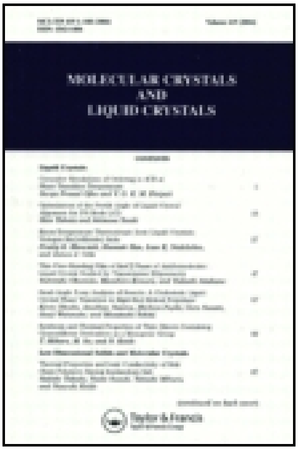

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Optical and ESR Studies of Na Clusters in Zeolite FAU

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Na clusters are generated in zeolite FAU with Si-to-Al ratios of 2.8 (Y-type) and 1.25 (X-type). When the density of adsorbed Na atoms increases, the ESR spectrum with hyperfine structures becomes narrow into a single line. In the IR absorption spectrum, no Drude-like absorption is observed at any adsorption densities of Na atoms. The ESR narrowing is explained by the mean field theory of the exchange narrowing given by Anderson and Weiss, by using the experimentally observed antiferromagnetic exchange coupling energy between magnetic moments of clusters.

Keywords: cluster; zeolite; exchange narrowing

INTRODUCTION

Alkali metal clusters can be generated in the cage of zeolites by the intercalation of alkali metal. Novel properties have been found in optical spectrum, magnetic properties and electron spin resonance (ESR) spectrum, depending on the kind of zeolite, the kind of alkali metal and the loading density[1,2]. Zeolite FAU has β-cage with an inside diameter of about 7 Å. The β-cages are arrayed in a diamond structure, as shown in Fig. 1. The supercage of FAU has the inside diameter of about 13 Å, and is surrounded by four β-cages. In FAU with the higher Si-to-Al ratio, so called Y-type, Na_4^{3+} clusters are known to be generated in the β-cage by the exposure of Y to the Na vapor[3]. Harrison *et al.* [4] observed the narrowing of ESR spectrum in the highly Na-loaded Y-type FAU with the Si-to-Al ratio of 2. They have assigned the origin to the motional narrowing mechanism, and implicitly assumed a metallic state. However, there is no direct evidence of metallic state. The ^{23}Na-NMR analysis suggests that the Na clusters in Y-type FAU do not show the usual Korringa law at lower temperatures, indicating that the metallic state is quite questionable[5]. Ursenbach *et al.* investigated the structure of Na clusters in FAU by the *ab initio* calculation[6]. Their results suggest that the electron transfer energy between the adjacent β-cage clusters is too small to be metallic. In a general sense, the clusters should be in a Mott insulator.

In the present paper, we made Na clusters in X-type FAU with the Si-to-Al ratio of 1.25 as well as Y-type one with the Si-to-Al ratio of 2.8. We measured optical and magnetic properties as well as ESR spectrum. It is concluded that the Na clusters in FAUs are in Mott insulator and the narrowing mechanism of ESR spectrum is assigned to exchange type.

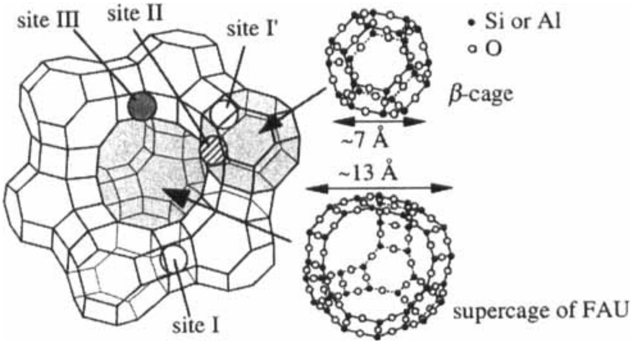

FIGURE 1 The schematic illustration of zeolite FAU and typical sites of Na cations.

ZEOLITE FAU

The chemical composition of zeolite FAU is given as $M_{m/r}Al_mSi_{192-m}O_{384}$ ($m \leq 96$). M is the r-valent exchangeable cation. As shown in Fig. 1, FAU framework is consisted of $Al_mSi_{192-m}O_{384}$, where the closed circles show Si or Al atoms and the open circles show O atoms. We call FAUs with the Si-to-Al ratios of less than 1.5 and larger than 1.5 by X- and Y-types, respectively. As shown in Fig. 1, Na cations are distributed at the sites I, I', II and III. The site I is at the center of double 6-ring prism. The site I' is at the center of 6-ring at the side of the double 6-ring prism. The site II is at the center of the single 6-ring. The site III is at the side of 4-ring in the supercage. Na cations are mainly distributed at the sites I and II in Y-type FAU, and at the sites I', II and partly III in X-type[7].

EXPERIMENTAL PROCEDURE

We used Na-type FAUs with Si-to-Al ratios of 1.25 and 2.8, and they are denoted by Na-FAU(1.25) and Na-FAU(2.8), respectively. The crystal size was about 1~2 μm. Distilled Na was adsorbed into fully dehydrated Na-FAU(1.25) and Na-FAU(2.8) in a vapor phase. We measured an optical diffuse reflection spectrum, an X-band ESR spectrum by using Bruker EPR EMX and a magnetic susceptibility by using Quantum Design MPMS-XL (SQUID magnetometer). The absorption spectra were obtained from the diffuse reflection spectra by the Kubelka-Munk transformation. The loading density of Na was estimated by the density of magnetic moment for the dilutely loaded samples, because each cluster has the paramagnetic moment with the spin quantum number of 1/2. In highly Na-loaded samples, the optical analysis was used for the estimation of loading density of Na[8].

We prepared samples with different Na-loading densities. The samples named #1a, #1b and #1c are Na-FAU(2.8) with the loading densities of much less than 0.01, ~0.01 and 0.4 ± 0.05 Na atom per β-cage (or supercage), respectively. The samples named #2a and #2b are Na-FAU(1.25) with the loading density of ~0.01 and 3 ± 0.2 Na atoms per β-cage (or supercage), respectively.

RESULTS AND DISCUSSIONS

Figures 2(a) and 2(b) show the ESR spectra of Na-loaded Na-FAU(2.8) and Na-FAU(1.25), respectively, measured at room temperature. The 13-line-hyperfine structure is seen in sample #1a in Fig. 2(a), and assigned to the paramagnetic cluster with the T_d symmetry, Na_4^{3+}, in β-cage. Sample #1b shows the narrowing in part. In sample #1c, the most part of ESR spectrum shows the narrowing into a single line at the center of spectrum. The full spectral width at half maximum is 30 Oe, and g-vale is 2.0009± 0.0002. In Fig. 2(b), the main component of sample #2a consists of 16-line-hyperfine structure, and the spectral shape can be reproduced by assuming Na_5^{4+}. The hyperfine structure has a period of ~27 Oe and the g-value of 2.0020 ± 0.0002. The spectral analysis suggests that a few percent of 10-line-hyperfine structure with a period of 20 Oe is involved in the spectrum. The 10-line-hyperfine structure can be assigned to Na_3^{2+}. The observed smaller period, 20 Oe, indicates the size

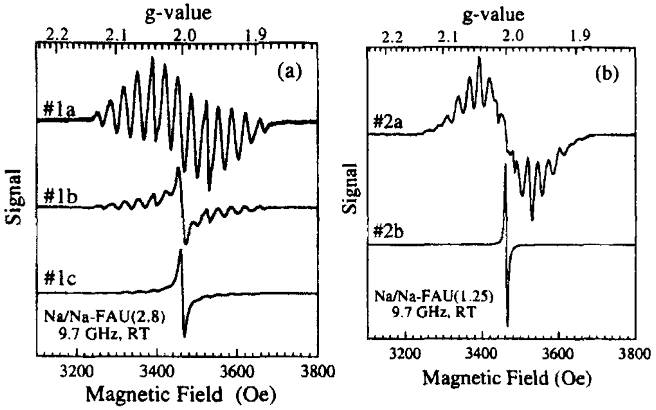

FIGURE 2 (a) ESR spectra of Na-loaded Na-FAU(2.8) at room temperature. The samples #1a, #1b and #1c are those Na-loaded at the densities of less than 0.01, ~0.01 and 0.4 Na atom per β-cage (or supercage), respectively. (b) ESR spectra of Na-loaded Na-FAU(1.25) at room temperature. The Na densities of the samples #2a and #2b are ~0.01 and 3 Na atoms per β-cage (or supercage), respectively.

of electron wave function of Na_3^{2+} is larger than that of Na_5^{4+}. Hence, Na_3^{2+} is located not in β-cage but in supercage. In sample #2b, a narrowing is clearly seen. The full width at half maximum is 8 Oe, and *g*-vale is 2.0011± 0.0002.

Figures 3(a) and 3(b) show the absorption spectra of Na-loaded Na-FAU(2.8) and Na-FAU(1.25), respectively, measured at room temperature. The dotted line in (b) shows the reflection spectrum of highly Na-loaded Na-FAU(1.25); namely sample #2b. In the spectrum of samples #1b and #1c, an absorption band is seen at 2.5 eV. The spectrum of #1b is basically the same as that observed by Kasai[9]. The spectrum of #1c is out of limit of the Kubelka-Munk transformation at the center of the absorption band, but the spectral shape is basically the same as that of #1b, although the ESR spectrum is quite different from each other in Fig. 2(a). The spectrum has no Drude term absorption at the IR region down to 0.3 eV, indicating that the samples #1b and #1c are insulating. The absorption spectrum of sample #2a in Fig. 3(b) has the bands at 2.5 and 1.9 eV, and they are assigned to Na_5^{4+} and Na_3^{2+} clusters, respectively. The Na_5^{4+} cluster in the β-cage has the excitation energy similar to that of Na_4^{3+} cluster observed in sample #1a or #1b. On the other hand, the Na_3^{2+} cluster is expected to be in the supercage from the ESR analysis, and should have the lower

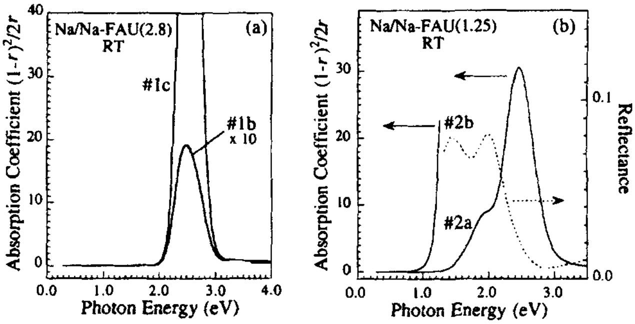

FIGURE 3 (a) Absorption spectra of Na-loaded Na-FAU(2.8); #1b and #1c. (b) Absorption and reflection spectra of Na-loaded Na-FAU(1.25); #2a and #2b.

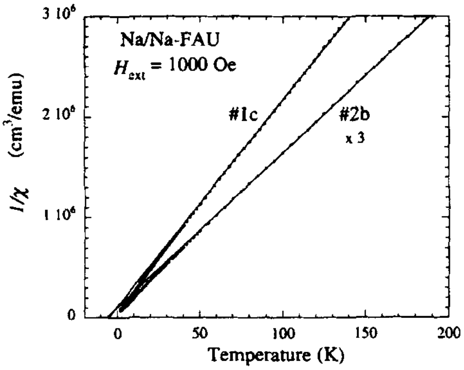

FIGURE 4 Temperature dependence of the reciprocal of magnetic susceptibility χ in highly Na-loaded Na-FAU(2.8); #1c, and Na-FAU(1.25); #2b. The applied magnetic field is 1000 Oe. The temperature independent magnetic susceptibility is subtracted from the observed value.

excitation energy, because of the larger size of the cluster. In highly Na-loaded sample #2b as well as dilutely Na-loaded sample #2a, the Drude-like absorption is absent in the lower energy region, indicating that both of them are insulating. The reflection spectrum may be due to the clusters generated in the supercage, because the energy is lower than that in the β-cage.

Figure 4 shows the temperature dependence of the reciprocal of magnetic susceptibility in highly Na-loaded samples #1c and #2b. Figure 4 shows a Curie-Weiss law with the negative Weiss temperature $T_w = -4 \pm 1$ in sample #1c and –6 ± 1 K in sample #2b. The effective magnetic moment per β-cage (or supercage) is estimated from the Curie constant at $T > 50$ K to be 0.7 and 1.3 μ_B in samples #1c and #2b, respectively, where μ_B is the Bohr magneton. These values indicates that ~20 and ~56 % of β-cages (or supercages) are occupied by the magnetic moment with $s = 1/2$ in samples #1c and #2b, respectively. The negative Weiss temperatures suggest that the magnetic moment of clusters interact with each other antiferromagnetically. According to the theory of exchange narrowing by Anderson and Weiss[10], the ESR spectral width ΔH_w is roughly given by

$$\Delta H_w = \left[\frac{3}{10}(\Delta H)^2 + (\Delta H_{fs})^2\right] \Big/ H_{ex}, \tag{1}$$

where ΔH is the broadening width by the dipole-dipole interaction, and ΔH_{fs} is the full width of the hyperfine structure. The value of H_{ex} is the exchange filed which corresponds to the exchange coupling energy. The value of H_{ex} can be estimated by using the exchange interaction energy J as

$$H_{ex} \sim \frac{\sqrt{2.8}J\sqrt{s(s+1)}}{g\mu_B} \quad , \tag{2}$$

where s is the spin quantum number, g the g-value. The value of J can be estimated from the Weiss temperature as $3kT_W = 2JZs(s+1)$ by using Weiss molecular field, where Z is the number of the nearest neighbors. If we use following values for the sample #1c, $s = 1/2$, $Z = 4$, $T_W = -4$ K, H_{ex} is estimated to be 21680 Oe. If we assume ΔH_{fs} as 400 Oe, ΔH_w is calculated to be 7 Oe by neglecting ΔH, because ΔH is much smaller than ΔH_{fs}. If we use following values for the sample #2b, $s = 1/2$, $Z = 4$, $T_W = -6$ K, H_{ex} is estimated to be 32520 Oe, and finally ΔH_w is calculated to be 5 Oe. The accuracy of this estimation is known to be not so good for small negative value of T_W, but the calculated widths 7 and 5 Oe in samples #1c and #2b roughly coincide with the respective experimental values 30 and 8 Oe. In case that the occupancy rate of paramagnetic clusters is much less than 100 %, such as ~20 % in sample #1c, the exchange interaction network may be incomplete. Hence, actual spectral width of ESR can be broader than that given by the above calculation, because an exchange narrowing may be incomplete.

SUMMARY

Na clusters were generated in Na-FAU(2.8) and Na-FAU(1.25). The narrowing of ESR spectrum is observed in highly Na-loaded samples, although no Drude-like absorption is observed. The negative Weiss temperature is observed in highly Na-loaded samples. According to the mean field theory given by Anderson and Weiss, the ESR narrowing can be well explained by the exchange mechanism.

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