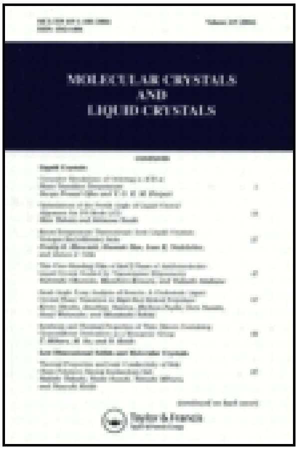

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Magnetic Properties Near the Ferromagnetic-Nonferromagnetic Phase Boundary in Potassium Clusters Incorporated into Zeolite LTA

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Magnetic and optical properties are investigated for K clusters incorporated into zeolite LTA at loading densities of K atoms, n, between 1.0 and 3.2 per cluster. No magnetic ordering is observed at $n < 2$. The spontaneous magnetization due to ferromagnetism is observed suddenly at $n > 2$. It is confirmed that the $1p$-like quantum electronic state of K cluster plays an essential role in the ferromagnetic phase.

Keywords: ferromagnetism; cluster; zeolite

INTRODUCTION

Recently, macroscopic phenomena in physical properties have been observed in three-dimensionally arrayed alkali metal clusters, such as a ferromagnetism[1], an antiferromagnetism[2] and a metal-insulator transition[3]. These clusters are created by the intercalation of guest alkali metals into the periodic space of zeolites. It is expected that the mutual interactions between clusters as well as the new quantum electronic state of cluster cause various macroscopic phenomena.

In zeolite LTA, the α cages with inside diameter of ~11 Å are arrayed in a simple cubic structure, as shown schematically in Fig. 1(a). The lattice constant is 12.3 Å. Closed circles show Si or Al atoms, and open circles show oxygen atoms. The chemical formula of the unloaded K-form LTA with the Si-to-Al ratio of unity is given as $K_{12}Al_{12}Si_{12}O_{48}$. K cations are distributed in the space of the framework. K clusters can be stabilized in α cages together with these K cations by the intercalation of guest K metal. The average number of 4s electrons per α cage, n, can be controlled up to ~ 7 by adjusting the loading density of K atoms without changing the simple cubic arrangement of clusters. The ferromagnetism has been observed most remarkable at the middle loading density, $n \sim 5$[4]. According to the optical study, 4*s* electrons occupy the 1*s*- and 1*p*-like quantum electronic states of K cluster depending on the loading density[5]. Two electrons occupy 1*s* state, and next electrons 1*p* state, as shown in Fig. 1(b). In this case, the loading density at $n = 2$ should be critical for the electronic properties. In the present study, *n* is systematically changed near 2 in detail, in order to clarify the relation between the magnetic properties and the quantum electronic state of K cluster. It is confirmed that the spontaneous magnetization of ferromagnetic state is observed only at $n > 2$, and that the degenerate 1*p*-like state of K cluster plays an essential role in the mechanism of ferromagnetism.

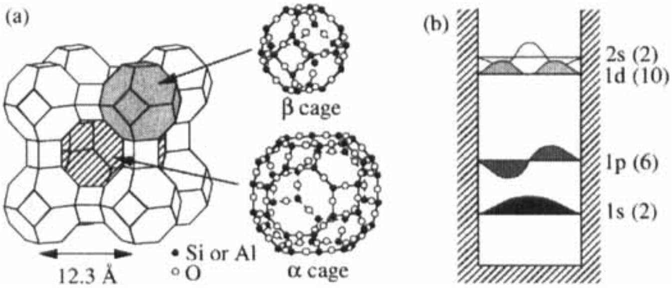

FIGURE 1 (a) Schematic illustration of the framework structure of zeolite LTA, (b) One-electron quantum states in the spherical well potential with the infinite depth. The states 1*s*, 1*p*, 1*d* etc. appear in the increasing order of energy. The degeneracy including the spin is shown in the parenthesis.

EXPERIMENTAL PROCEDURE

Distilled potassium was adsorbed into fully dehydrated K-form LTA through the vapor phase in a quartz glass tube. Samples with various average loading densities of K atoms per α cage *n*, $1.0 \leq n \leq 3.2$, were prepared. The value of *n* is equal to the electron concentration per cluster. The value of *n* is estimated from the optical analysis normalized by the chemical analysis[5]. This analysis has the ambiguity of about 5 %. The optical absorption spectra were obtained from the diffuse reflection spectra. Magnetic measurements were performed by the use of a SQUID system (Quantum Design, MPMS-XL) and the physical property measurement system (Quantum Design, PPMS). The temperatureindependent diamagnetic magnetization from both the quartz glass tube and zeolite framework is subtracted from the observed magnetization, and checked by the temperature dependence of the spin susceptibility of ESR.

EXPERIMENTAL RESULTS

In the infrared absorption spectra down to 0.3 eV, there appears no evidence of the Drude-like absorption tail in all of the samples, indicating that the K clusters are in the insulating state. Therefore, the present samples are assigned to be insulators.

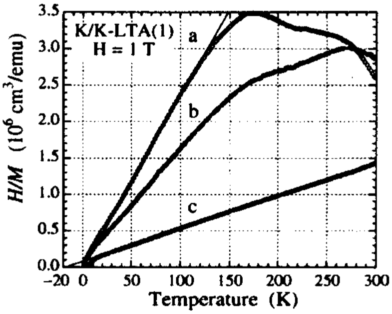

FIGURE 2 Temperature dependence of the reciprocal of magnetic susceptibility in K clusters in LTA. The external magnetic field is 1 T. Curves a, b and c correspond to the samples with n = 1.0, 1.9 and 2.3, respectively.

In Fig. 2, the temperature dependence of the reciprocal of magnetic susceptibility at the external magnetic field of 1 T is shown. The values of n are 1.0, 1.9 and 2.3 for curves a, b and c, respectively. In curves a and b, the Curie law is seen below ~120 K, and no ferromagnetic phase transition occurs down to 1.8 K. The effective magnetic moment is estimated to be 0.62 and 0.76 μ_B per α cage from the Curie constant below 120 K for curves a and b, respectively. A deviation from the Curie law is remarkable above ~120 K. The magnetic susceptibility increases with increasing the temperature above ~170 K and ~270 K in curves a and b, respectively. On the contrary in curve c, the Curie-Weiss law is kept up to 300 K. A ferromagnetic transition is observed at T_C ~ 4 K. The Curie temperature T_C is estimated from the Arrott plot analysis of the magnetization curve. The Weiss temperature T_W is estimated to be −17 K. The observed magnetic properties can be explained by the ferrimagnetism where the antiferromagnetic ordering of non-equivalent magnetic sub-lattice shows a spontaneous magnetization[6]. The effective magnetic moment M_{eff} is estimated to be 1.41 μ_B per α cage from the Curie constant. The values of T_C, T_W and M_{eff} are still smaller than those in the sample with much higher loading densities, for example, the sample at $n = 3.5$[6, 7] shows $T_C = 7.5$ K, $T_W = -35$ K and $M_{eff} = 1.76$ μ_B.

Figure 3 shows the external magnetic field dependence of the magnetization M at 2 K. In the right hand side of scale, the magnetic moment per cluster (or cage) is shown. The values of n are 1.0, 1.9 and 2.3 for curves a, b and c, respectively. In curve c, M quickly increases at low magnetic field due to the spontaneous magnetization, and continues to increase gradually at higher magnetic fields up to 7 T. In curves a and b, the major part of M shows typical paramagnetic behavior, and is gradually saturated at high magnetic field as calculated by the Brillouin function. At very low magnetic fields, a very small mount of spontaneous magnetization is found in the samples $n < 2$. This value decreases by improving the homogeneity of K-loading density. In the present samples $n < 2$, the residual spontaneous magnetization is less than 10 % of paramagnetic magnetization at 100 Oe, for example. Hence, we neglect them in the following discussion. In ferromagnetic samples at $n > 2$, the spontaneous magnetization is several orders of magnitude larger than those in the samples $n < 2$.

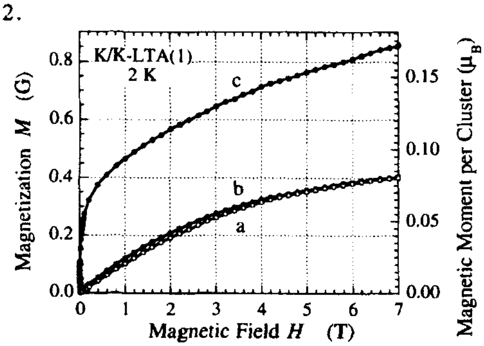

FIGURE 3 Magnetization curves for K clusters in LTA at 2 K. Curves a, b and c correspond to the samples with $n = 1.0$, 1.9 and 2.3, respectively.

In Fig. 4, the magnetization, M, measured at 100 Oe and 2 K is plotted as a function of the average electron concentration per cluster in the full range of K-loading density. The magnetization M dramatically increases about two orders of magnitude above $n \sim 2$. Then, M shows a peak at $n \sim 5$, and rapidly decreases to paramagnetic values.

DISCUSSIONS

The jump in M at $n \sim 2$ in Fig. 4 shows the sudden appearance of spontaneous magnetization of ferromagnetism. There is no doubt that the ferromagnetic phase boundaries at $n \sim 2$ is in close relation to the electron occupation of the $1p$-quantum electronic state of K cluster. By the way, the occupancy rate of the magnetic moment per α cage can be estimated from the effective magnetic moment. If we assume the spin quantum number $s = 1/2$, the effective magnetic moment per cage, 0.62 μ_B, observed in the sample $n = 1.0$ corresponds to the 13 % occupation of α cage with the $s = 1/2$ magnetic moment at low temperature. If all of cages are identical, the sample at $n = 1.0$ should have the cluster with $s = 1/2$ in 100% of α cage. However, the observed value is much smaller than above value. This result suggests that most of spins are considered to be in a singlet state at low temperatures by the pairing of up and down spins. With increasing the temperature above 120 K, some part of singlet states is easily dissociated into unpaired paramagnetic clusters, and the magnetic susceptibility increases as shown in Fig. 2. The singlet state is weakly coupled by the pairing of the adjacent clusters. The pairing may be stabilized by the cation displacement followed by the coupling of the adjacent $1s$-like cluster orbitals, like a hydrogen molecule. At $n = 2$, only the diamagnetism of the fully occupied $1s$ state should be observed according to the model presented here. The observed magnetic susceptibility at $n = 1.9$ is

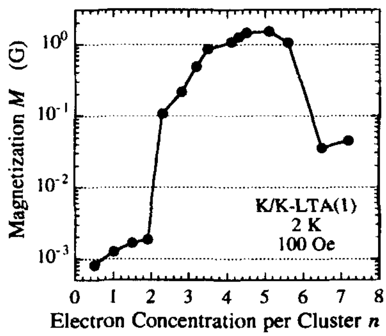

FIGURE 4 Magnetization at 2 K and 100 Oe of K clusters in LTA as a function of electron concentration per cluster n. The vertical axis is shown in the logarithmic scale.

smaller than that at n = 1.0 at room temperature, but finite. A further experiment is needed to analyze the temperature dependence of the magnetic moment at $n < 2$.

With increasing n higher than 2, the number of clusters with 1p-state electrons increases, and these clusters are adjacent to each other. They interact with each other. The increase in the number of these clusters may increase the volume of ferromagnetic regions. Then, they show the spontaneous magnetization and the finite values of Curie and Weiss temperatures, as seen in sample n = 2.3.

It is concluded that the 1p state of K cluster is responsible for the construction of the ferromagnetic phase in K-clusters in K-form LTA. The essential difference between the 1p state and 1s one is in the orbital degeneracy, because the 1p state has the orbital angular momentum. The degeneracy may play an important role in the ferromagnetic phase. Further investigation is still required to clarify the mechanism of ferromagnetism in K cluster in LTA with a careful consideration of the degeneracy of 1p state.

SUMMARY

A drastic increase of the magnetization is observed at the electron concentration per cluster of n = 2 in K clusters incorporated in LTA. It is obvious that the ferromagnetic properties in K clusters in LTA are closely related to the 1p-like quantum electronic state.

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