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Neutron-diffraction study on Na- and K-jarosites

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Abstract

Powder neutron-diffraction measurements of the frustrated kagomé lattice antiferromagnets Na- and K-jarosites ($AFe_3(OH)_6(SO_4)_2$: A = Na and K) were carried out. The determined magnetic structure at 10 K is the so-called $q = 0$ structure and found to be different from one reported previously for K-jarosite. The intensities of magnetic reflections show slow decreasing with increasing temperature near T_N and seem to imply successive phase transitions observed in a recent NMR study. © 1998 Elsevier Science B.V. All rights reserved.

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Frustrated magnetic systems show a variety of phase transitions, because the cancellation of the main interactions enhance the effects of relatively weak interactions or anisotropy. Recent detailed NMR and susceptibility measurements have revealed that successive phase transitions occur in the frustrated kagomé lattice antiferromagnets, jarosite family ($AFe_3(OH_6)(SO_4)_2$, A: alkali metal, etc.) [1]. Critical temperatures estimated from NMR measurements are $T_{N1} = 60$ K and $T_{N2} = 50$ K for A = Na and $T_{N1} = 64$ K and $T_{N2} = 48$ K for A = K [2]. In order to clarify the nature of these successive phase transitions, we carried out neutron powder diffraction measurements for Na-, K- and deuterized Na-jarosites.

Samples of normal Na- and K-jarosite were synthesized by one of the authors (MT) earlier [3]. Deuterized Na-jarosite was newly prepared according to the synthesis written in Ref. [4] with 99.75% D_2O solutions in order to reduce an incoherent background from protons. An X-ray diffraction pattern for the dueterized sample agrees very well with one in a database.

Neutron-diffraction measurements were performed at the JRR-3M reactor, Tokai, JAERI. Deuterized Na-jarosite was measured on the triple-axis spectrometer TAS-1 with a two-axis mode from 10 to 80 K and Na- and K-jarosite was measured on the powder diffractometer HRPD at 10 and 80 K.

In Fig. 1 we show the neutron powder diffraction pattern of the dueterized Na-jarosite measured at 10 K. The diffraction patterns of K- and normal Na-jarosites closely resemble each other and are almost in agreement with one reported by Townsend [5]. Magnetic reflections are indexed as shown in Fig. 1.

The normalized integrated intensities of the $(1\ 1\ \frac{3}{2})$, $(1\ 0\ \frac{5}{2})$ and $(0\ 1\ \frac{7}{2})$ magnetic reflections for the deuterized Na-jarosite are depicted in Fig. 2a as a function of temperature. Obviously, the upper critical temperature (T_{N1}) is evaluated to be about 58 K, being consistent with the NMR result. On the other hand, the lower critical temperature (T_{N2}) is not clear because of low statistics of the magnetic reflections. The intensities decrease with increasing temperature rather slowly toward T_{N1}, unlike a second-order phase transition. This probably indicates the existence of the intermediate (IM) phase.

Nuclear and magnetic structure refinements were made for six diagrams for K-, Na- and deuterized Na-jarosites measured at 10 and 80 K using a Rietveld refinement program RIETAN [6] with an extension of treating non-collinear magnetic structures. In the nuclear structure refinements we obtained R values 2–12%. The final structural parameters for all six diagrams are consistent with those in Ref. [5]. These results will be published elsewhere.

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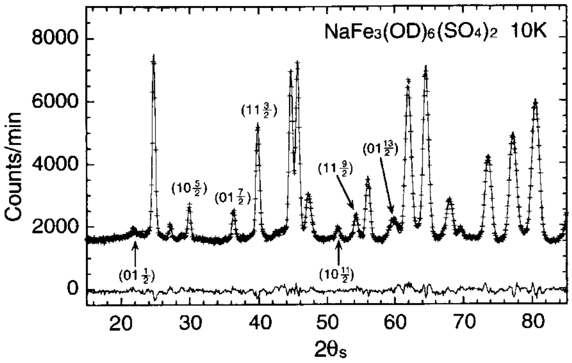

Fig. 1. Powder neutron diffraction pattern of the deuterized Na-jarosite at 10 K. Fit of Rietveld refinements is also shown.

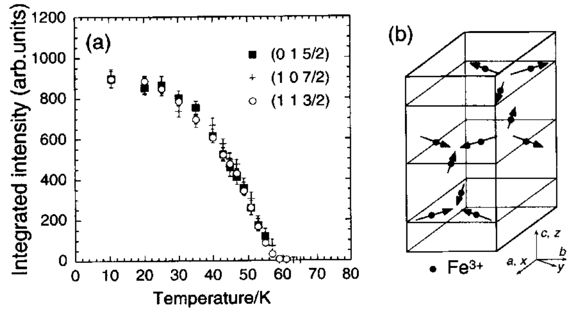

Fig. 2. (a) The temperature dependence of the integrated intensities for the magnetic reflections $(1\ 1\ \frac{3}{2})$, $(0\ 1\ \frac{5}{2})$ and $(1\ 0\ \frac{7}{2})$. The intensities are roughly normalized at 10 K. (b) The best model of the magnetic structure in the LT phase. Upper half with a reversed configuration is omitted for simplicity.

The magnetic structure is solved as follows: Because the Weiss constants are negative in these compounds, the most probable magnetic structures in a kagomé plane are so-called $q = 0$ structure and $\sqrt{3} \times \sqrt{3}$ structure. Since our data show that the magnetic unit cell is identical to the chemical unit cell in the *ab*-plane, we can assume a $q = 0$ structure. The spin configuration in a kagomé plane is represented by three spin directions with an angle of 120° to each other. Therefore, if we restrict the direction of a spin discretely by 30° step, the number of possible spin configurations in a kagomé plane becomes 24 ($360°/30° = 12$ choices times 2 choices of chirality). Since the magnetic unit cell contains six kagomé planes and since the direction of the spins in the upper half of the cell can be assumed to be a reversed configuration of the lower half, it is enough to calculate the magnetic structure factor for only 2×24^3 spin configurations. (A factor 2 comes from the direction of the spin plane. We calculated for xy and xz cases. In the xz case we averaged three symmetrically equivalent domains.)

There are 24 configurations which satisfy the extinction rule that $(1\ 1\ \frac{1}{2} + 3\ell)$, $(1\ 1\ \frac{5}{2} + 3\ell)$, $(1\ 0\ \frac{3}{2} + 3\ell)$ and $(0\ 1\ \frac{3}{2} + 3\ell)$ reflections (ℓ: non-negative integer) are forbidden. Two (equivalent) configurations of them coincide with the experimental fact that $(0\ 1\ \frac{1}{2})$ reflection is very weak. A same magnetic structure is found to be the best model for three compounds and it is shown in Fig. 2b. The ordered moments are confined in the xy-plane. From the magnetic structure refinements, Fe^{3+} moments were evaluated to be 3.3(1), 3.5(1) and 3.8(1) μ_B for Na-, deuterized Na- and K-jarosite, respectively.

It should be mentioned that the magnetic structure obtained in this study differs from one reported by Townsend et al. for K-jarosite [5]. A way of stacking of $q = 0$ structures is different between theirs and ours. The difference is partly seen in the experimental results. In our data, $(0\ 1\ \frac{1}{2})$ peak is invisible (in K- and normal Na-jarosites) or at most very weak (in deuterized Na-jarosite). On the other hand, $(0\ 1\ \frac{1}{2})$ peak has comparable intensity with other magnetic peaks in their data. Thus, the different magnetic structure might originate in the difference between the samples. The main reason, however, seems to be due to their overestimation of the integrated intensity of $(0\ 1\ \frac{1}{2})$ peak (see Fig. 4 in Ref. [5]). Recent NMR measurements support our result. In our structure a dipole field at 3a sites (Na or K) caused by Fe^{3+} magnetic moments is cancelled. This is consistent with a small internal field at Na sites [2].

Finally, we shortly mention about the IM phase. It is difficult to determine the magnetic structure unambiguously due to the low statistics of the reflections. However, as seen in Fig. 2a all magnetic reflections reside in the IM phase. Thus, if the transition at T_{N2} is of second order, the number of possible magnetic structures is greatly reduced.

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