Magnetic and Optical Properties of Rb and Cs Clusters Incorporated into Zeolite A

（ゼオライトＡ中の Rb および Cs クラスターの磁気的光学的性質）

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The zeolite A has the LTA-type framework structure which constructed by α and β cages with the inside diameter of 11 Å and 7 Å, respectively. They are arrayed in a simple cubic structure. Ferromagnetic properties have been found in K clusters generated in cages of zeolite A. This is quite novel magnetic material because the ordered magnetic state is realized by mutual interaction between *s*-electrons confined in the cluster. K cluster in zeolite A is assigned to a Mott insulator due to strong electron Coulomb repulsion in the cluster. Heavier alkali-atoms have smaller ionization energy, which may result in the larger electron-transfer energy t between clusters in adjacent cages, because the electronic potential of the cluster is expected to be shallower. The increase in t is expected to strongly affect the electronic properties. In this study, Rb and Cs clusters were incorporated into zeolite A at several loading-densities from dilute to near saturated ones, 5.5 for Rb case and 3.5 for Cs one. Their optical and magnetic properties are studied from the experimental results of optical spectra, magnetization, ESR and μSR measurements.

I newly find the ferromagnetic properties of Rb clusters in zeolite A at loading densities; the number of guest Rb atoms per unit, $n > 4$. Magnetic susceptibility of all samples obeys the Curie-Weiss law with negative Weiss temperatures indicating antiferromagnetic interaction between the magnetic moments. The optical absorption spectra of Rb clusters show absorption peak at 1.2 eV and 3.0 eV which are respectively assigned to optical transition of clusters formed in α and β cages of the zeolite A. The infrared absorption spectra show clear absorption gap at $n \leq 2.5$ indicating the insulating phase, but at $n > 2.5$ relatively large absorption coefficient exists even at 0.05 eV. This result can be explained by the metallic state realized by the 1*p*-band of the α-cage network. It is quite different from the case of the K clusters in zeolite A, where the insulating phase is confirmed in the full range of n. As the origin of the ferromagnetic properties, a ferrimagnetic model is proposed for Rb clusters in zeolite A, where two magnetic sub-lattices are assumed as the α-cage clusters and the β-cage clusters. In the α-cage network, itinerant ferromagnetic or weakly ferromagnetic state is realized by the narrow band of 1*p*-state and it is coupled antiferromagnetically with the localized magnetic moment in the β cage.

Cs clusters formed in the α cage of zeolite A is confirmed as the observation of a clear peak at ~1.2 eV in the optical absorption spectrum of a dilutely Cs-loaded sample. This absorption can be assigned to the optical transition from 1*s* to 1*p* state of the clusters stabilized in the α cage of A, as seen in K and Rb clusters. Magnetic susceptibility of all samples obeys Curie-Weiss law with negative Weiss temperature indicating antiferromagnetic interaction between magnetic moments. Electronic properties of Cs clusters in zeolite A systematically change with loading n, have a critical point at $n \sim 2.0$ and are also explained by an energy band model rather similar to that of Rb clusters.