Magnetic order and interaction in garnet lattice antiferromagnets AgCa$_2$$M_2$V$_3$O$_{12}$($M$=Mn, Co, Ni) and NaPb$_2$Mn$_2$V$_3$O$_{12}$

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Abstract. We have investigated the magnetic orderings and the magnetic interactions in garnet antiferromagnets AgCa$_2$$M_2$V$_3$O$_{12}$($M$=Mn, Co, Ni) and NaPb$_2$Mn$_2$V$_3$O$_{12}$, using the powder neutron diffraction and magnetization measurements. In the neutron diffraction measurements, we revealed that the magnetic structures in all samples measured are simple two sublattice antiferromagnetic structures with collinear magnetic moments. We also determined the exchange interactions from the critical magnetic fields $H$$_{sat}$ observed in the high field magnetization processes up to 30 T.

1. Introduction

For a long time, garnet magnets have been attracted much attention for their interesting magnetic and optical properties such as the magneto-optical effect[1] and novel magnetic properties[2]. The garnet type structure has the cubic symmetry with the space group $Ia$3$d$ of No. 230. The general chemical formula can be written as $\{C\}_3[A]_2(D)3$O$_{12}$ with eight of these formula units per the chemical unit cell. The cations on the C, A and D-sites are surrounded by dodecahedron (24c), octahedron (16a) and tetrahedron (24d) constructed by oxygen O$_{2}^-$ ions, respectively. Because of the much complex crystal structure, it might be difficult to understand the magnetic interactions among inter- and intra-sublattices. Nevertheless, it is much important to properly investigate the magnetic interactions in the complex garnet systems for understanding interesting properties in garnet magnets.

In the present study, in order to purely investigate the magnetic interactions among spins on octahedral A-site, we have performed the powder neutron diffraction measurements and the high field magnetization measurements on AgCa$_2$M$_2$V$_3$O$_{12}$($M$=Mn, Co, Ni) and NaPb$_2$Mn$_2$V$_3$O$_{12}$ with magnetic ions occupied on only A-site, which were synthesized by Awaka et al.[3, 4]. Hereafter, we use abbreviations ACMVO, ACCVO, ACNVO and NPMVO for AgCa$_2$Mn$_2$V$_3$O$_{12}$, AgCa$_2$Co$_2$V$_3$O$_{12}$, AgCa$_2$Ni$_2$V$_3$O$_{12}$ and NaPb$_2$Mn$_2$V$_3$O$_{12}$, respectively. In the recent bulk measurements, all the samples exhibit antiferromagnetic phase transitions and...
the Neel temperatures $T_N$ were determined to be 25 K in ACMVO[5], 6.39 K in ACCVO[6], 7.21 K in ACNVO[6] and 14 K in NPMVO[5].

2. Experimental detail
The powder samples of ACMVO, ACCVO, ACNVO and NPMVO were prepared with the previously reported procedures.[3, 4] The neutron diffraction experiments were carried out with the double axis diffractometer MUSASI installed at T2-3-2 beam port in guide hall at JRR-3 in Tokai. The powder samples putting into a vanadium cell were mounted into a closed cycle He-gas refrigerator. The incident neutron wave length was 2.47 Å which was obtained using pyrolytic graphite monochromator. The magnetization measurements under static magnetic field up to 30 T were performed using extraction methods with a hybrid magnet at NIMS.

3. Results and Discussion
3.1. Neutron diffraction
Figure 1 shows the powder neutron diffraction profiles at 4 K in all the samples. For all the samples, we can assign the indexes to the nuclear and magnetic peaks in the same manner, apart from the slightly different peak positions caused by the difference in the lattice constants. The nuclear peak indexes are represented by only index such as 211 and 321, and the magnetic ones are represented by “M” after indexes such as 200M and 222M, which is shown in figure 1(a). The nuclear reflections observed in the present measurements are consistent with the previous X-ray diffraction measurements.[3, 4] Several unidentified peaks were also observed, which might be originated from foreign phases. As shown in figure 2, we confirmed that these magnetic peaks appear below Neel temperatures that are determined by the previous bulk measurements.[5, 6]

As the results of the Rietveld analysis using the program FullProf,[7] we found that the antiferromagnetic structures in all the samples are the two-sublattice magnetic structure. The magnetic ions on the A-site construct the body center cubic (bcc) lattice with the two times

![Figure 1](imageurl)
smaller bases of \((a/2, a/2, a/2)\) than the chemical ones. In the determined two-sublattice model, the spins on the corner of the bcc are antiparallel to the spins on the center. Although the orientation of the magnetic moments cannot be determined owing to the high symmetric cubic crystal structure, we can determine the absolute values of the ordered magnetic moments. The determined magnetic moments are 3.82±0.04 \(\mu_B\) in ACMVO, 1.62±0.02 \(\mu_B\) in ACCVO, 1.61±0.04 \(\mu_B\) in ACNVO, and 3.59±0.04 \(\mu_B\) in NPMVO, where \(\mu_B\) is Bohr’s magneton. Although these values are considerably smaller than the theoretical values expected from fully localized moments, the case of the reduction has been unsolved at the present stage.

It should be noted that the two-sublattice magnetic structure is very simple and can be simply explained by the nearest neighbor antiferromagnetic exchange interactions, \(J\), connecting the spins on corner and center of the bcc. We thus conclude that the nearest neighbor antiferromagnetic exchange interaction is dominant for the intra-A-site exchange interactions in AgCa\(_2\)M\(_2\)V\(_3\)O\(_{12}\)(M=Mn, Co, Ni) and NaPb\(_2\)M\(_2\)V\(_3\)O\(_{12}\) systems.

### 3.2. High field magnetization

As shown in figure 3, the linear increment of magnetization as a function of magnetic field was observed in all the samples. In addition, no significant anomaly such as spin flop and metamagnetization was observed. Therefore, the magnetic anisotropy in all the systems is considered to be small compared with the exchange energy. In ACNVO, ACCVO and NPMVO, the magnetizations reach these saturation values in the critical magnetic fields, \(H^{\text{sat}}\), of 26.0 T, 11.5 T and 23.5 T, respectively. As for the ACMVO, \(H^{\text{sat}}\) can be estimated to be 40 T by the extrapolation of the magnetization curves up to the theoretically expected saturation value of 5 \(\mu_B\) (\(S=5/2\) and \(g=2\) in high spin state of Mn\(^{2+}\)).

Considering the linear increment of magnetization and the simple two-sublattice magnetic structure above mentioned, we expect that this system can be explained by the simple Hamiltonian, \(\mathcal{H} = -\sum_{i,j} J_{i,j} \vec{S}_i \cdot \vec{S}_j - g\mu_B \sum_i S^z_i H\), where \(J_{i,j}\) denotes the nearest neighbor exchange coupling constant connecting two spins \(\vec{S}_i\) and \(\vec{S}_j\), \(g\) is Lande factor and \(S^z\) is the spin component parallel to the magnetic field (\(H\)). In this case, the critical magnetic field can be written by \(H^{\text{sat}} = -zJS/\mu_B\), where \(z\) is a coordination number. Using the experimentally determined \(H^{\text{sat}}\) above mentioned and the coordination number \(z=8\) in the A-site, we can determine the nearest neighbor exchange constants: \(J^{\text{ACMVO}} = 2.7\) K, \(J^{\text{ACCVO}} = 6.7\) K, \(J^{\text{ACNVO}} = 5.0\) K and \(J^{\text{NPMVO}} = 1.6\) K. In these estimations, we also used the previously determined \(g\) and \(S\) values that were \(g=2\) and \(S=5/2\) of the high spin state of Mn\(^{2+}\) in ACMVO, \(S=1/2\) and \(g=3.5\) of the low spin state of ACCVO, \(S=1\) and \(g=2.28\) of the high spin state of Ni\(^{2+}\) in ACNVO, and \(S=5/2\) and \(g=2\) of the high spin state of NPMVO.[5, 6]

In this paper, we assumed that Co\(^{2+}\) in ACCVO could be of the low spin state at 2 K and has
Figure 3. The magnetization processes in AgCa$_2$Mn$_2$V$_3$O$_{12}$, AgCa$_2$Co$_2$V$_3$O$_{12}$, AgCa$_2$Ni$_2$V$_3$O$_{12}$ and NaPb$_2$Mn$_2$V$_3$O$_{12}$ at 2 K.

$g = 3.5$ by the fact that the saturation magnetization is $2.0 \mu_B$ after subtracting the Van Vleck paramagnetism shown by dotted line in figure 3. The spin state of Co$^{2+}$ in ACCVO has been discussed in detail in the previous paper.[6]

4. Summary

We have investigated the magnetic orderings and the magnetic interactions in garnet antiferromagnets AgCa$_2$M$_2$V$_3$O$_{12}$($M=$Mn, Co, Ni) and NaPb$_2$Mn$_2$V$_3$O$_{12}$, using the powder neutron diffraction and magnetization measurements. In the neutron diffraction measurements, we revealed that the magnetic structures in all the samples are simple two sublattice antiferromagnetic structures. The ordered moments in ACMVO, ACCVO, ACNVO and NPMVO are $3.82 \pm 0.04 \mu_B$, $1.62 \pm 0.02 \mu_B$, $1.61 \pm 0.04 \mu_B$ and $3.59 \pm 0.04 \mu_B$, respectively. Taking account of the simple two-sublattice magnetic structure that can be explained by the nearest neighbor antiferromagnetic exchange interactions, we conclude that the nearest neighbor antiferromagnetic exchange interaction is dominant for the intra-A-site exchange interactions in AgCa$_2$M$_2$V$_3$O$_{12}$($M=$Mn, Co, Ni) and NaPb$_2$Mn$_2$V$_3$O$_{12}$ systems. We also determined the nearest neighbor exchange interactions from the critical magnetic fields $H^\text{sat}$ observed in the high field magnetization processes up to 30 T. The determined exchange coupling constants are $J^{\text{ACMVO}} = 2.7$ K, $J^{\text{ACNVO}} = 5.0$ K, $J^{\text{ACCVO}} = 6.7$ K and $J^{\text{NPMVO}} = 1.6$ K.

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References

[1] Teale R W and Temple D W 1967 Phys. Rev. Lett. 19 904
[2] Petrenko O A, Ritter C, Yethiraj M and Paul D M M$^s$K 1998 Phys. Rev. Lett. 80 4570
[3] Awaka J, Kijima N, Uemura M, Kawashima Y and Nagata S 2005 J. Phys. Chem. Solids 66 103
[4] Awaka J, Kijima N, Akimoto J and Nagata S 2007 J. Phys. Chem. Solids 69 1740
[5] Awaka J et al. unpublished
[6] Awaka J, Ito M, Suzuki T and Nagata S 2004 J. Phys. Chem. Solids 66 851
[7] Rodriguez-Carvajal J 1993 Physica B 192 55