CHAPTER 1

Geometrically frustrated spinel systems and ordering of charges – A brief review

Electron correlation in condensed matter always seems to throw up a plethora of novel, exotic and complex phenomena that routinely destabilize every attempt to formulate or formalize understanding. In the last few decades several challenges are posed by the high temperature superconductors, colossal magneto resistance materials, spin glasses, frustrated systems and so on. Experimental and theoretical tools have been stretched to their limits to comprehend the complexities, but the horizon of convergence appears to recede farther and farther. Amongst the complex, correlated condensed matter systems, ‘frustrated systems’ are a class in itself and they exhibit novel ground states like spin liquids, spin ice and valence bond solids. The spinel compounds amongst these are unique in exhibiting such unconventional ground states. Ordering of the charge degree of freedom in a spinel system is a rare and contested phenomenon. Very few spinel compounds have shown coupling of the charge degree of freedom with the lattice as against a number of those that have shown frustration and ordering of spin degrees of freedom. Charge ordering out of a frustrated lattice has been observed in the spinel compounds like Fe₃O₄ [1], AlV₂O₄ [2], LiMn₂O₄ [3], LiRh₂O₄ and CuIr₂S₄ [4]. LiV₂O₄ is another unique spinel compound where charge and spin remain frustrated down to very low temperatures (<1K) and charge ordering occurs under pressure [5]. Interestingly this is the only compound that shows heavy fermion behaviour in transition metal
compounds. Another spinel oxide of relative similarity namely, LiTi$_2$O$_4$ is a type II superconductor with a $T_c$ of about 13K [6]. Apart from the coupling of charge and spin degrees with the lattice, coupling of orbital degrees with lattice is observed in some spinel compounds. For instance MgTi$_2$O$_4$ shows orbital ordering by the formation of dimers [7]. The formation of ‘multimers’, like dimers, trimers, heptamers and octomers is believed to be the path through which the system moves from a charge frustrated state to a charge ordered state. Experimental evidence through electron diffraction and x-ray diffraction support the formation of such multimers below the charge ordering transition temperature. Yet direct observation of charge ordering is still elusive. It is also to be noticed that among the few known materials mentioned above, no unique mechanism has emerged, to explain the observed phenomenon of order from frustration. A lot more experimental and theoretical efforts are called for.

This introductory chapter is divided into various sections to contextualize and motivate the present thesis. Section 1 reviews the concept of geometrical frustration. Section 2 explains frustration in the context of water ice. Section 3 describes the cation ordering in the pyrochlore lattice. Section 4 and 5 present a short review and summary of the spinel oxides exhibiting charge frustration. Section 6 summarizes the motivation and organization of this thesis.

1.1 The concept of Geometrical frustration – Historical development

Whenever a conflict arises between some fundamental interaction and the underlying lattice geometry, a geometrical frustration is said to result. The effect of such a geometrical frustration is the finite entropy at zero Kelvin indicating existence of a degenerate ground state. The recognition of the existence of such a geometrical
frustration dates back to 1936 when Giaque and Stout [8] measured specific heat on hexagonal water-ice and showed finite entropy (0.8 cal/deg/mole) at zero Kelvin which was explained by Linus Pauling [9] by considering the configurational entropy using the Bernal-Fowler [10] ice-rules. In general frustration can be of two types. Geometrical frustration is one of them and the other is frustration in accommodating two components with minimum energy configuration irrespective of the underlying geometry of the space. Spin glasses [11-12] form good example of the latter.

Figure 1.1 Pair wise anti aligning interaction on a (a) triangular arrangement and (b) Tetrahedron arrangement; Two dimensional lattices that sustain frustration (c) triangular lattice and (d) kagome’ lattice.

A typical example of geometrical frustration is anti-ferromagnetic interaction of Ising spins on a triangular lattice. In such a lattice the pair-wise anti-aligning of spins is incompatible with the underlying triangular lattice and the ground state becomes de-
generate. The number of possible ground state configurations increase as one moves from a triangular lattice to a pyrochlore lattice. There are a few lattices which have inherent tendencies for geometrical frustrations to occur. They are the triangular lattice and the kagome’ lattice in two dimensions and the pyrochlore lattice in three dimensions. To understand the existence of degenerate ground states accompanying geometric frustration, consider the case of pair-wise anti aligning of spins on a triangle as shown in Figure 1.1 (a). On a triangle after positioning the two anti-aligned spins, the third one can be placed either up or down. So the ground state can keep flipping between the two possibilities without an extra cost in energy. A similar situation exists on a tetrahedron as shown in Figure 1.1 (b). Once again if pair-wise anti aligning of spins has to be realized on this geometry, it shows incompatibility and hence frustration. But a configuration with two spins up and two spins down can still be attempted. There are eight such possibilities which are energetically favorable, thereby resulting in 8-fold degenerate ground state.

The pyrochlore lattice with parallel Ising spins is also frustrated and is similar to the ‘water ice’. Discovery of finite residual entropy in Ho$_2$Ti$_2$O$_7$ [13] demonstrated the first experimental observation of ‘spin ice’ on a pyrochlore lattice. In general minimization of the number of underlying constraint maximizes the ground state degeneracy of the interacting species. In all of these lattices severe frustration results, for example, when pair-wise anti parallel spin interaction have to be incorporated. A variety of experimental and theoretical works have been carried out in the case of frustrated magnetism [14]. A similar scenario as in the case of ‘water ice’ is anticipated if multivalent cations occupy the pyrochlore sub-lattices present in cubic spinel systems. In comparison with the frustrated magnetic systems, very few compounds have shown
frustration of charges. Since, it all started with ‘water ice’, it is essential to understand the nature of geometrical frustration in hexagonal ice.

1.2 Geometric frustration in ‘water ice’

Figure 1.2 shows the crystal structure of Ice Ih (Space Group P63/mmc (194); Symmetry: D$_{6h}$ [15]. In a hexagonal ice crystal each H$_2$O molecule has four nearest neighbors arranged near the vertices of a regular tetrahedron centered about the molecule of interest.

![Crystal structure of Hexagonal Ice](image_url)

**Figure 1.2 Crystal structure of Hexagonal Ice**

The oxygen atom of each molecule is strongly covalently bonded to two hydrogen atoms, while the molecules are weakly hydrogen bonded to each other. When projected
onto the plane perpendicular to the c-axis, the molecular stacking sequence is . . . ABBAABBA . . . The lattice parameters are: $a = 4.523 \, \text{Å}$ and $c = 7.367 \, \text{Å}$. The $c/a$ ratio (1.628) is very close to the ideal ratio (1.633) and is independent of temperature. The ice Ih unit cell is relatively open (packing factor less than 0.34), and this accounts for ordinary ice being less dense than water. In building this structure, Bernarl-Fowler proposed a rule that must be followed for the stability of the structure for the ideal crystal based on the assumptions that:

Each oxygen atom is bonded to two hydrogen atoms at a distance of 0.95Å to form a water molecule.

Each molecule is orientated so that its two hydrogen atoms face two, of the four, neighboring oxygen atoms that surround in tetrahedral coordination;

1. The orientation of adjacent molecules is such that only one hydrogen atom lies between each pair of oxygen atoms;

2. Ice (Ih) can exist in any of a large number of configurations, each corresponding to a certain distribution of hydrogen atoms with respect to oxygen atoms.

Based on these assumptions, the Bernal-Fowler rule states that “two protons stay near each of the oxygen and one proton must be on each O-O bond”. Each of the oxygen is at a distance of 2.76 Å and the retained O-H bond distance is 0.95 Å. Each oxygen must have two hydrogen at 0.95 Å and two hydrogen at 1.81 Å. The structural constraint demanding tetrahedral positioning of oxygen coupled with the requirement of molecular integrity of H₂O leads to frustration in proton-proton (hydrogen ion) interaction. In
general the protons would like to be far apart from the considerations of electrostatic interaction.

The possible configurations of organizing the frustrated protons on a tetrahedron can be enumerated as follows. Representing the protons by arrows as shown in figure 1.3, with an arrow pointing in implying ‘near’ and an arrow pointing out implying ‘far’, it can be seen that in general there are sixteen possibilities. This reduces to six when the ‘ice rule’, (namely, two-near and two-far) is applied. These six configurations, with two-in and two-out, are presented within the box.

![Possible configurations with two-in and two-out criterion](image)

**Figure 1.3** Possible configurations with two-in and two-out criterion.
It must also be considered that, of the four hydrogen bonds (between the oxygen ions) in which one water molecule participate, two are occupied by its hydrogen atoms and two are unoccupied. The chance that a given direction is available to a hydrogen atom is therefore 1/2, and as there are two hydrogen atoms to be placed, the probability that this can be done is \( \frac{1}{2} \cdot \frac{1}{2} = \frac{1}{4} \). Thus if there are a total of \( N \) molecules, the total number of configurations is then \( W = (\frac{6}{4})^N = (\frac{3}{2})^N \) contributing to finite entropy.

\[
S_0 = k_B \ln(\Omega) = N k_B \ln(\frac{3}{2}) = 0.81 \text{ Cal/deg/mol}
\]

This agrees well with the experimentally measured entropy value \([1]\). Thus frustration leads to ground state degeneracy.

### 1.3 Cation ordering in the pyrochlore spinel sub-lattice and the Verwey transition

Analysis of the ordering of the ions in the hexagonal ice demonstrates that whenever pyrochlore lattice is to be occupied by species with a specific pair-wise interaction a degenerate ground state can be anticipated. The recognition of frustration and finite entropy in water ice has resulted in modeling spins on triangular and pyrochlore lattices. Earliest calculations by Wannier \([16]\) consider the case of Ising spins on triangular lattice and show that the ground state of the model is macroscopically degenerate while occupying such a tetrahedron. Subsequent calculations by Anderson consider ordering of cations on the octahedral sites of an inverse spinel system and spins in a normal spinel system. A formula unit in the spinel system is represented as \( \text{AB}_2\text{O}_4 \), where, in the case of normal spinel the 8A ions form tetrahedron and the 16 B-ions form octahedral lattice. In the case of inverse spinel, 8-B ions form the tetrahedron and (8A+8B) ions form the octahedral. Focusing attention on the octahedral site, it is easy to
anticipate that there can be cation disorder due to the multiple possibilities of occupation of the octahedral sites by the A and B ions. The lattice formed by this octahedral site is like that of a pyrochlore i.e. corner sharing tetrahedron. Figure 1.4 shown here depicts the pyrochlore lattice. Each of the black dots (lattice points) is decorated by a basis of octahedral unit with a cation at the center of the octahedra and oxygen ions at the vertices.

Figure 1.4 The pyrochlore sub-lattice in spinel

Such a corner sharing tetrahedral lattice possesses an underlying diamond cubic symmetry as against the hexagonal symmetry observed in the case of tetrahedrons present in the water ice. Anderson imposed a criterion [17] that, if the A and B ions are represented by ‘+’ and ‘-’, then according to this criterion the ‘+’ and ‘-’ arrange themselves so that there is maximal number of ‘+;-’ pairs. This implies that in each tetrahedron 2 ‘+’ and 2 ‘-’ are placed. At this stage the similarity between the present case and the water ice emerges clearly and there are as earlier six possible ways of
arranging the two ‘+’ and two ‘-’ on any one tetrahedron. It can be observed from the figure that there are two sets of tetrahedral (each set inverted with respect to the other) and that the tetrahedron of one set touches only the tetrahedron of the other. If there are N lattice points there are N/4 tetrahedra on one set and similarly N/4 on the other. Considering the probability that any one tetrahedra has the correct configuration is 3/8, the number of possible correct configurations (two ‘+’ and two ‘-’) works out to be:

\[ W = \left( \frac{3}{8} \right)^{N/4} \cdot 6^{N/4} \]

Thus the cations on the pyrochlore lattice can transform from an infinite random occupation possibilities to a finite number of possibilities and hence the Verwey transition indicating choice of one such possibility.

1.4 A short review of the spinel oxides exhibiting charge ordering from frustration

1.4.1 Recent results of structural analysis of Fe\(_2\)O\(_4\) below Verwey transition

Verwey showed that in Fe\(_2\)O\(_4\) there exists an electrical and magnetic transition, at around 125 K. He proposed that Fe\(^{3+}\) (3d\(^5\) \(_{\text{HS}}\)) and the Fe\(^{2+}\) (3d\(^6\) \(_{\text{HS}}\)) order periodically on the B sub-lattice causing such a transition. Ever since the proposal, this structural model claiming ordering of Fe has been highly debated. Analysis of single crystal neutron diffraction data [18] showed that no charge ordered pattern emerged. This claim too was disputed because of the twinning of the crystal domains that comes in the way of resolving the single crystal data. Later another analysis based on combined refining of neutron and X-ray diffraction data [19], claimed a weak charge modulation breaking up
the structure into 1-d stripes. This model was again contested and lost ground based on the results of resonant scattering experiments [20].

![Figure 1.5 Structural model for Fe$_3$O$_4$ proposed by Verwey](image)

Figure 1.5 Structural model for Fe$_3$O$_4$ proposed by Verwey

Very recent high energy X-ray diffraction experiments [21] from an almost single domain (40µm) grain claim that Verwey’s hypothesis of 1:1 order of Fe$^{2+}$ and Fe$^{3+}$ is correct to a first approximation. The low temperature structure condenses to Cc super structure with 16 in-equivalent octahedral B-sites. However the absence of bimodal distribution of formal Fe charge, considerations of Fe-O bond distances, associating the anomalously short Fe$^{2+}$-Fe$^{3+}$ distance with delocalization of a single charge over one Fe$^{2+}$ and two adjacent Fe$^{3+}$, this study predicts formation of ‘trimerons’ as the quasi particles of the system. Hence the current picture on Fe$_3$O$_4$ is that the ordered Cc structure is a super cell of the parent cell with $\sqrt{2}a \times \sqrt{2}a \times 2a$ – New order parameter $-t_{2g}$ occupancies. The Verwey model is replaced by an orbital ordering picture involving charge disproportionation. In the recent times, it is recognized that Fe$_3$O$_4$ is a multiferroic
[22], apart from being ferrimagnetic ($T_N=851K$), below the Verwey transition temperature. Thus the spinel Fe$_3$O$_4$ is still being studied, even 75 years after the discovery of Verwey transition and it appears that every attempt to understand this system throws up more questions than answers.

1.4.2 Columnar ordering of charges in LiMn$_2$O$_4$

LiMn$_2$O$_4$ is an important battery electrode material and is synthesized using a variety of techniques and studied extensively. It goes through a structural transition at around 290 K [23] which in fact comes in the way of tapping the full potential of this battery material. Initially this structural transition was attributed to the Jahn-Teller distortion of Mn $3^+$ ions and efforts to increase the oxidation state of Mn by incorporating Li for Mn were carried out [24-25].

![Columnar charge ordering in LiMn$_2$O$_4$](image)

**Figure 1.6** Columnar charge ordering in LiMn$_2$O$_4$ – Projection along [001]; Green-Li; Blue- Mn $3^+$; Magenta- Mn $4^+$; Oxygen atoms are removed for clarity.
Later detailed analysis of neutron diffraction data [26] showed that the LiMn$_2$O$_4$ undergoes a structural phase transition from the high temperature cubic structure to an orthorhombic structure with the formation of 3a x 3a x a superstructure of the high temperature cubic cell. The most significant factor that characterizes the charge ordered state is the Mn-O bond distance. While in the charge frustrated cubic (Fd-3m) spinel phase there is a unique Mn-O distance of 1.9609(3) Å, the charge ordered orthorhombic (Fddd) structure with five different Mn sites as in figure 1.6, shows two different Mn-O distances; two of the Mn sites show an Mn-O distance of 1.91 Å indicating the existence of Mn $4^+$ and the other three of them show an Mn-O of 2.01 Å that correspond to Mn $3^+$. EXAFS measurements [27] carried out as a function of temperature confirms the existence of two different Mn-O distances.

This study also brings forth the presence of a large static lattice disorder due to the slightly varying Mn-O distances around each Mn ion. The charge ordering occurs as a columnar ordering of Mn $3^+$ and Mn $4^+$, in such a way that two kinds of columns of Mn $3^+$ one including a Li at the center and the other without a Li are surrounded by octagonal cylinders of Mn $4^+$. Magnetic ordering in this material is still unsettled, since there is wide difference in the results of neutron diffraction experiments. Low temperature neutron diffraction [28] study shows anti ferromagnetic ordering and hence complete removal of spin frustration in this system. Yet another study shows coexistence between anti-ferromagnetic long range ordering and diffuse scattering [29]. One more study claims complete absence of magnetic ordering [30]. Susceptibility measurements have shown an abrupt jump at the transition temperature and the Curie constant and Weiss temperature are estimated to be $C=4.86$ (15) emu K mol$^{-1}$ and $\theta = -300$ (20) K, respectively [21].
Around 65 K there is a splitting between the field cooled (FC) and zero field cooled (ZFC) susceptibility. On further cooling, the FC susceptibility reaches a maximum at 45 K. These observations imply AFM fluctuations in the material and probably an ordering of spins at 45 K. Electrical resistivity shows an upturn at the transition, characteristic of the charge ordering transition going from semi-conducting to localized behavior [29].

**1.4.3 Octamer formation in CuIr$_2$S$_4$**

CuIr$_2$S$_4$ is another spinel system which has shown charge ordering from frustration. In this system Cu assumes a valency of $^{1+}$ and hence Ir has to exist as a multivalent ion and it assumes $^{+3}$ and $^{+4}$ formal oxidation states.

![Figure 1.7](image)

**Figure 1.7** Formation of octamers of Ir$^{3+}$ (red) and Ir$^{4+}$ (blue) in CuIr$_2$S$_4$ when viewed in the [111] cubic direction [31]

It shows metal-insulator transition at 230 K accompanied by a complete loss of magnetic moments [31]. Determination of crystallographic structure below this temperature shows a charge ordered state that is attributed to a unique formation of spin dimers. The charge ordered state described by the triclinic structure is supposed to be made of isomorphic octamers as shown in Figure 1.7, involving isovalent bi-capped hexagonal rings. Spin
dimer formation is strictly expected only in 1-d system due to the coupling of spins to the lattice degree of freedom as in spin Peierls compounds like CuGeO$_3$ [32]. In the case of CuIr$_2$S$_4$ it is the Ir$^{4+}$ with unpaired electrons in the $d_{xy}$ orbitals that show varying Ir-Ir distances within the octamers and thus are supposed to form the spin dimers. Of all the charge ordered spinel compounds CuIr$_2$S$_4$ is studied extensively. They have shown that the metal-insulator transition in CuIr$_2$S$_4$ is very delicate and is easily destroyed under irradiation with X-rays [33] or, substitution of Ni at A-site or Ti, Rh and Cr at B-site [34] (and references there in).

1.4.4 Novel heptamer formation in AlV$_2$O$_4$

The spinel compound AlV$_2$O$_4$ opens up another new way of ordering of charges. Aluminum, a trivalent cation resides on the A site, and vanadium occupies the pyrochlore B-lattice with an average valency of 2.5. Interestingly AlV$_2$O$_4$ shows a semiconductor to insulator transition at around 700 K with a slight reduction in magnetization. A structural transition from cubic to rhombohedral (R-3m) has been observed to accompany the resistive transition indicating charge ordering. Thus AlV$_2$O$_4$ gives a unique opportunity of probing the charge ordered state at ambient temperatures.

![3:1 ordering of vanadium ions in AlV$_2$O$_4$](image)

**Figure 1.8** 3:1 ordering of vanadium ions in AlV$_2$O$_4$
When charge ordering from frustration was discovered in AlV2O4,[2] to maintain charge neutrality, it was proposed that the vanadium ions with an average valency of 2.5 in the cubic phase splits into V1 ions with valency 2.5-δ and V2 ions with valency 2.5+3δ. It was thought that this compound is a good example of ordering of vanadium ions as 3:1 (V1:V2) in every vanadium tetrahedral as shown in Figure 1.8. But subsequent detailed analysis of electron diffraction data indicated super lattice peaks at (½ ½ ½) kind of positions which required a totally different structural model to explain the observation. Based on the observation of super lattice spots and refinement of synchrotron powder diffraction data, a totally novel ‘heptamer’ clustering of vanadium ions with a left out ‘lone’ vanadium ion has been proposed to model the structure [35]. Vanadium occupies a single site in the frustrated spinel state, but in the charge ordered rhombohedral phase (R-3m), there are three different V sites V1, V2, V3. Based on the V-O bond distances it is assumed that the valence state of V1, V2 and V3 are +3, +2 and +2.5. When viewed from the [1 1 1] direction of the cubic cell, the three vanadium are arranged as layers of V1-V3-V2-V3-V1-V3-V2-V3 …

This structural model is shown in figure 1.9. The V3 trimers (brown) of adjacent planes along with the V2 (pink) form the heptamer cluster of seven vanadium atoms. The V1 (red) are considered to be loners as they do not bond with the neighbors. The magnetic susceptibility below 600 K could be fitted with a Curie-Weiss term and spin gap term. Existence of Curie-Weiss term till very low temperatures implies suppression of magnetic ordering. In AlV2O4 it implies that, though the charges have ordered below 700 K, the spins on vanadium continue to remain frustrated. This work also brings out that substitution of Mg for Al and Cr for V suppress the charge ordering. $^{51}$V and $^{27}$Al
NMR measurement [36] observes variation of knight shift $^{51}\text{K}$ and $^{27}\text{K}$ as a function of temperature.

**Figure 1.9** Structure of rhombohedral $\text{AlV}_2\text{O}_4$ in the hexagonal setting. $V1$ atoms are represented by red, $V2$ atoms by pink and $V3$ by dark brown octahedra, aluminum atoms are surrounded by light blue tetrahedron and oxygen atoms are in green. Notice the presence of vanadium heptamers.

The observed knight shifts could be fitted using the expression for susceptibility suggested in terms of spin gap and Curie–Weiss terms. At the local level it confirms existence of spin singlet behavior of the heptamer clusters and triplet behavior of the lone vanadium $V1$. Interestingly the hyperfine coupling constant ($B$) measured from the ratio of the knight shift and the susceptibility works out to be $-82\pm 8$ kOe /$\mu_B$ which in terms of orbital occupancy translates to a value comparable to $\text{VO}_2$ (one valence electron) and
less than \( V_2O_3 \) (two valence electrons). It is to be noted that the nature of charge distribution is still very interpretative in \( AlV_2O_4 \).

Results of the first principles density functional theory computations [37] confirm heptamer clustering within the rhombohedral charge ordered structure. From the V-V distance obtained on the converged structure, it is proposed that the charge distribution on the vanadium ions may be \( V_1^{2.5-\delta_1}, V_2^{2.5+\delta_2} \) and \( V_3^{2.5+(\delta_1-\delta_2)/6} \) with \( \delta_1 > \delta_2 > 0 \); Electron energy loss spectroscopy measurements on \( AlV_2O_4[38] \) record a unique three peak structure in the O-K edge and an average charge state of 2.5 on the vanadium ions. The origin of the heptamer formation is supposed to emerge from 1-D orbital (V-d\(_{xy}\)) chains [39]. From these studies it can be concluded that the low temperature charge ordered structure is explained by the heptamer cluster formation of vanadium ions. This kind of cluster formation is unique and it is to be examined how robust is this heptamer cluster in the presence of various parameters. The available results indicate that the cluster formation may be very delicate. It is also observed that charge distribution on the vanadium ions is yet to be established conclusively.

**1.4.5 Frustration to order in LiRh\(_2\)O\(_4\)**

Very recently another new spinel compound LiRh\(_2\)O\(_4\) has been synthesized [40] and observed to show a valence bond solid ground state following a band Jahn Teller effect. Rh in the B site has probably 1:1 ratio of \( Rh^{3+} \) \( (S = 0, 4d^6) \), and \( Rh^{4+} \) \( (S = 1/2, 4d^5) \). In contrast with the other charge frustrated spinel systems, LiRh\(_2\)O\(_4\) shows two transitions. Initially on cooling from ambient temperature down to 230 K, the resistivity
remains flat. At 230 K, it appears to show a weak increase till down to 170 K. But at 170 K, the resistivity increases several orders of magnitude.

![Structure of LiRh$_2$O$_4$ in the cubic phase](image)

**Figure 1.10 Structure of LiRh$_2$O$_4$ in the cubic phase [40]**

Also the ambient temperature cubic structure transforms to a tetragonal structure (I 4/am d) at 230 K and it further undergoes a transition to orthorhombic structure at 170 K. At present the transition at 230 K is identified as band Jahn–Teller transition and the other one at 170 K is considered to be a charge ordered transition induced by the band Jahn-Teller effect. Magnetic susceptibility shows that the system moves from an orbital disordered paramagnetic metal to orbital ordered paramagnetic metal to a charge and orbital ordered, insulating non magnetic valence bond solid. Specific heat measurements made using DSC indicate a large change in entropy 0.24 R/mole Rh$^{4+}$ and 0.70 R/mole Rh$^{4+}$. The density of states near the Fermi surface is predominantly from the transition metal ions and they make a flat band in the case of charge ordered materials. This density of states, couple with the degeneracy in the orbital degree of freedom in the case of
LiRh$_2$O$_4$, resulting in band Jahn-Teller instability. An increased thermo electric power (80 $\mu$V/K at 800 K) measured in LiRh$_2$O$_4$ is supposed to auger well with this argument. Eventually this band Jahn-Teller instability is supposed to drive the system to a valence bond solid state.

1.5 Short summary of the spinel compounds exhibiting charge order from frustration

To sum up, the five spinel compounds Fe$_3$O$_4$, LiMn$_2$O$_4$, CuIr$_2$S$_4$, AlV$_2$O$_4$ and LiRh$_2$O$_4$ known so far, have shown charge frustration. In all of them the high temperature charge frustrated state is characterized by the cubic structure. They explore the configuration space in a completely different manner as they relieve the frustration with finitely many possible ground states to a particular charge ordered state, sometimes through orbital ordering. All of them apart from Fe$_3$O$_4$ are normal spinels existing in a cubic structure (Fd-3m). In all of them, the pyrochlore B sub-lattice is randomly occupied by the multiple valent transition metal ions. All of them show a “Verwey transition” like increase in resistivity of varying magnitudes as they are cooled. The resistive transition is accompanied by a structural transition.

But they assume totally different structures in their charge ordered state. None of them satisfy the Anderson’s 1:1 criterion and some of them show charge disproportionation with non integral charge states. Superlattice reflections observed in the electron diffraction patterns, have served as important input in arriving at the structural model in each of these compounds. Thus the study of frustrated spinel systems compellingly takes us to unknown territories with unpredictably plenty of possibilities into a hitherto unchartered and unexplored ground state landscapes.
Spinels exhibiting charge order

Figure 1.11 The five spinel systems that exhibit charge frustration in the cubic structure Fd-3m. All of them relieve the frustration through structural transition by farming unique clustering brought about by the participation of orbitals.

Owing to the complex nature of the structure and ordering, these charge frustrated spinel systems are very challenging to synthesize, to solve the crystal structure in the ordered state and to understand the role of various parameters on the charge ordered state. As it is evident a lot more needs to be studied about these just emerging systems in terms of experimentation and theoretical formulation to explore further and to reach ultimately to the mechanism of ordering from frustration. With this background it becomes essential to express the reason behind the specific choice of AlV_2O_4 and LiMn_2O_4 as the two compounds chosen for study under this thesis.
1.6 Motivation and thesis organisation

Amongst the spinel systems showing charge ordering from frustration, AlV$_2$O$_4$ stands apart, since it is the only spinel compound known so far that shows charge ordering at around 700 K. This unique feature offers a possibility to access the charge ordered state at ambient temperature. The ordering of charges itself appears to be through a novel clustering of vanadium ions in the form of a heptamer molecular unit. LiMn$_2$O$_4$ offers another interesting scenario since it shows partial charge ordering through the formation of octagonal columnar structures. Though abundantly studied for its functionality as a battery material, the charge ordering aspect is still less probed. Only a few published works exist indicating the challenges posed by these materials and hence it is motivating to synthesize and study these systems in some more detail. Also, in the parlances of strongly correlated electronic systems with myriads of surprises under their fold, the phenomenon and the physics of charge ordering itself is highly contested, more so from frustration, and hence it motivates further probing.

Thus, the present thesis engages in studying these two charge frustrated spinels (AlV$_2$O$_4$ and LiMn$_2$O$_4$) by tweaking the thermodynamic variables like pressure and temperature and tuning the charge concentration by substitution. Condensed matter tools like powder diffraction, resistivity measurement, electron energy loss spectroscopy measurements and computation of electronic structure are used in this thesis.

Thesis organization

The above review of the conceptual aspects of frustration including typical examples of charge ordering from frustration with respect to spinel system and motivation for the
investigation carried out in the present thesis work form Chapter 1. Chapter 2 discusses the aspects of synthesis and powder X-ray diffraction characterization of AlV$_2$O$_4$ and the results of the systematic high temperature powder XRD measurements confirming the structural transition from room temperature charge order phase to high temperature charge frustrated phase. Chapter 3 describes the results of synchrotron powder XRD measurements in a diamond anvil cell under hydrostatic and non hydrostatic pressures showing for the first time that the charge ordered AlV$_2$O$_4$ is driven back to frustration under high pressure. Results of the electron energy loss spectroscopy measurements and Density Functional calculations are presented in chapter 4. In chapter 5, synthesis, characterization, results of four probe resistance measurement and results of the low temperature synchrotron powder XRD measurements of another interesting charge frustrated spinel compound LiMn$_2$O$_4$ with partial substitution of Ru for Mn is presented. Finally, chapter 6 describes the conclusions of the present thesis and lists the scope for future study.

References


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