Antiferromagnetic Orderings of Alkali-metal Nanoclusters Arrayed in Sodalite Crystal Studied by μSR and Other Microscopic Probes

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Abstract: Alkali metal clusters with an unpaired electron can be periodically arranged in a body-centered cubic structure in sodalite, a type of aluminosilicate zeolite, to form a Mott insulator accompanied with an antiferromagnetic ordering. This system does not contain any magnetic elements and is a novel magnetic system in which the magnetic order is realized by alkali metal s-electrons. In order to investigate the origin of the s-electron magnetism in detail, we present examples of studies using muon spin rotation/relaxation (μSR), synchrotron radiation Mössbauer spectroscopy, and neutron diffraction techniques. The spatial expansion of the s-electron wave functions of the nanoclusters with increasing alkali metal content has been directly observed by these experimental methods. This enhances the exchange interaction and increases the transition temperature (Néel temperature). A very simple model material of the Mott-Hubbard system is realized in s-electrons. We also point out that there are great expectations for the future contribution of computer science to this material system, especially to μSR experiments.

Keywords: Alkali-metal cluster, Zeolite, Sodalite, Antiferromagnetism, Mott insulator, Muon spin rotation/relaxation, Synchrotron radiation Mössbauer spectroscopy, Neutron diffraction

1 Introduction

Magnetic materials usually contain transition metal elements and/or rare earth elements. The reason for this is that the highly localized d- and f-electrons carry the magnetic moment and the magnetic order is realized by the exchange interaction between them. However, some materials have been discovered that overturn such common sense. The magnetic ordering of p-electrons (π-electrons) in organic magnets is an example, and that of s-electrons in this article is one of the best examples. The periodic arrangement of nanosized alkali metal clusters can be achieved by adsorbing alkali metals into zeolite crystals having an arrayed nanospace (cage structure). In this case, s-electrons confined in a cage occupy discretized levels due to quantum size effects and exhibit magnetic order due to exchange interactions between periodically arranged clusters. There are various types of crystal structures of zeolites, and ferromagnetic, antiferromagnetic, and ferrimagnetic orderings have been found depending on the combination of alkali metals [1–7]. In this system, s-electrons of alkali metals, which are considered to be the furthest from magnetism, exhibit magnetic order. In this article, we present examples of antiferromagnetic order in alkali-metal clusters in sodalite, which is the simplest system among these materials, studied by using microscopic magnetic probes, namely, muon spin rotation/relaxation (μSR), synchrotron radiation Mössbauer spectroscopy, and neutron diffraction techniques.

Sodalite is a type of aluminosilicate zeolite, which has the simplest crystal structure. As shown in Figure 1 (a), a truncated octahedral β-cage (inner diameter of about 7 Å) consisting of a Si-O-Al covalent bond network is arranged in a body-centered cubic (bcc) structure. This network is negatively charged in the
number of Al atoms, and the charge is compensated by the distribution of alkali cations in the space (cations are omitted in Figure 1 (a)). The chemical composition is $A_3\text{Al}_3\text{Si}_3\text{O}_{12}$ ($A$: alkali element) per cage. When one alkali metal atom is absorbed here, one s-electron is confined to the cage and is shared by four cations to form an $A_4^{3+}$ cluster (Figure 1 (b)) [8]. The clusters have unpaired electrons and antiferromagnetic order develops when all cages are occupied [3, 9, 10]. The antiferromagnetic transition temperature (Néel temperature) is about 50 K and 72 K for the Na and K clusters, respectively, and depends on the alkali elemental species [11–16]. These materials are just-half-filled Mott insulators with one electron at each site (cage), and the exchange interaction between s-electrons through the cage window is considered to be the origin of the magnetic order. The characteristic feature of this system is that s-electrons spread in nano-sized clusters are responsible for the magnetism. In conventional magnetic materials, the atomic wave function, such as d-orbitals and f-orbitals, is responsible for the magnetism, which is well known. On the other hand, the shape and spatial extent of the s-electron wave function in alkali-metal nanoclusters are non-trivial. The motivation for this research is to elucidate the mechanism of s-electron magnetism by studying these points in detail using various microscopic probes including quantum beams.

2 Experimental Results

In the present study, we prepared three materials. The Na-form sodalite loaded with Na atoms is abbreviated to Na/Na$_3$-SOD, which contains Na$_3^{3+}$ clusters. The K-form sodalite loaded with K atoms is abbreviated to K/K$_3$-SOD, which contains K$_3^{3+}$ clusters. The K-form sodalite loaded with Rb atoms is abbreviated to Rb/K$_3$-SOD, which contains K-Rb alloy clusters with the average composition of (K$_3$Rb)$_3^{3+}$.

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The most direct proof of long-range magnetic order is probably the neutron diffraction experiment. However, in this study, only one Bohr magneton ($\mu_B$) per tens of atoms exists in the material, and the moment is spread out to nanosize. Thus, the magnetic scattering was expected to be extremely weak. Powder samples of 3–4 grams were synthesized and subjected to neutron powder diffraction using 5G PONTA at JRR-3 (Japan Research Reactor 3). Figure 2 shows the experimental results of the K clusters in sodalite. Below the Néel temperature, the 001 reflection grows with lowering temperature. This reflection is forbidden in the crystal structure. We also observed the 111 reflection in the Na cluster, which will be described later. These peaks are thought to be magnetic diffraction peaks, and are inferred to be magnetic structures in which the magnetic mo-
ments of the clusters at the apexes of the cubic lattice and at the body center are anti-parallel. These results are the first case of direct observation of magnetic ordering of s-electrons by neutron diffraction [17, 18]. Although the magnetic scattering intensity is only about 0.1% of the nuclear scattering intensity, we attempted to analyze it more quantitatively. Figure 3 shows the wavenumber dependence of the magnetic form factor estimated from the ratio of the magnetic scattering intensity to the nuclear scattering intensity. The magnetic form factor corresponds to the Fourier transform of the spatial distribution of the electron spin density, and is shown as a dashed line in the Figure, assuming a β-cage inner diameter of 7 Å and the 1s wave function of electrons confined in a spherical well potential. Reflecting the large wave function, the form factor decreases sharply with the wavenumber, and the experimental results for sodium clusters are in good agreement with this calculation. The result shows that the magnetic properties of this system are exactly those of electrons spread in a nano-sized cage, as schematically shown in Figure 1 (b). Since neutron diffraction is a probe of the reciprocal space, only the average structure is obtained. That is, even if there are, for example, heterogeneities between cages, they are averaged out. Nevertheless, it is surprising to see such a good agreement between experimental results and calculations assuming a single Bohr magneton and a simple spherical potential well. A more robust and homogeneous magnetic ordering is realized by s-electrons than one might expect. On the other hand, the form factor of the K clusters is smaller than that of the Na cluster at the wavenumber of the 001 reflections, as indicated by the blue closed circle, and the 111 reflections could not be observed within the experimental error range [18]; the form factor decays faster in the K clusters and the spatial extent of the s-electron wave function is larger than that of the Na cluster. This will be understood in relation to the origin of the Neel temperature rise, which will be discussed later.

Muons, a kind of elementary particle lepton with spin \( s = \frac{1}{2} \), are produced by the spallation of pions in a carbon target using a proton accelerator. Thanks to the helicity of the concurrently produced neutrinos, the positive muon \( \mu^+ \) spin is 100% polarized in the opposite direction to the direction of the beam. Therefore, an external magnetic field is not required to polarize the spin at all. This, together with a gyromagnetic ratio three times higher than that of protons, makes \( \mu \text{SR} \) an extremely sensitive magnetic probe. The implanted \( \mu^+ \) stops at interstitial sites in the material and feels the local magnetic field. Hence, \( \mu^+ \) is a probe of the real space. We performed zero-field (ZF-) \( \mu \text{SR} \) measurements on samples of Na metal, K metal and K-Rb alloy clusters in sodalite crystals using the GPS spectrometer in the Paul Scherrer Institute (PSI), Switzerland. Spin-polarized \( \mu^+ \) beams were implanted into the samples, and the emitted positrons were detected by forward and backward counters located on the upstream and downstream sides of the beam, respectively. The asymmetry is defined as
\[
A(t) = \frac{N_F(t) - \alpha N_B(t)}{N_F(t) + \alpha N_B(t)}
\]
where \( N_F(t) \) and \( N_B(t) \) indicate the time evolution of the number of positrons at the forward and backward counters, respectively. \( \alpha \) is a calibration factor of the efficiency of the counters. Then, we can observe the time evolution of the spin polarization of \( \mu^+ \) stopping in the sample. Figure 4 shows the ZF-\( \mu \text{SR} \) time spectra of three samples. The vertical axis values are shifted appropriately. In all the samples, oscillations of the asymmetry are clearly seen. This signal is due to a coherent precession of the \( \mu^+ \) spins, indicating that homogeneous internal magnetic fields arise in the antiferromagnetic ordered states [12]. We analyzed the spectra using the following equation:
\[
A(t) = A_0 \exp\left[-(\lambda_1 t)^b\right] \cos\left(\gamma_\mu H_{int} t\right) + A_2 \exp\left(-\lambda_2 t\right) + B,
\]
where the first term is the precession component of the internal magnetic field of $H_{\text{int}}$ with a damping which comes from the field distribution, and $\gamma \mu$ stands for the gyromagnetic ratio of muon ($2\pi \times 13.55 \text{ kHz/G}$). The second term is a slowly relaxing component. The term $B$ is for a time- and temperature-independent baseline. The fitting results are shown by black curves in Figure 4. The temperature dependence of the internal magnetic field is shown in Figure 5, which shows typical behavior of the second-order phase transition. The solid line is a phenomenological fitting, and the critical exponent is estimated to be $\beta = 0.38-0.40$, which indicates a Heisenberg-type antiferromagnet. The internal magnetic field at low temperatures was about 92, 142 and 155 Oe for Na, K and K-Rb, respectively, indicating that the internal magnetic field was stronger for samples with heavier composition and higher Néel temperature.

Potassium isotope $^{40}$K is known to be a Mössbauer nucleus. However, conventional Mössbauer measurements using radioisotope sources are not possible because there is no parent nucleus that forms an excited state of $^{40}$K (29.83 keV). For this reason, only a few experiments using nuclear reactions such as neutron capture were conducted in the 1960s. Recently, a new method to obtain Mössbauer absorption spectra of various radionuclides using synchrotron radiation was developed by Seto et al. at SPring-8 [19]. We have prepared K clusters enriched with about 5% of $^{40}$K in sodalite and applied this technique to successfully observe the Mössbauer absorption spectrum of $^{40}$K for the first time using synchrotron radiation at BL09XU, SPring-8 [20]. Below the Néel temperature of 72 K, the absorption dip deepened and widened. The ground and excited state spins of $^{40}$K are $I = 4$ and 3, respectively, and the absorption spectrum splits into 21 lines due to the hyperfine interaction with the electron spins. However, we were not able to observe them separately. The data were analyzed by calculating the exact spectral shape based on nuclear resonant scattering theory. We found that a hyperfine field of $92 \pm 30$ kOe is generated on the $^{40}$K nucleus at the temperature of 8 K because of the antiferromagnetic order [20].
Discussion

We summarize the results obtained by using three different quantum beams. Neutron diffraction clearly shows that the antiferromagnetism in this system is a long-range magnetic order. Magnetic form factor analysis suggests that the spatial distribution of the spin density is wider for K clusters than for Na clusters. This may be closely related to the fact that the Néel temperature is higher in the K cluster. Heavier alkali metal atoms have lower ionization energies and weaker electron-lattice interactions. Therefore, the cluster’s potential for s-electrons becomes shallow and the spatial extent of s-electrons increases. As a result, the electron transfer energy $t$ through the window to the adjacent cage is expected to increase. Since the Coulomb repulsion energy $U$ is still high ($U > t$) when two electrons are accommodated in the same cage, the Mott insulator state is realized, but the antiferromagnetic exchange interaction is considered to increase with the decrease in $U/t$. In this way, the parameters of the Mott-Hubbard model can be controlled by changing the alkali metal species. These results agree qualitatively with theoretical predictions [21–23].

The μSR study systematically showed a stronger internal magnetic field for samples with heavier average composition of alkali atoms and higher Néel temperature. Since the number density of the electron spins in the sample is one per cage in all samples, this result cannot be explained by considering only the dipole field created by the electron spins. Although the μSR is an extremely sensitive magnetic probe that can be used in zero magnetic field, the weakness of this method is that the stopping position of $\mu^+$ in the crystal cannot be determined easily, unlike NMR or Mössbauer spectroscopy where we usually know the position of the nuclei used as probes. The stopping position of $\mu^+$ is mainly determined by the electrostatic potential, and it is generally believed that $\mu^+$ stops near negatively charged oxygen atoms in various oxides [24, 25]. Therefore, we consider the four-membered ring window connecting the second neighboring cage as the $\mu^+$ stopping position in the sodalite crystal where the most negative charges (or oxygen atoms) are concentrated (Figure 6). In the antiferromagnetically ordered state, the spins in the cages on both sides of this site are ferromagnetically aligned because the two cages are the second neighbors. We then assume that $\mu^+$ has a finite Fermi contact interaction with the tail of the s-electron wave function of both cages. The systematic increase in the local magnetic field at the $\mu^+$ position can be explained qualitatively if we consider that the spatial extent of the s-electron wave function increases with the heavier alkali metal clusters, as discussed above. On the other hand, Mössbauer spectroscopy of the $^{40}$K nucleus showed a hyperfine field nearly three orders of magnitude higher than that of μSR. As shown schematically in Figure 6, the nuclear position of the alkali cation implies a much higher electron spin density at the nuclear position of the alkali cation than the $\mu^+$ site at the tail of the s-electron wave function. For the future, it is necessary to construct a wave function that satisfies all the results obtained by the three probes using the theoretical calculation to understand the system more deeply.

Figure 6. (a) Schematics of alkali-metal clusters formed in sodalite crystal. Two β-cages, the second nearest neighbors, are shown. They are connected via a 4-membered ring. Alkali cations are located inside the cages. The s-electron wave function is delocalized in the cage. The electronic spins are ferromagnetically coupled between the second nearest neighbors in the bcc lattice of sodalite. (b) Calculation result of $\mu^+$ stopping sites by assuming the O-μ bond with the length of 1 Å and point charges. Two $\mu^+$ sites are expected within this assumption.
4 Summary and Prospects

The antiferromagnetism of alkali-metal clusters in sodalite was investigated using μSR, neutron diffraction, and synchrotron radiation Mössbauer spectroscopy. The combination of these methods has given us a new insight into the spatial distribution of the wave function of s-electrons in the nanoclusters, which is responsible for magnetism, unlike the d- and f-electrons in conventional magnets. It is also demonstrated that the materials studied in this work realizes a very simple model system of the Mott-Hubbard physics.

As mentioned above, it is difficult to determine the exact position of μ\(^+\) in μSR experiments. The future contribution of computer science to the search for this problem is highly anticipated. What has been said before in oxides is that μ\(^+\) form O-μ bonds and stop at the lowest electrostatic potential at a distance of 1 Å from oxygen [24, 25]. We also programmed and calculated it for alkali-metal clusters in sodalite crystal. Each atom is assumed to have a point charge, without taking into account the influence of the broadening of the s-electron wave function and the effect of the presence of μ\(^+\) to the lattice. The results are shown in Figure 6 (b), where a site close to the 6-membered ring (μ\(^+\)1) and a site close to the 4-membered ring (μ\(^+\)2) were obtained. In addition, almost the same sites are obtained in the electrostatic potential calculations using the density functional method without considering the muon effect [26]. This result is slightly different from the speculated site of the 4-membered ring shown in Figure 6 (a). However, in all cases, the calculated dipole fields, assuming a point dipole at the cage center, are far from the experimental values. Therefore, the issue of muon position in this system is not yet resolved. It is expected that both the Fermi contact interaction with the s-electrons of the cluster and the lattice distortion due to the μ\(^+\) stopping should be taken into account in the calculation of the μ\(^+\) stopping position and the local magnetic field. This is not a simple task, but it holds great promise for the future of computer science. The lattice distortion induced by the implanted μ\(^+\) has been very precisely calculated for small systems such as fluorides [27, 28]. It is hoped that such precise calculations can be applied to materials with a large unit cell size, such as the objects of this study. For the Fermi contact interaction, μSR measurements under strong transverse magnetic fields are now underway to measure the so-called muon Knight shift.

On the other hand, μSR experiments with negative muons μ\(^-\), have been developed very recently. Whereas positive muons stop at the interstitial sites of the crystal, negative muons are captured in the nucleus to form muon atoms. Since each muon atom has different lifetimes depending on the species of nuclei, the μSR experiment at the target nuclear site can be performed if the analysis is done well. During the capturing of negative muons in the nucleus, the muon spin polarization is reduced to about 1/6th of its original value, which has been difficult to experiment with from the viewpoint of statistical accuracy. However, it is becoming possible to perform experiments in a realistic beamtime because of the developments of J-PARC MLF. The nuclear magnetic field of hydrides and its dynamics have been successfully observed very recently [29–31]. This method is also expected to be applied to the study of magnetic materials. Thus, the complementary use of positive and negative muons and computer science methods is expected to enhance our understanding of the magnetism of this material system.

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