* **215,** 270 (1967).
28. E. Dempsey and D. H. Olson, *J. Phys. Chem.* **74,** 305 (1970).
29. D. H. Olson, *J. Phys. Chem.* **72,** 4366 (1968).
30. J. Stankowski, A. Więckowski, and Saber Hedewy, *J. Magn. Res.* **15,** 498 (1974).
31. J. A. Rubio, J. Soria, and F. H. Cano, *J. Colloid Interface Sci.* **73,** 312 (1980).
32. Z. Dudzik, R. Fiedorow, W. Przystajko, and A. Więckowski, *Bull. Acad. Pol. Sci., Sér. Sci. Chim.* **23,** 955 (1975).
33. M. Sharnoff, *J. Chem. Phys.* **42,** 3383 (1965).
34. H. Yokoi and A. W. Addison, *Inorg. Chem.* **16,** 1341 (1977).
35. V. F. Anufrenko, M. G. Maksimov, V. G. Shinkarenko, A. A. Davydov, Yu. A. Lokhov, N. N. Bobrov, and K. G. Ione, *in* "Application of Zeolites in Catalysis" (G. K. Boreskov and Kh. M. Minachev, Eds.), pp. 109–152, Akad. Kiadó, Budapest (1979).
36. E. Bullugiu, G. Dascola, D. C. Giori, and A. Vera, *J. Chem. Phys.* **54,** 2191 (1971).
37. S. K. Hoffmann and J. Goslar, *J. Solid State Chem.* **44,** 343 (1982).
38. Ch. Ch. Chao, *J. Magn. Reson.* **10,** 1 (1973).
39. J. H. Lunsford, "Proceedings, 2nd International Symposium on Magnetic Resonance in Colloid and Interface Science, Menton 1979," p. 67. Reidel, Dordrecht (1980).
40. T. Ichikawa and L. Kevan, *J. Amer. Chem. Soc.* **105,** 402 (1983).
41. M. Narayana and L. Kevan, *J. Chem. Phys.* **78**(II), 3573 (1983).
42. I. V. Ovchinnikov and V. N. Konstantinov, *J. Magn. Res.* **32,** 179 (1978).