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Impact of orbital degrees of freedom on geometrical frustration in the kagome-like magnet $SrV_xGa_{12-x}O_{19}$

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We studied kagome-like magnets, $SrV_xGa_{12-x}O_{19}$ with V^{3+} ($3d^2$ in the triply degenerate t_{2g} states), as a geometrically frustrated spin system with orbital degrees of freedom. We observed a suppression of low-temperature spin entropy and an anomalous contraction of the V triangles on the kagome lattice, which can be regarded as the V trimerization with spin-singlet formation. This result, which is in clear contrast to their Cr^{3+} ($3d^3$) analogs exhibiting a spin-liquid behavior, indicates a substantial impact of orbitals on geometrically frustrated magnets.

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Spontaneous formation of higher-order structures in crystals, as exemplified by charge ordering and orbital ordering in transition-metal oxides, is of current interest in the field of strongly correlated electron systems. The interest in such higher-order structures arises not only from their uniqueness as crystal structures, but also from their impact on the electronic and/or magnetic states of the systems. For example, many charge-ordering and orbital-ordering transitions in transition-metal oxides cause the opening of a charge gap and induce metal-insulator transitions.[1] In the present Rapid Communication, we studied the impact of the spontaneously formed higher-order structure on the magnetic state of geometrically frustrated spin systems.

Geometrically frustrated spin systems are characterized by a large degeneracy of the ground states caused by the competing antiferromagnetic interactions on the triangle-based lattices, for example, triangular lattice, kagome lattice, and pyrochlore lattice.[2] The spin systems on those lattices exhibit various intriguing behaviors, for example, spin-liquid, spin-glass, and spin-ice behaviors. In particular, the geometrically frustrated magnets with Heisenberg spins, for example, the magnets having Cr^{3+} ($3d^3$),[2–8] Ni^{2+} ($3d^8$),[9] or Cu^{2+} ($3d^9$) (Refs. 10 and 11) exhibit unique low-energy excitations emerging from their degenerate ground states, as observed in low-temperature specific heat and neutron scattering. On the other hand, an increasing number of studies have indicated that the existence of the orbital degrees of freedom qualitatively alters the physical properties of geometrical frustrated magnets. For example, $LiVO_2$, where V^{3+} ions ($3d^2$ in the triply degenerate t_{2g} state) exist on the triangular lattice, exhibits a spin-singlet state with V trimerization, and it was proposed that the orbital ordering of the triply degenerate t_{2g} states in the V ion is the origin of the spin-singlet state.[12] Similar orbital ordering in the geometrically frustrated systems is observed in spinel ZnV_2O_4 (Refs. 13 and 14) and AlV_2O_4.[15]

In this Rapid Communication, we report experimental results of kagome-like magnets with V^{3+} ($3d^2$), $SrV_xGa_{12-x}O_{19}$. The compounds with the same crystal structure (magnetoplumbite structure) having Cr^{3+} ($3d^3$), $SrCr_xGa_{12-x}O_{19}$, have been studied extensively as a prototypical geometrically frustrated magnet with $S=3/2$ Heisenberg spins.[2–7] We synthesized the V^{3+} analog of $SrCr_xGa_{12-x}O_{19}$ for the first time, and found that, in contrast to $SrCr_xGa_{12-x}O_{19}$ that exhibits a low-energy excitation typical of a spin-liquid state, $SrV_xGa_{12-x}O_{19}$ exhibits a nearly spin-singlet state, which can be attributed to the orbital ordering of the t_{2g} state in the V^{3+} ions.

Polycrystalline samples of $SrV_xGa_{12-x}O_{19}$ with $0 \leq x \leq 8$ were synthesized by a solid-state reaction in a sealed quartz tube.[16] Stoichiometric amounts of $SrGa_4O_7$, V_2O_3, and Ga_2O_3 were mixed, pressed into pellets, sealed in a quartz tube, and sintered at 1050 °C for 120 h with one intermediate grinding. $SrGa_4O_7$ was made by calcining $SrCO_3$ and Ga_2O_3 in air. We also made polycrystalline $SrCr_8Ga_4O_{19}$ for a comparative study. Magnetization was measured by a superconducting quantum interference device magnetometer. Specific heat was measured by a physical properties measurement system (PPMS) with a relaxation technique. Synchrotron x-ray powder diffraction measurement was performed with an incident wavelength of 0.7778 Å at SPring-8 BL02B2.[17] Rietveld analysis of the diffraction data was performed with Rietan-2000.[18]

Figure 1(a) shows the inverse magnetic susceptibility ($1/\chi$) per V mole of $SrV_xGa_{12-x}O_{19}$ with various values of x. For $x=2$, $1/\chi(T)$ is almost linear against temperature T indicating a simple Curie-Weiss behavior. With increasing x, the slope of $1/\chi(T)$ below 50 K increases; i.e., the magnitude of a Curie constant per V mole decreases as summarized in the inset. In addition, $1/\chi(T)$ up to 600 K for larger x exhibits a nonlinear behavior against T, and $1/\chi(T)$ for $x=8$ exhibits a clear S-shape T dependence. Such a S-shape $1/\chi(T)$ has been observed in spinel AlV_2O_4,[15] where $\chi(T)$ is given by the sum of a Curie-Weiss term and a spin-gap term. In the present $SrV_xGa_{12-x}O_{19}$ with large x, a similar interpretation is probable as discussed below.

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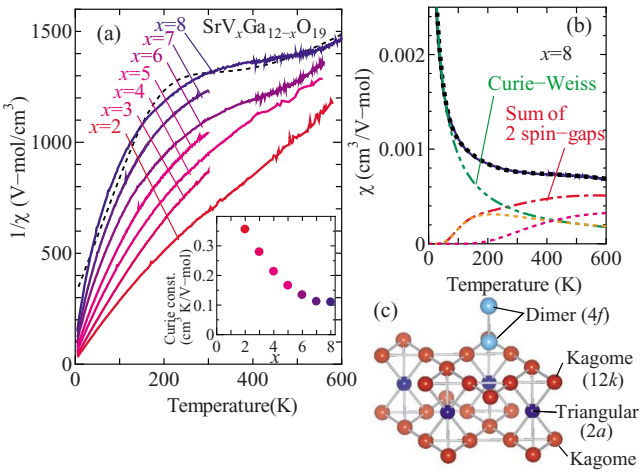

FIG. 1. (Color online) (a) Inverse magnetic susceptibility of $SrV_xGa_{12-x}O_{19}$ per V mole with various values of x at 0.1 T. The dashed line indicates the result of the fitting for $x=8$ by the sum of one Curie-Weiss term and one spin-gap term. The inset shows the x dependence of a Curie constant per V mole below 50 K. (b) Magnetic susceptibility data of $x=8$ (a solid line) and the fitting result (a dashed line, barely seen because it follows the solid line) by the sum of a Curie-Weiss term (a dot-dot-dashed line) and two spin-gap terms (each by dashed lines and the sum by a dot-dashed line.) (c) Schematic picture of the arrangement of the V ions in $SrV_xGa_{12-x}O_{19}$.

A distinct difference between $SrV_xGa_{12-x}O_{19}$ and $SrCr_xGa_{12-x}O_{19}$ is observed in the low-T specific heat $C(T)$. It is known that in $SrCr_xGa_{12-x}O_{19}$, a large broad peak of specific heat appears below 20 K, as also observed in the present experiment [Fig. 2(a)]. This peak arises from the removal of the spin entropy of the Cr^{3+} ions ($S=3/2$), which survives down to low temperatures because of the absence of long-range ordering, and the corresponding entropy amounts to ~50% of the total spin entropy.[7] However, such a large peak of the magnetic specific heat is absent in $SrV_xGa_{12-x}O_{19}$, as shown in Fig. 2(a). Instead, a small increase in $C(T)/T$ is observed for $x>0$, which can be attributed to a part of the spin entropy for the V ions ($S=1$).

To estimate the spin entropy per V ions, $C(T)$ of $SrGa_{12}O_{19}$ (without V) with appropriate rescaling was subtracted as the phonon contribution from all other data, and

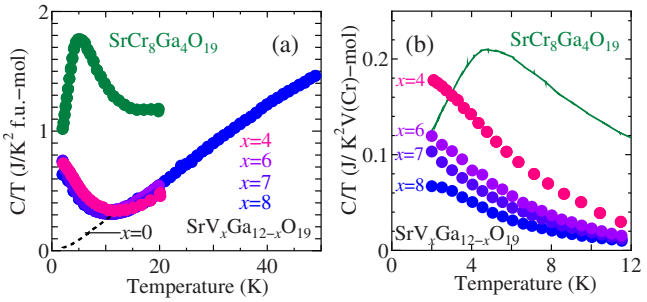

FIG. 2. (Color online) (a) Specific heat of $SrV_xGa_{12-x}O_{19}$ and $SrCr_8Ga_4O_{19}$ per formula-unit ($SrV_xGa_{12-x}O_{19}$) mole. (b) Magnetic specific heat per V (or Cr) mole divided by temperature for $SrV_xGa_{12-x}O_{19}$ and $SrCr_8Ga_4O_{19}$.

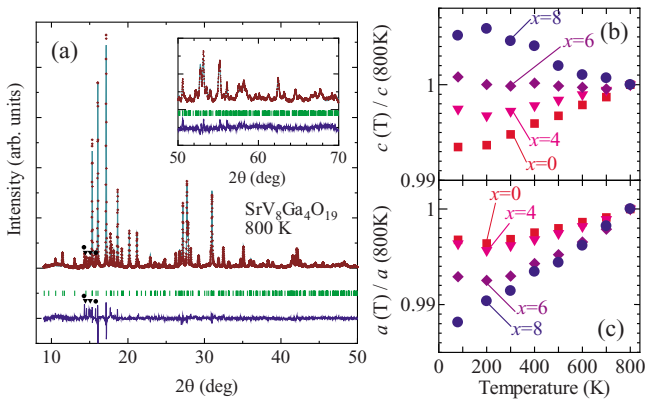

FIG. 3. (Color online) (a) Synchrotron x-ray powder diffraction patterns (plus marks) and Rietveld refinement patterns (solid lines) of $SrV_8Ga_4O_{19}$ at 800 K with $\lambda=0.7778$ Å. The vertical marks indicate the position of Bragg peaks, and the solid line at the bottom corresponds to the difference between observed and calculated intensities. Small closed circles and triangles are those from nonmagnetic impurity phases ($Sr_3V_2O_8$ and $Sr_{10}V_6O_{25}$). The inset is the expanded figure at higher angles $2\theta=50-70°$. [(b) and (c)] Temperature dependence of a and c lattice constants normalized to the values at 800 K.

the magnetic part of $C(T)/T$ per V mole was obtained and plotted in Fig. 2(b). As can be seen, the magnetic part of $C(T)/T$ per V mole decreases with increasing the V contents x. The magnitude of the spin entropy can be estimated by integrating $C(T)/T$ over T shown in Fig. 2(b). By assuming the T^2 relation of $C(T)$, which is the case for Cr,[7] as the extrapolation of the data below 2 K, the spin entropy for $x=8$ is estimated as 0.43 J/V-mol K.[19] This value is only ~5% of the total spin entropy of the V spins ($S=1$), R log 3=9.13 J/V-mol K, indicating that most of the spin entropy of V are removed at higher temperatures. It should be noted that no other anomaly of specific heat is observed up to 50 K, and no anomaly is observed in magnetic susceptibility up to 600 K. Thus, it is unlikely that there is an antiferromagnetic ordering at higher temperature and that is the reason of the suppression of the low-T spin entropy in $SrV_xGa_{12-x}O_{19}$.

In order to obtain the information about how spin entropy is removed at higher temperatures from a structural viewpoint, we measured the synchrotron x-ray powder diffraction of $SrV_xGa_{12-x}O_{19}$ with various values of x and temperatures between 80 and 800 K and made a Rietveld analysis of the data. As an example, the diffraction pattern and the result of the Rietveld analysis of $SrV_xGa_{12-x}O_{19}$ with $x=8$ at 800 K is shown in Fig. 3(a),[20] and the parameters obtained from the analysis are listed in Table I. Figures 3(b) and 3(c) show the temperature dependence of the a and c lattice constants. For $x=0$, both the a and the c lattice constants exhibit a gradual decrease with decreasing T, which can be attributed to a normal thermal expansion. On the other hand, for $x=8$, the a lattice constant exhibits a larger decrease whereas the c lattice constant exhibits an increase with decreasing T, i.e., negative thermal expansion. It should be noted that the unit-cell volume $V \propto a^2c$ shows an almost comparable T dependence for different x values.

TABLE I. Atomic parameters of $SrV_xGa_{12-x}O_{19}$ with $x=8$ at 800 K from the Rietveld analysis of the synchrotron x-ray powder diffraction data. Space group is $P6_3/mmc$, and lattice constants are $a=5.8215(1)$ Å and $c=23.3360(4)$ Å. Site occupation numbers are 0.5 for Ga at 4*e*, 0.79/0.21 for V/Ga at 2*a* (triangular lattice), 0.82/0.18 for V/Ga at 4*f* (dimer), and 0.93/0.07 for V/Ga at 12*k* (kagome lattice). No occupation of V for the Ga (4*e*) and the Ga (4*f*) sites was confirmed also by Rietveld analysis and is set to zero in the present analysis. $R_{wp}=12.21\%$ and $R_e=3.37\%$. The Debye-Waller factors *B* of the oxygens are the same from the constraint in the analysis.

Atom (site)	*x*	*y*	*z*	*B* (Å^2)
Sr (2*d*)	2/3	1/3	1/4	3.32(8)
V/Ga (2*a*)	0	0	0	0.4(1)
Ga (4*e*)	0	0	0.2642(2)	0.8(1)
Ga (4*f*)	1/3	2/3	0.0282(1)	0.53(5)
V/Ga (4*f*)	1/3	2/3	0.1930(1)	1.1(1)
V/Ga (12*k*)	0.1722(2)	0.3444(4)	−0.10755(7)	0.67(4)
O (4*e*)	0	0	0.1485(4)	0.87(7)
O (4*f*)	1/3	2/3	−0.0516(5)	0.87(7)
O (6*h*)	0.185(1)	0.370(2)	1/4	0.87(7)
O (12*k*)	0.1604(8)	0.321(2)	0.0525(3)	0.87(7)
O (12*k*)	0.5046(7)	0.009(1)	0.1509(2)	0.87(7)

Next, let us see how V-V length is varied with *T*. In the kagome-lattice layer of $SrV_xGa_{12-x}O_{19}$ with the magnetoplumbite structure, there are two crystallographically inequivalent V triangles [Fig. 4(b)]. One V triangle (A) is connected to a V ion on the triangular-lattice layer next to the kagome-lattice layer with a tetrahedral configuration, which is then connected to a V triangle A in the next kagome-lattice layer also with a tetrahedral configuration [see also Fig. 1(c)]. The other V triangle (B) is not directly connected to any V ions with a tetrahedral configuration. As shown in Fig. 4(a), for $x=0$ ($SrGa_{12}O_{19}$), the Ga-Ga length in triangle A is larger than that in triangle B by ~2%, which is almost comparable to that of the Cr-Cr length in $SrCr_8Ga_4O_{19}$.[6] However, with increasing *x*, the difference of the V-V length in triangle A and B becomes larger (~14% for $x=8$ at low temperature), and furthermore, the V-V length exhibits a large *T* dependence; that in triangle B decreases whereas that in triangle A increases with decreasing *T*. The contraction of triangle B for $x=8$ amounts to 4% from 800 to 100 K, more than the change of the *a* lattice constant, and this can be regarded as the "trimer" formation of the V ions on the kagome lattice. The larger decrease in the *a* lattice constant with *T* for larger *x* shown in Fig. 3(c) is dominated by this V trimerization. On the other hand, we could not find any specific V-V bonds along the *c* axis to exhibit anomalous *T* dependence. One possible origin of the negative thermal expansion along the *c* axis for $x=8$ is the long-range strain of the crystal to keep the thermal volume change modest; a too large contraction along the plane inevitably leads to the elongation along the *c* axis.

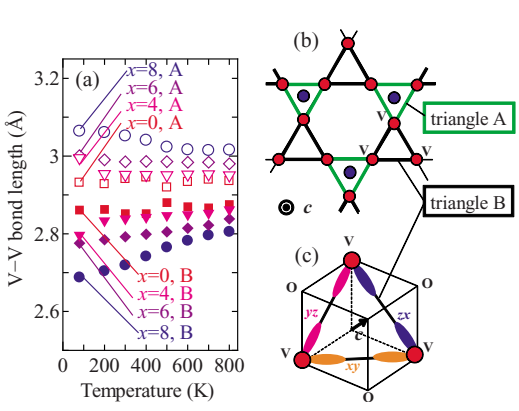

FIG. 4. (Color online) (a) V-V (Ga-Ga) bond length on triangle A (open symbols) and B (closed symbols) for $SrV_xGa_{12-x}O_{19}$. (b) Kagome lattice with two inequivalent triangles, A and B. (c) Orbital ordering of the t_{2g} states (*xy*, *yz*, and *zx* states) for three V ions on triangle B.

This trimerization of the V ions on the kagome lattice resembles that observed in $LiVO_2$ with the V triangular lattice. According to Pen *et al.*,[12] the trimerization of the V ions and the formation of the spin-singlet state at 500 K in $LiVO_2$ is caused by the ordering of the t_{2g} orbitals in the V ions. A similar orbital-ordering scenario can be applied to the V trimerization of the present compounds: on each of the three V-V bonds on triangle B, a bonding state consisting of either two *xy* orbitals, two *yz* orbitals, or two *zx* orbitals is formed, which can accommodate two electrons, and thus, six electrons supplied by three V^{3+} ions ($3d^2$) are accommodated in three bonding states and form a spin-singlet state [Fig. 4(c)]. (Note that a similar trimerization and a spin-singlet state on the V kagome lattice was reported for ferromagnetic NaV_6O_{11}.[21–23]) It should be pointed out that there are several differences between $LiVO_2$ and $SrV_xGa_{12-x}O_{19}$. (a) Since triangles A and B are crystallographically inequivalent from the beginning, there is no phase transition to form the orbital-ordered spin-singlet state in $SrV_xGa_{12-x}O_{19}$. (b) Though all the V ions on the kagome-lattice layer can form a spin-singlet state, there are two other sites for the V ions, the "dimer" sites and the "triangular-lattice" sites, as shown in Fig. 1(c). Even though the V ions at the dimer sites can form a spin-singlet state as spin pairs, which is the case even for $SrCr_xGa_{12-x}O_{19}$ with $S=3/2$,[6] the V ions on the triangular-lattice site between two adjacent kagome-lattice layers cannot easily form a spin singlet.

On the basis of this spin-structure model, let us discuss the *T* dependence of magnetic susceptibility $\chi(T)$ and specific heat $C(T)$. The spin-singlet ground state of the V kagome lattice contributes to a spin-gap term in $\chi(T)$, $D/[T\{3+\exp(E_g/k_BT)\}]$, whereas the V spins on the triangular lattice contribute to a Curie-Weiss term, $C/(T-\theta)$. We first fitted $\chi(T)$ of $SrCr_xGa_{12-x}O_{19}$ with $x=8$ by assuming one spin-gap term and one Curie-Weiss term. The result of the fitting is shown by a dashed line in Fig. 1(a). Though the fitting can reproduce the overall feature of the S-shape $\chi(T)$, it quantitatively deviates from the experimental data, particularly at low *T*. We next fitted the data by assuming two spin-gap terms and one Curie-Weiss term, and the result of the fitting and each component are shown by dashed lines in Fig. 1(b). The obtained

parameters are as follows: $D_1=0.53$ cm^3 K/mol, $E_{g1}=3.4\times10^2$ K, $D_2=1.93$ cm^3 K/mol, $E_{g2}=1.16\times10^3$ K, $C=0.11$ cm^3 K/mol, and $\theta=-17$ K. One possible interpretation for the existence of two spin-gap terms is that each corresponds to that for the trimers on the kagome lattice and that on the dimer sites. Considering the number of the V sites on the kagome lattice (=6) and on the dimer (=2), it is likely that E_{g1} corresponds to the dimer and E_{g2} to the trimer. Another possibility is that the magnitude of the spin-gap term is distributed in the sample probably due to the randomness effect arising from a small amount of Ga substitution, and such a distribution of the spin-gap magnitude is represented by the two spin-gap terms. From the fitting, the number of the $S=1$ spins contributing the Curie-Weiss term was estimated as ~10% of the total V ions. This value is almost comparable to the number of V at the triangular-lattice site (=1/8 if all the sites are occupied by V).

The low-T increase in the specific heat can be also attributed to the V spins on the triangular lattice.[24] One may argue that the entropy of this part (5% of the total spin entropy) is too small compared with the number of the V ions on the triangular lattice (1/8 of the total V ions). However, even in $SrCr_xGa_{12-x}O_{19}$, in which all the Cr spins contribute to spin frustration, the spin entropy below 100 K reaches only 50% of the total spin entropy. Thus, it is reasonable to assume that frustrating spins with $S=1$ exist on the triangular lattice between spin-singlet kagome layers, which contribute to the low-T specific heat. It should be also pointed out that both magnetic susceptibility [Fig. 1(a)] and specific heat [Fig. 2(b)] indicate the increase in the number of spins per V with decreasing the number of V (or increasing the number of Ga). This can be attributed to the appearance of magnetic moment on the kagome lattice associated with the collapse of the spin-singlet V trimers with nonmagnetic Ga doping.

In conclusion, we studied kagome-like magnets having V^{3+} ions ($3d^2$), $SrV_xGa_{12-x}O_{19}$ with magnetoplumbite structure. We found that V trimers with spin-singlet states are formed on the kagome lattice, presumably caused by the ordering of the t_{2g} orbitals, whereas the V ions on the triangular lattice (between two kagome-lattice layers) remain as $S=1$ frustrated spins. The present result indicates a spontaneous formation of spin singlet states and frustrated spins in one crystal, in which orbital degrees of freedom play an important role.

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