An orbital glass state of a nearly metallic spinel, CoV$_2$O$_4$

R. Koborinai, 1 S.E. Dissanayake, 2 M. Reehuis, 3 M. Matsuda, 4 S.-H. Lee, 2 and T. Katsufuji 1, 5

1Department of Physics, Waseda University, Tokyo 169-8555, Japan
2Department of Physics, University of Virginia, Charlottesville, Virginia 22904, USA
3Helmholtz-Zentrum für Materialien und Energie, 14109 Berlin, Germany
4Quantum Condensed Matter Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, U.S.A
5Kagami Memorial Research Institute for Materials Science and Technology, Waseda University, Tokyo 169-0051, Japan

(Dated: May 20, 2015)

Strain, magnetization, and unpolarized and polarized neutron diffraction measurements were performed to study the magnetic and structural properties of spinel CoV$_2$O$_4$. Magnetostriiction measurements indicate that a subtle distortion of the crystal along the direction of magnetization, $\Delta L/L \sim 10^{-4}$, exists and varies from elongation to contraction in a second order fashion upon cooling. Unpolarized and polarized single-crystal neutron experiments indicate that upon cooling the ferrimagnetic structure changes from collinear to noncollinear at $T \sim 90$ K, where the elongation of the crystal is maximized. These results imply the existence of an orbital glassy state in the nearly metallic frustrated magnet CoV$_2$O$_4$.

PACS numbers: 75.25.Dk,75.25.-j,75.80.+q,75.50.Gg

The interplay between magnetic frustration and orbital degree of freedom has been extensively studied in various transition-metal oxides. Among them, spinel vanadates AV$_2$O$_4$, in which the magnetic V$^{3+}$ [t$_{2g}$] ions form a highly frustrated three-dimensional corner-sharing network of tetrahedra, are model systems to search for novel emergent phases. With non-magnetic A$^{2+}$ ions (A = Zn, Cd), upon cooling the system undergoes a first order structural phase transition due to an orbital long range order followed by a bi-partite magnetic order [1-3]. With magnetic A$^{2+}$ ions such as Mn, Fe and Co, additional spin exchange interactions between A$^{2+}$ and V$^{3+}$ ions come into play to exhibit more complex behaviors. For example, the insulating MnV$_2$O$_4$ [4, 13] exhibits a first order structural phase transition from cubic to tetragonal (with a shorter c axis) and ferrimagnetic order with a noncollinear V spin structure [2] simultaneously at $T_C = 57$ K. This phase transition is dominated by the Kugel-Khomskii-type interactions that are the intersite interactions between orbital and spin degrees of freedom of the V ions. Another insulating FeV$_2$O$_4$ [14-22], exhibits, upon cooling, successive structural phase transitions from a cubic to a high-temperature tetragonal to an orthorhombic, and to a low-temperature tetragonal phase (with a longer c axis), which are caused not only by the orbital degree of freedom of V ions but also of Fe$^{3+}$ (3d$^6$, e$_g^2$t$_{2g}$) ions [14].

The spinel CoV$_2$O$_4$ [Co$^{2+}$: e$_g^4$t$_{2g}^3$, V$^{3+}$: t$_{2g}^2$] provides a unique situation due to its close proximity to itineracy [22-28]. Unlike in the insulating AV$_2$O$_4$ (A = Mn, Fe), no observed crystal distortion has been observed in CoV$_2$O$_4$ down to 10 K by x-ray diffraction, while a similar ferrimagnetic order as in the insulating compounds was detected below $T_C \simeq 150$ K by DC magnetization [23]. More recently, a neutron scattering study on Mn$_{1-x}$Co$_x$V$_2$O$_4$ proposed, by extrapolating from $x \leq 0.8$, the disappearance of orbital order for higher Co concentration ($x \geq 0.8$) due to the enhancement of itineracy [28]. On the other hand, bulk magnetization ($M_{\text{bulk}}(T)$) data obtained from polycrystalline samples of CoV$_2$O$_4$ showed two cusps centered at 60 and 100 K, and specific heat, $C_V$, data exhibited one peak at 60 K and a broad peak centered at $T_C$, which was attributed to a short-range orbital order [23]. This contradicts a previous single crystal study that reported one cusp in $M_{\text{bulk}}(T)$ at 75 K and no corresponding anomaly in $C_V$ [24]. More recently, dielectric measurements on a single crystal reported a contraction along the direction of the applied magnetic field below 30 K [27]. Despite the conflicting results, the anomalies below $T_C$ observed in the different measurements suggest that the orbital degree of freedom might be playing an important role also in this compound although the associated lattice distortion might be too small to be easily detected. This calls for the use of experimental probes that are more sensitive to such subtle changes in magnetic and structural properties that might exist in this nearly metallic spinel.

In this paper, we report on the strain, magnetization, and unpolarized and polarized neutron diffraction measurements of single crystals and polycrystalline samples of CoV$_2$O$_4$. The most salient feature of our data is that, upon cooling, the system undergoes weak lattice elongation below $T_C$, of an order of $\Delta L_{\text{max}}/L \sim 10^{-4}$ in a second order fashion, which differs from the strong, first order crystal distortions due to orbital long range order found in the other insulating vanadium spinels. Upon further cooling, the distortion continuously changes from elongation ($\Delta L/L > 0$) to contraction ($\Delta L/L < 0$). The structural change is accompanied by changes in the ordered magnetic state. We argue that the unusual structural and magnetic behaviors are due to the system’s proximity to the itineracy that incompletely suppresses
the orbital degree of freedom leading to a glassy orbital state.

The single crystals of CoV$_2$O$_4$ were grown by the floating zone technique. When a polycrystalline rod with a stoichiometric amount of Co and V ($= 1:2$) is used, a large single crystal of CoV$_2$O$_4$ cannot be grown because of the precipitation of the V$_2$O$_3$ impurity phase. Thus, the single crystals in this study were grown with extra Co. The Co-V ratios of the #1 and #2 single crystals were estimated by induction-coupled plasma analysis and found it to be 1.21:1.79 and 1.3:1.7, respectively. At the same time, polycrystalline samples with excess amounts of Co, Co$_{1+x}$V$_{2-x}$O$_4$ ($x = 0, 0.1$ and $0.2$) were synthesized for comparison in sealed quartz tubes. The bulk magnetization measurement on the samples was performed using a SQUID magnetometer. Strain measurements were performed using a strain-gauge technique. Neutron powder diffraction measurements were carried out on the BT1 powder diffractometer at the NIST Center for Neutron Research with a Cu(311) monochromator ($\lambda = 1.5398$ Å), and the Rietveld refinements were carried out using the FULLPROF program. Single crystal neutron diffraction measurements were performed on the four-Circle Diffractometer E5 at the BERII reactor of the Helmholtz-Zentrum Berlin with neutron wavelengths of $\lambda = 2.4$ Å and 0.9 Å. Polarized elastic neutron scattering experiments were performed at HB1 Polarized Triple-Axis Spectrometer at the High Flux Isotope Reactor, Oak Ridge National Laboratory with neutron energy of 13.5 meV. A vertical guide field of 3 T was applied using 8 T Vertical Asymmetric Field Cryomagnet.

Fig 1 (a) shows the temperature ($T$) dependence of $M_{bulk}$ obtained from a single crystal of CoV$_2$O$_4$ (#1) with an applied magnetic field ($H$) of 0.1 T along the [100] direction. $M_{bulk}(T)$ increases below the ferrimagnetic transition temperature $T_C \sim 165$ K (black circles). Unlike in the case of polycrystalline samples, anomalies in $M_{bulk}(T)$ below $T_C$ are barely visible in the single crystal data. When the same crystal was ground to a powder, however, $M_{bulk}(T)$ exhibits a clear anomaly at $T_p = 45$ K (red circles). The weak anomaly at $T_p$ can also be seen in $M_{bulk}(H)$ measured at several different temperatures around $T_p$. As shown in Fig. 1 (b), $M_{bulk}(H)$ exhibits hysteresis due to the presence of ferromagnetic components. The inset shows the $T$-dependence of the coercive field $H_c$ at which $M$ becomes zero. $H_c(T)$ exhibits a dip centered at $T_p = 45$ K.

Fig. 2 shows the strain ($\Delta L/L$) data obtained from the #1 single crystal when the magnetic field is applied along the [100] direction, $H \parallel [100]$, as a function of $H$ and $T$. As shown in Fig. 2 (a) and (b), upon ramping up, the strain, both parallel ($\Delta L_{//}/L$) and perpendicular ($\Delta L_{\perp}/L$) to $H$, do not show any response to $H$ for $T > T_C$. Below $T_C$, however, the strain exhibits a strong response. Interestingly, the strain response to $H$ shows an opposite behavior between the two temperature regimes, above and below $\sim 40$ K. For $40 \leq T < T_C$, as $|H|$ increases up to 0.2 T, $\Delta L_{//}/L$ sharply increases while $\Delta L_{\perp}/L$ sharply decreases by a much smaller amount. Upon further ramping, the change in $\Delta L/L$ becomes gradual. For $T \leq 40$ K, however, the strain response is opposite; upon ramping up to 0.2 T, $\Delta L_{//}/L$ sharply decreases by a small amount while $\Delta L_{\perp}/L$ sharply increases by a much larger amount.

The $T$-dependence of the sharp response at low field,
measured with $|H| = 0.2$ T is shown in Fig. 2 (c). Upon cooling, $\Delta L_{ij}/L( T, |H| = 0.2$ T) (red circles) starts increasing gradually below $T_C$, reaches its maximum value of $\sim 2 \times 10^{-4}$ at $\sim 100$ K. Upon further cooling, it decreases, and becomes negative below $\sim 45$ K to reach $\sim -4 \times 10^{-5}$ at $\sim 10$ K. On the other hand, upon cooling, $\Delta L_{ij}/L( T, |H| = 0.2$ T) (blue triangles) decreases gradually to $\sim -2.5 \times 10^{-5}$ at $\sim 100$ K, then starts to increase to become positive below $\sim 45$ K and reaches its maximum value of $\sim 2 \times 10^{-4}$ at $\sim 10$ K. The opposite strain response to $H$ between the two $T$ regimes, below and above $\sim 45$ K, is clearly illustrated in the $T$–dependence of the difference $\Delta L_{\text{diff}}/L = (\Delta L_{||} - \Delta L_{\perp})/L$ with $|H| = 0.2$ T shown as the black circles in Fig. 2 (d).

$\Delta L_{\text{diff}}/L$ is the measure of distortion from cubic phase, $\Delta = 1$, where $\alpha$ and $c$ are the lattice constants, assuming that the crystal is tetragonal and the magnetic moments are along the $c$ direction. It should be noted that the temperature, $\sim 45$ K, at which $\Delta L_{\text{diff}}/L$ changes its sign coincides with $T_p$ where $M_{\text{bulk}}(T)$ exhibits a weak anomaly and $H_{c}(T)$ a minimum (see Fig. 1). We emphasize that the crystal distortion $\Delta L_{\text{diff}}/L = \Delta - 1$ changes upon cooling from elongation to contraction, both of which occur in a second order transition. The second order crystal distortion in the nearly metallic CoV$_2$O$_4$ is in stark contrast with the sharp first-order contraction observed in the insulating MnV$_2$O$_4$ (red circles in Fig. 2 (d)).

To investigate how the magnetic state evolves with the changes in the crystal structure, neutron diffraction experiments were performed on polycrystalline and single crystal samples of CoV$_2$O$_4$. Figure 3 (a) shows the neutron powder diffraction data collected at 5 K ($< T_C$) and 180 K ($> T_C$). The overall crystal structure remains cubic with $Fd\bar{3}m$ symmetry down to 5 K. An obvious difference between the 5 K and 180 K data is the strong (111) Bragg intensity at 5 K, which is due to the ferromagnetic order with the characteristic wave vector of $\mathbf{k}_{m} = (0, 0, 0)$. The refinement of the diffraction data at 5 K indicate that the Co$^{2+}$ magnetic moments are ferromagnetically aligned along one principal axis of the cubic spinel (whose direction is defined as the $c$ axis) and the $c$-component of the $V^{3+}$ moments are antiparallel to the Co$^{2+}$ moments. In addition, the V moments are canted from the $c$ axis by $\sim 20(2)^{\circ}$ to the (110) direction, and the $ab$-plane components of the neighboring $V^{3+}$ moments are antiferromagnetically aligned with each other. This magnetic structure is reproducible by the $\Gamma_3$ irreducible representation for the $Fd\bar{3}m$ space group with $\mathbf{k}_{m} = (0, 0, 0)$, as illustrated in Figs. 3 (b). This magnetic structure is similar to that of FeV$_2$O$_4$ at low temperatures [14]. The magnitude of the ordered Co moment at 5 K, $(M_{\text{Co}}) = 2.89(3) \mu_B$, is close to the expected value for the high-spin state of Co$^{2+}$ (3 $\mu_B$), while that of the V moment $(M_V) = 0.71(3) \mu_B$, is much less than the expected value for $V^{3+}$ (2 $\mu_B$) when it is fully polarized. The reduction of the V moment is due to strong frustra-

FIG. 3: (Color online) Neutron powder diffraction data of CoV$_2$O$_4$ measured at (a) 5 K and (b) 180 K. Circles are the experimental data and black lines represent the calculated intensities. Green bars represent nuclear and magnetic Bragg peak positions and blue lines indicate difference between experimental data and calculation. (c) A sketch of the magnetic structures for CoV$_2$O$_4$. Four-circle neutron diffraction measurements on a single crystal (\#2) using a neutron wavelength of $\lambda = 2.4$ Å were also performed as a function of $T$ at several different Bragg $Q$ points. As shown in Fig. 4 (a) and (b), upon cooling, most of the Bragg peaks such as (400), (202), (313), (511) and (111) increase below 169 K $\sim T_C$, exhibit a broad maximum at $\sim 100$ K, and a dip at $\sim 40$ K. This $T$-dependence coincides with the $T$-dependence of the strain: $\Delta L_{ii}/L(H = 0.2$ T) exhibits a broad peak at $\sim 100$ K, and below $\sim 40$ K $\Delta L_{ij}/L(H = 0.2$ T) becomes larger than $\Delta L_{ij}/L(H = 0.2$ T). An exception is the (002) peak that is a forbidden nuclear peak by the $Fd\bar{3}m$ symmetry, and thus expected to be purely magnetic. The (002) peak exhibits a gradual increase below $T_C$ down to 10 K with a very weak dip at $\sim 40$ K.

In order to identify the $T$-dependences of the nuclear and magnetic contributions for the Bragg peaks, we have performed two different measurements. Firstly, unpolarized four-circle diffraction using a neutron wavelength of $\lambda = 0.9$ Å was performed to reach high $Q$ values where magnetic contributions are negligible due to the fall-off
The spin-flip scattering of the (002) Bragg vertical guide field of 3 T was applied along the [1,-1,0] crystal was aligned in the (HHL) scattering plane and a vertical guide field of 3 T was applied along the [1,1,0] direction. The spin-flip scattering of the (002) Bragg reflection, shown in Fig. 4 (d) is proportional to the square of the antiferromagnetic in-plane (110) moments of the V$^{3+}$ ions. Fig. 4 (d) shows the data as a function of T. The (002) intensity remains almost zero for 90 K < T < T_C, and below ~ 90 K it increases sharply and exhibits a maximum at ~ 40 K. The unpolarized and polarized neutron scattering data indicate that upon cooling below T_C the V$^{3+}$ and Co$^{2+}$ moments order ferromagnetically and upon further cooling the V$^{3+}$ moments start canting at T ~ 90 K. By refining the 10 K single crystal diffraction data (see Fig. 4 (e)), the canting angle of the V$^{3+}$ moments is determined to be ~ 10(2)°, which is close to the value of 20(2)° obtained from the powder diffraction. Similar cantings of the V$^{3+}$ moments have been observed in MnV$_2$O$_4$ with the canting angle of ~ 65° [6, 7] and FeV$_2$O$_4$ with that of ~ 55° [10], and they were suggested to closely relate to an orbital order of V$^{3+}$ ($t_{2g}$) ions and the resulting change in their magnetic interactions. The fact that in CoV$_2$O$_4$ the canting occurs at temperatures where the strain $\Delta L/L$ is maximized ($T_{\text{max}}$ ~ 90 K for the #2 crystal [29]) indicates that an orbital order appears at ~ 100 K as well. Unlike in the insulating compounds, MnV$_2$O$_4$ and FeV$_2$O$_4$, where the orbital order occurs in a first order fashion, however, the structural distortion of CoV$_2$O$_4$ is subtle and gradual as a function of temperature. Thus, we conclude that in CoV$_2$O$_4$ its close proximity to the itineracy incompletely suppresses the orbital degree of freedom of the V$^{3+}$ ions, leading to an orbital glass state.

In summary, our bulk magnetization, magnetostriction, and neutron scattering data obtained from polycrystalline and single crystals of the nearly metallic vanadium spinel, CoV$_2$O$_4$, show that upon cooling the system undergoes two successive second order phase transitions at T_C ~ 160 K from a paramagnet to a collinear ferrimagnet, and at ~ 100 K to a noncollinear ferrimagnet and orbital glassy state. Our results suggest that the combination of the magnetostriction and polarized and unpolarized neutron scattering techniques may be powerful in studying the subtle interplays between the orbital and spin degrees of freedom in other materials as well in which fluctuations of the V orbitals are supposed to play an important role.

The work at Waseda university was partly supported by JSPS KAKENHI Grant No. 25287090. Research at UVA was supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under Award No. DE-FG02-07ER46384. We acknowledge the support of the National Institute of Standards and Technology, U. S. Department of Commerce, in providing the neutron research facilities for powder diffraction measurements used in this work. This research at ORNL’s High Flux Isotope Reactor was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy.
Email: sachithd83@gmail.com
Email: katsufu@waseda.jp

[1] Y. Ueda, N. Fujiwara, and H. Yasuoka, J. Phys. Soc. Jpn. 
66, 778 (1997).
[2] S.-H. Lee et al., Phys. Rev. Lett. 93, 156407 (2004).
[3] Z. Zhang et al., Phys. Rev. B 74, 014108 (2006).
[4] T. Suzuki, M. Katsumura, K. Taniguchi, T. Arima, and 
T. Katsufuji, Phys. Rev. Lett. 98, 127203 (2007).
[5] H. D. Zhou, J. Lu, and C. R. Wiebe, Phys. Rev. B 76, 
174403 (2007).
[6] J. H. Chung, J. H. Kim, S. H. Lee, T. J. Sato, T. Suzuki, 
M. Katsumura, and T. Katsufuji, Phys. Rev. B 77, 
054412 (2008).
[7] V. O. Garlea, R. Jin, D. Mandrus, B. Roessli, Q. Huang, 
M. Miller, A. J. Schultz, and S. E. Nagler, Phys. Rev. 
Lett. 100, 066404 (2008).
[8] V. Hardy, Y. Breard, and C. Martin, Phys. Rev. B 78, 
024406 (2008).
[9] S.-H. Baek, N. J. Curro, K.-Y. Choi, A. P. Reyes, P. L. 
Kuhns, H. D. Zhou, and C. R. Wiebe, Phys. Rev. B 80, 
140406 (2009).
[10] S. Sarkar, T. Maitra, R. Valentí, and T. Saha-Dasgupta, 
Phys. Rev. Lett. 102, 216405 (2009).
[11] G.-W. Chern, N. Perkins, and Z. Hao, Phys. Rev. B 81, 
125127 (2010).
[12] Y. Nii, N. Abe, and T. Arima, Phys. Rev. B 87, 085111 
(2013).
[13] S. L. Gleason, T. Byrum, Y. Gim, A. Thaler, P. Abbamonte, 
G. J. MacDougall, L. W. Martin, H. D. Zhou, and S. L. Cooper, 
Phys. Rev. B 89, 134402 (2014).
[14] T. Katsufuji, T. Suzuki, H. Takei, M. Shingu, K. Kato, 
K. Osaka, M. Takata, H. Sagayama, and T. Arima, J. 
Phys. Soc. Jpn. 77, 053708 (2008).
[15] S. Sarkar and T. Saha-Dasgupta, Phys. Rev. B 84, 
235112 (2011).
[16] G. J. MacDougall, V. O. Garlea, A. A. Aczel, H. D. Zhou, 
and S. E. Nagler, Phys. Rev. B 86, 060414 (2012).
[17] Q. Zhang, K. Singh, F. Guillou, C. Simon, Y. Breard, 
V. Caignaert, and V. Hardy, Phys. Rev. B 85, 054405 
(2012).
[18] Y. Nii, H. Sagayama, T. Arima, S. Aoyagi, R. Sakai, 
S. Maki, E. Nishibori, H. Sawa, K. Sugimoto, H. Ohsumi, 
et al., Phys. Rev. B 86, 125142 (2012).
[19] J.-S. Kang, J. Hwang, D. H. Kim, E. Lee, W. C. Kim, 
C. S. Kim, S. Kwon, S. Lee, J.-Y. Kim, T. Ueno, et al., 
Phys. Rev. B 85, 165136 (2012).
[20] S. Kawaguchi, H. Ishibashi, S. Nishihara, M. Miyagawa, 
K. Inoue, S. Mori, and Y. Kubota, J. Phys.: Condens. 
Matter 25, 416005 (2013).
[21] Z. H. Huang, X. Luo, L. Hu, S. G. Tan, Y. Liu, B. Yuan, 
J. Chen, W. H. Song, and Y. P. Sun, J. Appl. Phys. 115, 
034903 (2014).
[22] D. Choudhury, T. Suzuki, D. Okuyama, D. Morikawa, 
K. Kato, M. Takata, K. Kobayashi, R. Kumai, H. Nakao, 
Y. Murakami, et al., Phys. Rev. B 89, 104427 (2014).
[23] A. Kismarahardja, J. S. Brooks, A. Kisman, K. Matsubayashi, 
R. Yamanaka, Y. Uwatoko, J. Whalen, T. Siegrist, and H. D. Zhou, Phys. Rev. Lett. 106, 056602 
(2011).
[24] A. Kisman, J. S. Brooks, J. Lu, J. Whalen, T. Siegrist, 
and H. D. Zhou, Phys. Rev. B 84, 205138 (2011).
[25] Y. Huang, Z. Yang, and Y. Zhang, J. Phys., Condens. 
Matter 24, 056003 (2012).
[26] R. Kaur, T. Maitra, and T. Nautiyal, J. Phys.: Condens. 
Matter 26, 045505 (2014).
[27] A. Kismarahardja, J. S. Brooks, H. D. Zhou, E. S. Choi, 
K. Matsubayashi, Y. Uwatoko, and Y. Uwatoko, Phys. Rev. B 87, 054432 (2013).
[28] J. Ma, J. H. Lee, S. E. Hahn, T. Hong, H. B. Cao, A. A. 
Aczel, Z. L. Dun, M. B. Stone, W. Tian, Y. Qiu, et al., 
Phys. Rev. B 91, 020407 (2015).
[29] T dependence of $M$ and $\Delta L/L$ for other single crystals 
and polycrystalline Co$_{1+x}$V$_{2-x}$O$_4$ are shown and discussed in the supplementary material.
[30] In neutron scattering of a real crystal, which can be regarded as a bunch of many crystal blocks with nearly the same orientation, an incident neutron beam is reflected from many crystal blocks if there is small misorientation between the blocks. However, if the orientation of the crystal blocks are perfect, an upstream crystal block depletes the beam before it reaches a downstream crystal block that has exactly the same orientation and is supposed to reflect the same beam as the upstream crystal. This effect (extinction effect) reduces the scattering intensity of the beam.

[31] In neuron scattering of a real crystal, which can be regarded as a bunch of many crystal blocks with nearly the same orientation, an incident neutron beam is reflected from many crystal blocks if there is small misorientation between the blocks. However, if the orientation of the crystal blocks are perfect, an upstream crystal block depletes the beam before it reaches a downstream crystal block that has exactly the same orientation and is supposed to reflect the same beam as the upstream crystal. This effect (extinction effect) reduces the scattering intensity of the beam.