

## NOTES

On Electron Spin Resonance Spectra of  $Mn^{2+}$  Ions for Various Cation-Exchanged Synthetic Zeolites

The parameters of five types of  $Mn^{2+}$  spectra obtained for various cation-exchanged zeolites by the ESR  $Q$ -band technique have been tabulated in preceding papers (1,2). Each type corresponds to specific symmetry of the electric field around the  $Mn^{2+}$  ion. Further study of water adsorption on zeolites predehydrated at 450°C (3), and a more detailed investigation of initial dehydration stages (pumping at room temperature and at 50°C) revealed another spectrum of  $Mn^{2+}$  overlooked by us before. The parameters of this spectrum (designated as 1') differed from those for spectrum 4 (that corresponds to  $Mn^{2+}$  localization at site  $S_1$ ) only in the  $D$  parameter. Therefore it appears that the dehydration stages observed earlier displayed not spectrum 4, as believed before (1,2), but spectrum 1'. More accurate estimation of the  $D$  parameter showed a value of  $155 \pm 15$  Oe for spectrum 4, and 100 Oe or less for spectrum 1'. The latter coincided with that of  $Mn^{2+}$  in a polycrystalline solid with  $D < 100$  Oe (4). In the  $X$ -band the spectrum consisted of monotonically broadening hfs components and of forbidden transition lines with  $\Delta m_i \neq 0$ . In the  $Q$ -band the hfs components were of the same width and the forbidden transition lines were virtually absent.

Spectrum 1' appeared as single in zeolites ZnY-81, LaY-72, and YY-70 upon adsorption of 10-14 water molecules/cavity. For Ca and Cd zeolites it appeared

together with spectrum 3 upon adsorption of 4 molecules only.

On dehydration of cation-exchanged zeolites spectrum 1' appeared at early stages of dehydration. For CdY this spectrum was recorded together with spectrum 3 up to 100°C dehydration. With cations more hydrophilic than  $Mn^{2+}$  spectrum 1' was recorded up to higher temperatures: 150°C for MgY and ZnY, 200°C for LaY, and 400°C for YY. At higher dehydration temperatures spectrum 1' was replaced by spectrum 4 for all specimens studied.

Comparing the conditions for 1' with the results obtained earlier (5) on water adsorption by the sodalite, we suggested that this spectrum was due to  $Mn^{2+}$  localized in the water-filled sodalite cage. Indeed, the spectra of  $Mn^{2+}$  ions in the sodalite have shown complete identity of their parameters with those of spectrum 1'. The sodalite used has been described earlier (5,8). Such a localization of  $Mn^{2+}$  was suggested also in (6) for ion exchange in various cation-exchanged zeolites Y. The whole amount of water in a sodalite cage can be detected by X-ray analysis (7). This means that the mobility of water molecules in sodalite cages is limited and this might provide an explanation to the low  $D$  value and the relevant low widths of certain hfs components in spectrum 1'.

According to the above, Table 2 in Ref. (2) must be corrected as shown in Table 1.

Thus the dehydration process seems to occur as follows. Pumping at room temper-

TABLE 1<sup>a</sup>  
TYPES OF SPECTRA

Cationic forms	Temp (°C)										
	Original	Pump, at room temp	50	100	150	200	250	300	350	400	450
<b>Yttrium</b>											
YY-70	1	1'	1'	1'3	1'3	1'	1'	1'	1'	1'	4
YY-98	1	1'	1'	1'3	1'3	1'	1'	1'	1'	1'	1'
<b>Lanthanum</b>											
LaY-72	1	1'	1'	1'3	1'3	1'3	4	4	4	4	4
LaY-93	1'	1'	1'	1'	1'	1'	1'	1'	1'	1'	1'
<b>Zinc</b>											
ZnY-81	1	1'	1'	1'	1'	1'	4	4	4	4	4
<b>Magnesium</b>											
MgY-60	1	1'	1'	1'	1'	—	4	4	4	4	4
MgY-81	1'	1'	1'	1'	1'	4	4	4	4	4	4
<b>Cadmium</b>											
CdY-43	1	1'3	1'3	1'3	1'3	34	34	4	4	4	4
CdY-83	1	—	—	3	34	34	34	34	345	345	345
<b>Calcium</b>											
CaY-35	1	1'	3	3	3	34	34	4	4	4	4
CaY-65	1	1'3	1'3	3	3	3	34	345	345	345	45

<sup>a</sup> Corrected Table 2 in Ref. (2).

ature results in removal of molecular water from supercavities in all cation-exchanged forms. The remaining water would stay in the sodalite cages, its content being dependent on the cation hydrophilicity. In zeolites with trivalent cations water can remain in sodalite cages up to 400°C.

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