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**Citation for published version:**

Browne, AJ, Kimber, SAJ & Attfield, JP 2017, 'Persistent three- and four-atom orbital molecules in the spinel AIV<sub>2</sub>O<sub>4</sub>', *Physical Review Materials*, vol. 1, no. 5, 052003. <https://doi.org/10.1103/PhysRevMaterials.1.052003>

**Digital Object Identifier (DOI):**

[10.1103/PhysRevMaterials.1.052003](https://doi.org/10.1103/PhysRevMaterials.1.052003)

**Link:**

[Link to publication record in Edinburgh Research Explorer](#)

**Document Version:**

Peer reviewed version

**Published In:**

Physical Review Materials

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## Persistent three- and four-atom orbital molecules in the spinel $\text{AlV}_2\text{O}_4$

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**Electronic instabilities in transition metal compounds may lead to ground states containing orbital molecules when direct metal-metal orbital interactions occur. The spinel  $\text{AlV}_2\text{O}_4$  was reported to contain  $\text{V}_7^{17+}$  orbital heptamers that emerge below a 700 K charge ordering transition. Our X-ray total scattering analysis of  $\text{AlV}_2\text{O}_4$  between 300 and 1100 K reveals a very different picture as the postulated heptamers are found to be pairs of spin-singlet  $\text{V}_3^{9+}$  trimers and  $\text{V}_4^{8+}$  tetramers, and these orbital molecules persist to at least 1100 K in a disordered high temperature cubic phase.**

Notable electronic and magnetic properties arise from the ordering of charge, orbital, and spin degrees-of-freedom in transition metal ( $M$ ) oxides and related compounds [1,2]. When  $M$ - $M$  distances are short, for example, through edge- or face-sharing of  $\text{MO}_6$  octahedra, molecule-like clusters of metal cations may be formed if ordering localizes electrons into appropriately oriented  $d$ -orbitals [3]. Clusters of metal-metal bonded cations formed below an orbital ordering transition have thus been termed ‘orbital molecules’ [4]. A classic exemplar is  $\text{VO}_2$ , where a metal-insulator transition and accompanying structural (Peierls) distortion at 340 K leads to the formation of  $(\text{V}^{4+})_2$  dimers within one-dimensional chains from V ions that are uniformly spaced above the transition [5,6]. The importance of molecule-like bonding interactions in driving the dimerization in  $\text{VO}_2$ , and related materials such as  $\text{Ti}_4\text{O}_7$ ,  $\text{V}_4\text{O}_7$  and  $\text{NbO}_2$ , has recently been highlighted [7]. More complex arrangements of orbital dimers are found in  $\text{CuIr}_2\text{S}_4$  [8] and  $\text{MgTi}_2\text{O}_4$  [9], and formation of disordered  $(\text{Mo}^{4+})_2$  orbital dimers has recently been identified at the spin glass transition of the pyrochlore  $\text{Y}_2\text{Mo}_2\text{O}_7$  [10].

Orbital molecules of more than two  $M$  ions are less common. Triangular  $(\text{V}^{3+})_3$  clusters are found in  $A_x\text{VO}_2$  ( $A = \text{Li}, \text{Na}$ ) materials and  $\text{BaV}_{10}\text{O}_{15}$  [11,12,13], whilst linear  $\text{Fe}_3^{8+}$  ‘trimerons’ are observed in the complex electronic order of magnetite ( $\text{Fe}_3\text{O}_4$ ) below the much-studied Verwey transition [14,15], and coexisting dimers and trimers are reported in the related material  $\text{Fe}_4\text{O}_5$  [16]. The largest orbital molecules claimed to date are heptameric clusters, reported in  $\text{AlV}_2\text{O}_4$  below a charge and orbital ordering transition accompanied by a rhombohedral to cubic structural distortion at  $T_{\text{CO}} = 700$  K [17]. The ground state was reported as having formal charge distribution  $\text{Al}_4[\text{V}_7^{17+}\text{V}^{3+}]\text{O}_{16}$  where the  $\text{V}_7^{17+}$  heptamer has 18  $3d$ -electrons occupying nine localized orbitals with overall spin  $S = 0$ , while the remaining  $S = 1$   $\text{V}^{3+}$  cation is paramagnetic. The spin singlet nature of the heptamers was confirmed by  $^{51}\text{V}$  NMR measurements [18] and further studies revealed that the long-range charge and orbital ordering is suppressed by replacing V with 5% Cr [19], or by applying pressures over 21 GPa [20].

The conventional picture of orbital molecule formation is that these quantum states emerge by displacive distortions from a structurally uniform high temperature phase below some electronic and structural transition temperature, ranging from the Peierls transition in  $\text{VO}_2$  to an intersecting one-dimensional orbital-ordering wave description of the heptamer order in  $\text{AlV}_2\text{O}_4$  [21]. However, recent studies of local structure through analysis of the pair distribution function (PDF) obtained from total scattering measurements have shown that disordered  $4d$  orbital dimers persist above the transition in  $\text{LiRh}_2\text{O}_4$  where  $(\text{Rh}^{4+})_2$  dimers persist up to 350 K, well above their 170 K ordering temperature [22], and in  $\text{Li}_2\text{RuO}_3$ , where  $(\text{Ru}^{4+})_2$  dimers order below 540 K but are evident to at least 920 K [23]. However, similar PDF studies of  $\text{CuIr}_2\text{S}_4$  and  $\text{VO}_2$  (the only  $3d$ -transition metal material investigated in this way) have reported that the orbital dimers disappear from both the long range and local structure above their transition temperatures [24,25]. To investigate whether large orbital molecules can persist to high temperatures we have studied the long range and local structure of  $\text{AlV}_2\text{O}_4$ , and in this Rapid Communication we report a very different picture of the electronic ordering in this material than that previously described.

Polycrystalline  $\text{AlV}_2\text{O}_4$  was synthesized from powdered Al,  $\text{V}_2\text{O}_5$  and  $\text{V}_2\text{O}_3$  ground together in the stoichiometric ratio, pressed into pellets, and sealed in evacuated quartz ampoules for three heatings up to 1150 °C for a total of 96 hours, with intermediate regrinding and pelleting.  $\text{V}_2\text{O}_3$  was prepared by reduction of  $\text{V}_2\text{O}_5$  under flowing  $\text{H}_2$  at 900 °C. Magnetization measurements shown in Supplemental Material are similar to those in the literature [17]. High energy X-ray total scattering data were collected on beamline ID22 at the European Synchrotron Radiation Facility using wavelength  $\lambda = 0.206547 \text{ \AA}$ . The  $\text{AlV}_2\text{O}_4$  sample was held in a 0.7 mm diameter quartz capillary and heated to temperatures between 300 and 1100 K using a hot air blower. Rietveld fits to the X-ray patterns were carried out using the GSAS program [26]. For PDF analysis, background-corrected scattering functions  $S(Q)$  were transformed to pair distribution functions  $G(r)$ , using PDFgetX3 [27], for momentum transfers  $Q$  between 0.5 and 25.8  $\text{\AA}^{-1}$ . Structural models were refined against the PDF data using the PDFgui program [28], including simulation of termination ripples, over the interatomic distance range  $1.5 \leq r (\text{\AA}) \leq 12$ . As a further check that orbital molecule features extracted from the  $\text{AlV}_2\text{O}_4$  PDFs are not the result of termination errors or other data artefacts, comparable X-ray data were also collected at 300 K from the cubic spinel  $\text{LiV}_2\text{O}_4$  which is of interest for heavy fermion behavior [29]. Fits to the  $\text{LiV}_2\text{O}_4$  PDF do not evidence orbital molecule or other deviations from the cubic spinel structure. These and further structural results for  $\text{AlV}_2\text{O}_4$  are in Supplemental Material [30].

$\text{AlV}_2\text{O}_4$  is reported to have the cubic spinel structure (Fig. 1a) at high temperatures, and a rhombohedral ordered arrangement of  $\text{V}_7$  heptamers (space group  $R\bar{3}m$ ) below  $T_{\text{CO}} = 700 \text{ K}$  (Fig. 1b) [17]. However, the  $R\bar{3}m$  heptamer model was found to give a poor fit to the PDF derived from 300 K X-ray scattering data, particularly in the 2.4 - 3.2  $\text{\AA}$  range where nearest-neighbor V-V distances lie (Fig. 2a). This indicates that the heptamer description of short-range V-V bonding is incorrect. Modifications to the orbital molecule structure were investigated, and a simple change was found to bring the fit into agreement with the PDF in the V-V region. Allowing the central V atom of the heptamers (atom V2 in the structural model) to move in the  $z$ -direction towards one of the two triangular end-faces greatly improves the overall fit (Fig. 2a). This displacement forms separate triangular  $\text{V}_3$  and tetrahedral  $\text{V}_4$  clusters within which

V-V distances are short ( $<2.7 \text{ \AA}$ ), indicative of bonding, while intercluster V-V distances are much longer ( $>2.9 \text{ \AA}$ ). Previous measurements indicated that the apparent  $V_7^{17+}$  heptamers have a spin singlet ground state [17,18], and the same condition is met by a combination of  $S = 0 V_3^{9+}$  trimers and  $S = 0 V_4^{8+}$  tetramers. These result from simple two-centre two-electron V-V bonding: three  $3d^2 V^{3+}$  ions form two bonds each, giving  $V_3^{9+}$  triangles, and four  $3d^3 V^{2+}$  ions are each bonded to three others in  $V_4^{8+}$  tetrahedra. The charge distribution in the ground state of  $AlV_2O_4$  is thus  $Al_4[V_4^{8+}V_3^{9+}V^{3+}]O_{16}$ , showing an unprecedented coexistence of two large orbital molecules.

The  $Al_4[V_4^{8+}V_3^{9+}V^{3+}]O_{16}$  model was fitted to the low temperature PDF data by allowing all V2 atoms to displace in the same direction which lowers the space group symmetry to polar  $R3m$ , although  $R\bar{3}m$  symmetry constraints were applied to all other atoms to reduce the number of variables. The long range ordering of pairs of  $V_3^{9+}$  and  $V_4^{8+}$  orbital molecules in this  $R3m$  model (Fig. 1c) is polar and could give rise to ferroelectricity. A simple ordering of antiparallel V2 displacements to give an alternative antiferroelectric order is frustrated in rhombohedral symmetry as the V2 sites are arranged in triangular layers, so the alternative ground state has the disordered structural average shown in Fig. 1d where a half-occupied split V2 site models the disorder within each orbital molecule pair. Rietveld fits (shown in Supplemental Material) of the ferroelectric ordered pair model gave poorer fits than the disordered antiferroelectric average model, hence the latter is taken as our proposed ground state structure for  $AlV_2O_4$  corresponding to a long range ordered array of disordered pairs of  $V_3^{9+}$  and  $V_4^{8+}$  orbital molecules, as shown in Fig. 1e, equivalent to the split V2 site model of Fig. 1d in the crystallographic average.

Above  $T_{CO} = 700 \text{ K}$  the structural symmetry of  $AlV_2O_4$  changes from rhombohedral to cubic. The cubic  $Fd\bar{3}m$  normal spinel structure (Fig. 1a) has one electronically-averaged  $V^{2.5+}$  site, and all nearest-neighbor V-V distances are equal. However this model gives a poor fit to the PDF derived from 1100 K X-ray data in the relevant  $2.4 - 3.2 \text{ \AA}$  region (Fig. 2b) suggesting that local V displacements are still present above  $T_{CO}$ . To explore whether the  $V_3^{9+}$  and  $V_4^{8+}$  orbital molecules survive to high temperatures, the  $R3m$  model (Fig. 1c) was used to fit the PDFs above 700 K. The hexagonal lattice parameters  $a_H$  and  $c_H$  were constrained to give a metrically cubic lattice ( $c_H/a_H = \sqrt{24}$ ), consistent with the average structure, and all V-V distances within the two orbital molecules were constrained to be equal to improve refinement stability at high temperatures. This model greatly improves the fit to the PDF data (Fig. 2b) and the derived V-V distances are found to evolve continuously between the rhombohedral and cubic phases (Fig. 3a). Even at 1100 K, bonding V-V distances within orbital molecules are  $2.78 \text{ \AA}$  and non-bonding distances vary between  $2.93 \text{ \AA}$  and  $3.06 \text{ \AA}$ , whereas the standard cubic spinel description predicts all V-V distances to be  $2.92 \text{ \AA}$ . To describe the disordered orbital molecules within the cubic average structure of  $Al_4[V_4^{8+}V_3^{9+}V^{3+}]O_{16}$  in Rietveld fits we used a split-site  $Fd\bar{3}m$  model in which  $7/8$  of the V scattering (representing the proportion of vanadium atoms in orbital molecules) is displaced to two sites either side of the ideal position that holds the remaining  $1/8$ . This leads to an improved fit to all the high temperature profiles, as shown in Supplemental Material. Whether the orbital molecules have significant dynamics

with motions coupled to the phonon modes at high temperatures is unclear from the present data, and inelastic scattering experiments will be needed to test this possibility.

Comparison of V atom displacements derived from the PDF fits and split-site Rietveld refinements in Fig. 3b shows that they agree well, with the V displacement decreasing from  $\sim 0.2$  Å at 300 K to  $\sim 0.1$  Å at 1100 K. Extrapolation indicates that zero displacement (i.e. a uniform cubic spinel arrangement) would be reached above  $\sim 2000$  K, which is far above the  $\sim 1400$  K synthesis temperature for  $\text{AlV}_2\text{O}_4$ . Previous measurements showed little change in magnetization or conductivity through the transition at  $T_{\text{CO}} = 700$  K ( $\text{AlV}_2\text{O}_4$  is a semiconductor with activation energy  $\sim 0.4$  eV) [31], which corroborates the validity of the  $\text{Al}_4[\text{V}_4^{8+}\text{V}_3^{9+}\text{V}^{3+}]\text{O}_{16}$  description at high temperatures as smaller species derived from the breakdown of the  $S = 0$   $\text{V}_3^{9+}$  and  $\text{V}_4^{8+}$  orbital molecules would either lead to large increases in paramagnetic susceptibility from electron-localized states, as the theoretical Curie constant per V atom changes from  $C = 0.125$  emu K mol $^{-1}$  for  $\text{Al}_4[\text{V}_4^{8+}\text{V}_3^{9+}\text{V}^{3+}]\text{O}_{16}$  towards 1.44 emu K mol $^{-1}$  for paramagnetic  $\text{AlV}^{2+}\text{V}^{3+}\text{O}_4$ , or to increased conductivity through electron delocalization. Hence,  $\text{AlV}_2\text{O}_4$  has remarkably stable  $\text{V}_3^{9+}$  and  $\text{V}_4^{8+}$  orbital molecules that are disordered within the high temperature cubic spinel phase to at least 1100 K, and form an ordered array of disordered pairs below the apparent charge ordering transition at 700 K.

The structural insights derived from this study demand substantial revision of theoretical descriptions for the electronic transition in  $\text{AlV}_2\text{O}_4$  and the physics of large orbital molecule formation. The ground state of  $\text{AlV}_2\text{O}_4$  is found to contain pairs of spin-singlet  $\text{V}_3^{9+}$  trimers and  $\text{V}_4^{8+}$  tetramers, rather than  $\text{V}_7^{17+}$  heptamers as previously reported. The upper size limit of known orbital molecules is thus reduced from seven- to four-atom clusters. This provides a more consistent size distribution for the known species, with many dimers, a few trimers, and tetrameric  $\text{V}_4^{8+}$  orbital molecules as the largest example.  $\text{AlV}_2\text{O}_4$  is thus notable for containing a mixture of the two largest known orbital molecules. The  $\text{V}_3^{9+}/\text{V}_4^{8+}$  orbital molecules within each pair in the ground state appear to be disordered, but could lead to a novel ferroelectric state if ordered. High temperature studies demonstrate that disordered  $\text{V}_3^{9+}$  and  $\text{V}_4^{8+}$  orbital molecules ‘hidden’ in the crystallographic cubic average structure of  $\text{AlV}_2\text{O}_4$  persist to at least 1100 K, far above the apparent charge ordering transition at 700 K. The conventional picture of orbital molecules emerging displacively from a structurally uniform phase below the electronic and structural transition is thus incorrect for this spinel. The ideal cubic structure is apparently unstable over all its existence range with respect to local charge and orbital ordering that produces orbital molecules, and their disorder to pairwise order transition leads to the cubic to rhombohedral structural change observed on cooling below  $T_{\text{CO}}$ . The temperature scales for the formation and the long range ordering of orbital molecules are thus very different for  $\text{AlV}_2\text{O}_4$ , unlike in  $\text{VO}_2$  in which they are the same [25], showing that orbital molecule phenomena in these apparently similar  $3d$ -metal oxides can originate from real-space (molecular) or momentum-space (Fermi surface) electronic instabilities. Reinvestigation of similar materials using local structure methods will thus be important to discover whether ‘hidden’ orbital molecules are present in other apparently uniform average structures.

We thank Mauro Coduri for help with data collection. This work was supported by the ERC and access to ESRF was provided by STFC. Part of this work was supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, at the Oak Ridge National Laboratory.

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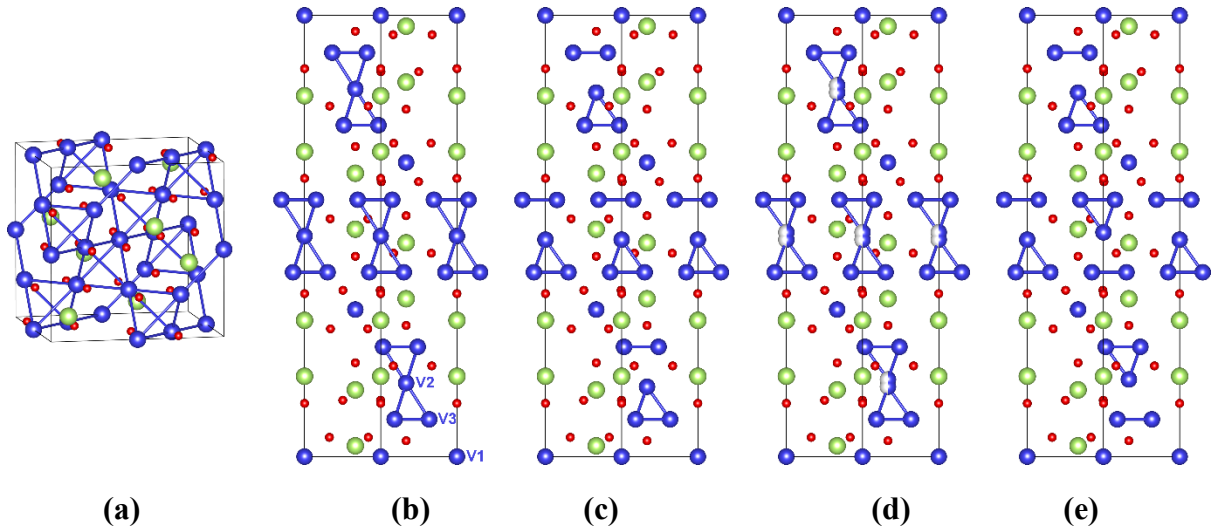


FIG. 1. Structural models for  $\text{AlV}_2\text{O}_4$  where Al/V/O are green/blue/red atoms. (a) The cubic spinel structure, showing nearest-neighbor V-V connections which are all equivalent. (b) The previously reported  $\text{V}_7$  cluster model with  $R\bar{3}m$  symmetry. The three symmetry-independent vanadium sites are labelled: site V1 is occupied by paramagnetic  $\text{V}^{3+}$  cations, whilst each heptamer comprises a central V2 atom between two triangles of V3 atoms. (c) The  $R3m$  model used for PDF fitting, in which  $\text{V}_3$  and  $\text{V}_4$  orbital molecules have long range ferroelectric order. (d) The split site  $R\bar{3}m$  model used to describe the disordered antiferroelectric average crystal structure in the Rietveld fits. (e) A local configuration showing a statistical distribution of the clusters corresponding to the split site average in (d). The rhombohedral unit cells in (b) to (e) are projected on the (110) plane with the  $c$ -axis vertical, and short ( $<2.90 \text{ \AA}$ ) orbital molecule V-V distances are shown.



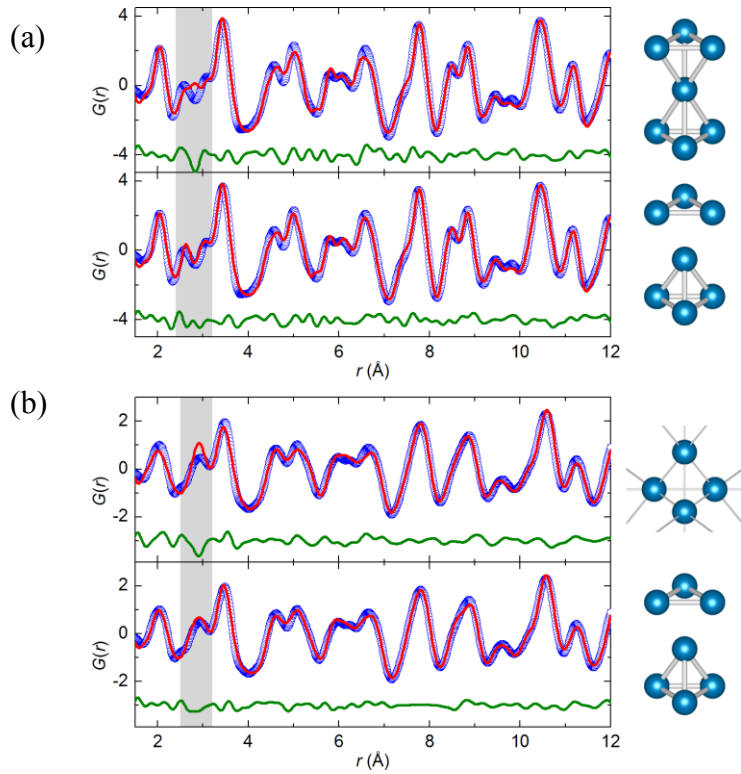
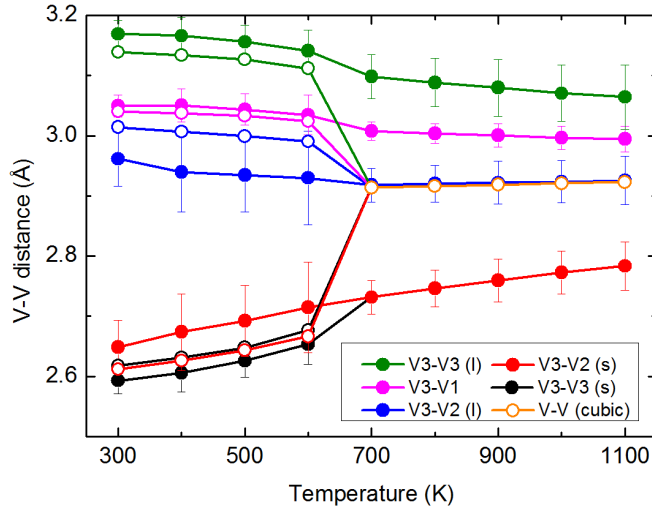
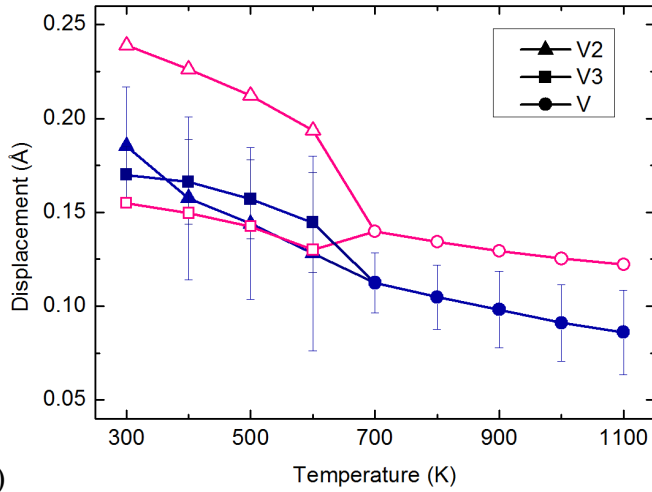


FIG. 2. Comparisons of fits to pair distribution functions (PDFs) of  $\text{AlV}_2\text{O}_4$  where nearest neighbor V-V distances lie in the shaded region at  $r = 2.4 - 3.2 \text{ \AA}$ . The local vanadium species in each structural model are shown to the right. (a) 300 K PDF, where the upper fit (residual  $R_w = 16.3\%$ ) of the  $R\bar{3}m$   $\text{V}_7$  heptamer model (Fig. 1b), agrees poorly in the V-V region, but allowing the central V to move off-centre to form  $\text{V}_3$  and  $\text{V}_4$  orbital molecules in the  $R3m$  model (Fig. 1c) gives the improved fit shown below ( $R_w = 13.6\%$ ). (b) 1100 K PDF, where the upper fit of the ideal cubic  $Fd\bar{3}m$  spinel model (Fig. 1a) gives a poor fit in the shaded region ( $R_w = 16.6\%$ ), but the lower fit of  $\text{V}_3$  and  $\text{V}_4$  orbital molecules in a  $R3m$  model (Fig. 1c) constrained by metrically cubic cell parameters greatly improves the agreement ( $R_w = 11.6\%$ ).



(a)



(b)

FIG. 3. (a) Comparison of V-V nearest neighbor distances in  $\text{AlV}_2\text{O}_4$  from PDF fits (filled symbols) using the  $R\bar{3}m$  structural description, and Rietveld analyses (open symbols) using the split site  $R\bar{3}m$  and cubic  $Fd\bar{3}m$  spinel models respectively below and above  $T_{\text{CO}} = 700$  K. Rietveld V-V distances all converge to a single value above  $T_{\text{CO}}$  because disordered orbital molecules are not described by a cubic average spinel structure, but PDF fitting shows that they persist above  $T_{\text{CO}}$ . (The two bonding V-V distances were constrained to be equal in the PDF fits above  $T_{\text{CO}}$  for refinement stability.) (b) Displacements of V atoms from their ideal sites due to orbital molecule formation, from PDF (filled symbols) and the split site Rietveld (open symbols) analyses. Both sets of displacements decrease smoothly on heating, but evidence the persistence of orbital molecules to 1100 K.