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Low-Dimensional Ferromagnetic Properties of $SrCuV_2O_7$ and $BaCuV_2O_7$

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The crystal structure of isostructural $SrCuV_2O_7$ and $BaCuV_2O_7$ consists of one-dimensional (1D) zigzag chains of Cu atoms with next-nearest-neighbor interaction. The main intrachain interaction was found to be ferromagnetic and estimated at 4.6 K (Hamiltonian $H \sim -2J$). $SrCuV_2O_7$ and $BaCuV_2O_7$ are new examples in the scanty family of 1D ferromagnets. Isothermal magnetization measurements at 0.08 K and specific heat data showed that $MCuV_2O_7$ exhibits antiferromagnetic long-range ordering at $T_N = 1.36$ K for $SrCuV_2O_7$ and $T_N = 1.47$ K for $BaCuV_2O_7$. Spin-flop transitions were observed in the antiferromagnetic state at 0.08 K near 0.5 kOe in $SrCuV_2O_7$ and 2 kOe in $BaCuV_2O_7$. In air, $SrCuV_2O_7$ and $BaCuV_2O_7$ melted incongruently above 983 and 1018 K, respectively.

1. Introduction

The properties of low-dimensional magnets continue to be of great interest to physicists and chemists.[1] One of the reasons for such interest is to understand superconducting properties of the two-dimensional copper oxides. Of the many possible combinations of dimensionality and spin quantum number (S), one combination which has been conspicuous by the lack of realizations is the one-dimensional (1D) $S = 1/2$ Heisenberg ferromagnet.[2−4] The numerous studies on 1D magnetic systems have been on antiferromagnets, for example, $S = 5/2$ Heisenberg (Mn^{2+}), $S = 1$ (Ni^{2+}, Haldane system), $S = 1/2$ Ising (Co^{2+}), and $S = 1/2$ Heisenberg (Cu^{2+}) systems. However, there are only few examples of the 1D $S = 1/2$ Heisenberg ferromagnets, for example, $(CH_3)NCuCl_3$,[2] $[(CH_3)_3NH]_3Cu_2Cl_7$,[2] $K_2Cu_{0.59}Zn_{0.41}F_4$ (diluted two-dimensional ferromagnet),[5] some organic radical compounds,[3,4,6] and the most studied $(C_6H_{11}NH_3)CuBr_3$ and $(C_6H_{11}NH_3)CuCl_3$.[7−9] The 1D $S = 1/2$ Ising ferromagnets are presented, for example, by $CoCl_2*2H_2O$, $CoBr_2*2H_2O$, $RbFeCl_3*2H_2O$, and $CoCl_2(NC_5H_5)_2$.[7]

1D ferromagnets are particularly of interest because quantum effects are expected to be most pronounced in them. The anisotropies of J values (Ising-type contribution), even if they are very small, give rise to a qualitative change in the thermodynamical quantities, especially in an applied field, for 1D ferromagnets in comparison with 1D antiferromangets.[2,3,9] Theoretically, the 1D $S = 1/2$ Heisenberg ferromagnet has been investigated a lot.[10−12] However, the comparison of theory and experiments is restricted by a very small number of the 1D $S = 1/2$ Heisenberg ferromagnets.

Magnetic sublattice in two isostructural compounds $SrCuV_2O_7$ (space group *Pnma*, $a = 14.470$ Å, $b = 5.4704$ Å, and $c = 7.4201$ Å)[13] and $BaCuV_2O_7$,[14] whose magnetic properties have not been investigated yet, can be presented, from the structural point of view, by a model of the double chain or by a model of the uniform zigzag chain with next-

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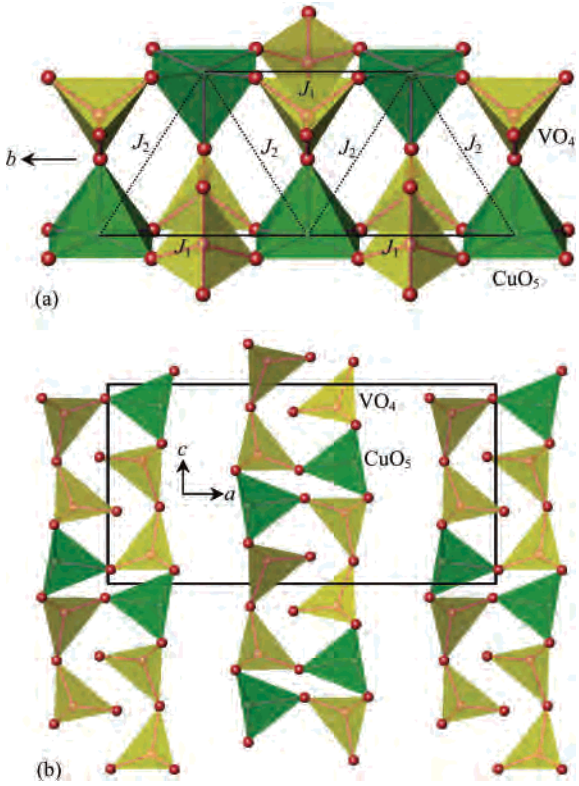

Figure 1. (a) The double Cu chain in $SrCuV_2O_7$ along the *b* axis (or uniform zigzag chain with next-nearest-neighbor interaction). (b) The arrangement of the double Cu chains in the crystal structure of $SrCuV_2O_7$: projection along the *b* axis.

nearest-neighbor (NNN) interaction[15] (Figure 1a) along the *b* axis (Figure 1b). These models are described by two exchange constants, J_1 and J_2. There is one Cu site in $MCuV_2O_7$ (M = Sr and Ba), and the Cu atom has a square pyramidal coordination. The Cu atoms are connected with each other through super-superexchange interactions[16] including two Cu−O···O−Cu paths, where the O···O is an edge of VO_4 groups (Figure 1a). The basal planes of the CuO_5 pyramids lie on one plane and the Cu−O···O angles are 134.3° and 134.6° (for $SrCuV_2O_7$). Such a type of connection between magnetic ions usually gives rather strong antiferromagnetic interaction ($J_1 \sim -50$ K, Hamiltonian $H = -2J_1\Sigma S_iS_{i+1}$).[17] On the other hand, the connection between Cu atoms responsible for J_2 includes long apical Cu−O bonds (Figure 1a), and one of the Cu−O···O angles (149.3° and 98.0° for $SrCuV_2O_7$) is close to 90°. J_2 was therefore expected to be very small. As a result, we expected vanadates $MCuV_2O_7$ (M = Sr and Ba) to be simple uniform 1D $S = 1/2$ linear chain Heisenberg antiferromagnets such as phosphates $SrCuP_2O_7$[17] and $BaCuP_2O_7$.[18] However, phosphates $SrCuP_2O_7$ and $BaCuP_2O_7$ have different crystal structures in comparison with vanadates $MCuV_2O_7$ (M = Sr and Ba).

Surprisingly, magnetic properties of $MCuV_2O_7$ (M = Sr and Ba) resembled those observed for the 1D $S = 1/2$ Heisenberg ferromagnets. In This Paper, we present the results of specific heat and dc and ac magnetization measurements in different static magnetic fields. These results evidence on the 1D ferromagnetic properties of $MCuV_2O_7$ (M = Sr and Ba). $SrCuV_2O_7$ and $BaCuV_2O_7$ are new examples in the scanty family of the 1D $S = 1/2$ ferromagnets.

2. Experimental Section

Synthesis. $SrCuV_2O_7$, $BaCuV_2O_7$, and $BaZnV_2O_7$ were synthesized from stoichiometric mixtures of $SrCO_3$ (99.99%), $BaCO_3$ (99.99%), CuO (99.9%), ZnO (99.99%), and V_2O_5 (99.8%) by the solid-state method. The mixtures were pressed into pellets and allowed to react at 943 K ($SrCuV_2O_7$ and $BaCuV_2O_7$) and 873 K ($BaZnV_2O_7$)[19] for 200 h with four intermediate grindings on Pt plates. X-ray powder diffraction (XRD) data collected with a RIGAKU RINT 2500 diffractometer (2θ range of 5−60°, a step width of 0.02°, and a counting time of 1 s/step) showed that the three samples were monophasic. $SrCuV_2O_7$ and $BaCuV_2O_7$ were khaki green and $BaZnV_2O_7$ was pink. $BaZnV_2O_7$ is isotypic[19] with $BaCuV_2O_7$ and can be used to estimate the lattice contribution in the specific heat. $SrZnV_2O_7$ crystallizes, however, in a different structure type (space group $P2_1/n$).[20]

Magnetic and Specific Heat Measurements. Direct current (dc) magnetic susceptibility ($\chi = M/H$) was measured on a Quantum Design SQUID magnetometer (MPMS XL) between 2 and 300 K in an applied field of 100 Oe under both zero-field-cooled (ZFC) and field-cooled (FC) conditions. Isothermal magnetization curves were recorded between −50 and +50 kOe at 2, 3, 4, 5, 10, and 15 K. Magnetization data at 0.08 K were taken in a pulsed magnetic field up to 150 kOe by an induction method using a multilayer pulse magnet at KYOKUGEN, Osaka University. Alternating current (ac) susceptibility measurements were performed with a Quantum Design PPMS instrument in the temperature range of 1.8−30 K (on cooling) at frequencies (f) of 10, 10^2, 5×10^2, and 10^3 Hz, applied oscillating magnetic field (H_{ac}) of 1 Oe, and different static magnetic fields (H_{dc}) ranging from 0 to 20 kOe. Specific heat, C_p versus T, of $SrCuV_2O_7$ and $BaCuV_2O_7$ was recorded between 0.45 and 300 K (between 1.8 and 170 K for $BaZnV_2O_7$) on cooling at zero magnetic field by a pulse relaxation method using a commercial calorimeter (Quantum Design PPMS). At magnetic fields of 5, 10, 30, 50, and 90 kOe, the C_p versus T data were taken between 2 and 21 K for $SrCuV_2O_7$ and $BaCuV_2O_7$.

Thermal Analysis. Thermal stability of $SrCuV_2O_7$, $BaCuV_2O_7$, and $BaZnV_2O_7$ was examined under air with a MacScience TG-DTA 2000 instrument. The samples were placed in Pt crucibles, heated, and then cooled with a rate of 10 K/min. $SrCuV_2O_7$ was heated to 1013 K, $BaCuV_2O_7$ up to 1058 K, and $BaZnV_2O_7$ up to 1073 K. Differential thermal analysis (DTA) showed peaks at 993 and 998 K on heating and at 976 and 917 K on cooling for $SrCuV_2O_7$; at 1029, 1033, and 1047 K on heating and a very broad peak at 887 K on cooling for $BaCuV_2O_7$; and at 1047 K on heating and broad peaks at 978 and 905 K on cooling for $BaZnV_2O_7$. Such inconsistency of heating and cooling behavior suggests that $SrCuV_2O_7$, $BaCuV_2O_7$, and $BaZnV_2O_7$ melt incongruently above 983, 1018, and 1033 K, respectively. No structural phase transition was detected by DTA in $BaZnV_2O_7$ at 943 K.[19]

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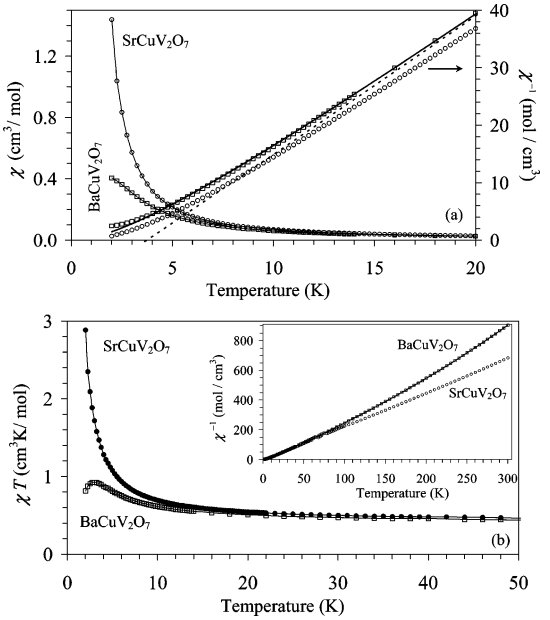

Figure 2. (a) The χ vs T (symbols with line) and χ^{-1} vs T (symbols) curves measured at 100 Oe for $SrCuV_2O_7$ and $BaCuV_2O_7$. The solid line for the χ^{-1} vs T curve shows the fit to eq 2 and the dashed line presents the fit to eq 1 for $BaCuV_2O_7$ as an example. (b) The χT vs T curves between 2 and 50 K for $SrCuV_2O_7$ and $BaCuV_2O_7$. Inset gives the χ^{-1} vs T curves for $SrCuV_2O_7$ and $BaCuV_2O_7$ between 2 and 300 K with the Curie−Weiss fit for $BaCuV_2O_7$.

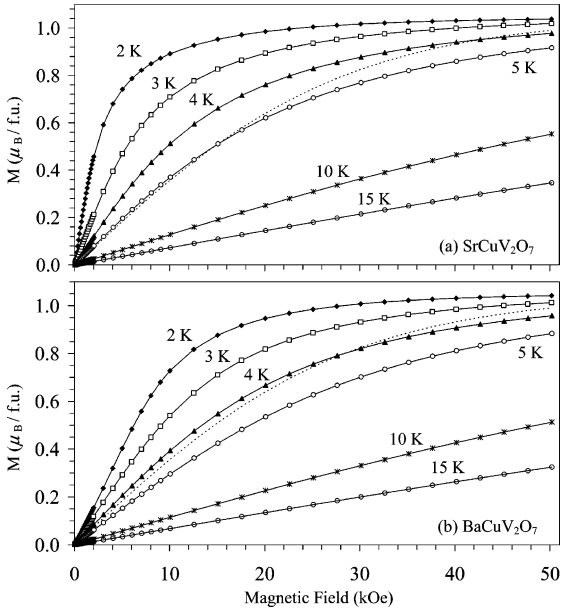

Figure 3. Isothermal magnetization curves, M vs H, at 2, 3, 4, 5, 10, and 15 K for (a) $SrCuV_2O_7$ and (b) $BaCuV_2O_7$. The dotted lines are the $S = 1/2$ Brillouin function with $g = 2.1$ at 2 K.

3. Results and Discussion

Figure 2a depicts the χ versus T and χ^{-1} versus T curves for $SrCuV_2O_7$ and $BaCuV_2O_7$. No noticeable difference was found between the ZFC and FC curves. The χ versus T curves showed no broad maxima characteristic of low-dimensional antiferromagnets. The χ values increased with decreasing temperature in the whole temperature range of 2−300 K. Thus, $SrCuV_2O_7$ and $BaCuV_2O_7$ are not low-dimensional antiferromagnets. The χ^{-1} versus T data at 15−300 K were fitted by a modified Curie−Weiss expression

$$\chi(T) = \chi_0 + C/(T - \theta) \qquad (1)$$

with temperature independent term $\chi_0 = -6(7) \times 10^{-6}$ cm^3/mol, Curie constant $C = 0.440(2)$ cm^{3}K/mol, and Weiss constant $\theta = 3.4(2)$ K for $SrCuV_2O_7$ and $\chi_0 = -3.17(2) \times 10^{-4}$ cm^3/mol, $C = 0.4219(5)$ cm^{3}K/mol, and $\theta = 3.75(7)$ K for $BaCuV_2O_7$. The positive Weiss constant indicates that the main interaction between Cu atoms is ferromagnetic. Below about 15 K, the χ^{-1} versus T curves deviated from the Curie−Weiss law. The similar behavior of the χ^{-1} versus T curves was observed in other 1D ferromagnets.[3,4,12] The χT versus T curve for $SrCuV_2O_7$ demonstrated the sharp increase at low-temperature region while the χT versus T curve for $BaCuV_2O_7$ exhibited a broad maximum at 3 K (Figure 2b). Taking into account the structural features of $SrCuV_2O_7$ and $BaCuV_2O_7$, the positive Weiss constants are the first indication that $SrCuV_2O_7$ and $BaCuV_2O_7$ are a 1D $S = 1/2$ ferromagnetic system.

To roughly estimate the main intrachain interaction, we used the model of the uniform 1D $S = 1/2$ Heisenberg ferromagnet,[3,4] that is, assuming that J_1 is dominant ($J_1 \gg J_2$) or J_2 is dominant ($J_2 \gg J_1$)

$$\chi(T) = \chi_0 + \frac{Ng^2\mu_B^2}{4k_BT}\left[1 + \left(\frac{J_1}{k_BT}\right)\right] \qquad (2)$$

where N is Avogadro's number, g is the spectroscopic splitting factor (g-factor), μ_B is the Bohr magneton, and k_B is Boltzmann's constant. Equation 2 is valid for $k_BT/J_1 > 1$. The fitting of the χ^{-1} versus T curves to eq 2 between 5 and 300 K yields $\chi_0 = 1.0(7) \times 10^{-5}$ cm^3/mol, $g = 2.151(5)$, and $J_1/k_B = 4.6(2)$ K for $SrCuV_2O_7$ and $\chi_0 = -3.10(1) \times 10^{-4}$ cm^3/mol, $g = 2.1131(9)$, and $J_1/k_B = 4.58(6)$ K for $BaCuV_2O_7$.

The real part of the ac susceptibility curves, χ' versus T, at zero static magnetic field almost coincided with the dc χ versus T curves measured at 100 Oe. Strong dependence of the χ' versus T curves on static magnetic field, H_{dc}, was found and a broad maximum appeared on the χ' versus T curves from $H_{dc} = 2$ kOe for $SrCuV_2O_7$ and $H_{dc} = 10$ kOe for $BaCuV_2O_7$.[7] No noticeable difference was found for the χ' versus T curves measured at different frequencies.

Isothermal magnetization curves are given in Figure 3. No hysteresis was observed on the M versus H curves. The saturation of magnetization occurred at about 40 kOe for $SrCuV_2O_7$ and 50 kOe for $BaCuV_2O_7$ at 2 K. The saturation value of about 1.05 μ_B/mol was expected for $S = 1/2$ and $g \approx 2.1$. Such magnetization curves were observed in other 1D $S = 1/2$ ferromagnets.[2,8,12] The experimental magnetization data for $SrCuV_2O_7$ and $BaCuV_2O_7$ saturated much faster than expected for the $S = 1/2$ Brillouin function with $g = 2.1$ (Figure 3). This fact shows the dominating ferromagnetic interaction between Cu^{2+} ions.

Figure 4 depicts the M versus H and dM/dH versus H curves for $SrCuV_2O_7$ and $BaCuV_2O_7$ at 0.08 K, that is, below the temperatures of long-range magnetic ordering (see the

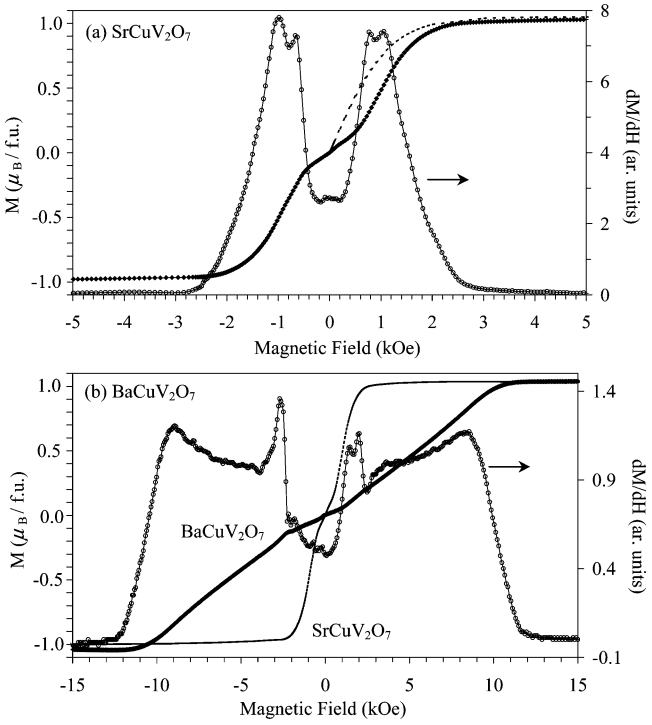

Figure 4. (a) The M vs H and dM/dH vs H curves for $SrCuV_2O_7$ at 0.08 K between −5 and 5 kOe. The dotted line is the $S = 1/2$ Brillouin function with $g = 2.1$ at 0.08 K. (b) The M vs H and dM/dH vs H curves for $BaCuV_2O_7$ at 0.08 K between −15 and 15 kOe. The M vs H curve for $SrCuV_2O_7$ is also shown for comparison.

specific heat data). The saturation magnetization was the same, 1.05 μ_B/mol. At low magnetic fields, the magnetization increased linearly with the field and slower than expected for the $S = 1/2$ Brillouin function with $g = 2.1$. No hysteresis was found and the M versus H curves passed through the origin. These facts indicate that the 1D ferromagnetic chains are ordered antiferromagnetically in both $SrCuV_2O_7$ and $BaCuV_2O_7$. At about 0.5 kOe for $SrCuV_2O_7$ and 2 kOe for $BaCuV_2O_7$, the slope change of the M versus H curve because of a spin flop transition was detected in the antiferromagnetic state. The small value of the magnetic field for the spin flop transition reflects the very small value of the interchain interaction. The dM/dH versus H curve for $SrCuV_2O_7$ clearly exhibited two peaks near 0.5 kOe. Thus, two-step spin flop transition is possible.

The C_p/T versus T curves for $SrCuV_2O_7$, $BaCuV_2O_7$, and $BaZnV_2O_7$ are given in Figure 5a. The C_p was almost the same in the temperature range of 40−300 K for $MCuV_2O_7$ (M = Sr and Ba). The M sublattice seems to give the same constant contribution to the specific heat. This behavior is quite unusual because in the series of isostructural compounds, the heavier atoms give the larger contribution to C_p.[17,21] On the other hand, the specific heat of $BaZnV_2O_7$ was larger than that of $BaCuV_2O_7$ in the temperature range of about 13−150 K (Figure 5). This fact shows that the sublattice of the transition-metal ion has a very strong effect on C_p, that is, even a small change in the mass results in the strong change in C_p. The estimation of the lattice contribution, C_l, in $MCuV_2O_7$ (M = Sr and Ba) was therefore not straightforward. The lattice contribution was estimated between 16 and 21 K using the equation

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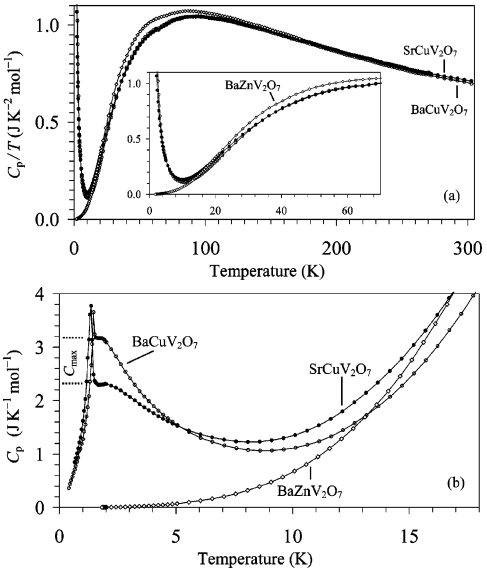

Figure 5. (a) Temperature dependence of C_p/T for $SrCuV_2O_7$, $BaCuV_2O_7$, and $BaZnV_2O_7$. Inset shows the enlarge fragment of the figure. (b) The C_p vs T curves up to 18 K for $SrCuV_2O_7$, $BaCuV_2O_7$, and $BaZnV_2O_7$.

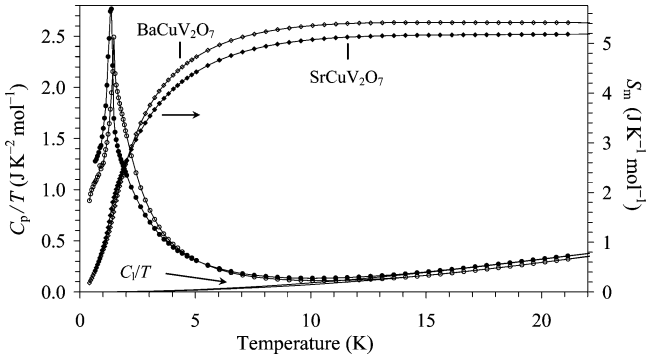

Figure 6. The C_p/T vs T and S_m vs T curves for $SrCuV_2O_7$ and $BaCuV_2O_7$. The solid lines show the lattice contribution (C_l/T vs T curves).

$$C_l\,(=C_p) = \beta_1 T^3 + \beta_2 T^5 \qquad (3)$$

with $\beta_1 = 9.38 \times 10^{-4}$ J K^{-4} mol^{-1} and $\beta_2 = -3.56 \times 10^{-7}$ J K^{-6} mol^{-1} for $SrCuV_2O_7$ and $\beta_1 = 7.21 \times 10^{-4}$ J K^{-4} mol^{-1} and $\beta_2 = -3.86 \times 10^{-9}$ J K^{-6} mol^{-1} for $BaCuV_2O_7$. Then, this equation was extended to the lower temperature region.

The magnetic entropy, $S_m(T) = \int(C_m/T)dT$, where $C_m = C_p - C_l$, was close to $R \ln 2 \approx 5.76$ J K^{-1} mol^{-1} expected for the $S = 1/2$ systems (5.17 J K^{-1} mol^{-1} for $SrCuV_2O_7$ and 5.42 J K^{-1} mol^{-1} for $BaCuV_2O_7$; Figure 6). This fact gives the support that the estimation of C_l is reasonable. However, the reduced values of S_m show that the C_l was overestimated.

The very large difference in the values of broad maximum, C_{max}, of the zero-field specific heat curves (Figure 5) for $SrCuV_2O_7$ ($C_{max} = 2.30$ J K^{-1} mol^{-1}) and $BaCuV_2O_7$ ($C_{max} = 3.16$ J K^{-1} mol^{-1}) was quite noticeable. This fact shows that the ferromagnetic intrachain interaction is affected by

different J_2 (if J_1 is dominant) or J_1 (if J_2 is domimant), interchain interactions, or anisotropies.[10,22] In the series of isostructural 1D $S = 1/2$ antiferromagnets, for example, $MCuP_2O_7$ (M = Ca, Sr, and Pb),[17,18] the values of C_{max} are almost the same ($C_{max} \approx 3.0$ J K^{-1} mol^{-1}) and are consistent with the theoretical value. In addition to the broad maxima, the specific heat data also exhibited the sharp peaks at 1.36 K for $SrCuV_2O_7$ and 1.47 K for $BaCuV_2O_7$ because of long-range antiferromagnetic ordering (Figures 5). The C_p versus T curves for $SrCuV_2O_7$ and $BaCuV_2O_7$ were strongly affected by static magnetic field as for other 1D ferromagnets.[3,6,8−10]

A spin exchange constant, J, is expressed as $J = J_{AF} + J_F$, where J_{AF} and J_F are the antiferromagnetic and ferromagnetic contributions, respectively.[23] J_{AF} is proportional to OI^2, where OI is the overlap integral between magnetic $x^2 - y^2$ orbitals of Cu^{2+} ions. Therefore, when OI is almost zero, the J_F will dominate and the spin exchange becomes ferromagnetic.

Strong dependence of the sign and strength of J values on the Cu−O−Cu bridge angle is well-known in copper dimers bridged by two Cu−O−Cu paths.[24,25] The exchange interaction is usually ferromagnetic for the Cu−O−Cu angle less than 97° and antiferromagnetic for the larger angles. However, this simple rule does not work in some compounds, for example, organic complexes containing tetranuclear or trinuclear clusters of Cu^{2+} ions.[26−28] In ref 28, the ferromagnetic interaction was found between Cu^{2+} ions having the Cu−O−Cu angles of 139.2−140.5°.

In $SrCuV_2O_7$ and $BaCuV_2O_7$, the situation is more complicated because Cu^{2+} ions are connected through super-superexchange interactions, Cu−O···O−Cu. The strength and sign of exchange interaction obviously depend on many parameters including bond length and angles and the nature of the chemical bonds in TO_4 (T = P or V) tetrahedra. In particular, the overlap between two Cu^{2+} magnetic orbitals associated with the Cu−O···O−Cu paths depends on the overlap between two p orbitals of oxygen residing on the O···O contact. Intuitively, the shorter the O···O distance (i.e., the edge of TO_4 tetrahedron), the larger the overlap between p orbitals.[16] For phosphate groups, PO_4^{3-} or $P_2O_7^{4-}$, the O···O distance is usually 2.5−2.55 Å. On the other hand, for vanadate groups, VO_4^{3-} or $V_2O_7^{4-}$, the O···O distance is about 2.7−2.8 Å. This fact can qualitatively explain why J is antiferromagnetic in such one-dimensional compounds as $SrCuP_2O_7$,[17] $BaCuP_2O_7$,[18] and $(VO)_2P_2O_7$,[29] while J is ferromagnetic in $SrCuV_2O_7$ and $BaCuV_2O_7$ despite the fact that they have similar connections between magnetic ions, that is, including Cu−O···O−Cu or V−O···O−V paths.

We hope that this work will encourage theoreticians to investigate the model shown in Figure 1a for (anti)-ferromagnetic J_1 and (anti)ferromagnetic J_2 in more details. The exact quantitative description of $SrCuV_2O_7$ and $BaCuV_2O_7$ and determination of J values requires numerical calculations and experiments using single crystals. In particular, the first principle calculations may help to distinguish between two possibilities: (1) coupled ferromagnetic chains ($J_1 > J_2$) and (2) zigzag chains with NNN interaction ($J_2 > J_1$).

In conclusion, all the results obtained and the structural features of $SrCuV_2O_7$ and $BaCuV_2O_7$ confirm that these two compounds behave as the 1D $S = 1/2$ ferromagnets. The typical features of 1D ferromagnets observed in $SrCuV_2O_7$ and $BaCuV_2O_7$ include (1) positive Weiss constant in the Curie−Weiss fitting, (2) strong field dependence of the specific heat and the real part of the ac susceptibility, (3) strong composition dependence of the value of broad maximum of the specific heat, and (4) fast saturation of the isothermal magnetization curves. $SrCuV_2O_7$ and $BaCuV_2O_7$ are therefore new examples in the scanty family of the 1D $S = 1/2$ ferromagnets.

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Supporting Information Available: Experimental XRD patterns for $SrCuV_2O_7$, $BaCuV_2O_7$, and $BaZnV_2O_7$ (Figures S1−S2). TG and DTA curves for $SrCuV_2O_7$, $BaCuV_2O_7$, and $BaZnV_2O_7$ (Figure S3). The real part of the ac susceptibility, χ' versus T, at different static magnetic fields for $SrCuV_2O_7$ and $BaCuV_2O_7$ (Figures S4 and S5). The C_m versus T and excess heat capacity curves at different static magnetic fields for $SrCuV_2O_7$ and $BaCuV_2O_7$ (Figures S6 and S7) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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