Phase Transitions of $\alpha$-Sr$_2$VO$_4$ with K$_2$NiF$_4$-type Structure

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Abstract
The electronic ground state of $\alpha$-Sr$_2$VO$_4$ has been a matter of interest for a decade because of a possible competition between a small Jahn-Teller effect, spin-orbit interactions, and exchange interactions. Nevertheless, the phase transitions of the compound have not been clearly characterized by experiments due to a difficulty in synthesizing good samples. In this study, three phase transitions were recognized at $T_1 = 101$ K, $T_2 = 127$ K, and $T_N = 10$ K by magnetic and thermal measurements for well-characterized samples. The transitions at $T_1$ and $T_2$ are independent structural transitions, and so the existence of an intermediate phase between them is strongly suggested. The transition at $T_N$ is a canted antiferromagnetic or ferrimagnetic ordering. Some anomalous bendings were observed in magnetization curves below $T_N$. These facts are discussed based on the theoretical models proposed.

Keywords: Sr$_2$VO$_4$, phase transition, orbital, octupole

1 Introduction
$\alpha$-Sr$_2$VO$_4$ was first synthesized by Cyrot et al. in 1990 immediately after the discovery of high $T_C$ cuprates [1]. Since then, it has attracted attention because it is a counter compound of the high $T_C$ cuprates regarding the electron-hole symmetry [2, 3]. Recently, the electronic ground state of the compound has become a matter of great interest owing to the predictions of non-trivial spin- and orbital-order [4, 5] and magnetic octupole order [6].

The V compound has K$_2$NiF$_4$-type structure with $I4/mmm$ space group. The VO$_6$ octahedron with one 3$d$ electron is elongated along the $c$-axis, and so the electron occupies the doubly-degenerated $d_{yz}$ and $d_{zx}$ orbitals according to the crystal field approximation. The $d_{xy}$ orbital is located at the energy level about 80 meV higher than that of the degenerated orbitals. The non-trivial order is theoretically found to be caused by quantum fluctuations assuming some plausible ordering patterns, although the exact ordering pattern likely depends on the system size for the calculation [4, 5]. Interestingly the quantum fluctuations enhance the occupancy of the electrons in the $d_{xy}$ orbitals. In this case, the ground state is less affected by spin-orbit interaction [5], which is typically about 30 meV for the V ions. On the other hand, if the spin-orbit interaction is taken into consideration for a single V ion with the crystal field, the interactions between two V ions lead to the magnetic octupole order because of in-plane
anisotropy by Hund’s coupling [6]. In cases where there is no covalency between V and O ions, the magnetic dipole moments completely disappear.

Experimental elucidation of the electronic state is obviously important. It is believed that a drop in the magnetic susceptibility near 97 K is a key transition for the elucidation [7]. However, no consensus has been established about the origin of the drop. The fact that good samples were hard to synthesize has harassed experimental advance in the research. Indeed, magnetic properties, such as the magnitude of the drop and absolute value of magnetic susceptibility even at high temperatures, depended strongly on samples as seen in reference [8]. We recently succeeded in establishing the synthesis method of the compound, and found that magnetic dipole order appears only below $T_N \sim 8$ K [9]. This fact naively seems to support the non-trivial order, but the magnetic octupole order has not been ruled out, because inelastic neutron scattering measurements have revealed the excitation between the Kramers doublets expected by the spin-orbit coupling [10]. Even if the spin-orbit interactions are of primary importance, small dipole moments are caused by the covalency and their ordering may coexist with the octupole ordering below $T_N$ due to a minor axial anisotropy. In this situation, after all, the origin of the drop near 97 K is presumably a key to solving the ground state, and so the characterization of the phase transitions in a good sample is highly desired.

This is a part of proceedings of ICM 2015, where magnetic properties of isostructural Sr$_2$CrO$_4$ will be presented together with those of the V compound. In this paper, the characterization of the phase transitions of the latter compound is focused because the other parts of the presentation have already been reported elsewhere [9, 11].

2 Experimental

α-Sr$_2$VO$_4$ powder sample was synthesized by structural transformation from β-Sr$_2$VO$_4$ [9]. β-Sr$_2$VO$_4$ was sealed in Pt capsule in a glove box filled with Ar gas, pressed using a belt-type press at 7.7 GPa, and heated at 1700°C for 1hr. The temperature was quenched to room temperature after the synthesis and the pressure was gradually released to ambient. The sample was taken out of the Pt capsule in the glove box. In the previous report [9], the transformation was carried out under 4 GPa at 1300°C for 2hrs. However, sample quality becomes better as higher pressure and temperature are applied within $P \leq 7.7$ GPa and $T \leq 1700$°C. Data was also collected using a different sample, which was made by transformation under 7.5 GPa at 1500°C for 1 hr from the mixture with the nominal composition of Sr$_4$VO$_{4.01}$.

The oxygen content of the β-Sr$_2$VO$_{4+\delta}$ sample was estimated from weight increase by oxidation into SrO and Sr$_3$V$_2$O$_8$, to be $\delta = 0.005 \pm 0.002$. About 200 mg sample was weighed in the glove box within the accuracy of 0.01 mg, using electronic balance, XP205DR (Mettler Toledo). Repeatability of the weight was perfect for several measurements. The sample was heated at 800°C in flowing oxygen gas for several hours in the tube furnace, and then the oxygen gas was stopped to flow Ar gas. The gas exchange is needed to prevent a part of SrO from changing into SrO$_2$ while the sample is cooled down. Without this process, weight increase is overestimated and so the $\delta$ value is largely underestimated. Such a $\delta$ value is irreproducible and unreliable. For example, the $\delta$ values of $-0.27$ and $-0.15$ were obtained without the gas exchange. The error of $\pm 0.002$ was estimated assuming the weights of the sample before and after the oxidation include the error of 0.015 mg according to the specification of the balance. The $\delta$ estimation was performed for four batches of samples with the nominal composition of $\delta = 0$, and no difference was observed. The $\delta$ value estimated by this method is always 0.004–0.005 larger than nominal compositions even for off-stoichiometric samples.

Sample characterization was performed using powder X-ray diffraction (XRD) with X’Pert
Pro MPD (PANalytical). No impurity phase was detected for the stoichiometric sample, whereas small peaks assignable to Sr$_3$V$_2$O$_8$ were observed for the off-stoichiometric sample with the nominal composition of Sr$_2$VO$_4$$_{01}$. The off-stoichiometry of $\delta = 0.015$ causes 1.5 mol. % of Sr$_3$V$_2$O$_8$ and SrO, the latter of which easily absorbs water in air and so is hard to detect by the XRD measurements. The appearance of Sr$_3$V$_2$O$_8$ indicates that the oxygen content of the main phase becomes maximum at the synthesis condition, and strongly suggests that the $\delta$ value of the stoichiometric sample is null because Sr$_3$V$_2$O$_8$ would have appeared if the $\delta$ value were negative. No significant difference in magnetic susceptibility was observed between the stoichiometric and off-stoichiometric samples. Specific heat data of the two samples also agree with each other except around the transitions at 101 K and 127 K; the specific heat of the off-stoichiometric sample were apparently about 10% larger than that of the stoichiometric sample although the peak temperatures are completely the same between them.

Magnetic measurements were carried out using MPMS-XL (Quantum Design). Zero-field cooling data was obtained, as the sample was cooled to 2 K after the superconducting magnet of MPMS-XL was heated above the superconducting transition temperature to eliminate as much residual current as possible. The temperature dependence of magnetic data between 70 K and 150 K was obtained as temperature continuously increased and decreased with the rate of 0.5 K/min. Magnetization curve was measured with decreasing field from 7 T to −0.1 T at each temperature. Specific heat data were collected using PPMS (Quantum Design) by the relaxation method. The absolute values of the specific heat around the transitions shown below may be inaccurate because the relaxation method is, in principle, unsuitable for measuring a first-order phase transition. This is one of the main reasons why the 101 K peak size of the off-stoichiometric sample is different from that of the stoichiometric sample. In addition, thermal contact between a sample and sample stage always became poor at around 101 K due to a large structural change [7]. In this paper, $T$, $H$, $M$, $\chi$, and $C_p$ represent temperature, magnetic field, magnetization, magnetic susceptibility, and specific heat, respectively. The magnetic susceptibility is defined simply as $\chi = M/H$ or as the slope of the magnetization curve at low fields. A spontaneous magnetization is defined to be the value at which magnetization curve intersects the $M$ axis. All the data shown here were collected using only two samples of the stoichiometric and off-stoichiometric ones, although the reproducibility of the data was confirmed using some samples made individually.

3 Results & Discussion

Temperature dependence of magnetic susceptibility measured under 1 T are shown in Fig. 1. In addition to the large drop below $T_1 = 101$ K, a small hump is detected at $T_2 = 127$ K. Specific heat also has anomalies at these exact temperatures. In the previous report [7], it was deduced that, although a short-range orbital order started to develop below 122 K, the transition occurred only at 97 K, where the magnetic susceptibility showed a minimum. The present data clearly indicate that there are two phase transitions at $T_1$ and $T_2$, and that they correspond to the maximum of the susceptibility and the hump, respectively.

Magnetic susceptibility and specific heat data collected on cooling and heating are shown in Fig. 2. The small thermal hysteresis with approximately 1 K width is seen for the transition at $T_1$, showing that the transition is of the first order. Magnetic susceptibility measured on cooling is slightly larger than that on heating just below $T_1$. The difference becomes smaller with decreasing temperature and disappears around 60 K. On the other hand, the other transition has no clear hysteresis, and so the order of the transition is unclear just from these data. These transition temperatures depend less on magnetic field as shown in Fig. 1b.
Figure 1: Temperature dependences of magnetic susceptibility under 1 T (a) and specific heat under various fields (b). The dotted lines show \( T_1 \) and \( T_2 \). The solid lines in panel a show the fit lines by Curie-Weiss law (see the text). The broken lines in panel b just connect the data points.

It has been considered that two phases coexist between 94 K and 122 K, because in this temperature region x-ray diffraction revealed the splitting of the (200) Bragg peak [7]. We also have observed similar split between \( \sim 95 \) K and 125 K by powder x-ray and neutron diffraction measurements. However, considering the existence of two phase transitions and the small or absent hysteresis, it is less plausible that the two-phase region is so extensive; an intermediate phase most likely exists [12]. Namely, the high-temperature phase is changed into the intermediate phase at around \( T_2 \), and then the intermediate phase is transformed into the low-temperature phase with a narrow temperature region of two-phase coexistence. Indeed, in our case, the ratio of the diffraction peak intensity of the split peaks appeared almost constant at higher temperatures [12].

Curie constant, \( C \), and Weiss temperature, \( \Theta \), were estimated from the reciprocal susceptibility data between 20 K and 60 K (low), and between 200 K and 300 K (high), to be \( C_{\text{low}} = 0.089 \text{ emu K/mol} \) and \( \Theta_{\text{low}} = -19 \text{ K} \), and \( C_{\text{high}} = 0.29 \text{ emu K/mol} \) and \( \Theta_{\text{high}} = -75 \text{ K} \), respectively. As seen in Fig. 1a, the fits depend, to some extent, on the temperature range of the fit. However, certainly the \( C_{\text{high}} \) value is significantly smaller than the theoretical value of \( C_{\text{theory}} = 0.375 \text{ emu K/mol} \) for \( g = 2 \) and \( S = 1/2 \). According to the current fit, the \( C_{\text{high}} \) value is only 78% of \( C_{\text{theory}} \). Covalency between V and O ions, quantum fluctuations, and existence of orbital moments may be considered as possible origins of the reduction. From the \( \Theta_{\text{high}} \) value, the superexchange interaction between neighboring V ions may be estimated to be 19 K (\( \approx 1.6 \text{ meV} \)), assuming only the nearest-neighbor interactions within the mean-field theory. This seems to justify the theoretical treatment to consider the spin-orbit interactions and crystal field prior to exchange interactions. On the other hand, the Curie constant at low temperatures are approximately 31% of that at high temperatures. Naively thinking, the number of magnetic moments becomes about 1/3, or the effective moment on each V site shrinks by 45%. However, it should be noted that simple Curie-Weiss law may not be applicable based on either the theoretical model of the non-trivial order or the magnetic octupole order. In the former model, magnetic moments caused by the spins on the V sites may heterogeneously interact with each other because of the various orbital states; Kugel-Khomskii type interactions [13] should be considered in the orbital ordered state. In the latter model, Zeeman splitting for
the dipole moments at V sites is extremely inhomogeneous when magnetic field is applied for a powder sample; only the $g$ value along the $c$ axis becomes finite with the covalency [6].

Magnetic dipole ordering occurs at $T_N = 10$ K as seen in Fig. 3. Small spontaneous magnetization appears below $T_N$. The muon spin rotation measurements proved the staggered dipole ordering [9]. Thus, the spontaneous magnetization can be due to canting of the antiferromagnetically ordered moments. However, if the $I4/mmm$ space group is preserved below $T_N$, there is an inversion symmetry between two adjacent V ions, which indicates no Dzyaloshinsky-Moriya interaction between them. So, the canted antiferromagnetic ordering is unlikely under this assumption. It should be noted that ferrimagnetic ordering may occur in a non-trivial ordered state, in which the expectation values of magnetic moments on the V sites are not uniform [4, 5].

The entropy corresponding to the shaded area in Fig. 3 was estimated to be 0.71, which is only 12% of Rln2 (R: gas constant). It suggests that the transition there is of the first order. Indeed, small jump appears to exist at $T_N$ in the specific heat data. The transition temperature is almost independent of magnetic field as shown in Fig. 4, which can be attributed to the first-order nature; in case of a conventional second-order magnetic ordering with appearance of spontaneous magnetization, there appears a crossover, not a transition, from a paramagnetic to a magnetically ordered state under a finite magnetic field. This is because the symmetry breaking is caused by the magnetic field even in the paramagnetic state, and so the crossover temperature usually increases with increasing field. The first order nature of the magnetic transition, of course, does not prevent the development of magnetic correlations. Indeed, in addition to the small jump, the critical behavior is partially seen just above $T_N$. Thus, it is reasonable to consider the possibility that the development of magnetic correlations induces electrical quadrupole (orbital) ordering to cause the first-order transition.

The magnetic transition at $T_N$ was always observed when the transitions at $T_1$ and $T_2$ appeared. So, the transition itself is robust. On the other hand, the spontaneous magnetization was rather scattered, for example, between $\sim 0.001 \mu_B/f.$ u. and $\sim 0.002 \mu_B/f.$ u. at 2 K. There
Figure 3: Temperature dependence of magnetic susceptibility measured on cooling under 0.001 T(a) and specific heat under zero field.

may still remain a room to improve the synthesis condition or the sample characterization, although residual magnetic fields during the magnetization curve measurements might cause the variation.

Magnetization curves below $T_N$ usually show three small anomalies at around 1 T, 4 T, and 6 T at 2 K, as seen in the differentiated curve in Fig. 5. Although these anomalies were not observed in all samples, at least the anomaly at the lowest field is related to the magnetic ordering at $T_N$ because the characteristic field decreases with increasing temperature and disappears at $T_N$ as shown in Fig. 5b. The phase diagram is depicted as shown in Fig. 5c, assuming that the 1T anomaly is caused by a transition. At present, it is uncertain whether the anomaly is due to a transition or crossover. This behavior is far from the typical temperature dependence of spin-flop transition in a field, which is almost constant with temperature because magnetic anisotropy is less dependent on temperature. In case that the anomaly is a spin-flop
Figure 5: Magnetization curve and the differentiated curve at 2 K for the stoichiometric sample (a), the differentiated magnetization curves of the off-stoichiometric sample at various temperatures (b), phase diagram below 14 K up to 2.1 T (c). The broken lines in panel b just connect the data points. In panel c, the black circles are the peak fields of the differentiated magnetization curves of the off-stoichiometric sample, and the black and red squares are the peak temperatures of the specific heat of the off-stoichiometric and stoichiometric samples, respectively. The field dependence of $T_N$ of the former sample is expected to be almost the same as that of the latter because the specific heat of the former under 0 T, 4.5 T and 9 T had the peaks at 9.8 K, 9.8 K, and 9.6 K, respectively.

transition, it seems that the phase diagram is similar to that of Mn$_2$XS$_4$ (X = Si, Ge) [14, 15], although the present compound has spontaneous magnetization even at 0 K under zero magnetic field. The thermal or quantum fluctuations may play a certain role in the spin-flop-like anomaly, as in the case of Mn$_2$XS$_4$. As another possibility, the phase diagram may be a reflection of the ordering of two kinds of degrees of freedom in the ground state. Certainly, it is hard to simply conclude that they show critical behaviors toward $T_N$ and $H = 0$, because all the phase boundaries likely have first-order nature even if the anomaly seen in the magnetization curve is a transition. Nevertheless, it should be pointed out that a similar phase diagram will be derived if the magnetic dipole moments and electrical quadrupole moments (orbital degree of freedom) shows critical behaviors, which happen to be cut off by the weak first-order transitions due to structural modification related with the orbital/electrical quadrupole ordering.

As is seen in Fig. 5, the appearance of the anomalies is dependent on the samples. It is not due to the excess oxygen. The sample with the nominal composition of Sr$_2$VO$_4$.02 showed a less prominent anomaly at 1 T than the stoichiometric sample. No clear origin of the difference in the appearance has been detected although more than 20 kinds of samples were used to find out factors related to the appearance of the anomalies. The fragility may suggest that the electronic ground state is very sensitive to small perturbations like crystal defects.

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