Communication

Hydrostatic pressure dependence on the collapsing of heptamer clusters in the charge ordered spinel AlV$_2$O$_4$

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A B S T R A C T

Charge frustrated spinels have engaged the interest of condensed matter studies due to the novel formation of multimer molecular sub units that lifts the degeneracy in the ground state. An exhaustive study on the stability of these molecular sub units is not available in the literature. In the present study, evidence has been obtained for the first time that hydrostatic pressure beyond 21 GPa, destabilizes the vanadium heptamer molecular sub units reversibly in the unique ambient temperature charge ordered spinel AlV$_2$O$_4$. The bulk modulus and its pressure derivative of the charge ordered phase are constrained. In addition a systematic structural analysis as a function of temperature shows destabilization of vanadium trimers those stack up to make the heptamer units. The crystal structure and total energy have been calculated using first principles density functional formalism (GGA approximation) as a function of pressure. The results obtained corroborate the stability of the frustrated phase beyond 20 GPa.

1. Introduction

Charge ordering from frustration in a spinel system is a rare phenomenon known to occur only in a few compounds so far. Structural transitions observed in the spinel systems like Fe$_3$O$_4$ [1,2], LiMn$_2$O$_4$ [3], CuIr$_2$S$_4$ [4], AlV$_2$O$_4$ [5] and LiRh$_2$O$_4$ [6] have been attributed to be due to the ordering of charges from frustration. In general, geometrical frustration is said to result whenever a conflict arises between some fundamental interaction and the underlying lattice geometry. The underlying geometry that is in conflict with the interaction is inherently provided by the pyrochlore or the cubic spinel lattices and the fundamental interaction may involve spins or charges or even orbitals. While spin frustration on spinel lattices has been explored in a variety of systems, charge frustration has been observed only in a few compounds in the spinel system mentioned above. In fact it was the Verwey transition, observed in Fe$_3$O$_4$ that has opened the field of charge ordering from frustration about six decades ago. To date, the theoretical understanding and also the experimental studies have been limited in this area. Formation of molecular multimer units have been proposed to relieve of charge frustration in the spinels [7]. For instance formation of trimers in Fe$_3$O$_4$, octamers in CuIr$_2$S$_4$ and heptamers in AlV$_2$O$_4$ have been identified in the charge ordered state

[1,2,4,5]. In the case of AlV$_2$O$_4$, the heptamer molecule [7] that forms in the charge ordered state is known to be made up of two vanadium trimers linked via a central vanadium atom.

Among the spinel compounds that show charge ordering from frustration, AlV$_2$O$_4$ is unique in adopting a charge ordered rhombohedral structure at ambient temperature. In all other compounds the charge order transition takes place at lower temperatures. Thus, it offers an opportunity to probe and perturb the charge ordered state at ambient temperature. In the case of AlV$_2$O$_4$, our earlier work using synchrotron powder XRD studies under non-hydrostatic pressure [8] has shown that there is pressure- induced frustration above 20 GPa that persists after decompression. The motivation of the present work is to go beyond and examine the role of hydrostatic pressure in the transformation from order to frustration. We have also carried out ab-initio electronic structure calculations to determine the stability of the phases under the application of pressure. In addition a systematic study of the transformation at ambient pressure and high temperature is also performed.

2. Experimental

The charge frustrated spinel compound AlV$_2$O$_4$ is synthesized using

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stoichiometric quantities of Al (Alfa Aesar 99.97%), V_2O_3 (Alfa Aesar 99.7%) and V_2O_5 (Alfa Aesar 99.99%) [5]. Powder X-ray diffraction data are collected at ambient conditions in a slow scan mode using Cu K_α radiation in a STOE diffractometer. High Temperature Powder XRD measurements are also carried out using a high temperature (HT) attachment to the SIEMENS-D500 diffractometer at various temperatures from room temperature up to 550 °C at every 10 °C step by loading the powder on a Ta Sample holder. The hydrostatic pressure experiments on AlV_2O_4 powder have been carried out at the West - B1 beam line at the Cornell High Energy Synchrotron Source (CHESS), USA. A pair of brilliant cut gem quality diamonds with culet size 300 μm has been used in a symmetric-type diamond cell. A Steel gasket with 100 μm size of the hole and thickness of 60 μm is used to contain the sample. A few grains of ruby served as the pressure marker. The beam size is 10×10 μm. A mixture of methanol and ethanol in the ratio 4:1 has been used as pressure transmitting medium. Powder diffraction data is collected using a MAR 345 image plate detector. Sample to image plate distances and angles of detector tilt have been calibrated with CeO_2 using Fit-2d [9].
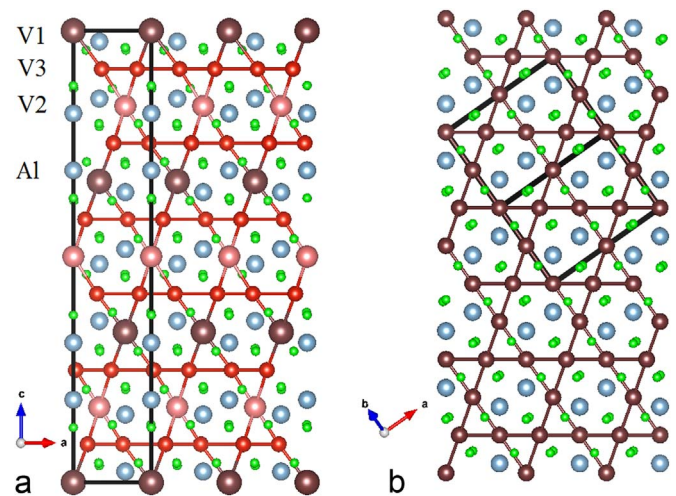
Ab-initio electronic structure calculations within the density functional formalism have been performed for the charge ordered rhombohedral phase and the charge frustrated cubic spinel phase of AlV_2O_4 [10] to estimate the relevant bulk properties from the total energy. Properties of AlV_2O_4 in both the rhombohedral (R-3 m, 166) and cubic spinel (Fd-3 m, 227, 2nd setting) structures have been carried out using the full potential linearized augmented plane wave (FP-LAPW) method as implemented in the all electron WIEN2k [11] code. The Wu-Cohen [12] formulation of the generalized gradient approximation (GGA) has been used to estimate the exchange and correlation functionals. Experimental cell parameters under pressure have been used as input to compute the total energy with the same criterion for convergence as mentioned in [10].

3. Results and discussion

Fig. 1 shows the results of the Rietveld refinement carried out on the powder diffraction data, which confirm the Heptamer structural model [8] of charge ordered AlV_2O_4 including both the major pure phase and the minor impurity (Al_2O_3) phase. All the peaks corresponding to the major AlV_2O_4 phase can be indexed to R-3 m structure with three different vanadium ion sites in the charge ordered state. The refined lattice parameters (a= b=5.7613 (2) Å and c=28.6876(10) Å
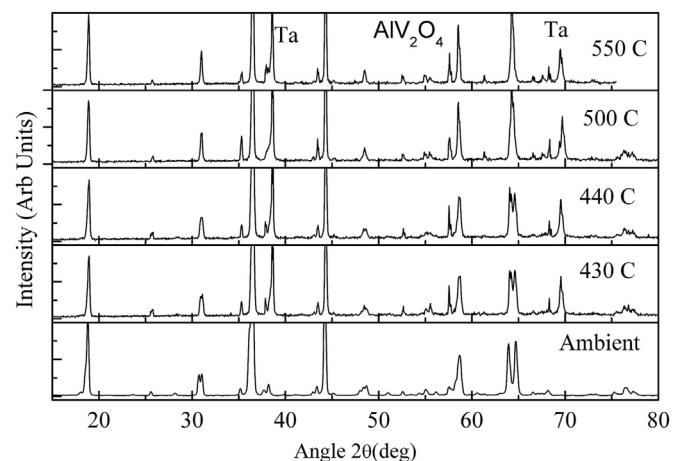

Fig. 2. Structure of AlV_2O_4 drawn using VESTA (A Three-dimensional visualization system for electronic and structural analysis [13]); (a) Rhombohedral phase in the 0–10 projection; (b) Cubic phase in the 0–11 projection.

(hexagonal notation) and the cell volume (V=824.65(4) $Å^3$) agree well with those quoted in the literature [7].

The crystal structure of AlV_2O_4 is drawn with VESTA [13] and presented in Fig. 2 to get a perspective of the system. The figure outlines the heptamer cluster formed by the V2 and V3 vanadium ions in the charge ordered structure and the presence of a single vanadium ion in the frustrated cubic structure. Fig. 2(a) shows the rhombohedral phase in the 0–10 projection with three different vanadium ions. Fig. 2(b) shows the cubic phase in the 0–11 projection with one type of vanadium ions. It is also known from the heptamer model proposed by Horibe et al. [7], that V3 atoms form a kagomè network built via the formation of V3 trimers while the V2 atoms form a triangular lattice.

Results of our powder diffraction measurements as a function of temperature carried out in this study are presented in Fig. 3. The ambient temperature powder diffraction pattern shows that the rhombohedral phase is characterized by reflections corresponding to the (0 1 8), (1 1 0) planes (around 2θ=30°) and those corresponding to the (0 2 16) and (2 2 0) planes (2θ=64°). The corresponding reflections from the cubic phase within this angular region are from the (2 2 0) and (4 2 0) planes. The merging of the rhombohedral splitting can be observed at 500 °C.

Fig. 4 shows the variation of the d- spacing values corresponding to the (0 2 16) and (220) reflections as a function of temperature. The

Fig. 1. Rietveld refinement confirming with the heptamer structural model for the charge ordered AlV_2O_4. The peaks of impurity Al_2O_3 are marked with asterisks. Short solid lines indicate expected peak positions for the major and impurity phases. The difference plot between the observed and calculated intensities is shown at the bottom.

Fig. 3. High temperature powder diffraction of AlV_2O_4 using Cu K_α radiation. Beyond 440 °C the (018) rhombohedral (R) and the (1 1 0) R reflections (around 30° two theta) merge to (2 2 0) cubic(C) and the (0 2 16) R and the (2 2 0) R peaks (around 64° two theta) merge to become the (4 4 0) C.
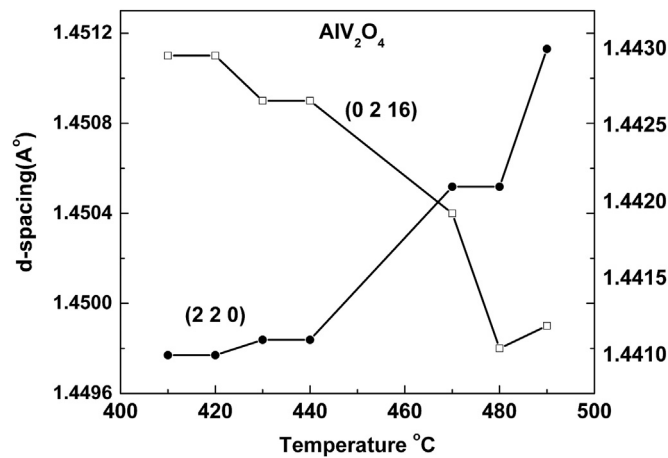
Fig. 4. Variation of the d-spacing corresponding to the (0 2 16) plane and (220). planes as a function of temperature.

Fig. 6. Powder diffraction data under hydrostatic pressure showing transformation from rhombohedral (charge ordered) to cubic (frustrated) structure. The indices of charge ordered (R) and charge frustrated (C) phase are marked. Asterisks indicate the impurity (Al_2O_3) peaks. The gasket peaks are denoted by G.

signature reflections of the rhombohedral system. From 21.3 GPa onwards, the reflections of the rhombohedral phase disappear and the pattern could be indexed to the cubic structure. In the case of non-hydrostatic pressures the frustration occurs around 22–23 GPa [8]. The sample was decompressed after application of 33.7 GPa, and the diffraction pattern collected is shown in Fig. 6. The pattern corresponding to complete decompression shows the characteristic reflections from (0 2 16) and (2 2 0) planes of the rhombohedral phase, unlike the non-hydrostatic conditions, where the cubic phase is retained irreversibly on decompression [8].

The unit cell volume per formula unit plotted as a function of pressure in Fig. 7 shows a decrease till about 21 GPa, beyond which the transition to the cubic phase occurs. There is a notable shift in volume associated with the transition, indicating that the transition is first order in character. This is in accord with previous high temperature results [5], as well as with the observed hysteresis in the transition on
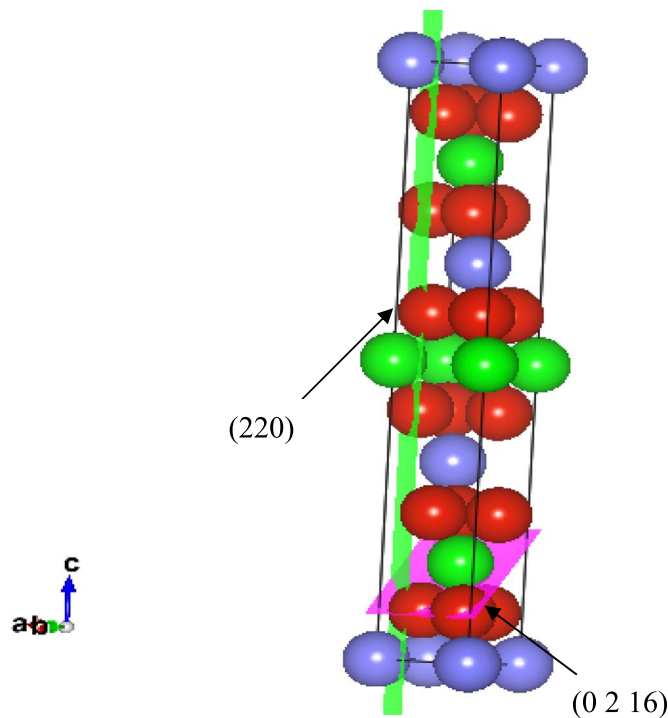

Fig. 5. The charge ordered rhombohedral cell with only vanadium atoms. Aluminum and oxygen atoms have been removed for clarity.

(220) plane spacing increases as a function of temperature, while the d-spacing corresponding to the (0 2 16) plane containing two of the vanadium atoms forming V3 trimers decreases on heating. They are viewed as bonding with the V2 vanadium ions at the center of the heptamer via orbital interactions [7,8]. These two planes are shown in Fig. 5 where the rhombohedral unit with vanadium atoms alone has been shown for clarity. This anomalous behaviour of the (0 2 16) plane relative to the (2 2 0) plane implies that the increase in temperature disturbs the V3 trimers. Basically, temperature modifies the V-3d and O-2p hybridization resulting in the charge redistribution leading to a decrease of the d- spacing corresponding to the (0 2 16) planes thereby inducing the structural transition.

The powder diffraction pattern obtained under hydrostatic pressure is shown in the Fig. 6. The results are completely hydrostatic up to ~10.4 GPa, and methanol: ethanol mixtures have modest stress gradients at higher pressures [14]. All the observed peaks are indexed. The pattern corresponding to the lowest pressure of 1.6 GPa shows the
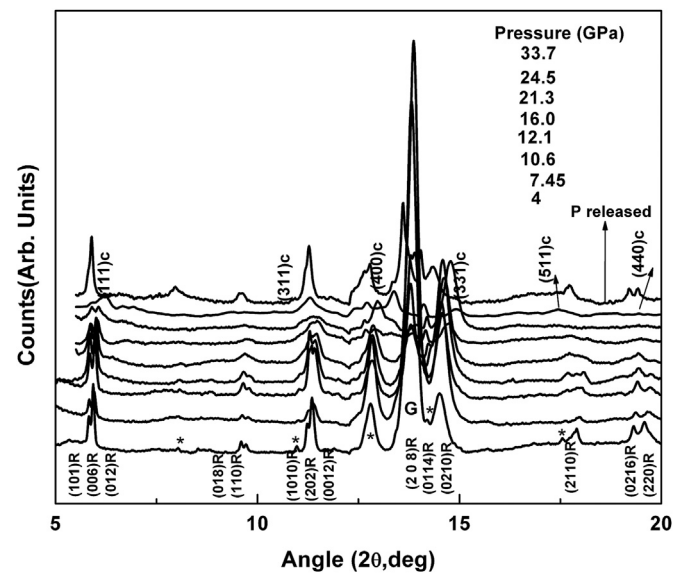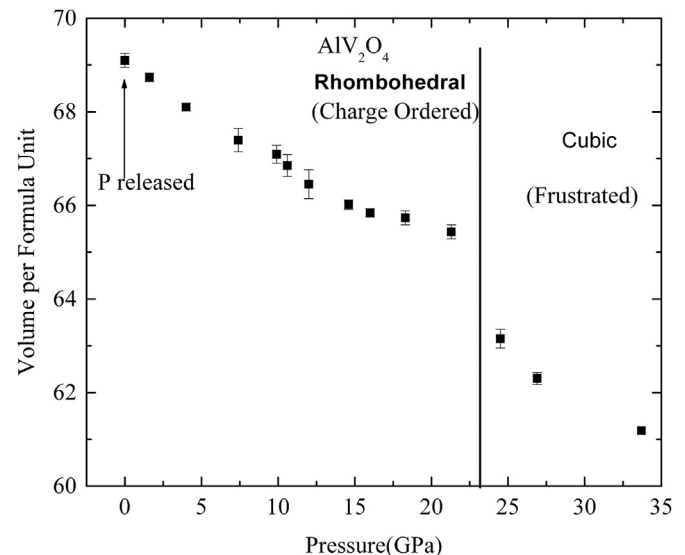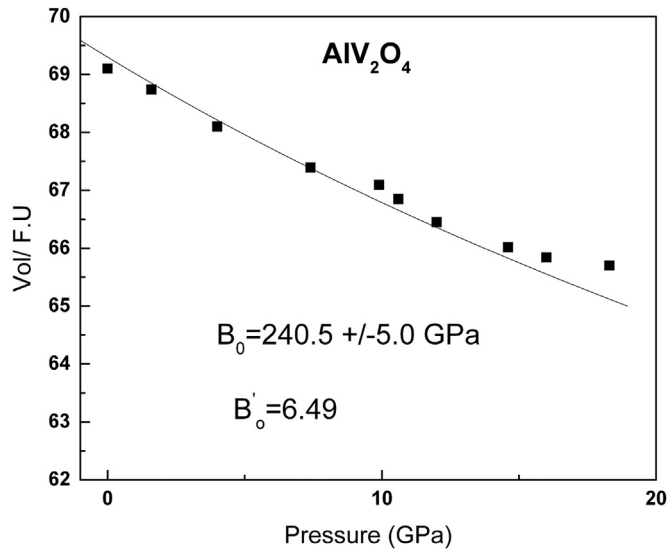

Fig. 7. Variation of volume/formula unit as a function of pressure in the charge ordered rhombohedral and frustrated cubic phases. The cell volume corresponding to decompression is indicated by the arrow mark.

Fig. 8. Equation of state of the charge ordered AlV_2O_4 obtained by fitting the P-V data to the third order Birch-Murnaghan equation. Dots–experimental data. Solid line–fit to the third–order Birch-Murnaghan equation of state.

decompression.

On increasing the pressure beyond 23 GPa, the volume per formula unit within the cubic phase also decreases with respect to the applied pressure at a substantially more rapid rate than in the case of the rhombohedral phase till the highest value of the applied pressure. Thus, from a thermo-chemical/ volumetric standpoint, the stability of the frustrated cubic phase appears to be substantially favored at high pressures.

An estimate of the bulk modulus of AlV_2O_4 is carried out by fitting the P–V data obtained from the high-pressure experiments, to the third order Birch-Murnaghan equation of state,

$$P(V) = \frac{3}{2}B_0 \left[\left(\frac{V_o}{V}\right)^{\frac{7}{3}} - \left(\frac{V_o}{V}\right)^{\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4}(B_o' - 4) \left[\left(\frac{V_o}{V}\right)^{\frac{2}{3}} - 1 \right] \right\}$$

where V_o, B_o, B_o' are the zero-pressure volume, bulk modulus and the first derivative of the bulk modulus with respect to pressure, respectively..

Fig. 8 shows the result of the fitting. The experimental data are indicated by dots and the fitting is represented by the solid line. The bulk modulus (B_0) corresponding to the rhombohedral phase is estimated to be 240.5+/- 5 GPa, and the value of the first derivative (B_0') is 6.49. This value of the bulk modulus is comparatively large among oxides; notably, another mixed valence vanadium compound, V_3O_5 has been observed to have a similarly high bulk modulus of 269(± 3) GPa [15]. Hence the possibility exists that highly incompressible behaviour may be an endemic property of mixed valence vanadium compounds, and the directional bonding associated with these phases is likely to contribute to their incompressibility.

The variation of d-spacings corresponding to the (0 2 16) and (220) planes as a function of pressure is presented in Fig. 9. The variaion in the (2 2 0) spacing is small relative to the (0 2 16) spacing, implying that the c-axis may be more compressible than the a- or b- axes. This probably has an implication to the transformation back to the frustrated cubic phase under pressure since the direct interaction between electrons in the V-d_{xy} orbitals may become more repulsive.

To examine the stability of the system under pressure total energy calculations have been carried out for both the charge ordered rhombohedral phase (R-3 m) and the charge frustrated cubic phase (Fd-3 m) of AlV_2O_4 by varying the volume/formula unit.

Fig. 10 shows the results of the computation. The experimental initial volumes are shown by filled circles (rhombohedral phase) and
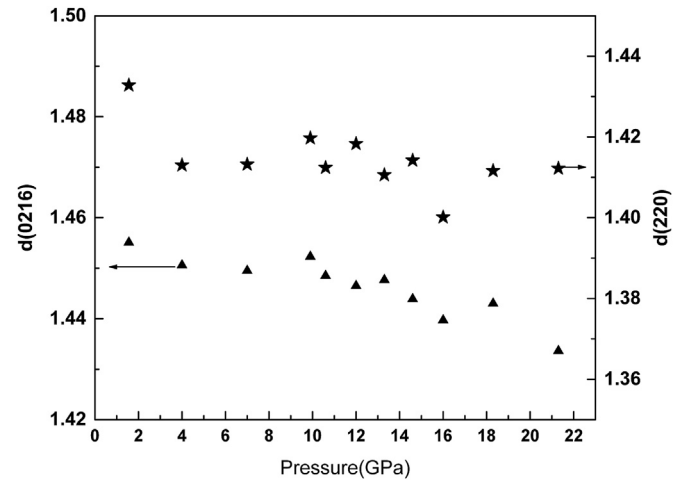
Fig. 9. Variation of the d-spacing corresponding to the (0 2 16) (triangles) and (220) (stars) planes as a function of hydrostatic pressure.
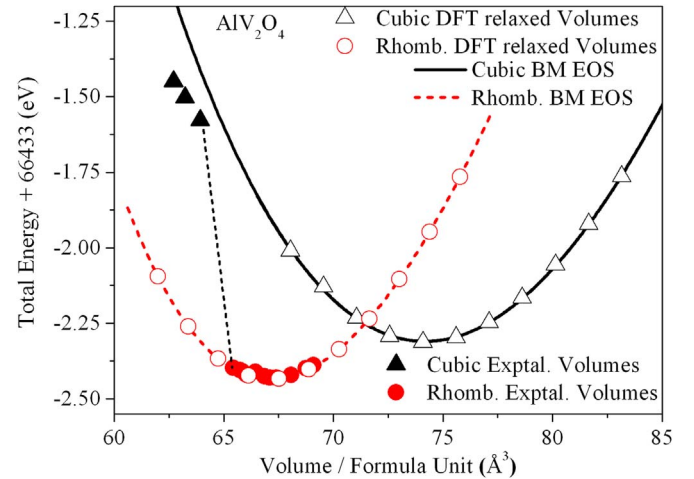
Fig. 10. Total energy as a function of volume per formula unit for AlV_2O_4. Filled triangles and filled circles represent the experimentally observed volume/FU; open triangle and circles–relaxed volumes/FU for the cubic and rhombohedral phase. Solid line–fit to the Birch-Murnaghan equation of state.

filled triangles (cubic phase) and the relaxed values are shown as open circles (rhombohedral phase) and open triangles (cubic phase). A very good agreement is observed between the experimental and relaxed volumes in the case of the charge ordered rhombohedral phase. In the case of the charge-frustrated cubic phase, the agreement between the experimental and relaxed volumes is not as good. This may be due to the uncertainties in the lattice parameter estimation from the broadened diffraction peaks at pressures above 20 GPa, or from theoretical uncertainties arising from magnetic or thermal effects within this vanadate structure. Despite this likely overestimate of the energy of the cubic phase at smaller volumes, it is clear that the ambient temperature charge ordered structure is driven to a frustrated state on the application of pressure.

The rhombohedral to cubic structural transition is a largely diffusionless phase transition, which involves only a small reorganization of atoms as shown in Fig. 2. Therefore, it can be conjectured that there may be a critical range of lattice strain below (high pressure) and above (high temperature) which the delicately balanced orbital overlap is inhibited, collapsing the relatively fragile heptamer cluster assembly and driving the system back to frustration. At present, the formation of the heptamer vanadium molecular unit has been proposed to be brought about by the orbital overlap of V2 and V3 vanadium [16]. This model has been claimed to be valid based on NMR experiments

[17]. But electron energy loss spectroscopy and band structure calculations [10,18] have indicated the possibility of more complex charge disproportionation scenarios on all the three vanadium ions, and hence a complex ordering of orbitals in this system. Further experiments and computations examining the role of orbitals are essential to decipher the mechanism that leads the formation or collapse of multimer units in avoiding a degenerate ground state in the inherently frustrated systems.

4. Conclusion

The unique ambient temperature charge-ordered spinel AlV_2O_4 undergoes a pressure- induced transition to frustration in low differential stress environments at about 21 GPa. Decompression from hydrostatic pressure reversibly takes the system back to the ordered phase. First principle electronic structure calculations based on density functional formalism confirms that the frustrated cubic and charge-ordered rhombohedral phases lie close in energy under pressure. Structural analysis of the high temperature diffraction reveals that the V3 trimers forming the kagome' lattice in the charge ordered rhombohedral phase get disrupted as the temperature is increased and this disruption may drive the system to frustration. Thus application of high hydrostatic pressure or thermal energy leads to collapsing of the vanadium heptamer sub units and drive the system to frustration. The specific role of pressure and temperature on the vanadium orbitals still remains unclear at this juncture.

Acknowledgement

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