Ferromagnetism of Potassium Clusters Incorporated into Zeolite LTA

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Potassium clusters are incorporated into supercages of zeolite LTA crystals, with the supercages arrayed in a simple cubic structure at a number density of 5.3×10^{20} cm^{-3}. About four 4*s* electrons of K atoms are included in each cluster. The ac magnetic susceptibility increases dramatically with decreases in temperature below 8 K, and shows ferromagnetism below about 4 K. The effective magnetic moment per supercage is estimated to be about $0.13\mu_B$ at 1.7 K. Magnetic properties resemble those of a reentrant spin glass.

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An isolated metal cluster of a nonmagnetic element is expected to exhibit a magnetic moment when it has an odd number of electrons [1]. The temperature dependence of the magnetic susceptibility of these clusters is expected to be of the Curie type [2]. If such clusters are arranged periodically and their magnetic moments mutually interact, the resulting materials are expected to be significantly different, with respect to magnetic properties, not only from the isolated clusters but also from the original bulk material.

Very recently, ferromagnetism has been reported in organic molecular crystals with no magnetic element, such as *p*-NPNN [3] and C_{60}TDAE [4]. In these materials, ferromagnetism may be realized by the mutual interaction between molecular magnetic moments or by itinerant electrons.

The framework of zeolites is crystalline, and includes well defined cages specific to the type of zeolite. Cations, for example, Na^+, are distributed in the space of the framework. The chemical formula is given as $M_nAl_nSi_mO_{2(n+m)}$, where M denotes the kind of cation. Alkali metal clusters of various sizes are generated in zeolites by introducing guest alkali metal atoms. Extensive optical and magnetic measurements have been performed on these materials [5–10].

In LTA, which is a type of zeolite, supercages with an inner diameter of 11 Å are arrayed in a simple cubic structure with a number density of 5.3×10^{20} cm^{-3}, and are connected by shared windows with an inner diameter of 5 Å. In the present paper, K clusters are generated in the supercages of K-exchanged LTA, and the electronic interaction between K clusters is realized through the windows between the supercages. Such arrayed clusters are called a *cluster crystal* [11]. It is confirmed by the optical reflection spectrum that each K cluster includes about four 4*s* electrons of guest K atoms. It is revealed from the measurement of the ac magnetic susceptibility that the K cluster crystal shows ferromagnetism below about 4 K.

Original Na-form LTA powder was transformed by ion exchange into K form in the KCl aqueous solution, and washed with distilled water. The Si-to-Al ratio of LTA was unity. The chemical formula is given as $K_{12}Al_{12}Si_{12}O_{48}$. This zeolite is abbreviated K-LTA(1) hereafter. The powder size was 3–10 μm. K-LTA(1) powder was dehydrated throughout in a vacuum, and sealed in a quartz glass tube together with both a distilled K source and a small amount of helium gas for the heat exchange. K was adsorbed in zeolite cages through the vapor phase by elevating the temperature to 160 °C. Before the K loading, K-LTA(1) powder was white and did not exhibit any optical absorption between 0.4 and 6 eV. After the K loading, the powder was colored dark brick red. K^+ ions of zeolite are expected to participate in the cluster with the guest K atoms. The maximum number of loaded K atoms in a supercage may not exceed ten, because about ten atoms fill up the space of a supercage.

The spectrum of the reflection R plus the transmission T of a zeolite powder particle was obtained from that of the diffuse reflection r by the equation $R+T=4r/(1+r)^2$. The ac magnetic susceptibility was measured in a modulation magnetic field of ±78 mOe and 400 Hz. The external dc magnetic field was applied parallel to the modulation field. The magnetic susceptibility of the zeolite powder without guest K atoms is less than 10^{-6} emu/cm^3 over the measured temperature range.

Figure 1 shows the $R+T$ spectrum of K-loaded K-LTA(1) at room temperature. In the present sample, the absorption coefficient above 0.6 eV is so large that the transmitted light of each zeolite powder particle is extremely weak compared with the reflected light. Hence, the obtained spectrum is equivalent to the reflection spectrum R above 0.6 eV. Below 0.6 eV, the transmission cannot be neglected, and the spectrum shows $R+T$.

In Fig. 1, a strong reflection band is seen around 2 eV, and relatively small structures are seen at 0.7 and 1.15 eV. In a free K atom, the main optical transition occurs at 1.6 eV. In a bulk K metal, the reflectivity is very high and energy independent below 3.5 eV. The observed spectrum, however, differs widely from those expected both from free K atom and from bulk K metal. The total oscillator strength is estimated to be 4 per unit cell of LTA from the analysis of the reflection curve in Fig. 1. This value means that about four 4*s* electrons of K atoms

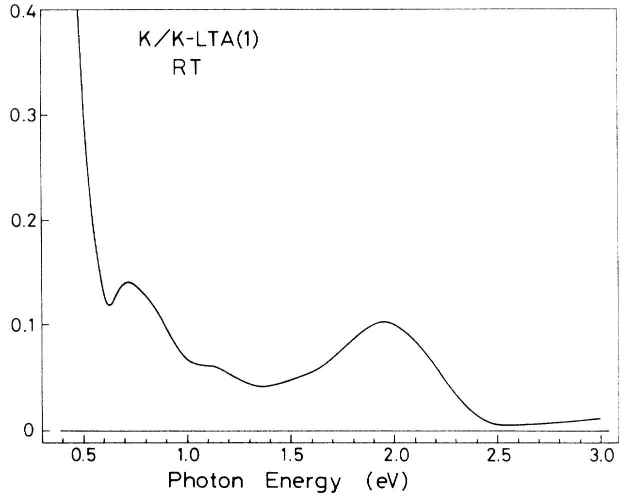

FIG. 1. The sum spectrum of the reflection R and the transmission T of K-loaded K-LTA(1) crystal at room temperature.

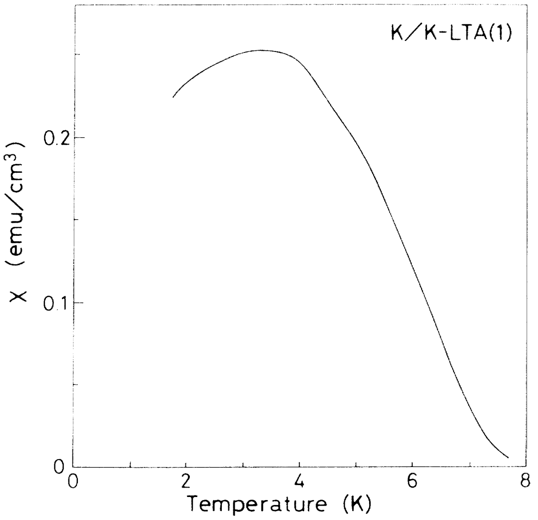

FIG. 2. Temperature dependence of the ac magnetic susceptibility χ in K-loaded K-LTA(1) powder.

are introduced to each unit cell by the K loading. The framework of LTA includes small cages called sodalite cages. In the case of Na-LTA(1), the optical transition of an electron localized in a sodalite cage has been observed at 3 eV [10], but a corresponding band cannot be found in Fig. 1. Therefore, it is confirmed that all four of the electrons are distributed in the supercage in the present sample.

It is expected that the attractive potential for electrons is realized by host and guest K^+ ions distributed in the supercage. The effective diameter of a free K atom is about 5 Å. This size is so large that it is impossible for there to be four independent K atoms in a supercage. The 4s orbits of K atoms overlap with each other. Therefore, four electrons and some K^+ are expected to be stabilized in each supercage as a K cluster. As stated later, the existence of K clusters is confirmed by the reflection spectrum in Fig. 1. The electron wave function of a K cluster is expected to be partly extended to adjacent supercages through the window.

Reflection structures in Fig. 1 are assigned as follows: The reflection band at 2 eV exhibits an oscillator strength of 3. This value is much larger than unity. Hence, the optical response is caused by the collective motion of more than three electrons. Such a collective motion is referred to as a surface plasmonlike oscillation in an approximate sense [12]. Hence, the reflection band at 2 eV is assigned to the surface plasmonlike state of a K cluster. A similar band has been observed in Na clusters incorporated into Na-LTA(1) [10]. Also, in a free K cluster, a surface plasmonlike absorption band has been observed at 2 eV [13].

When the effective potential for an electron in a supercage is assumed to have a spherical shape with a diameter of 11 Å, the transition energy between 1s and 1p quantum electronic states is calculated to be 1.3 eV. The energies of the small reflection structures in Fig. 1, 0.7 and 1.15 eV, coincide well with this value. Hence, the reflection structures are assigned to the individual excitation of electrons in a K cluster. Similar bands have been observed in Na clusters incorporated into Na-LTA(1) [10].

Figure 2 shows the ac magnetic susceptibility χ of K-loaded K-LTA(1) powder as a function of the temperature. With decreasing temperature, χ increases dramatically, shows a peak value of 0.25 emu/cm^3 around 3.3 K, and then, decreases gradually. At this level of susceptibility, the demagnetizing field is so significant that the susceptibility is saturated. Generally, the saturation value depends on the shape of the sample. The shape of the present zeolite powder is cubic in most cases, and the maximum value is close to that of the spherical sample, $3/4\pi$ emu/cm^3. Therefore, the compensated susceptibility is much larger than the value given in the figure, especially at the peak. The drastic temperature dependence and the absolute value of χ indicate a ferromagnetism below about 4 K.

The curve in Fig. 2 resembles that in the spin-glass state of a spherically shaped *Au*Fe alloy for the dense Fe region (Fe at.% > 12%) [14]. In Au-22-at.%-Fe alloy [14], for example, the ac magnetic susceptibility increases remarkably with decreasing temperature, and shows ferromagnetism below 230 K. The magnetic susceptibility reaches the maximum value of 0.223 emu/cm^3 at 220 K, and gradually decreases with decreasing temperature. At much lower temperatures, the magnetic susceptibility decreases remarkably, for example, below 30 K for Au-19-at.%-Fe alloy [15]. This phenomenon is referred to as reentrant spin-glass behavior. At low temperatures, the increase in the average hyperfine field in the Mössbauer

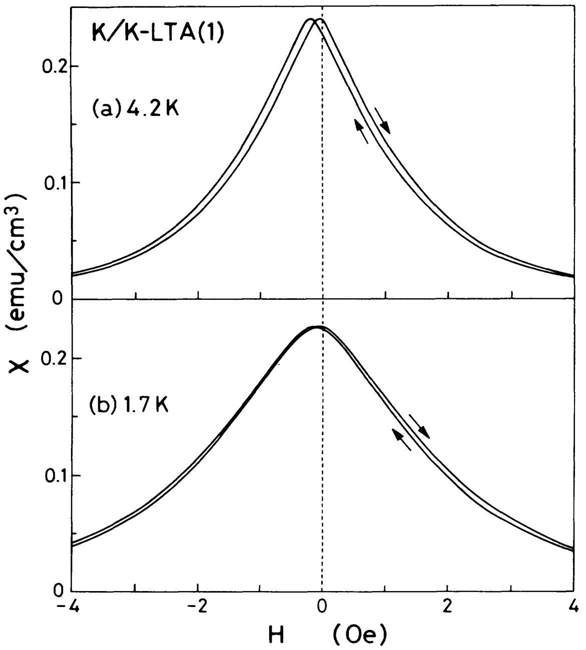

FIG. 3. External dc magnetic field (H) dependence of the ac magnetic susceptibility (χ) of K-loaded K-LTA(1) powder at 4.2 (upper) and 1.7 K (lower). The arrow indicates the direction of field variation.

experiment and the irreversibility in the magnetization process have been observed in an *Au*Fe alloy [16].

Figure 3 shows the ac magnetic susceptibility χ at 4.2 and 1.7 K as a function of the external dc magnetic field H, where the arrow indicates the direction of field variation. The internal dc magnetic field is much smaller than the external field, because of the demagnetizing effect. The center of the curve is slightly shifted from the origin, because the weak magnetic field due to the terrestrial magnetism remains unscreened. The magnetic susceptibility decreases under a very weak dc magnetic field. Under applied fields of about 1 and 2 Oe at 4.2 and 1.7 K, respectively, the magnetic susceptibility is reduced to half of the peak value. Such an applied field sensitivity has also been observed in *Au*Fe alloy [14]. The curves in Fig. 3 show a weak hysteresis as a function of the applied dc magnetic field. This indicates the existence of weak residual magnetization. Generally, in the case where hysteresis exists, the differential susceptibility is larger than the ac susceptibility (or the reversible susceptibility). Hence, strictly speaking, the ac susceptibility obtained in Fig. 3 is slightly smaller than the differential susceptibility.

The curves in Fig. 4 show the magnetization M as a function of H, where M is obtained from the integral of χ with respect to H in Fig. 3. The values obtained may be slightly smaller than those obtained from the integral of the differential susceptibility, because of the weak hysteresis. Here, we neglect this difference, because the hysteresis is weak. In Fig. 4, saturation magnetization up to 150 Oe is estimated to be 0.54 and 0.65 G at 4.2 and 1.7 K, respectively. From these values, the effective magnetic moment per supercage is estimated to be $0.11\mu_B$ and $0.13\mu_B$ at 4.2 and 1.7 K, respectively.

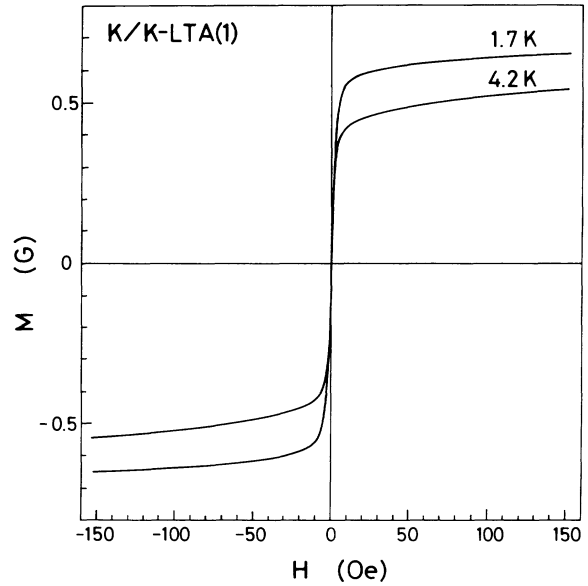

FIG. 4. External magnetic field (H) dependence of the magnetization (M) of K-loaded K-LTA(1) powder at 4.2 and 1.7 K.

The above magnetic properties of K-loaded K-LTA(1) resemble those in Fe-rich *Au*Fe alloy. Hence, it is expected that K clusters with magnetic moments are distributed in zeolite crystals, and that their magnetic moments are interacting with each other.

The precise mechanism of the magnetic properties of the present substances is not well known, but the interim interpretation is as follows: If we start from the localized electron model, the magnetic moment of the cluster arises from the partly filled electronic state localized in the supercage. We assume a spherical quantum-dot potential with an infinite barrier in the supercage for simplicity. The quantum states of $1s,1p,1d,2s,\ldots$ are expected there, and $2,6,10,2,\ldots$ electrons can occupy the respective orbits in sequence. In the present case, about 4 electrons are localized in each supercage on average, and, therefore, the $1p$ state is partly occupied. In the zeolite crystal, the total number of K^+ ions in each supercage is not uniform, because this number varies statistically. Hence, the number of trapped electrons in each supercage may differ from one to another. If we ignore Hund's rule, a cluster with an odd number of electrons shows a magnetic moment of μ_B.

Two types of mechanisms are considered as the origin of the interaction between clusters having magnetic moments. One is the direct exchange interaction between adjacent clusters, and the other is the RKKY interaction through the itinerant electrons. In the former case, the electrons localized in adjacent supercages partly overlap through the window between the supercages. In the latter case, some parts of the electrons are delocalized, and the remaining parts are localized in the supercage. In the present optical measurement above 0.4 eV, however, direct evidence of itinerant electrons has not been obtained.

In conclusion, ferromagnetism is observed in K-loaded K-LTA(1) below about 4 K. The interactions between the magnetic moments of K clusters indicate a ferromagnetic state similar to the reentrant spin-glass phenomenon.

The change in the cluster-spin density will cause a drastic change in the magnetic properties. The spin density of the present cluster system can be controlled by changing the loading density of the guest K atoms. The density dependence experiment is currently in progress, and will be reported elsewhere.

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