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Crystal Field Effects in Ion-Exchanged Faujasites

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Paramagnetic spin resonance spectroscopy has been applied to the study of small amounts of Cu^{2+} in synthetic faujasites containing K^+ through Mg^{2+} as the major compensating cation. Dehydration results in spectral changes corresponding to a transition from distorted octahedral to square-planar symmetry for the Cu^{2+} ion. As the cation changes from K^+ to Mg^{2+}, its increasing polarizing power, e/r, results in a shift of electron charge distribution to these ions, with an increased energy of the $d_{x^2-y^2}$ levels of the copper.

INTRODUCTION

The catalytic properties of faujasite-type zeolites are greatly affected by the nature of the cations occupying the supercage positions (*1, 2*). The preceding paper has demonstrated that the ability of these cations to form radical cations from aromatic molecules with low ionization energies varies exponentially with the electron affinity of the cation (*3*). Furthermore, a synergistic effect on Cu^{2+} ions in the presence of other cations was noted.

Nicula *et al.* (*4*) have shown that Cu^{2+} is an ideally suited component for the paramagnetic spin resonance study of crystalline environments in the supercage. Small concentrations of Cu^{2+} display a characteristic hyperfine spectrum which is consistent with the expected crystallographic coordination in the faujasite. The hyperfine splitting constants are sensitive to hydration of the Cu^{2+} ion and to the strength of the crystal field acting on the ion or, alternatively, to the ligand bonding involved.

A series of 2% Cu in various ion-exchanged faujasites is a favorable subject for the study of any crystal field variations arising from different neighboring cations around the Cu^{2+}.

EXPERIMENTAL

The starting material was a sample of synthetic sodium faujasite. Chemical and thermogravimetric analyses showed the composition to be $Na_{57}(AlO_2)_{57}(SiO_2)_{135} \cdot 264\ H_2O$.

Conventional ion-exchange techniques were used under conditions yielding maximum exchange. A series of faujasites containing K, Na, Li, Ba, Ca, and Mg were prepared in this manner. These samples were further ion-exchanged with copper nitrate solution to give 2% Cu^{2+} by weight in each sample. The exact copper content was determined chemically and by magnetic susceptibility measurements, using an apparatus described elsewhere (*5*).

The paramagnetic resonance spectrometer was a Strand Labs Inc. Model 600 EMR spectrometer modified with a Varian Associates V201B Klystron and V-4531 Cavity, a 100-kc Field Modulation and Control Unit, and a Varian Model V-4012A 12-inch electromagnet. The instrument operated in the X-band at 9400 Mc/sec, measured with a Hewlett Packard Co. Model X530A Frequency Meter. The magnetic field was measured and recorded using a Bell Inc. "240" Incremental Gaussmeter. Exact values of g were determined by scanning the sample together with an internal standard of DPPH. The low-range scale of the recording gaussmeter was calibrated from the hyperfine splittings of $MnSO_4$ solution. The g values and hyperfine splitting constants so obtained were of sufficient accuracy for the purposes discussed below.

RESULTS AND DISCUSSION

Figure 1 shows a typical spectrum of the Cu^{2+} ion for the hydrated 2% Cu-Mg faujasite. Figure 2 is the same sample after dehydration at 400°C. These spectra are similar to those of Nicula *et al.*, who discussed thoroughly the dehydration of Cu-Na Linde Y structures. These authors summarized the theoretical background developed in detail by others (*6–10*).

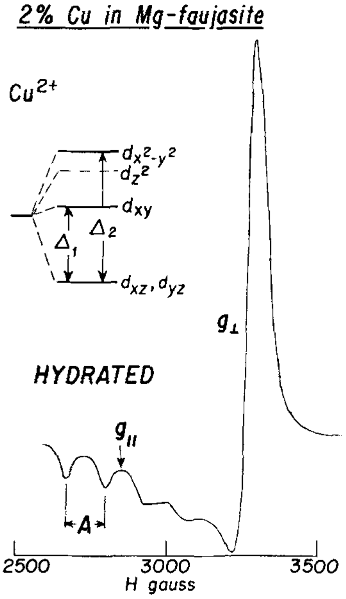

FIG. 1. Paramagnetic resonance spectrum of the hydrated Cu^{2+} ion in Mg faujasite.

It has been assumed that the Cu^{2+} ions occupy only the supercage positions close to the puckered six-membered oxygen rings. This assumption was also made by Nicula but is questioned by Rabo *et al.* on the basis of incomplete and unpublished data (*11*). In this position the Cu^{2+} ion is considered to have perturbed square-planar or tetragonally distorted octahedral coordination with the oxygen ions. Theoretically derived spectra based on this structure agree very well with experiment (*4*) and therefore give some basis for further interpretation.

Nicula *et al.* (*4*) used detailed theoretical expressions for the analysis of their results. This enabled them to deduce parameters such as the degree of in-plane σ-bonding, the in-plane π-bonding and the out-of-plane π-bonding, as well as the energy level separations. It is doubtful whether the accuracy of the data presented by these authors justifies this elaborate treatment. It is believed that the less sophisticated theory of Owen (*6*) is more pertinent. In this case

$$\begin{aligned} g_{\parallel} &= 2[1 - \alpha^2(4\lambda_0/\Delta_1)] \\ g_\perp &= 2[1 - \beta^2(\lambda_0/\Delta_2)] \\ A &= [(g_{\parallel} - 2) + \tfrac{3}{7}(g_\perp - 2) - \tfrac{4}{7} - K]P \\ B &= [(g_\perp - 2) - \tfrac{3}{14}(g_{\parallel} - 2) + \tfrac{2}{7} - K]P \end{aligned} \tag{1}$$

where $g_{\parallel}$, $g_\perp$, A, and B are the measured parameters; Δ_1, and Δ_2, the level splittings shown in Fig. 1; α^2, β^2, and K, measures of covalency associated with the bonding; and λ_0 and P, the usual spin–orbit coupling constant (-848 cm^{-1}) and overlap parameter (0.036 cm^{-1}).

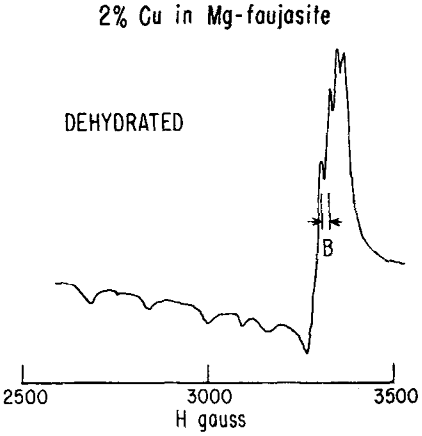

FIG. 2. Paramagnetic resonance spectrum of the dehydrated Cu^{2+} ion in Mg faujasite.

The equations allow α^2, β^2, and K to be evaluated when Δ_1 and Δ_2 are assigned assumed values. Alternately, complete ionic bonding may be assumed so that $\alpha^2 = \beta^2 = 1$ and

$$\begin{aligned} g_{\parallel} - 2 &= -(8\lambda_0/\Delta_1) \\ g_\perp - 2 &= (2\lambda_0/\Delta_2) \end{aligned} \tag{2}$$

giving Δ_1 and Δ_2 as the deduced parameters. It is assumed for the comparative purposes discussed below that this latter treatment is sufficient. This is then simply the crystal field approach with no covalency involved. The crystal field acting on the d electrons of the Cu^{2+} ion originates from the surrounding oxygen ions, themselves fully ionized.

Figure 3 shows the measured $g_{\parallel}$ and $g_{\perp}$ splittings and their variation both with dehydration and change of neighboring cation. Figure 4 gives the crystal field energy levels calculated from these values.

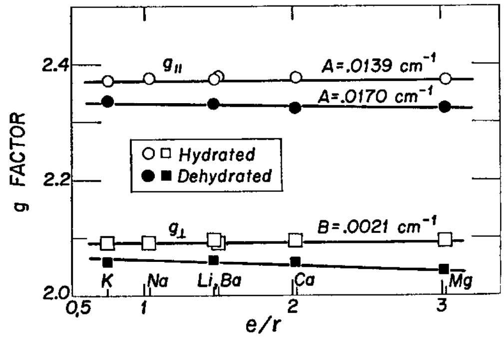

FIG. 3. Dependence of $g_{\parallel}$ and $g_{\perp}$ on e/r of the majority cations.

The situation for the hydrated case is demonstrated in Fig. 5. Here the coordination is not square-planar, as discussed above, but rather tetragonally distorted octahedral. The levels for such a scheme are shown in Fig. 5. The highest levels are the $d_{x^2-y^2}$ and d_{z^2} and these are the ones represented by the dotted lines in Fig. 4. Equations (2) still apply but Δ_1 and Δ_2 now refer to the splittings of the $d_{x^2-y^2}$ and d_{z^2} levels, respectively. These levels are very close together, as expected, and do not vary with changing cations. The water molecules tend to stabilize or shield the environment of the copper ions, thus preventing any purturbations from the neighboring cations.

The dehydrated cation, however, is best described by the square-planar model. The energy level arrangement is shown in Fig. 5 with the $d_{x^2-y^2}$ and d_{xy} levels the highest. The dehydration results in a large increase of the $d_{x^2-y^2}$ splitting, which again is consistent with the predicted behavior of square planar versus octahedral coordination (an increase >1.3 is expected). The d_{xy} increases only slightly with increasing values of e/r, whereas $d_{x^2-y^2}$ increases by about 30% as the cation changes from K^+ to Mg^{2+}. This indicates that the $d_{x^2-y^2}$ orbitals, situated almost in the plane of the six-membered oxygen ring, react strongly to the change of environment, but the d_{xy} orbitals show little effect.

What then is responsible for the increased splitting of the $d_{x^2-y^2}$ levels? Crystal field theory predicts that such an increase would occur if either the Cu^{2+} ion becomes more positive or else the center of electron charge distribution in the ligand moves closer to the oxygen ion. This corresponds physically to a movement of charge distribution away from the oxygen–copper bond and results

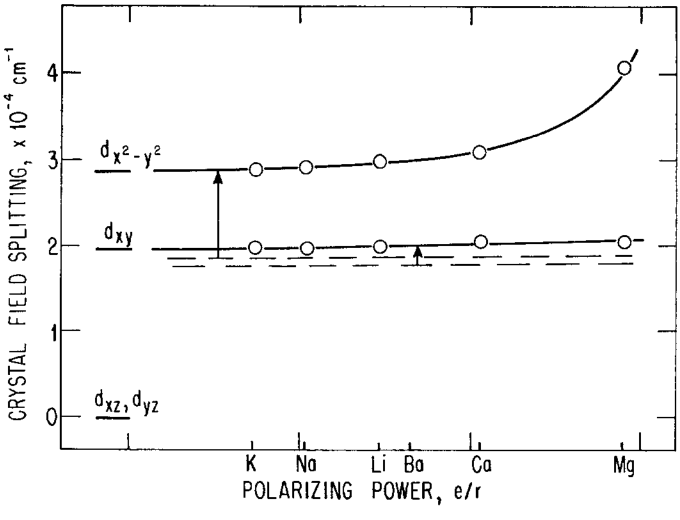

FIG. 4. Variation of crystal field splitting parameter with e/r. The arrows show the effect of dehydration.

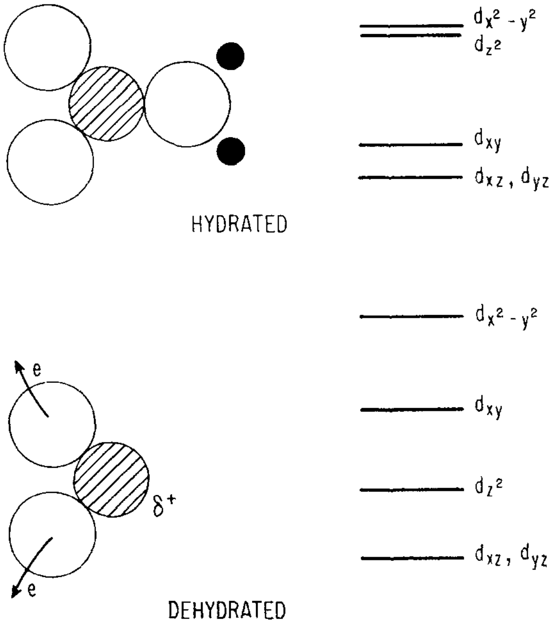

Fig. 5. Crystal field splitting of the hydrated and dehydrated Cu^{2+} levels.

from an attraction of charge by the more strongly polarizing Mg^{2+} ion. The higher field of the Mg^{2+} ion acts not directly but through the intermediate oxygen atoms. This mechanism requires mobility in the charges present to compensate the aluminum ions, but there is no reason to consider them rigidly fixed.

Conclusions

The nature of the cation has a measurable effect on the splitting of the Cu^{2+} levels. The explanation given above is based on the crystal field theory and is perhaps the simplest approach possible. The conclusions from this interpretation are that the electron cloud of the O—Cu bond is pulled away from the Cu^{2+} by the attraction of the cation on the electron distribution in the crystal. These conclusions fit into the model of acid sites in zeolites developed in the following paper (*12*). More elaborate interpretations are perhaps possible but are not necessary or justified.

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