FERROMAGNETISM OF ALKALI-METAL CLUSTERS INCORPORATED IN THE PERIODIC SPACE OF ZEOLITE LTA

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Magnetic properties are reported for rubidium and potassium clusters arrayed in a simple-cubic structure in zeolite LTA crystal. A ferromagnetism is observed, although no magnetic element is contained there. The result clearly indicates the intercluster interaction. The ferromagnetic properties vary depending on the average number of ns electrons of cluster. Optical properties reveal quantum electronic levels of cluster. The ferromagnetism is interpreted qualitatively in terms of the itinerant electron model based on the quantum levels of cluster. The magnetic properties of various clusters observed in zeolites are discussed from the microscopic point of view.

1. Introduction

The quantum-size effect in metal clusters makes a noticeable difference to their magnetic as well as optical properties. Electronic properties are expected to vary depending on the number of electrons occupying the quantum states of cluster. The electronic state of alkali-metal cluster has been well understood on the basis of a simple model, because an ns electron of alkali-metal atom has a weak interaction with the positive core. In the spherical-well potential model of cluster, quantum electronic states of 1s, 1p, 1d, etc., appear in the increasing order of energy. Although no magnetic element is contained in a cluster, it may have a magnetic moment when an odd number of electrons are confined in the cluster. When the degenerate quantum electronic state, such as 1p state, is partly occupied with electrons, a cluster may have a magnetic moment, because of the Hund coupling.

If these clusters are arrayed with a certain periodicity and have a mutual interaction, a macroscopic electronic property may be significantly different from that of isolated clusters. Zeolite crystals provide a periodic nanoscale space for clusters. An array of clusters can be supported there. Recently, guest materials, such as metals, semiconductors, molecules, and polymers, are incorporated into the internal space of zeolite, and new types of nanoscale materials are fabricated vigorously.

LTA, a type of zeolites, has a simple-cubic structure with a lattice constant of 12.3 Å, as shown in Fig. 1. LTA has the framework consisting of Al\textsubscript{12}Si\textsubscript{12}O\textsubscript{48}, and has the negative charge of $-12e$ for each unit cell. In K-type LTA, for example, 12K\textsuperscript{+} are sitting at certain sites in the space of framework. When guest K atoms are adsorbed onto dehydrated K–LTA, 4s electrons of K atoms will be shared with many cations, but repelled by the framework. Hence, cationic clusters will be generated by the alkali-metal adsorption. According to the optical measurement,\textsuperscript{1} cationic cluster of potassium is generated in the α cage which has the inside diameter of about 11 Å. A ferromagnetism has been observed depending on the number of guest potassium atoms.\textsuperscript{2} The ferromagnetism results from the intercluster interaction. A similar ferromagnetism has been observed in rubidium clusters.\textsuperscript{3} In the sodium clusters, however, magnetic properties indicate a diamagnetism.\textsuperscript{3} In zeolite FAU, paramagnetic clusters have been observed in ESR experiment.\textsuperscript{4} In the present paper, magnetic properties of alkali-metal clusters in zeolite are viewed. The microscopic mechanism of cluster formation and the stable electronic state are discussed.
in terms of the balance of the interaction between electrons, and between electron and cation.

2. Experimental

K and Rb metals were adsorbed through the vapor phase into fully dehydrated K- and Rb-form LTAs, respectively. Hereafter, K-form LTA with the Si/Al ratio of unity is denoted by K-LTA(1), and that of Rb-form by Rb-LTA(1). The maximum number of guest alkali-metal atoms was 7.3 and 5 for K and Rb, respectively. Ac magnetic susceptibility was measured with the Hartshorn inductance bridge. The absorption spectrum was obtained from the diffuse reflection spectrum. Detailed experimental procedures were shown in previous papers.\(^1,2\)

3. Paramagnetic Properties of Clusters in Zeolite FAU

An ESR measurement is very informative to the structural analysis of cluster, because the hyperfine structure gives us a clear information about consistent atoms and also the spin state. This measurement, however, is available in the case where an electron is localized in the cluster. When electrons are itinerant over clusters, we should rely on x-ray or neutron diffraction experiments for the structural analysis.\(^5,6\) These experiments, however, give us the average structural information on the position of cations (there are many available sites in zeolite). Some of them are fully occupied with cations, but others are partly occupied. The alkali-metal cluster involves some \(ns\) electrons. The x-ray diffraction experiment, however, does not give the information about \(ns\) electrons of cluster, because of miner electrons. The neutron scattering normally gives no information about electrons, because neutrons are scattered by nuclei. We can roughly image the structure of cluster from the result of the structural analysis, but we can confirm the structure model by the analysis of electronic properties which is a direct information about \(ns\) electrons of cluster. From this point of view, the analysis from many sides is desirable for the discussion of these materials.

The first observation of alkali-metal cluster in zeolite has been done in Na cluster incorporated into Na–FAU.\(^7,8\) A pink coloration with the peak energy of 2.5 eV and an ESR signal with 13 hyperfine structures were observed. It has been assigned to Na\(^{3+}\) paramagnetic cluster generated in the \(\beta\) cage of FAU. The inside diameter of the \(\beta\) cage is about 6.5 Å. According to the spherical-well potential model with the same diameter, the first excited state, 1p state, is located at the energy 3 eV higher than the 1s ground state. The experimental value of 2.5 eV is well coincide with this energy. A similar cluster, K\(^{3+}\), is known to be generated in K–FAU.\(^4\) The absorption spectrum is quite similar to that of Na\(^{3+}\).\(^1\)

As mentioned above, the \(ns\) electron is attracted by cations but repelled by framework potential. When electrons approach cations, cations move due to the electron–cation interaction. Hence, the wave function of the electron and cation positions of cluster are thought to be mutually adjusted by the quantum-mechanical balance of the attractive and repulsive potentials and the kinetic energy of electron. In FAU, \(\beta\) cages are connected in a diamond structure through the double six-membered ring. An electron in one cluster may move into an empty orbital of cluster in adjacent \(\beta\) cage. The ESR spectrum, however, indicates that the electron of Na\(^{3+}\) cluster is localized in the limit of dilute loading. In the dilute limit, most of cations have no electron, and are located at the position different from that of cations participating the cluster where cations are interacting with the electron. A guest cation will additionally deepen an electronic potential. In other words, the energy level in the electron-occupied cage is different from that in the electron-unoccupied cage. Hence, the electron can be transferred resonantly to the adjacent cage.
With increasing loading density of alkali metal, most of cages are occupied with electron. Guest cations are distributed here and there. An electron can find the equivalent cation configuration in adjacent cage, and be transferred resonantly to other cages successively. This is a metallic state of clusters. Indeed, the ESR measurement of high-density loading samples shows a spectral narrowing due to the motion of electron. In this situation, the electron-electron interaction will change the spin state from paramagnetism of localized electrons to Pauli paramagnetism of metal. The spin density estimated from the ESR signal intensity is considerably weaker than that estimated from the total number of ns electrons. The Curie–Weiss law with a small intercept of $-7$ K has been observed in the ESR signal of K-loaded K–FAU. This is not reminiscent of the antiferromagnetic state but of the metallic state of clusters.

For Cs clusters in FAU, the ESR signal shows a spectral narrowing even at dilute-loading density. This indicates that the electron transfer occurs over many cages at low cluster density. This is different from that observed in Na and K clusters. The difference is qualitatively explained by the model that the electronic potential of each cage is more uniform and shallower than those in Na and K clusters, because of the ionization energy of Cs atom is smaller than those of Na and K atoms. In this condition, an electron moves over many cages as in metal. The temperature dependence of ESR signal shows the Weiss temperature of $-40$ K. This result means that Cs clusters are most metallic.

The paramagnetic character of alkali-metal clusters, however, is not observed in Na-loading Na–LTA(1). Magnetic susceptibility of this system is $-1 \pm 1 \times 10^{-6}$ emu/cm$^3$, independent of the loading density. Most of the Na cluster are diamagnetic. This result strongly indicates that electrons make a singlet pair in each cluster. This result is quite different from that observed in clusters in FAU. Usually, a repulsive interaction between electrons tends to separate electrons into isolated ones. The pairing of electrons can be explained by the strong electron–phonon interaction. The ESR measurement and optical analysis have been reported for Na clusters in zeolite SOD.

### 4. Ferromagnetic Properties of Clusters in Zeolite LTA

When Rb metal is dilutely loaded into Rb–LTA(1), a remarkable absorption band appears at $\sim 1.2$ eV, as shown in Fig. 2. This absorption band is assigned to the $1s-1p$ electronic excitation of cluster generated in the $\alpha$ cage. The excitation energy well coincides with that calculated in the spherical quantum-well potential having the effective inner diameter of the $\alpha$ cage, $\sim 11$ Å. When the Rb loading density is lower than two atoms per $\alpha$ cage, ac magnetic susceptibility is of the order of $10^{-3}$ emu/cm$^3$ at liquid-helium temperature. This value is considerably smaller than that calculated in the isolated paramagnetic clusters, $10^{-4}$ emu/cm$^3$. Therefore, Rb clusters in Rb–LTA are thought to be in the metallic state, similar to Cs clusters in FAU or high-density Na and K clusters in FAU. With increasing Rb loading density higher than two atoms per cage, however, an ac magnetic susceptibility suddenly increases. In saturated sample, ac magnetic susceptibility shows a ferromagnetic value of the order of $10^{-2}$ emu/cm$^3$ at liquid-helium temperature. In Fig. 3, the reciprocal of magnetic susceptibility, $\chi^{-1}$, is shown for the sample whose loading density is higher than two Rb atoms per $\alpha$ cage. In the figure, the loading density increases in the order of samples (a) to (g). In sample (g), the Rb loading density is five atoms per $\alpha$ cage on average, and saturated. A broken line indicates the Curie law.

![Absorption spectrum of dilutely Rb-loaded Rb–LTA(1) at room temperature. A remarkable band is seen around 1.2 eV.](image)
calculated for paramagnetic clusters with spin $\hbar/2$, i.e., the magnetic moment of $1.73\mu_B$ in each $\alpha$ cage. Experimental results show a Curie–Weiss law with the common Curie constant. The localized magnetic moment is estimated to be $0.8\mu_B$ from the Curie constant. The Weiss temperature estimated from the result in Fig. 3 shifts from negative to positive value with increasing loading density.

In Fig. 4, a temperature dependence of magnetization at the external magnetic field of 20 Oe is shown for sample (g) of Fig. 3. The reciprocal of magnetic susceptibility is also shown in the figure. The Curie temperature is roughly estimated to be 2.7 K. The magnetization at 200 Oe is also shown in the figure and is much larger than that at 20 Oe. This result means that the magnetization is not saturated easily for the external magnetic field. This is one of the typical phenomena of a weak ferromagnetism of itinerant electrons. The maximum magnetic moment estimated from magnetization is $0.05\mu_B$ which is much smaller than that estimated from the Curie constant, $0.8\mu_B$. This is one of the typical phenomena of an itinerant electron ferromagnetism. The negative value of Weiss temperature in Fig. 3 does not mean an antiferromagnetism but is reminiscent of a Pauli paramagnetism as discussed above.

A sudden change of magnetic susceptibility at the average density of two Rb atoms per $\alpha$ cage is strongly indicative of a change in the electronic state at the Fermi level. In zeolite LTA, $\alpha$ cages are arrayed in a simple-cubic structure. The intercage electron transfer of a regular lattice forms an energy band. Figure 5 indicates a schematic representation of the energy band calculated in the tight-binding model. Lower and upper bands originate from 1s and 1p quantum states of cluster, respectively. The 1p band splits into two branches due to the $\sigma$ and $\pi$ transfers of electron in 1p orbitals. Two electrons per $\alpha$ cage fill up the 1s band, and next six electrons fill up the 1p band. When an electron density is less than two, the Fermi level is across the 1s band. When an electron density is between two and eight, the Fermi level is across the 1p band. The sudden change of magnetic properties well coincides with the change of the energy band at the Fermi level. In the 1p state, the electronic state is triply degenerate. Therefore, a Hund’s coupling will stabilize a higher spin state of cluster. This may contribute to a ferromagnetic stability.

The electronic potential of each cage may not be uniform due to the difference in the configuration and number of cations. Hence, the energy of cluster orbitals may be different from one to another. If the electron-transfer energy, however, is sufficiently larger than the energy difference of orbitals, electrons
propagate coherently. The electronic configuration of Rb clusters in Rb–LTA(1) may be close to that of alloy where atoms occupy a regular lattice site but have different potentials depending on the kind of atom.

When K is loaded into K–LTA(1), basically similar but somewhat different results have been observed for magnetic and optical properties.$^{1,2}$ In the case of K clusters, however, the maximum loading density of guest K atoms is 7.3 per cage. This value implies that the maximum electron concentration is 7.3 per cluster. This value is larger than that of Rb clusters, ~5. Figure 6 shows the magnetization of K-loaded K–LTA(1) at 1.7 K and 100 Oe as a function of the electron concentration per cluster. Each circle indicates the results of each sample, and they are connected by straight lines. The maximum magnetization is found around the electron concentration of ~5 per cluster. The maximum value of 1.17 G corresponds to the 0.24μB per cluster. This value is much smaller than that of iron, 2.2μB per atom, but comparable with the value of nickel, 0.6μB per atom.

The electron-concentration dependence of the magnetization in Fig. 6 have been well explained by the energy-band model.$^2$ At five electrons per cluster, the density of state at the Fermi level will take the maximum. The Stoner condition of the itinerant electron ferromagnetism satisfies most favorably a ferromagnetism. With increasing intercluster electron-transfer energy, the energy bandwidth increases, but the density of states at the Fermi level decreases. The intercluster transfer energy of K clusters is expected to be smaller than that of Rb clusters, because of the difference in the ionization energy of the atom. Hence, the density of states in K clusters is expected to be higher than that in Rb clusters at the same electron concentration. The Stoner condition for K clusters may be better than that for Rb clusters. The observed ferromagnetism in K clusters is more remarkable than that in Rb clusters. The difference is qualitatively interpreted in terms of the expected difference of the band parameter. In Na clusters, the energy bandwidth is expected to be smaller than those in K and Rb clusters. The diamagnetism, however, has been observed in Na clusters independent of the Na loading density, as mentioned in Sec. 3. In Na clusters in LTA, the electron–phonon coupling may overcome the Hund coupling as well as the electron–electron repulsion interaction.

Very recently, it is pointed out theoretically that the ferromagnetism may not be realized at the just five electrons per cluster in the nearest-neighbor intercluster electron-transfer model.$^{18}$ An antiferromagnetism should appear at this electron concentration. They have found the ferromagnetic phase at the just half-filled condition of the degenerate Hubbard model by the introduction of the next-nearest-neighbor electron transfer.
Properties of ac magnetic susceptibility of K clusters is slightly different from that usually expected in homogeneous materials.\(^1\) A ferromagnetic phase has shown slow dynamics observed usually in re-entrant spin glass. In a nonferromagnetic phase, susceptibility has shown an external magnetic field sensitive behavior, as observed in spin-glass state. Spin-glass phenomenon is not observed in Rb clusters. In K clusters, the inhomogeneity of electronic potential is expected to be larger than that in Rb clusters, because the ionization energy of K atom is larger than that of Rb atom.

5. Summary

Ferromagnetism is found in Rb and K clusters incorporated into Rb– and K–LTA(1), respectively. In Rb clusters, a magnetic susceptibility suddenly increases when the loading density of Rb exceeds two atoms per \(\alpha\) cage. In K clusters, the magnetization has the maximum at the five electrons per cluster. These results are well interpreted on the basis of the magnetic properties of ns electrons which are occupying the energy band originating from the quantum electronic state of cluster. Detailed analysis is still required to clarify the mechanism of ferromagnetism quantitatively.

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