

## Spontaneous Formation of Vanadium “Molecules” in a Geometrically Frustrated Crystal: $\text{AlV}_2\text{O}_4$

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We investigated the charge-ordered (CO) state in spinel  $\text{AlV}_2\text{O}_4$  by electron diffraction, synchrotron x-ray diffraction, and magnetic measurements. It was found that the CO structure appearing below 700 K is characterized by the formation of V clusters (heptamers), each of which is consisting of 7 vanadium atoms and is in a spin-singlet state as a total. Theoretical consideration indicates that this unique molecularlike V heptamer is stabilized by a strong bonding of vanadium  $t_{2g}$  orbitals.

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Often in the crystal with a fractional number of electrons per site, the electron density, which is uniform over the entire crystal at high temperatures, becomes periodically inhomogeneous at low temperatures. This state, called a charge-ordered (CO) state, is generally observed in strongly correlated electron systems like transition-metal oxides. A famous example of the CO state is a “stripe” state, observed in cuprates [1], nickelates [2], and manganites [3], where doped holes (electrons) on the tetragonal lattice condense into a stripe shape, and the number of electrons at each site become integer. One of the driving forces for the formation of the stripe state is Coulomb repulsion; holes or electrons in the crystal are localized and aligned in a stripe shape to minimize the Coulomb repulsion energy between them. However, in many cases, CO is accompanied by spin and orbital ordering, as best exemplified by the charge ordering in perovskite manganites. In those compounds, a concomitant spin and orbital ordering occurs with CO [4], implying that not only charge but also spin and orbital degrees of freedom play important roles for the formation of such a state. The CO in spinel  $\text{CuIr}_2\text{S}_4$  recently reported [5], which is a rare example of CO in a perfect cubic crystal, is also driven by spin-singlet formations of  $\text{Ir}^{4+}$  dimers [6].

$\text{AlV}_2\text{O}_4$ , in which the average valence of V is  $2.5+$  ( $3d^{2.5}$ ), is another example showing CO on a cubic spinel structure [7,8]. Upon the phase transition into the CO state at 700 K, the electrical resistivity sharply increases and the magnetic susceptibility is suppressed. Previous studies proposed a structural model of the CO, in which the V ions on the kagome lattices and those on the triangular lattices with different valences stack alternately along the [111] direction. However, there are still unsolved problems in this model. For example, both x-ray powder diffraction and electron diffraction (ED) experiments show the pres-

ence of the superlattice structure with the wave vector  $q = 1/2[111]$ , which was not considered in the proposed model of the CO structure.

In this Letter, we show that the CO in spinel  $\text{AlV}_2\text{O}_4$  occurs in such a way that a “heptamer” composed of 7 V atoms and a left-alone V atom orders periodically. In this CO state, the number of electrons per site is still fractional, which is in clear contrast to the stripe state. We show that the stability of the V heptamer in  $\text{AlV}_2\text{O}_4$  is driven by the cooperation of charge, spin, and orbital degrees of freedom of the V ions, analogously to the formation of molecules in the free space.

The  $\text{AlV}_2\text{O}_4$ ,  $\text{AlV}_{2-x}\text{Cr}_x\text{O}_4$ , and  $\text{Al}_{1-x}\text{Mg}_x\text{V}_2\text{O}_4$  polycrystalline samples were synthesized by a conventional solid-state reaction method [7,8]. The electron microscope experiments were carried out in a JEM-2010 transmission electron microscope. Synchrotron x-ray powder diffraction experiments were performed both at the BL-4B2 beam line at the Photon Factory and at the BL02B2 beam line [9] at SPring-8. The x-ray diffraction profile in Fig. 1(c) was obtained using a wavelength of 0.12060 nm at the Photon Factory. Structure refinement was done by the Rietveld method with RIETAN-2000 [10]. Magnetic susceptibility was measured by a SQUID magnetometer.

First of all, we began with the determination of the correct space group of the CO structure to construct a new crystallographic structural model. We carefully investigated various ED patterns at room temperature (in the CO phase) characterized by the presence of the superlattice spots at the  $1/2\ 1/2\ 1/2$ -type positions, in addition to the fundamental spots due to the cubic spinel structure with the space group of  $Fd\bar{3}m$ . From the analysis of the ED patterns, we obtained a complete reciprocal lattice in the CO phase of  $\text{AlV}_2\text{O}_4$ , as shown in Fig. 1(a). The unit cell of the CO structure in  $\text{AlV}_2\text{O}_4$  was depicted schematically in

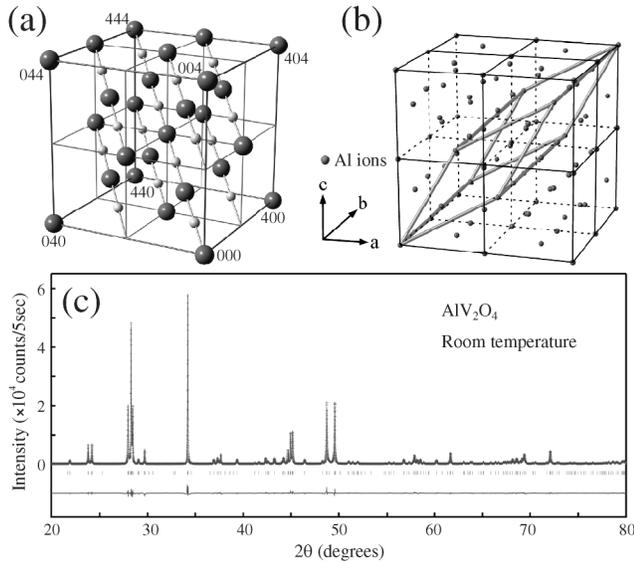


FIG. 1. (a) Complete reciprocal lattice in the CO phase of  $\text{AlV}_2\text{O}_4$ . Large and small circles show fundamental spots due to the cubic spinel structure ( $Fd\bar{3}m$  indexing) and superlattice spots at  $1/2$   $1/2$   $1/2$ -type positions, respectively. The solid line is a guide to the eye. (b) Thick solid lines indicate the rhombohedral unit cell in the CO phase. The small cubic (8 of which forms large cubic) refers to the unit cell of original cubic spinel lattice. Small circles depicted Al ions. (c) Portion of the Rietveld fit of the synchrotron x-ray powder diffraction pattern for  $\text{AlV}_2\text{O}_4$  at room temperature ( $\lambda = 0.12060$  nm.)

Fig. 1(b). We concluded that the CO phase of  $\text{AlV}_2\text{O}_4$  has a rhombohedral structure with the space group of  $R\bar{3}m$ .

As a next step, we have determined the magnitude and the direction of the atomic displacements in the CO phase by refining the synchrotron x-ray powder diffraction data. Here, the starting model for structural refinements was set up based on the reciprocal lattice obtained from the ED experiment. The displacement pattern of each atom was determined using the space-group representation theory. Using this starting model, a full, unconstrained refinement on the x-ray powder diffraction data was performed by the Rietveld method [10]. The overall quality of the fitting was fairly good: profile-weighted  $R$  factor  $R_{\text{wp}} = 7.82\%$ ,  $R$ -Bragg factor  $R_B = 2.10\%$ , and goodness of fit  $s = 1.6054$ . A portion of the Rietveld refinement plots for the synchrotron x-ray profile is shown in Fig. 1(c). The refined structure of the CO phase in  $\text{AlV}_2\text{O}_4$  is displayed in Fig. 2(a) with the V-V bond lengths. Atomic parameters in the CO phase can be shown in Table I.

One characteristic distortion in the CO phase of  $\text{AlV}_2\text{O}_4$  is V clustering. As shown in Fig. 2(a), there are three independent V sites in the hexagonal unit cell, 2 V atoms on the triangular lattice [V1 (yellow) and V2 (red)], and 1 V atom on the kagome lattice (V3, blue). On the kagome lattice, there are two kinds of V3-V3 bonds with different bond lengths [the shorter (red) is 2.6101 Å and the longer (gray) is 3.1413 Å], and V3 “trimers” are formed as a result. On the other hand, there are two inequivalent

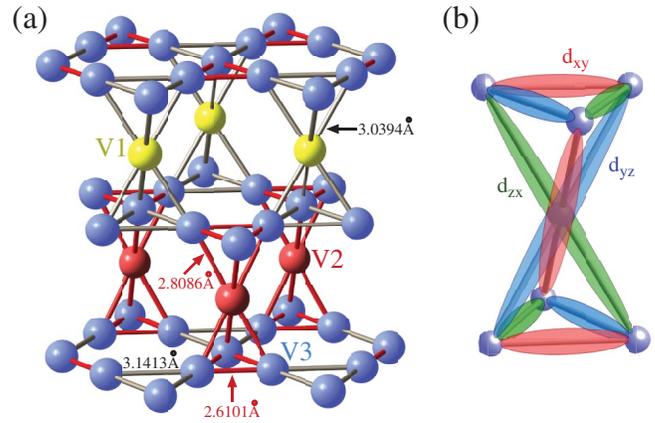


FIG. 2 (color). (a) The crystal structure in the CO phase of  $\text{AlV}_2\text{O}_4$  are shown schematically. There are three inequivalent V ions (V1, V2, V3), and V-V bond lengths are substantially different. Heptamers, each of which is made of one V2 (red) and six V3 ions (blue) connected by the shorter V-V bonds (shown by red lines) can be seen. The V1 (yellow) is a left-alone ion from the heptamer formation. (b) Schematic electronic bonds in the heptamer are shown. There are six “intratrimer bonds” and three “intertrimer bonds” in one heptamer. Each bond consists of  $d_{xy}$ ,  $d_{yz}$ , or  $d_{yz}$  orbitals, as illustrated by different colors.

triangular-lattice layers, composed of V1 atoms and V2 atoms, respectively. Here, all the V2 atoms are sandwiched by two V3 trimers, but none of the V1 atoms are. Furthermore, the V2-V3 bond length (2.8086 Å, red) is much shorter than the V1-V3 bond length (3.0394 Å, gray). These results indicate that the 7 V atoms, two V3 trimers, and one V2 atom in between, form a V cluster, or a “heptamer,” in the CO structure [shown by red lines in Fig. 2(a)], and a V1 atom (yellow) is left alone from the heptamer formation. It should be noted that the V1-O bond length is 2.0439 Å, close to the theoretical value for the  $\text{V}^{3+}\text{-O}^{2-}$  bond, and thus it is reasonable to interpret the “left-alone” V1 ion as trivalent ( $3d^2$ ).

Another unsolved problem for the CO state is the behavior of magnetic susceptibility. As shown in Fig. 3, the inverse magnetic susceptibility [ $1/\chi(T)$ ] shows a  $T$ -linear dependence below 100 K [11]. It was found that  $\chi(T) \times (T + \theta)$  with  $\theta = 22.6$  K is constant between 10 K and 120 K within 4% error (not shown), indicating that  $\chi(T)$  below 120 K is purely dominated by one Curie-Weiss component,  $\chi(T) = C/(T + \theta)$ . However,  $1/\chi(T)$  shows a clear bending around 200 K, which implies the evolution of another component at temperatures higher than 200 K. At the CO transition temperature (700 K), there is a kink in  $1/\chi(T)$ . Such a complicated behavior is in clear contrast to the simpler behavior of other spinel vanadates with  $\text{V}^{3+}$  ions ( $\text{MgV}_2\text{O}_4$ , for example, shown in Fig. 3), in which  $1/\chi(T)$  is almost linear down to the spin-ordering temperature.

We found that the magnetic susceptibility of  $\text{AlV}_2\text{O}_4$  below 600 K can be fitted by the sum of a Curie-Weiss term and a spin-gap term, given as follows:

TABLE I. Structural parameters of  $\text{AlV}_2\text{O}_4$  at room temperature from the Rietveld refinement of synchrotron x-ray powder diffraction data. The space group is  $R\bar{3}m$ . The lattice parameters are  $a = b = 5.75148(3) \text{ \AA}$ ,  $c = 28.85407(14) \text{ \AA}$ , based on the hexagonal notation. The profile-weighted  $R$  factor  $R_{\text{wp}}$ ,  $R$ -Bragg factor  $R_B$ , and goodness of fit  $s$  are 7.82%, 2.10%, and 1.6054, respectively.

Atom	Site	$x$	$y$	$z$	$B (\text{\AA}^2)$	$U (\text{\AA}^2)$
Al1	6c	0	0	0.18298(3)	0.146(12)	0.00185(12)
Al2	6c	0	0	0.30931(3)	0.103(11)	0.00130(14)
V1	3a	0	0	0	...	...
V2	3b	0	0	0.5	...	...
V3	18h	0.84873(2)	0.15127	0.41786(1)	...	...
O1	6c	0	0	0.12132(6)	0.259(7)	0.00328(8)
O2	6c	0	0	0.37045(6)	0.259	0.00328
O3	18h	0.83153(8)	0.16847	0.53921(4)	0.259	0.00328
O4	18h	0.82972(8)	0.17028	0.29034(4)	0.259	0.00328
Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
V1	1388(155)	1388	86(8)	694	0	0
V2	659(15)	659	1762(18)	329	0	0
V3	2307(66)	2307	59(2)	467(79)	19(8)	-19

$$\chi(T) = \frac{C}{T + \theta} + \frac{D}{T[1 + \frac{1}{3} \exp(\frac{E_g}{k_B T})]} \quad (1)$$

A thick solid line in Fig. 3 is the result of the fitting ( $C = 0.125 \text{ cm}^3/\text{mol K}$ ,  $\theta = 22.6 \text{ K}$ ,  $D = 0.308 \text{ cm}^3/\text{mol}$ , and  $E_g = 844 \text{ K}$ ). Temperature dependence of each component (the Curie-Weiss and the spin-gap term) in  $\chi(T)$  is shown in the inset. As can be seen, the contribution of the spin-gap term is almost negligible below 100 K, and that is the reason for the  $T$ -linear behavior in  $1/\chi(T)$ . We also tried other functions for the fitting (e.g., a sum of two Curie-Weiss terms with different  $\theta$ , and a Curie-Weiss term + a  $T$ -constant term), but were unable to reproduce the experimental data. In particular, those functions fail to reproduce the  $T$ -linear behavior of  $1/\chi(T)$  below 100 K, since the second term does not vanish down to low  $T$  in those functions.

Such characteristics of magnetic susceptibility in this compound are closely correlated with the CO state. Figure 3 also shows  $1/\chi(T)$  of three derivatives of  $\text{AlV}_2\text{O}_4$ , in which the CO is suppressed down to the lowest temperature in different ways, Cr doping into the V site (as disorder) [8], Mg doping into the Al site (hole doping into V), and the introduction of excess oxygen (hole doping into V). With the suppression of CO, (1) the  $T$ -linear dependence of  $1/\chi(T)$  below 100 K is smeared out but  $1/\chi(T)$  becomes more round, and (2) the absolute values of  $\chi(T)$  around room temperature increase and approach that of  $\text{MgV}_2\text{O}_4$ . These results indicate that the peculiar behavior of  $\chi(T)$  in  $\text{AlV}_2\text{O}_4$  is characteristic of the CO state.

The Curie constant in the Curie-Weiss term of Eq. (1) estimated from the fitting ( $C = 0.125 \text{ cm}^3/\text{mol K}$ ) is consistent with the  $S = 1$  spins residing at one out of 8 V ions, and thus, this Curie-Weiss term should be attributed to the  $S = 1$  spins at the “left-alone” V1 ions ( $\text{V}^{3+}$ ,  $3d^2$ ) in the

CO state of  $\text{AlV}_2\text{O}_4$ . On the other hand, the spin-gap term can be attributed to the triplet excitation in the V heptamer. This means that the ground state of the V heptamer in the CO state of  $\text{AlV}_2\text{O}_4$  is spin singlet. The change of  $\chi(T)$  with suppressing CO by doping can be explained by the collapse of this spin-gap contribution and the appearance of Curie-Weiss components.

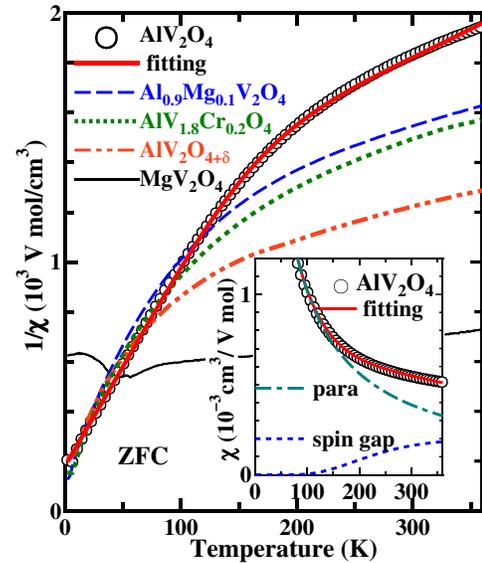


FIG. 3 (color online). Temperature variation of inverse magnetic susceptibility for the parent compound,  $\text{AlV}_2\text{O}_4$  (open circles), and three derivatives with no charge ordering,  $\text{Al}_{0.9}\text{Mg}_{0.1}\text{V}_2\text{O}_4$  (thin dashed line),  $\text{AlV}_{1.8}\text{Cr}_{0.2}\text{O}_4$  (dotted line),  $\text{AlV}_2\text{O}_{4.2}$  (dot-dashed line), and  $\text{MgV}_2\text{O}_4$  (thin solid line). A thick solid line is the fitting of the  $\text{AlV}_2\text{O}_4$  data by one Curie-Weiss term and one spin-gap term. The inset shows the magnetic susceptibility of  $\text{AlV}_2\text{O}_4$  (open circles), its fitting (solid line), and two components of the fitting function, a Curie-Weiss term (dot-dashed line) and a spin-gap term (dotted line).

How can the spin-singlet state be formed on the V heptamer? A spin-singlet state in  $\text{LiVO}_2$  with a similar V triangular lattice was proposed based on the ordering of  $t_{2g}$  orbitals [12], and it is reasonable to assume a similar state for the CO of the present  $\text{AlV}_2\text{O}_4$ . Here, the electron transfer is dominated by the  $d$ - $d$  direct overlap between  $t_{2g}$  orbitals, and there is a  $\sigma$  bond and a  $\pi$  bond for the overlap. Since the matrix element of the former is much larger than the latter, only the  $\sigma$  bond of the  $d$ - $d$  direct overlap is taken into account. Consequently, “intratrimer bonds” connecting two neighboring V3 sites within a trimer on the kagome lattice, and “intertrimer-bonds” connecting V3-V2-V3 on the straight line, exist in the heptamer, as shown in Fig. 2(b). Note that each bond is made of either the  $d_{xy}$ ,  $d_{yz}$ , or  $d_{zx}$  state of V  $t_{2g}$  orbitals because of the orbital-dependent anisotropy of the electron transfer. Accordingly, there are 6 intratrimer bonds and 3 intertrimer bonds in a heptamer. Since the left-alone V1 is trivalent ( $3d^2$ ), 1 V heptamer has 18 electrons ( $=2.5 \times 8 - 2$ ) in total; and therefore, they can be accommodated in the bonding states of these 9 bonds, and can form a stable spin-singlet state. Note that, since there are only  $2.5 \times 7 = 17.5$  electrons in a heptamer without CO, a half electron moves into the heptamer upon CO, and thus, the charge degrees of freedom also play an important role for the formation of V heptamers.

In the conventional CO state, the number of electrons at each site is integer, but in the CO state of  $\text{AlV}_2\text{O}_4$ , where electrons are distributed over the V heptamers, it is still fractional. This indicates that the stability of the CO state of  $\text{AlV}_2\text{O}_4$  is not given by the Coulomb repulsion between electrons, but by a strong electronic bonding inside a heptamer. Thus, the formation of V heptamers in the crystal has the same origin as that of molecules in the free space. Furthermore, a half electron transfers from a V1 ion to a V heptamer upon CO. Therefore, the CO state of  $\text{AlV}_2\text{O}_4$  is analogous to molecular complexes, in which cations (corresponding to the left-alone V1 ions) and anion molecules (corresponding to the V heptamers) order periodically.

As discussed above, such a large building block as a V heptamer is a consequence of cooperation between charge, spin, and orbital degrees of freedom of the V ions. In addition, the spinel lattice with geometrical frustration [13], on which the V ions are sitting, plays an important role, since spin systems on cubic or tetragonal lattices, which gives stronger constraint on the spin configuration, prefer simple spin-ordered states and thereby barely form a large building block of spins like the heptamer. Therefore, the formation of “molecular complexes” in  $\text{AlV}_2\text{O}_4$  can be regarded as a new type of self-organized state of electrons in the crystal with an underconstrained lattice, in other words, geometrically “soft” materials.

In summary, we demonstrated a unique CO structure in spinel  $\text{AlV}_2\text{O}_4$  characterized by a molecularlike V heptamer in a spin-singlet state and a left-alone  $\text{V}^{3+}$  ion with  $S = 1$ . Unlike the conventional CO states, the number of

electrons at each V site is still fractional in this CO state. The stability of the V heptamer is given by a strong bonding of vanadium  $t_{2g}$  orbitals, analogously to the formation of molecules in the free space.

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