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Arrangement of K Clusters in the K-Doped Zeolite K-LTA

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K clusters incorporated into zeolite K-LTA causes ferromagnetism below 8 K. Distribution of K^+ ions in its α-cages was studied by X-ray powder diffraction. On the basis of space group F23, electron-density distribution was determined by Rietveld analysis followed by iteration of analysis by a maximum-entropy method and whole-pattern fitting. K^+ ions were located in α-cages in such a way that K clusters between adjacent α-cages are not equivalent to each other, which will lead to the ferromagnetism with antiferromagnetic components.

Keywords: zeolite; cluster; X-ray powder diffraction; Rietveld analysis; maximum-entropy method

INTRODUCTION

K clusters incorporated into K-type zeolite K-LTA causes ferromagnetism below 8 K with its magnetic moment depending on the concentration of loaded K^+ ions[1–3]. Such a unique magnetic property is regarded as originating from 4s electrons of K^+ ions because K-doped K-LTA does not contain any magnetic atoms. The electrostatic potential of the 4s electrons distributed within each cluster is directly related to distribution of K^+ ions among α-cages. Therefore, detailed crystal data obtained by X-ray and/or neutron diffraction are indispensable for understanding the mechanism of the ferromagnetism in K-doped K-LTA. Though structural studies of K-doped K-LTA were reported by Tao and Seff[4] and Armstrong *et al.*[5], their samples did not exhibit ferromagnetism. Structural models consistent with a localized electronic structure revealed by an ESR study[6], *etc.* have not been proposed yet.

In this work, we have determined the structure of K-doped K-LTA using its X-ray powder diffraction (XRD) data measured under ultrahigh-vacuum conditions.

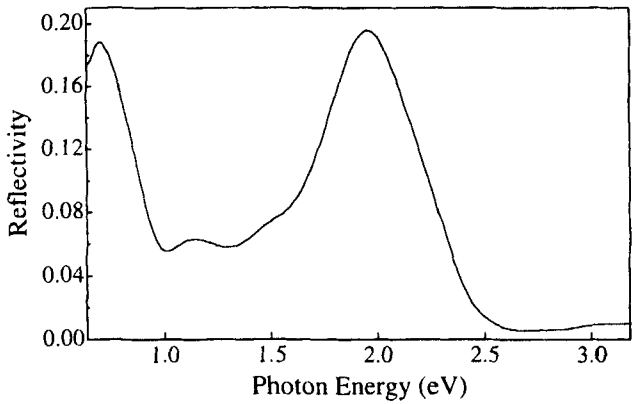

FIGURE 1 Reflection spectrum of $K_{5.2}$@K-LTA at room temperature.

The arrangement of K^+ ions has been visualized with electron-density maps obtained by combining Rietveld analysis and whole-pattern fitting based on a maximum-entropy method (MEM)[7]. The relation between the crystal structure and ferromagnetic interaction will be discussed on the basis of the resulting structural data.

EXPERIMENTAL

K-LTA with a chemical composition of $K_xSi_{98.96}Al_{95.04}O_{384}$ was fully dehydrated at 500 °C and *ca.* 10^{-6} torr for 12 h and loaded with K atoms by vapor transportation of K at 150 °C in an evacuated glass tube. A diffuse reflection spectrum of this sample was measured and transformed into a reflection spectrum (Fig. 1). The amount of adsorbed K atoms per a-cage was estimated at 5.2 by comparing the spectral shape and reflectivity of this spectrum with those reported before [2,8]. This sample will hereafter be abbreviated as $K_{5.2}$@K-LTA.

Magnetic properties of $K_{5.2}$@K-LTA were measured with a SQUID magnetometer. Its XRD data were collected at room temperature on a MAC Science MXP 3TZ powder diffractometer equipped with a pair of long Soller slits to decrease the angler aperture to 1°[9]. The sample was charged into a detachable sample container in a glove box filled with a high-purity He gas. Conditions of an XRD experiment were as follows: CuKα radiation, scan range of $4° < 2\theta < 100°$ with variable-width divergence and scattering slits, pressure inside the container below 2.4×10^{-8} torr. Intensity data were analyzed with a REMEDY software package[7] composed of a Rietveld-refinement program RIETAN-98[10] and an MEM program MEED[11] using our original structure-refinement technique: Rietveld analysis followed by iteration of MEM analysis and whole-pattern fitting.

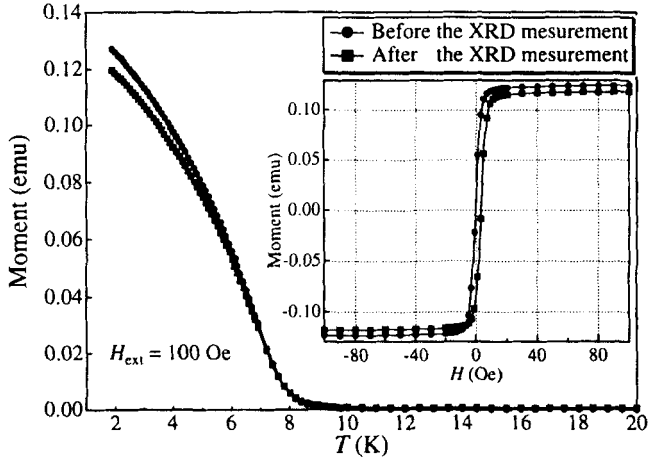

FIGURE 2 Temperature dependence of the magnetic moment, M, in an external magnetic field, H_{ext}, of 100 Oe for $K_{5.2}$@K-LTA. The inset shows the dependence of M on H_{ext} at 2 K.

RESULT AND DISCUSSION

The band at 2.05 eV in Fig. 1 is assigned to surface plasmon-like excitation. Bands at 1.5 eV and 0.7 eV are due to 1p–1d and 1s–1p transitions of molecular orbitals for K clusters[2], respectively. Figure 2 gives the temperature dependence of the magnetic moment, M, yielding a Curie temperature, T_C, of 8 K before and after the XRD experiment. This fact reveals that the sample was not degraded during the XRD measurement. M is also plotted as a function of the external magnetic field, H, in the inset of Fig. 2. These results, which clearly manifest the ferromagnetism in this system, reproduce the previous ones[2,3].

Reflection conditions derived by indexing reflections in the XRD pattern are $h + k$, $h + l$, $k + l = 2n$ for hkl, k, $l = 2n$ for $0kl$, $h + l = 2n$ for hhl and $h = 2n$ for $h00$, revealing the possible space group to be F23 (point-group symmetry T). F23 is noncentro-symmetric with lower symmetry than the space group of LTA: $Fm\bar{3}c$. Additional reflections, particularly those with h, k, $l = 2n+1$, whose profiles were broadened anisotropically were unequivocally observed. Although centrosymmetric space group $Fm\bar{3}m$ adopted by Armstrong *et al.*[5] has the same extinction rule as does space group F23, no ordering of Si and Al is allowed in $Fm\bar{3}m$ because of its higher symmetry. Hence, our structure refinement adopted F23. The fit between observed and calculated patterns was considerably improved by applying partial profile relaxation[7,9,10] to 18 reflections.

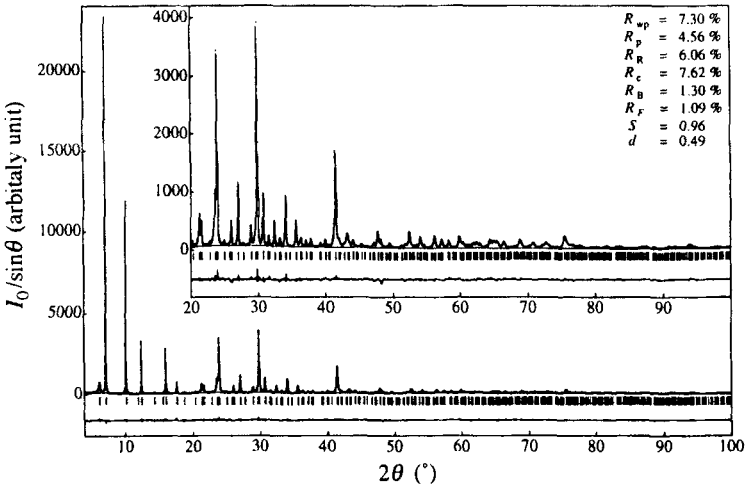

FIGURE 3 Result of MEM-based whole-pattern fitting for $K_{5.2}$@K-LTA. The inset shows magnified patterns from 20° to 100°.

Figure 3 show observed, calculated and difference patterns as well as *R* factors. The refined lattice constant, $a = 24.6685(3)$ Å, was larger than that of dehydrated K-LTA: $a \approx 24.57$ Å. Figure 4 illustrates the crystal structure of K-loaded K-LTA analyzed in the above way.

The amount of doped K^+ ions was estimated at 5.1 per α-cage from occupancies of 13 sites for K. This value is in fair agreement with 5.2 determined by the optical means, giving a chemical composition of $K_{137.6}Si_{98.96}Al_{95.04}O_{384}$. K^+ ions are distributed among 11 sites in a disordered manner. The sizes of K clusters in adjacent α-cages are not equivalent to each other. Such a structural feature forms a striking contrast to the previous model[5] that an α-cage containing an K_{12}^{4+} cluster neighbors on another α-cage with no K cluster. K^+ ions on a six-membered ring proved to split into two pieces, exhibiting positional disorder. The framework of LTA is distorted with slightly different inner-cage volumes between adjacent α-cages, which stems from our structural model adopting F23.

An electron-density map plotted for the (110) plane (Fig. 5) provides us with detailed information about the disordered configuration of K^+ ions. Localized electrons could not be detected in any significant amount in the β-cage around the center of the map. This finding presents evidence for the absence of an K_4^{3+} cluster in the β-cage and consistent with the interpretation of an ESR spectrum for K-loaded K-LTA by Woodall *et al.*[6]. The displacement of K^+ ions toward inner β-cages reduces the total electrostatic potential of this system. Electron densities

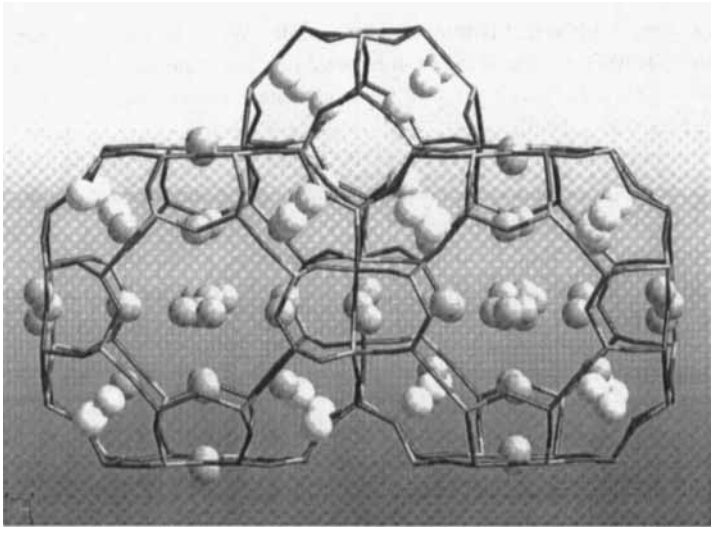

FIGURE 4 Structure of $K_{5.2}$@K-LTA viewed along the [100] direction. Different clusters in the neighboring α-cages and distortion of the framework can be clearly seen.

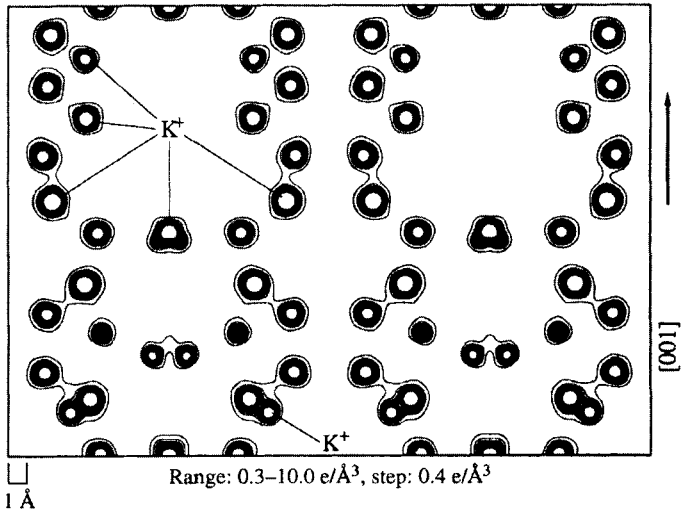

FIGURE 5 Electron-density map of the (110) plane for $K_{5.2}$@K-LTA. K^+ ions are distributed in the neighborhood of 4, 6 and 8-mebered rings.

for K^+ ions clearly revealed their positional disorder. We could also verify charge transfer between K^+ ions in the six-membered ring and O atoms. This finding reflects the fact that major part of K^+ ions contribute to maintaining the electrical neutrality of $K_{5.2}$@K-LTA.

The structural information obtained in the present study suggests that the ferromagnetism of $K_{5.2}$@K-LTA is explained in terms of an antiferromagnetic mechanism, *e.g.*, ferrimagnetism arising from different magnetic moments of K clusters in neighboring α-cages[12]. Calculation of a pseudo-potential for K^+ ions from our structure parameters also afforded quite different potential depths for adjacent inner α-cages.

SUMMARY

The structure of $K_{5.2}$@K-LTA was determined with its XRD data. It belongs to space group F23, which leads to distortion of the LTA framework. The electron-density map resulting from MEM-based whole-pattern fitting shows all K clusters to be distributed among α-cages. The sizes of K clusters in adjacent α-cages differ from each other. No K_4^{3+} clusters were found in the β-cages, in disagreement with the previous structural models[4,5].

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