Hierarchical ordering in kagomé lattice antiferromagnets, Jarosites

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Abstract

Jarosite compounds, $R\mathrm{Fe_3(OH)_6(SO_4)_2}$ [$R = \mathrm{K}$, Na, $\mathrm{NH_4}$], of the kagomé lattice antiferromagnets show the magnetic ordering below 65 K (T_{N1}). In addition to the transition at T_{N1}, some jarosite samples indicate the second transition at a lower temperature T_{N2}. The nature of the transitions was studied by the susceptibility and NMR experiments. The NMR results suggest the existences of the partial substitution of R^+ by $\mathrm{H_3O^+}$ and the deficiency of $\mathrm{Fe^{3+}}$ accompanied with the formation of $\mathrm{H_2O}$. The hierarchical orderings are considered to occur due to the effects of the substitutions, deficiencies, and the weak interplane interaction, that is, the two dimensional ordering occurs at T_{N1} in the domains formed by the substitutions and the three dimensional ordering occurs at T_{N2} between the kagomé planes.

Key words: kagomé lattice; frustration; jarosite; magnetic ordering

The kagomé lattice antiferromagnet is one of the geometrically frustrated magnetic systems. The ideal Heisenberg kagomé lattice antiferromagnet has no long range order down to zero temperature due to the continuous degeneracy of the ground state [1]. Jarosite compounds, $R\mathrm{Fe_3(OH)_6(SO_4)_2}$ [$R = \mathrm{K}$, Na, $\mathrm{NH_4}$], are examples of the kagomé lattice antiferromagnets. The magnetic ions $\mathrm{Fe^{3+}}$ ($S = 5/2$) form the kagomé lattice on the c-plane and couple antiferromagnetically with each other. The interplane exchange interactions are fairly weak because the adjacent kagomé planes are separated by some kinds of nonmagnetic ions. The jarosites show the magnetic ordering below about 65 K (T_{N1}) [2]. Some samples, moreover, show successive transitions at T_{N1} and T_{N2} ($T_{N1} > T_{N2}$) [3]. We have performed the magnetization and NMR experiments for $R\mathrm{Fe_3(OH)_6(SO_4)_2}$ [$R = \mathrm{K}$, Na, $\mathrm{NH_4}$] to investigate the successive transitions.

The samples were synthesized by hydrothermal treatment under two conditions. The potassium jarosite (sample K-J 1) was synthesized at about 200℃ in an autoclave and the other potassium jarosite (K-

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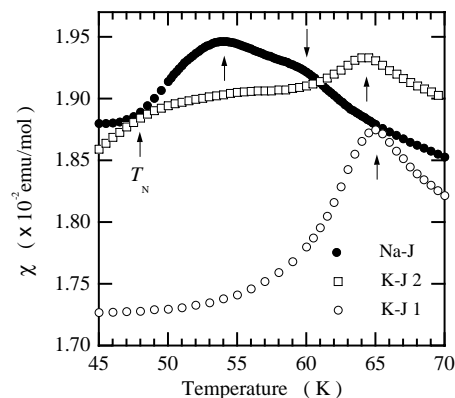[2] E-mail:maegawa@nmr.jinkan.kyoto-u.ac.jp

Fig. 1. Susceptibility of K-J 1, K-J 2 and Na-J. Arrows indicate the transition temperatures.

J 2) and sodium jarosite (Na-J) were synthesized at about 80℃ in beakers.

The susceptibility data of K-J 1, K-J 2, and Na-J are shown in Fig. 1. The K-J 1 shows the magnetic transition at only $T_{N1} = 65$ K, while K-J 2 shows successive transitions at $T_{N1} = 64.4$ K and $T_{N2} = 48.2$ K, and also Na-J shows ones at $T_{N1} = 60.0$ K and $T_{N2} = 54.0$ K.

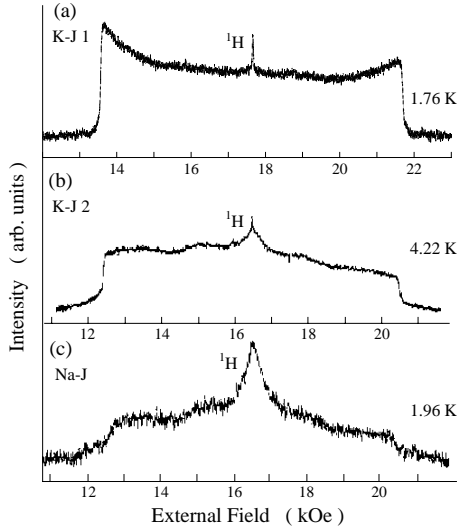The ^{1}H-NMR spectra of these jarosites in the para-

Fig. 2. ^{1}H-NMR spectra in the ordered phase: (a) K-J 1 at 75.1 MHz; (b) K-J 2 at 70.1 MHz; (c) Na-J at 70.1 MHz.

magnetic phase show sharp peaks with the half width of about 10 Oe. The widths increase up to about 4 kOe below T_{N1} and have no anomaly at T_{N2}. The spectra in the ordered phase are shown in Fig. 2. The spectrum of K-J 1 indicates the powder pattern of the antiferromagnet, in which all protons feel identical internal field from Fe^{+3} spins. The broad peaks come from ^{1}H in OH^-. This fact means that the ordered spin structure is the $\mathbf{q} = 0$ type of the $120°$ spin arrangement with $+1$ chirality [4], that is consistent with the neutron diffraction experiments [5]. The magnetic ordering and the spin structure are realized by the removal of the degeneracy due to the single-ion-type anisotropy [4,5].

On the other hand, the spectra for K-J 2 and Na-J in the ordered phases have narrow central peaks and medium peaks whose widths are about 2 kOe, in addition to the broad powder patterns which indicate the same spin structure with that of K-J 1. The central peaks remain sharp until 40 K and become abruptly broader below 40 K. Such behavior was also observed in $NH_4Fe_3(OH_6)(SO_4)_2$ at 20 K as the motional narrowing due to the rotation of NH_4^+. The partial substitution of H_3O^+ for R^+ and the deficiency of Fe^{3+}, which depend on the condition of the synthesis, have been reported in jarosites [6]. The behaviors of the central peaks are regarded as the motional narrowing of H_3O^+. Thus the central peaks come from ^{1}H in H_3O^+ substituting for R^+. The deficiencies of Fe^{3+} accompany the protonation of OH^- by H^+ to form H_2O. The medium peaks are considered to come from ^{1}H in these H_2O.

The echo signal intensities and the spin-lattice relaxation rates, $1/T_1$, of ^{1}H in OH^- for all samples show anomalies at T_{N1}, while the echo intensity and $1/T_1$ of

^{23}Na in Na-J show anomalies at T_{N2} [3]. The protons in OH^- exist nearly on the kagomé planes and ^{23}Na nuclei exist between the planes. The critical fluctuations which give rise to effects on $1/T_1$ are detected at the sites on the kagomé planes at T_{N1} and are detected at the sites between the planes at T_{N2}

It was reported that $H_3OFe_3(OH)_6(SO_4)_2$ shows no long-range order (LRO) down to 0.4 K and spin-glass like transition at 15 K [7]. The magnetic property of $H_3OFe_3(OH)_6(SO_4)_2$ is remarkably different from that of $RFe_3(OH)_6(SO_4)_2$ $[R = K, Na]$. It is considered that the partial substitutions of H_3O^+ for R^+ and the deficiency of Fe^{3+} play important roles for the transitions in the jarosites. The domains of 2D ordering might be formed in the kagomé planes at T_{N1}, but the 3D LRO between the planes is suppressed owing to the effects of substitutions, deficiencies, and the weakened interplane interaction. The 3D LRO occurs at lower temperature of T_{N2} owing to the development of the 2D ordering. The hierarchical orderings occur in K-J 2 and Na-J, while the 2D LRO and 3D LRO occur at the same temperature T_{N1} in K-J 1 because there is no substitutions and deficiencies.

It has been reported that the hierarchic transition is found in $CoCl_2$ graphite intercalation compound, which shows the 2D ferromagnetic LRO at 10 K and 3D LRO at 8 K [8]. The 2D LRO does not simultaneously induce the 3D LRO because of the formation of 2D domains and weak interlayer couplings.

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