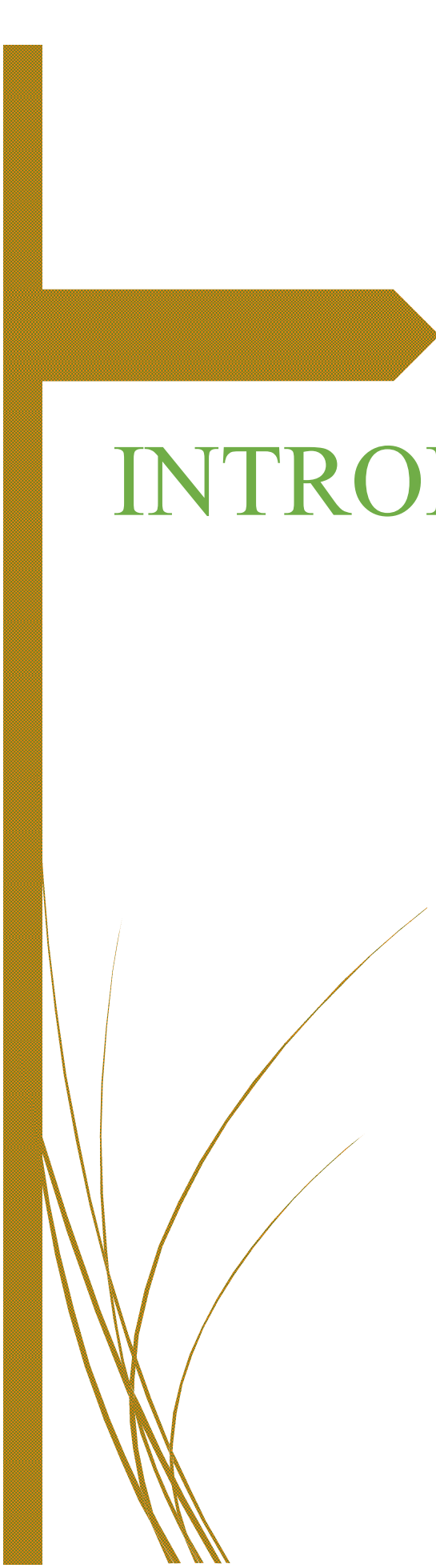
Chapter 1

INTRODUCTION



1. Introduction

In human history, technological achievement often deals with discovery and the use of new materials or -in some cases – a new employment of previously known ones. The development and application of new multifunctional materials has a strong effect in everyday's life, affecting our relationship with energy saving or production, communications and health care, just to mention some. This is apparent if one considers silicon chips, present in almost any electronic device; light emitting materials, which are at the heart of today's communications; novel liquid crystal displays, providing high performances and low energy consumption; magnetic materials, largely used in recording devices. The discovery of **multiferroic materials** is a milestone in the development of multifunctional devices as mentioned above.

1.1. Definitions of Multiferroics

The term multiferroic was coined relatively late, in 1994 by H. Schmid [1]. It refers to materials that have either two or more different ferroic orders at the same time: (anti)ferromagnetism, ferroelectricity and ferroelasticity. Multiferroics can be described as materials in which there are couplings between different types of ordering, including magnetic, charge, and elastic orders where magnetism and ferroelectricity are strongly coupled together. The question arises how different ferroic states can coexist in a single-phase material which is an important issue that can be elaborated in detail using symmetry arguments and Landau theory for continuous phase transitions, which shows that the spin structure alone can break spatial inversion symmetry leading to ferroelectric order [2,3].The condition of material to be a multiferroic is that at least two primary ferroic properties are coexist in one material in single phase and there may exist coupling between them. It means coupling between them is not a necessary condition to be a multiferroic material.

In those multiferroic compounds, complex spin order, which arises from frustrated and competing interactions, is established at low temperatures and induces ferroelectricity. The coupling between long range magnetic and ferroelectric order that is in which electric polarization switchable with magnetic field and magnetic polarization with electric field is known as **magnetoelectric coupling**. The materials exhibit these magnetoelectric coupling is termed as special class of multiferroic materials. The magnetoelectric coupling will allow the design of materials with novel electronic

properties and in selected cases bring them to application [4-6]. **Magnetoelectric coupling is a sufficient condition for multiferroicity not necessary because that materials which exhibits magnetoelectric coupling must be a multiferroic but multiferroic materials may be magnetoelectric or not**. From the application point of view, multiferroic materials which have strong coupling between ferroelectricity and magnetism are most important for the development of memory devices such as futuristic multistage memory devices with electrical writing and nondestructive magnetic reading operations [7, 8]. Schmid [1] introduced a name "**multiferroics**" for these materials.

"Crystals can be defined as multiferroic when two or more of the primary ferroic properties are united in the same phase."

Hans Schmid (University of Geneva, Switzerland) in: M. Fiebig et al. (ed.), *Magnetoelectric Interaction Phenomena in Crystals*, (Kluwer, Dordrecht, 2004)

The idea of Multiferrocity, not only cross-coupling responses of magnetization and polarization (i.e., the appearance of magnetization ***M*** in an electric field ***E***, or appearance of electric polarization ***P*** by the application of magnetic field ***H***) can exist in solids, but the systems in which two types of ordering: (ferro)magnetism (spontaneous magnetization) and ferroelectricity (spontaneous polarization),can exist simultaneously in one material in the absence of external electric and magnetic fields, brings much interesting twist in the field of multiferroic (Fig. 1.1) .

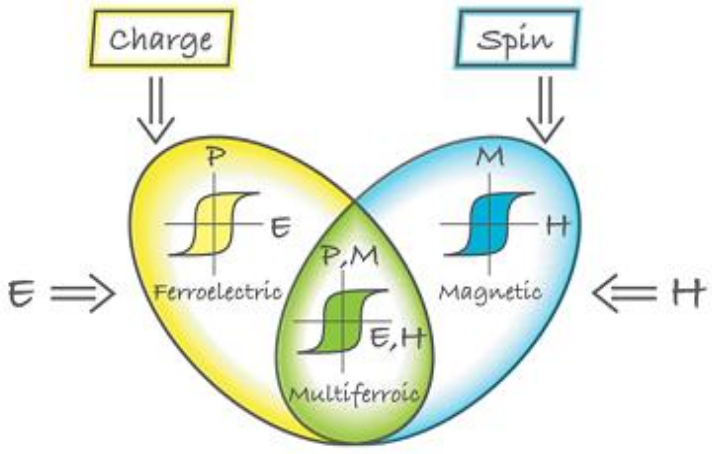


Fig.1.1: *Schematic diagram of multiferroic materials which combine the properties of ferroelectrics and magnets (courtesy: Khomskii, D., Physics 2, 20-27, 2009).*

There is a third type of ordering, spontaneous deformation, which leads to ferroelasticity included in this category. But, now-a-days multiferroic mainly applies to the coexistence of magnetism and ferroelectricity. Boracites were probably the first known multiferroics [9], and after that several other multiferroic materials were discovered or found in nature.

1.2. A brief review on historical background of Multiferroics

The study and development of functional materials (i.e. system able to perform more than two properties in one materials under a determined simultaneous) are thus mandatory, and compound displaying more than one degree of functionality (multifunctional materials) are promising in current rush toward miniaturization. In this wide category, electro-optic materials that currently lead the field of data transfer and manipulation, magnetoresistive compounds play a great role in the market of random access memory, ferromagnetic semiconductor offering interesting perspective in development of spintronics, and finally multiferroic materials offer to develop multiple control devices (e.g. electric field controlled-magnetic data storage and vice- versa).

Two independent phenomena point out the birth of magnetoelectric (ME): In 1888 Rontgen discovered that a moving dielectric magnetized when placed in an electric field [10] and the reverse effect was observed after 17 years latter (polarization of moving dielectric in magnetic field) [11]. In 1894 Curie pointed out the possibility of intrinsic ME behavior of crystals on the basis of symmetry considerations, in which the crystals can be polarized in the presence of a magnetic field and vice-versa. Theoretical details of the ME in a specific material Cr_2O_3 was developed by Dzyaloshinskii [12] and subsequently first experimental confirmation of ME effect (electric field induced magnetization) in Cr_2O_3 proved by Astrovin 1960, and he showed experimental confirmation of an electric field induced magnetization [13,14], and quickly the converse, magnetic field induced polarization was confirmed by Redo [15,16]. The subsequent search for alternative ME materials led scientists to synthesize new single phase compounds and found multiferroic and ME behavior in several families of materials. In 1972 Suchetelen introduced the idea of product property and later Boomgaard in 1978 laid the conceptual approach for preparation of magnetoelectric composites. Subsequently a series of single phase materials in single crystal, or ceramic

from such as [$Pb(Fe_{0.5}Nb_{0.5}O_3)$, $TbMnO_3$ and many other compounds] have been extensively investigated.

In recent years, many excellent reviews have been written summarizing the latest developments on different material combinations exhibiting interesting magnetoelectric properties [17-24]. In these review articles focus on the drawbacks in the developing technologies, and attention is drawn to overcome these drawbacks and understanding of some observations related to the physics of magnetoelectric materials. For better understanding the basic phenomena and achievements in the field of multiferroics, it has become necessary to classify the multiferroics on the basis of microscopic mechanisms that determine the coupling strength between magnetism and electricity and have been explained in detail by [25].

There are several families of multiferroic materials have been discovered, e.g. Pb-family: $Pb(Fe_{0.5}Nb_{0.5})O_3$, $Pb(Fe_{0.5}Ta_{0.5})O_3$, $Pb(Fe_{2/3}W_{1/3})O_3$ [26-32] perovskite oxide structure; Bi compounds $BiMnO_3$,$BiFeO_3$[33-37]; rare earth (RE) manganites $ErMnO_3$, $YbMnO_3$, $TbMnO_3$, $YMnO_3$, $LuMnO_3$ [38-41]; mixed perovskite solid solutions $PbTiO_3$, $Pb(Zr_{0.2}Ti_{0.8})O_3$, $Pb(Zn_{1/3}Nb_{2/3})O_3$, $Pb(Zr_{0.53}Ti_{0.47})O_3$ [42-49]; $REMn_2O_5$ family (RE=Tb, Dy, Eu, Gd, Ho, Y) [50-56], phosphates: $LiMPO_4$ (M= Ni, Co, Mn, Fe) [57-58], boracites: $M_3B_7O_{13}X$, where M = (Ni, Cu, Cr, Mn, Fe, Co) and X = (Cl, Br, I),[59-61], fluoride family $BaMF_4$, M = Mg, Mn, Fe, Co, Ni, Zn. [62-65], spinel chalcogenides $ZnCr_2Se_4$, $CdCr_2S_4$ [66-69], and delafossites, $CuFeO_2$ $CuCrO_2$ [70-71].

Multiferroic materials with cross-coupling effect (magnetoelectric coupling), have great potential for practical applications such as the ability to address magnetic memory electrically, introduction of new type of 4-state logic (i.e., with both up and down polarization and up and down magnetization), magnetoelectric sensors and many more, which leads to an extremely rapid development of the field of multiferroic [72-76].

1.3. Types of Multiferroic materials

In Multiferroic materials, mechanism of origin of ferroic properties and their coupling are most important to categorize them. On the basis of origin of ferroelectricity and magnetism, multiferroics materials are categorized in two types: Type I and Type II.

1.3.1. Type I Multiferroics

If the origins of ferroelectricity and magnetism are different and there exist a rather weak coupling between them or not are known as Type I multiferroics. Type I multiferroics are "older" and more numerous. These are good ferroelectrics and the ordering temperatures of ferroelectrics and magnetic transitions can be well above room temperature. But there is problem in that type of multiferroics materials, they cann't exhibit strong coupling between ferroelectricity and magnetism which is important from the application point of view. In general in these type I multiferroic materials the FE ordering temperature is much higher than the magnetic ordering. Type I multiferroics are also categorized in several different subclasses on the basis of microscopic mechanism (origin) of ferroelectricity in them. We will focus on four of the major subclasses, but there are certainly others.

1.3.1.1. Origin of ferroelectricity due to d^0-ness condition

Transition metal perovskites are the most promising multiferroic materials which exhibit a lot of magnetic materials with diverse properties among them; also most of the classical ferroelectrics, such as $BaTiO_3$ or (PbZr)TiO3 (PZT), belong to these class. In the past decades, to create multiferroic materials were mostly concentrated on these classes of compounds. In this class of compounds, there exist hundreds of magnetic perovskites; the good collection is presented in the tables compiled by Goodenough and Longo [77]. Another, even more extensive volume in the same Landolt-Börnstein series lists hundreds of ferroelectric perovskites [78]. The study of these tables indicates that there is practically no overlap between these two extensive lists of materials: magnetism and FE in perovskites seem to exclude one another but there are some exceptions in the stoichiometric (not mixed) perovskites are $BiFeO_3$ [79] and $BiMnO_3$ [80-81] and may be the recently synthesized $PbVO_3$ [82-83]. In fact even these examples do not violate this general `` exclusion'' rule for Perovskites that ferroelectricity in them apparently has a different source than in most of the FE of this class, such as $BaTiO_3$.

Then why this mutual exclusion? Answer is that all conventional ferroelectrics Perovskites contain transition metal ions with empty d orbitals such as Ti^{+3}, Ta^{+5}, W^{+6} whereas for magnetism one needs partially filled d or f orbitals. Ferroelectricity in these systems is due to the off-center shifts of the transition metal ion, which forms strong covalent bonds with one (or three) oxygen, using their empty *d* states [Fig. 1.2(a)]. On

the other hand, the presence of real *d* electrons in d^n configurations of magnetic transition metals suppress this process, preventing ferroelectricity in magnetic perovskites. This so called "d^0 vs d^n problem" was one of the first to be studied theoretically at the beginning of the recent revival of multiferroics [84-85].

1.3.1.2. Origin of ferroelectricity due to lone pair

In some multiferroic materials e.g. $BiMnO_3$ and $BiFeO_3$ both contain only magnetic TM (Transition Metal) ions as Mn^{+3} (d^4) and Fe^{+3} (d^5) and both exhibits ferroelectric and magnetic simultaneously, these are exception in the family of Perovskites multiferroic which violate the "exclusion" rule of d^0 vs d^n. It is clear that they are not violating the general rule of inducing ferroelectricity but in that case ferroelectricity is not due to transition metal ions as e.g. $BaTiO_3$, it is driven by the other A-ions, in the case Bi, in $BiFeO_3$. Most probably in $BiMnO_3$ and $PbVO_3$, Bi^{+3} and Pb^{+2} play the major role in the origin of ferroelectricity. Actually these ions (Bi^{+3} and Pb^{+3}) exhibits two outer 6s electron and they do not participate in chemical bonding, so it is called *lone pairs* [25]. This lone pair gives high polarizability of respective ions [Fig. 1.2(b)], which in classical theory of FE is believed to lead, or at least strongly enhance, the instability towards FE.

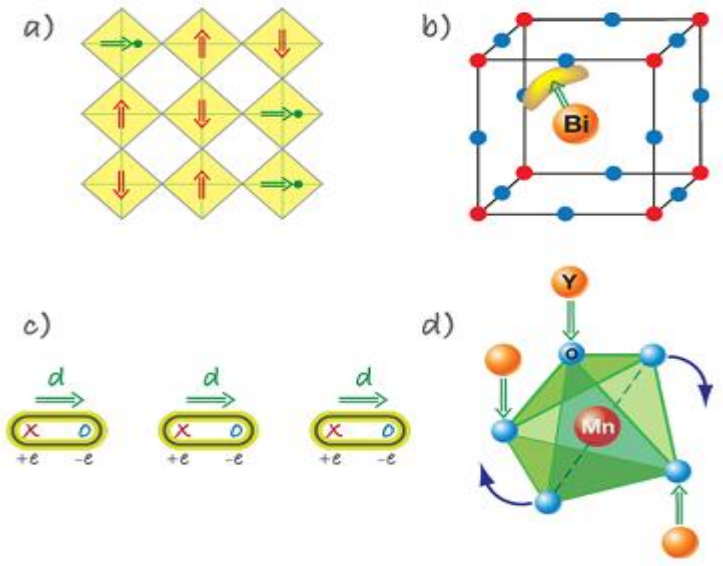


Fig.1.2: *Depending upon the mechanism of origin of the ferroelectricity, type-I multiferroics have been divided in (a) Multiferroic perovskites (b) Ferroelectricity due to lone pairs (c) Ferroelectricity due to charge ordering and (d) Geometrically frustrated Ferroelectricity (courtesy: Khomskii, D., Physics 2, 20-27, 2009) [25].*

From the microscopic point of view we can simply say that the particular orientation of these lone pairs, or dangling bonds, may create local dipoles, which finally can order in a FE or anti-FE fashion.

1.3.1.3. Ferroelectricity due to charge Ordering

In some Multiferroics, ferroelectricity occurs due to charge ordering (CO); CO means ordering of transition metal ions with different valencies or a site centered ordering of extra electrons or holes on a metal sublattice [Fig. 1.2(c)]. That have been observed in half doped manganites e.g. $R_xCa_{1-x}MnO_3$ (R= rare earth) as x= 0.5, $LaCaMnO_3$ where x≥ 0.5. In half-doped manganites, x=0.5 [86-87], one uses the picture of a checkerboard CO below figure 1.3 [88] shows alternation of Mn^{3+} and Mn^{4+} ions. (One should not take this terminology too literally: there is never a full charge localization with the formation of real Mn^{3+} and Mn^{4+} states, usually the degree of charge disproportionation is much.

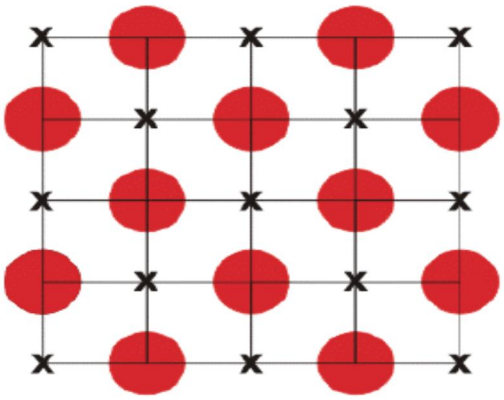


Fig.1.3 *Site centered charge ordering in half doped manganites like $Pr_{0.5}Ca_{0.5}MnO_3$ (D.I. Khomskii et al, JMMM 306 (2006) 1-8) [88].*

1.3.1.4. Geometrical ferroelectricity

In some perovskites ABO_3 where size of A-ions small enough there occurs tilting and rotation of BO_6octahedra to make a close packing of the structure and exhibits a structural transition from cubic to orthorhombic (or sometimes rhombohedra) structure (the so called $GdFeO_3$distortion) [fig. 1.2 (d)]. This tendency of distortion is calculated by the formula of tolerance factor $t=(r_A+r_O)/\sqrt{2}(r_B+r_O)$, where $r_{A,B,O}$ are the ionic radii of corresponding ions. Typical values of cubic – orthorombic transitions due to this mechanism are ~800, 1000 K. In the case of $YMnO_3$ and in similar systems: to achieve close packing, rigid MnO_5 trigonal biprysm tilted. But in this process perovskites does not

lead to FE, due to tilting BO_6 one rather shorten the A– O bond length. In the hexagonal structure of $YMnO_3$ such type of tilting leads to a loss of an inversion symmetry and to lead FE, with dipole moments mostly formed by Y – O pairs. Thus in a sense FE in these compounds is almost an ``accidental by-product'' of the tendency to close packing. It is not surprising then that also here the corresponding structural phase transitions occur at pretty high transition temperatures ~900 ¸ 1000 K [89].

1.3.2. Type II Multiferroics

If the origin of one ferroic property is connected to other, it means one ferroic property switchable with another and vice versa, these are known as Type II multiferroic materials. This is the most interesting discovery in the field of multiferroics in which ferroelectricity exists only in a magnetically ordered state and is due to a particular type of magnetism. It is known as novel class of multiferroics because there exist a strong coupling between ferroelectricity and magnetism. It indicates one ferroic order causes another ferroic order and they exhibits strong "magnetoelectric effect".

The coupling between long-range magnetic and ferroelectric order has been studied since the 1960s [90-91] and it was discovered in type II multiferroic materials in which magnetoelectric is strong. These strong Magnetoelectric coupling is most important in the field of novel potential applications e.g. four logic state memory devices because with strong coupling between the electric and magnetic state (ME coupling), there exist four switchable states, namely, (+P, +M), (+P, -M), (-P, +M), and (-P, -M) [92] and multiferroics and magnetoelectrics with cross-coupling can be used to develop of futuristic multistate memory devices with electrical writing and nondestructive magnetic reading operations [93-94].

That happens in the recently discovered multiferroic materials $RMnO_3$ (with perovskites structure; R=Tb, Gd) [95], in RMn_2O_5 (R different rare earths, such as Tb, Y etc.) [96], in $Ni_3V_2O_8$ [97], and in hexaferrite [98]. In all these systems FE appears in magnetically ordered state, in certain phase: the phase with the spiral ordering in $TbMnO_3$ [99], and in similar phases in other such systems. There are many other examples of multiferroics materials in which ferroelectricity occurred due to non collinear magnetic ordering (spiral or helicoidal) e.g $LiCu_2O_2$, and $LiCuVO_4$ etc. [100-104].

There is important question about microscopic mechanism behind the generation of FE by magnetic ordering in these systems, is actually not answered. But one general idea seems to be quite acceptable that in the most of these systems, FE appears in magnetic phases with the spiral (non-collinear spin ordering), or helicoidal magnetic structures [105-107]. So, we discuss the mechanism of ferroelectricity appears in the complex magnetic order such as spiral or helicoidal spin ordering.

1.3.2.1. Ferroelectricity due to spiral Magnetism

In the last past decades, there has been a great deal of interest in multiferroic community to discover such several metal compounds, where ferroelectricity is induced by a transition to a complex magnetic state (spiral or helicoidal). This class of materials are systems like $RMnO_3$ (R=Gd, Dy or Tb), RMn_2O_5 (R=Tb or Y), $MnWO_4$, $NiVa_2O_8$, $CoCr_2O_4$, $CuFeO_2$, CuO or some complex hexagonal ferrites like $(Ba,Sr)_2Zn_2Fe_{12}O_{22}$ [18,38, 108-110] and $LiCu_2O_2$, $LiCuVO_4$ [102-104]. In this class of materials, some of these systems show appreciable effects such as the ability of a magnetic field to rotate or stabilize an electrical polarization, as in the case of $TbMnO_3$ or $GdMnO_3$, respectively [111-113]. In this way qualitatively one can understand that the inversion symmetry is actually broken in the spiral phase of magnetic ordering and induce ferroelectricity in it.

Origin of ferroelectricity due to magnetism is a great issue to discuss the mechanism of the appearance ferroelectricity due to magnetic ordering. So, we discuss some theory to elaborate this issue which stated below.

1.3.2.2. Ginzburg-Landau theory (GL)

GL theory explains the mechanism of coupling of electric polarization P to the magnetization M due to which non-collinear magnetic ordering [Fig. 1.4] induces ferroelectricity. Actually in that case spin <S> breaks time reversal symmetry, t→-t and polarization <R> breaks space inversion symmetry which transforms P→P and M→-M, lowest order coupling occurs at $<S>^2<R>^2$ and lower-order terms involving spatial gradient $<S>^2<\text{grad } R>$ or <S><grad S><R> are possible.[114]

Generally one can write down GL terms like

$$F_I \sim \mathbf{P}\cdot\mathbf{M}(\nabla\cdot\mathbf{M}), \quad \mathbf{P}\cdot(\mathbf{M}\cdot\nabla)\mathbf{M}, \quad \mathbf{P}\cdot\nabla(\mathbf{M}^2)$$

that result in induced polarization

$$\mathbf{P} \sim \mathbf{M}(\nabla \cdot \mathbf{M}), \quad (\mathbf{M} \cdot \nabla)\mathbf{M}, \quad \nabla(\mathbf{M}^2)$$

(in the presence of magnetic ordering)

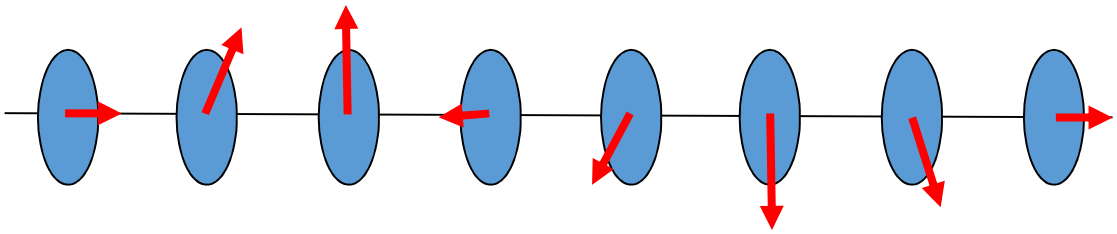


Fig. 1.4: *Non-collinear magnetic ordering (Spiral Spin Ordering).*

For spiral spins

$$\mathbf{M} = M_1\hat{x}\cos(\mathbf{k}\cdot\mathbf{r}) + M_2\hat{y}\sin(\mathbf{k}\cdot\mathbf{r})$$

induced polarization

$$\mathbf{P} \sim \mathbf{M}(\nabla \cdot \mathbf{M}), \quad (\mathbf{M} \cdot \nabla)\mathbf{M}, \quad \nabla(\mathbf{M}^2)$$

has a uniform component given by

$$\mathbf{M} = M_1\hat{x}\cos(\mathbf{k}\cdot\mathbf{r}) + M_2\hat{y}\sin(\mathbf{k}\cdot\mathbf{r})$$

$$\int d^3\mathbf{r}\mathbf{P} \sim \underline{M_1 M_2}\mathbf{k} \times (\hat{x} \times \hat{y})$$

uniform induced polarization depends on the product of $\mathbf{M_1}$ $\mathbf{M_2}$, when spin ordering is collinear ($M_1M_2 = 0$), they cannot induce polarization. If the spin ordering is non-collinear ($M_1M_2 \neq 0$), only non-collinear spin ordering have a chance to induce polarization. That quite consistent with experimental facts. No microscopic derivation of Mostovoy's free energy exists yet.

1.3.2.3. Inverse D-M (Dzyaloshinskii-Moriya) Interaction (Microscopic theory)

Dzyaloshinskii-Moriya explains first microscopic origin of induced electric polarization due to spin chirality (non-collinear ordering) in multiferroic materials. Dzyaloshinskii-Moriya plays an important role and has a profound effects on certain magnetic properties in both insulators and metals [115-116]. The DM interaction attracted much attention and has been subject of intensive study in the past decade. DM interaction has great importance related to the magnetoelectric coupling effects in multiferroics as it was proposed in spin current model [117-119] and in the so called

inverse DM interaction model. Actually DM interactions point out the mechanism of origin of spin chirality, it is due to spin orbit coupling. When considering spin orbit interaction for a spin spiral state then one can write down spin-polarization interaction term such as

$$\frac{1}{2}\sum_{\langle ij\rangle}\mathbf{P}_{ij}^{2}+\lambda\sum_{\langle ij\rangle}\mathbf{P}_{ij}\cdot(\hat{e}_{ij}\times\mathbf{S}_{i}\times\mathbf{S}_{j})$$

Where P_{ij} is Dzyaloshinskii-Moriya (DM) vector and e_{ij} direction of DM vector that fully consistent with symmetries and consistent with GL theory. Scheme of interaction is shown below in figure [Fig.1.5].

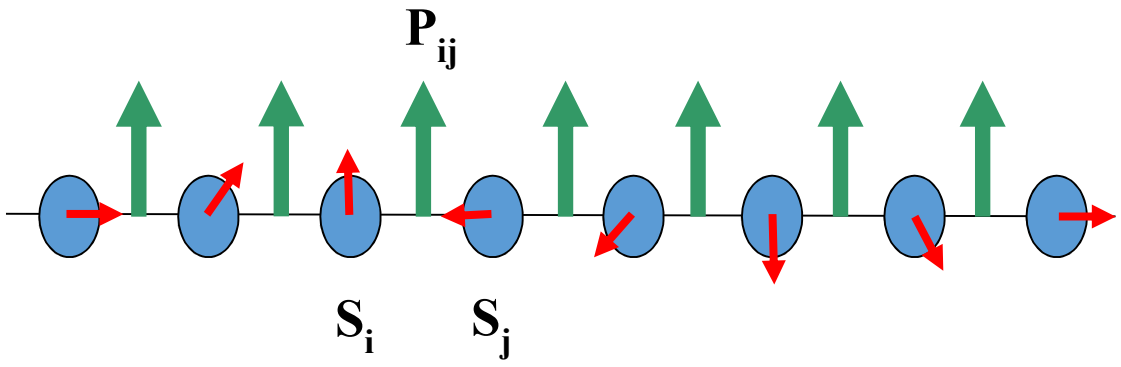


Fig.1.5: *Electric polarization (DM) vector in the presence Spiral magnetic ordering.*

1.3.2.4.: Theory of Katsura, Nagaosa, Balatsky (KNB-Model)

In this theory, they explained fully microscopic origins based on the electronic states and develop a theory of Magnetoelectric effect (ME) starting from the electronic Hamiltonian considering the spin-orbit coupling and showed the ME and spin current are directly related in non-collinear spin structure such as spiral state. Considering three atom model as shown below figure [Fig.1.6] [106] which represents the bond between two transition metal ion M1 and M2 through the oxygen atom O where e_1 and e_2 are generally in non-collinear configuration. In the presence of oxygen atom, there are hopping process between M site and O site. The Hamiltonian for electron transfer given as

$$H = H_{SO} + H_M + H_O + H_V$$

$$H_{SO} = \lambda S \cdot L$$

$$H_M = -U \sum_{a=r,l} m_a \cdot \left(\sum_{l=xy,yz,zx} S_{a,l} \right)$$

$$H_O = E_p \sum_{b=x,y,z} \sum_{\sigma} p^{+}_{b\sigma} p_{b\sigma}$$

$$H_V = V \sum_{\sigma} \left[\left(d^{+}_{l,xy\sigma} p_{y\sigma} + d^{+}_{l,zx\sigma} p_{z\sigma} \right) - \left(d^{+}_{r,xy\sigma} p_{y\sigma} + d^{+}_{r,zx\sigma} p_{z\sigma} \right) \right] + h.c.$$

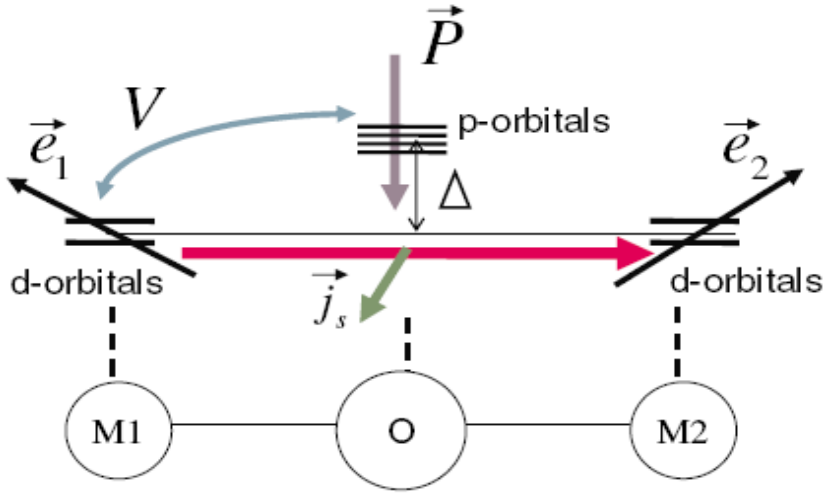


Fig. 1.6: *The cluster model with two transition metal ions M1, M2 with the oxygen atom O between them. With the noncollinear spin directions e~1 and e~2, there arises the spin current j~s / e~1 e~2 between M1 and M2. Here the direction of the vector j~s (denoted by the short arrow near the middle of the diagram) is that of the spin polarization carried by the spin current. The direction of the electric polarization P~ is given by P~ / e~12 j~s where e~12 is the unit vector connecting M1 and M2 [106]*

KNB Hamiltonian is solved assuming λ (spin-orbit) >Hund (U) and polarization defined as

$$\mathbf{P} \propto \mathbf{K} \times \langle \mathbf{S}_1 \rangle \times \langle \mathbf{S}_2 \rangle$$

Where polarization are orthogonal to spin rotation axis and modulation wave vector develops and spin current is essential for electric polarization.

There are many multiferroic materials discovered in which magnetoelectric coupling has been observed as explained above in Type II multiferroics. In these examples of multiferroics, $TbMnO_3$ and $LiCuVO_4$ are the most important. In $TbMnO_3$ non-zero electric polarization **P** appears below 30 K and shows strong magnetoelectric coupling when magnetic structure changes from the sinusoidal to a helicoidal one [120]. In $LiCuVO_4$ nonzero electric polarization appears below 2.3 K due to flop transition of sinusoidal spin structure to helicoidal [103] and gives low electric polarization value but it exhibits an **one-dimensional quantum spin chain** and behaves as **quantum magnet** that explain many quantum phenomena in condensed matter physics. So, we choose these two system for the present PhD project. $TbMnO_3$ crystallizes in orthorhombically perovskites structure (ABO_3 type) and $LiCuVO_4$ in distorted inverse spinel structure (AV_2O_4). Let us discussed these two types of structures in details below.

1.3.2.5. Perovskites Materials

Materials which exhibits perovskites type structure attracted more attention towards it because reach properties are governed by family of perovskites materials. Perovskites describe a crystal structure class, very stable structure, large number of compounds, variety of properties and many practical applications

- high T_c cuprate superconductors
- Colossal Magneto-Resistance ($La,SrMnO_3$)
- fast ion conduction (Li^+, O^{2-}), batteries, fuel cells
- mixed electronic/ionic conduction, fuel cells
- oxidation/reduction catalysts

- ferroelectric / piezoelectric ceramics ($BaTiO_3$, $Pb(ZrTi)O_3$)
- important mineral structure in lower mantle ($MgSiO_3$)

- **multiferroicity**

The general formulae of perovskites type structure is ABO_3 where A refers to the rare earth elements (Tb, Y, La, Pr etc.) or alkaline earth metals (Ba, Sr, Ca etc.) and B (Mn, Fe, Ti etc.) transition metals as shown in below figure 1.4. In this way transition metals form octahedral structure with oxygen (O) play a key role in ferromagnetism and ferroelectricity which are most important from the application point of view in the

development of future magnetic storage device (four logic state memory device), magnetic recording media, magnetic sensors, permanent magnet etc. $TbMnO_3$ is an important example of such perovskites, the structure of which is shown in figure [Fig. 1.7].

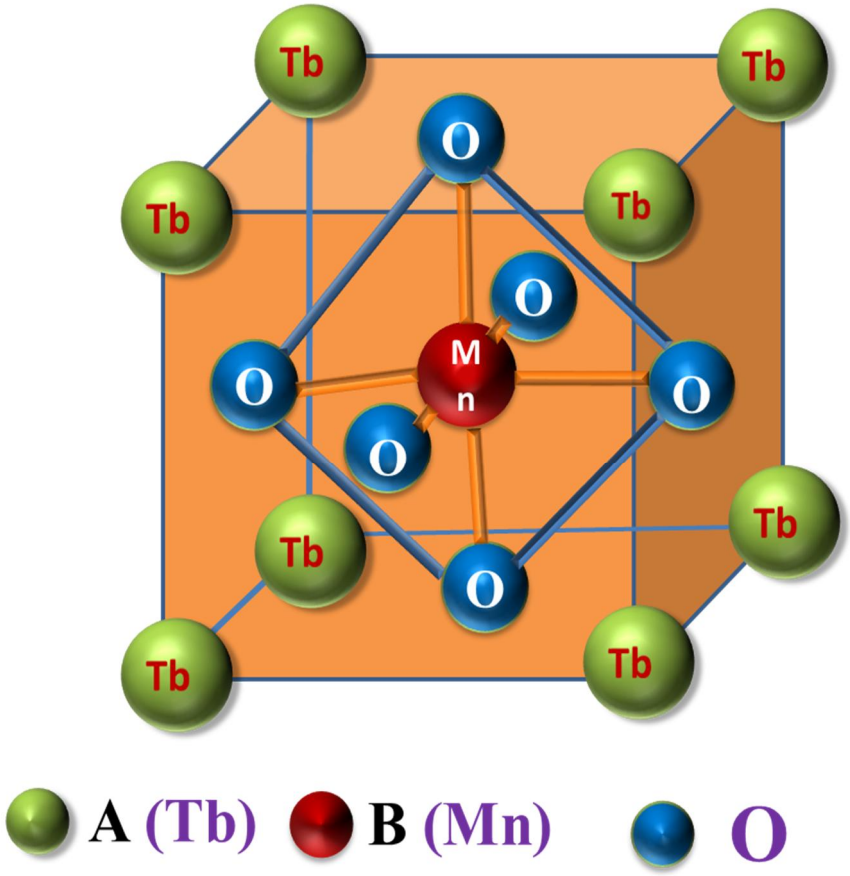


Fig. 1.7: *Perovskites structure of $TbMnO_3$*

This is an important system in which strong magnetoelectric coupling has been discovered. It crystallizes orthorhombically distorted perovskites structure with a lattice constant a = 0.5296 nm, b = 0.5837 nm, c = 0.7404 nm at room temperature [121]. It behaves as antiferromagnetic material which contains Mn^{+3} ions with occupied d orbitals with three t_{2g}^3 and two e_g^1 orbitals. It exhibits several magnetic transitions at low temperature. At T~41K, Mn^{+3} moments ordered antiferromagnetically in incommensurate sinusoidal spin ordering [122] and below T~27 K it flops into spiral (cycloidal) spin ordering. Below this Lock in temp (T_{Lock}~ 27 K) appearance of ferroelectricity have been observed in $TbMnO_3$. And at T~7 K magnetic ordering of Tb^{+3} occurs [123]. Existence of ferroelectricity below T~27K is related to the transition of

spin flop from sinusoidal to spiral spin ordering. It indicates that time reversal symmetry (TRS) is broken below 27 K and appearance of ferroelectricity has been also observed due to broken of spatial inversion symmetry. It shows ferroelectricity is induced due to the spiral magnetic structure. It is generally accepted that ferroelectric polarization is induced by the cycloidal spin ordering [124].

1.3.2.6. Normal and Inverse Spinel Structure

Normal Spinel structure:-The general formula for spinel structure is AB_2O_4, where A and B are some cation e.g. Li^{+}, Mn^{+3}, Zn^{+2}, Cu^{+2}, V^{+5}, V^{+3} etc. If A cations occupy tetrahedral site and B octahedral site in a crystal unit cell, then spinel structure is termed as **normal spinel structure** [125-126] e.g. $MgAl_2O_4$ as shown in below figure [Fig.1.8].

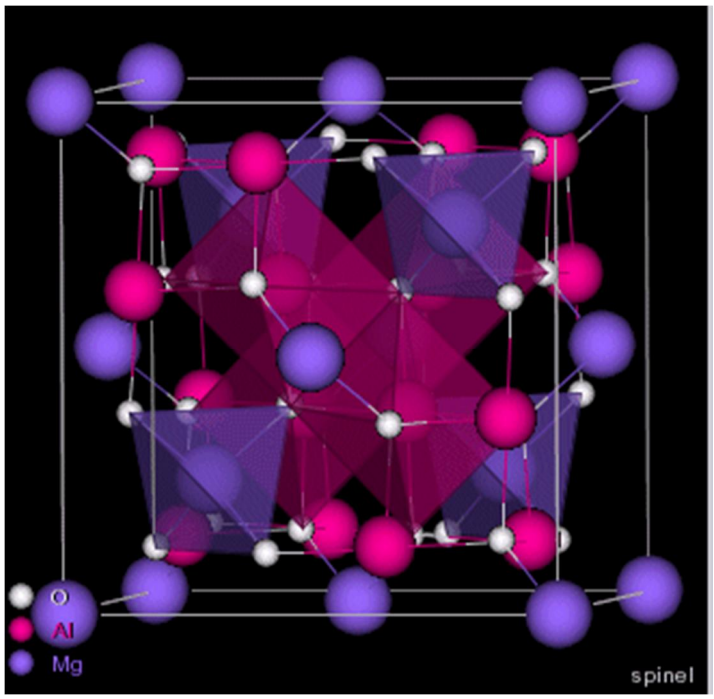


Fig. 1.8: *Normal spinel Structure of $MgAl_2O_4$.*

Inverse Spinel structure:- In AB_2O_4 spinel structure, if B occupy tetrahedral site and octahedral site is shared by both A & B actions then structure is known as **Inverse spinel structure** [125-126] because A and B cation invert their positions from octahedral to tetrahedral site coordinated with oxygen so it is called "inverse" spinel structure. The 1D cuprate $LiCuVO_4$=V[**LiCu**] O_4=B(AB)$O_4$with spin S=1/2 (in x^2–y^2 orbital) has only one crystallographically distinct Cu site (no multi-orbital or multisite effect) [127], and it crystallizes in an orthorhombic distorted inverse spinel structure, in which the non-

magnetic V^{5+} ($3d^0$) ions occupy the tetrahedral sites, whereas Li^+ and Cu^{2+} are arranged in an ordered way on the octahedral sites [128]. Both LiO_6 and CuO_6 octahedra form independent chains along the c direction as shown in below figure [Fig.1.9].

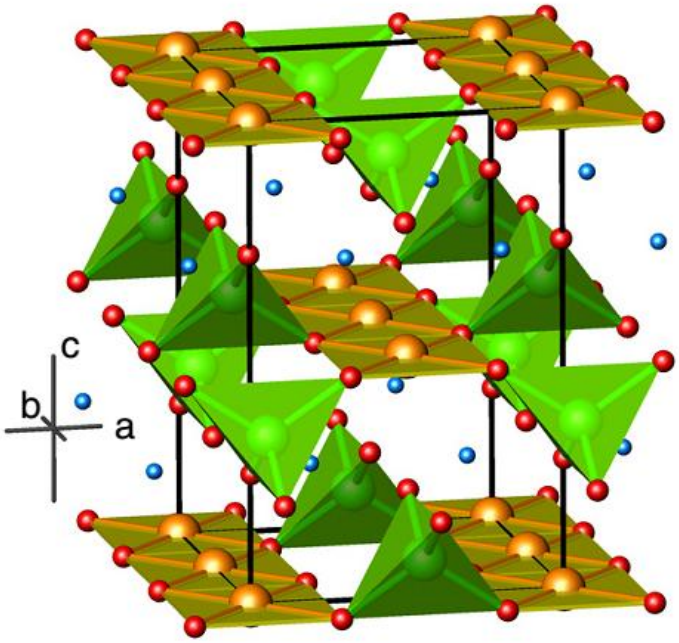


Fig. 1.9: *Orthorhombically distorted Inverse spinel structure of $LiCuVO_4$ (O^{-2} ions are highlighted in red, the Li^+ ions in blue,the VO_4 tetrahedra are highlighted in green, the CuO_2 chains in light olive)[A. S. Moskvin et al E P L , 81 (2008) 57004.]*

$LiCuVO_4$ is an important system because it behaves as quasi-one dimensional **quantum spin system (QSS)** and belong to low dimensional system which explains many ground state properties, quantum phenomena and gives exact solution of some theoretical models.

1.3.2.7. Quantum spin System

Quantum magnetism or quantum spin system (QSS) is one of the most active areas of research in the field of condensed matter physics. There is a significant research interest specially in low dimensional quantum spin system. The field of quantum spin system (QSS) or *quantum magnetism* has been originated since some decades ago. The Ising [129] and Heisenberg models [130] are the original ones introduced in this field. For Ising model the ground state on a hyperqubic lattice is an ordered configuration of the spins. On the other hand, the ground state of Heisenberg model is not just a simple

configuration of spins but alinear combination of several configurations. Althoughthe ground state of Ising model on the hyperqubic lattice can be represented simply by a configuration of spins theground state of Heisenberg model is not known exactly on two and three dimensional lattice. Even for one dimensional antiferromagnetic Heisenberg model the ground state of *N* spin 1/2 is given by a set of N coupled linear equations via Bethe Ansatz [131]. The main difference between the two models is related to the noncommuting terms which exist in Heisenberg model. In this sense the Ising model is a classical one and the Heisenberg model is a quantum one.

Quantum Magnets are spin system in which spins interact via a well-known exchange interaction. The interaction is purely quantum mechanical in nature and the type of interaction was derived simultaneously by Heisenberg and Dirac in 1926 [132]. The most well-known model of interacting spins in an insulating solid is the Heisenberg model with the Hamiltonian

$$H = \sum_{<i,j>} Jij\, \overrightarrow{Si}.\overrightarrow{Sj}$$

S_i and $S_j$is the spin operator located at the lattice site i and j respectively and J_{ij} denote the strength of exchange interaction. The spin $\left|\ \overrightarrow{Si}\ \right|$can have a magnitude ½ , 1, 3/2, 2/3, 2 ….etc. The lattice at which spins are located is d-dimensional e.g for linear chain (d=1), square lattice (d=2) and cubic lattice (d=3).

1.3.2.7.1. Role of Quantum magnetism in condensed Matter Physics

Understanding the properties of many particle interacting systems is a crucial issue in modern science. However interactions between relatively simple components give rise to complex behavior? Many questions like how does consciousness emerge from a collection of neurons? How is the large-scale Universe organized? And why do electrons superconduct in some materials and give rise to magnetism in others? These questions involves the emergence of macroscopic properties that are qualitatively distinct from the properties of the individual components [133]. In physics, we are interested in understanding and classifying the generic ways in which such macroscopic phenomena emerge, linking the microscopic properties of the components (including their environment) to the macroscale. This is usually the field of condensed-matter physics, in which innumerable interacting electrons in materials give rise to complex phenomena such as superconductivity, the quantum Hall effect and magnetic ordering.

Actually magnetism in condensed matter is ultimately a quantum phenomenon, most of its manifestations can be understood by means of classical concepts. Quantum effects are particularly significant at low temperatures in materials where magnetic ions with low spin moments (i.e. $S = 1/2,1$) form low-dimensional structural units. Despite *quantum-dominated* magnetism is the exception rather than the rule, the existence of exact theoretical models, the rich analogies with other problems involving interacting fermionic and bosonic particles, the undoubted central role of magnetism in condensed-matter systems of current interest (such as unconventional superconductors or heavy-fermions materials) is behind the intense activities in this field of research.

We start by discussing the three basic ingredients for enhancing the *quantum* aspects of magnetism, namely low spin, low dimensionality and low temperatures. First we describe how quantum mechanics introduces an effective additional dimension to the magnetic problem. The crucial role of dimensionality in determining the physical properties of a magnetic material is uncover many quantum magnetic phenomena in condensed matter physics.

1.3.2.7.2. Low Dimensional Quantum magnetism

Low dimensional systems often exhibit strong quantum fluctuation effects leading to the failure of conventional theories. This creates theoretical challenges which can sometimes be met using field theory, integrability and numerical techniques such as the Density Matrix Renormalization Group and Matrix Product States that are especially powerful in one dimension. What is one dimensional quantum magnetism? Actually when microscopic entities like electron, spin, charge and orbital are constrained to move or interact in one dimension (i.e. exchange interactions of spins are strong in one direction rather than the other) is termed as one dimensional system or low dimensional. The interest in one-dimensional (1D) quantum systems with several interacting particles arguably began back in 1931 when Bethe solved the famous Heisenberg model of ferromagnetism [131], but it was only in the 1960^s that people realized that the techniques developed by Bethe could be used to solve a host of different many-body models [134-138], It was subsequently realized that many 1D systems have universal low-energy behaviour and can be described by the paradigmatic Tomonaga-Luttinger-Liquid (TLL) theory [139-141]. This is really opened up the field of one-dimensional physics, which has remained a large subfield of condensed-matter physics ever since [141,142]. Recently, there has been a great revival of interest in 1D systems due to the realization

of 1D quantum gases in highly controllable environments using cold atomic gases [143-149]. This development in the field of one dimensional physics implies that it may now experimentally realize 1D systems with bosons or fermions and explore the interacting nature of their quantum behavior.

1.3.2.7.3. Fundamental Importance and Physical significance of Low dimensional System

After discovery of low dimensional physics many fundamental phenomena e.g. Quantum effects and fluctuations are important (disorder, quantum criticality, spin-liquid states), Excitation fractionalization by dimensional confinement (topological excitations with fractional quantum numbers (spinons) spin-charge separation, Luttinger liquid phase), dimensional cross-over and confinement of fractional excitations, Mott-insulating state in 1D and ground state properties in condensed matter physics have been explained by the theory of low dimensional physics. Many quantum spin systems of spin quantum number $s > 1/2$ or in spatial dimensions greater than 1D cannot be solved exactly and give some classical counterpart or quantum disorder in the solution due to "lack of integrability" comes from the competition between different bonds, as in quantum frustration.

In spite of this not very promising beginning, the field of low-dimensional magnetism developed into one of the most active areas of today's solid state physics. For the first 40 years this was an exclusively theoretical field. Theorists were attracted by the chance to find interesting exact results without having to deal with the hopelessly complicated case of models in 3D. They succeeded in extending the solution of Ising's (classical) model to 2D (which, as Onsager showed, *did* exhibit spontaneous order) and in calculating excitation energies, correlation functions and thermal properties for the quantum mechanical 1D Heisenberg model and (some of) its anisotropic generalizations. In another line of research theorists established the intimate connection between classical models in 2D and quantum mechanical models in 1D [150-152]. An important characteristic of low-dimensional magnets is the absence of long range order in models with a continuous symmetry at any finite temperature as stated in the theorem of Mermin and Wagner [153], and sometimes even the absence of long range order in the ground state [154]. It was only around 1970 when it became clear that the one- and two dimensional models of interest to theoretical physicists might also be relevant for real materials which could be found in nature or synthesized by ingenious crystal growers.

One of the classical examples are the early neutron scattering experiments on TMMC [155]. Actually, magnets in restricted dimensions have a natural realization since they exist as real bulk crystals with, however, exchange interactions which lead to magnetic coupling much stronger in one or two spatial directions than in the remaining ones. Thus, in contrast to 2D lattices (on surfaces) and 2D electron gases (in quantum wells) low D magnets often have all the advantages of bulk materials in providing sufficient intensity for experiments investigating thermal properties (e.g. specific heat), as well as dynamic properties (in particular quantum excitations) by e.g. neutron scattering.

1.3.2.7.4. Low Dimensional (1D) Magnetism a bridge between Theoretical and Experimental Research

The interest in low-dimensional, in particular one-dimensional magnets developed into a field of its own because these materials provide a unique possibility to study ground and excited states of quantum models, possible new phases of matter and the interplay of quantum fluctuations and thermal fluctuations. In the course of three decades interest developed from classical to quantum mechanics, from linear to nonlinear excitations.The field of one-dimensional magnets is characterized by strong interactions between theoretical and experimental research: In the early eighties, the seminal papers of Faddeev and Takhtajan [156] who revealed the spinon nature of the excitation spectrum of the spin- 1/2 antiferromagnetic chain, and Haldane [157] who discovered the principal difference between chains of integer and half-integer spins caused an upsurge of interest in new quasi-1D magnetic materials, which substantially advanced the corresponding technology. On the other hand, when the interest in the field seemed to go down, in the mid-eighties, a new boost came from the discovery of high temperature superconductors which turned out to be intimately connected to the strong magnetic fluctuations which are possible in low D materials. At about the same time a new boost for experimental investigations came from the new energy range opened up for neutron scattering experiments by spallation sources. Further progress of material science triggered interest in spin ladders, objects staying “in between” one and two dimensions [158]. At present many of the phenomena which turned up in the last decade remain unexplained and it seems safe to say that low-dimensional magnetism will be an active area of research good for surprises in many years to come. It is thus clear that the field of 1D magnetism is vast and developing rapidly. New phenomena are found and new materials appear at a rate which makes difficult to deliver a survey which would be to any extent complete. Although classical models played an important role in the early

stage of 1D magnetism, emphasis today is on models where quantum effects are essential.

In the aspect of theoretical point of view the field is extremely broad and provides a playground for a large variety of methods including exact solutions (using the Bethe Ansatz and the mapping to fermion systems), quantum field theoretic approaches (conformal invariance, bosonization and the semiclassical nonlinear $\sigma-$model (NLSM)), methods of many-body theory (using e.g. Schwinger bosons and hard core bosons), perturbational approaches (in particular high order series expansions) and finally a large variety of numerical methods such as exact diagonalization (mainly using the Lanczos algorithm for the lowest eigen values but also full diagonalization), density matrix renormalization group (DMRG) and Quantum Monte Carlo (QMC) calculations.

1.3.2.7.5. Examples of 1D (low-dimensional system) magnet

Most investigations in the field of low dimensional system on the material side concentrate on compounds with either Cu^{2+}-ions which realize spin- 1/2 or Ni^{2+}-ions which realize spin 1. Among the spin- 1/2 chain-like materials, $CuCl_2{\cdot}2NC_5H_5$ (Copperpyridinchloride = CPC) is important as the first quantum chain which was investigated experimentally [159]. Among today's best realizations of the spin- 1/2 antiferromagnetic Heisenberg model we mention $KCuF_3$ and Sr_2CuO_3. Another quasi-1D spin- 1/2 antiferromagnet which is widely investigated is $CuGeO_3$ since it was identified in 1992 as the first inorganic spin-Peierls material [160] [160]. There are many quasi-one dimensional spin-1/2 materials discovered and widely studied e.g. $LiCuVO_4$, $LiCu_2O_2$, Li_2CuO_2 and $NaCu_2O_2$ etc. Studies of these systems are very important from the application and physics both point of view. The prototype of ladder materials with spin- 1/2 is $SrCu_2O_3$; generally, the $SrCuO_2$ materials realize not only chains and two-leg ladders but also chains with competing interactions and ladders with more than two legs. Of particular interest is the material $Sr_{14}Cu_{24}O_{41}$ [161] which can be easily synthesized and consists of both CuO_2 zig zag chains and Cu_2O_3 ladders. A different way to realize spin- 1/2 is in chains with Co^{++}-ions which are well described by a pseudospin 1/2: The free Co ion has spin 3/2 , but the splitting in the crystal surrounding is so large that for the interest of 1D magnetism only the low-lying doublet has to be taken into account (and then has a strong tendency to Ising-like anisotropy, e.g. in $CsCoCl_3$). Among the spin-1 chain-like materials, $CsNiF_3$ was important in the classical era as a ferromagnetic xy-like chain which allowed to demonstrate magnetic solitons; for the

quantum S=1 chain and in particular the Haldane gap first ($Ni(C_2H_8N_2)_2NO_2(ClO_4)$ = NENP) and more recently ($Ni(C_5H_{14}N_2)$ $2N_3(PF_6)$ = NDMAP) are the most important compounds.

It should be realized that the anisotropy is usually very small in spin- 1/2 chain materials with Cu^{2+}-ions whereas S=1 chains with Ni^{2+}-ions, due to spin orbit effects, so far are typically anisotropic in spin space. An increasing number of theoretical approaches and some materials exist for alternating spin-1 and 1/2 ferrimagnetic chains and for chains with V^{2+}−ions with spin 3/2 and Fe^{2+}-ions with spin 2, however, to a large degree this is a field for the future. There are many compounds which may serve as 1D magnets can be found in earlier reviews [162].

1.3.2.7.5.1. $LiCuVO_4$ behaves as quasi-one dimensional quantum magnet

In this way we studied spin ½ Heisenberg antiferromagnetic quasi one-dimensional quantum spin system (QSS) $LiVCuO_4$ because it exhibits one dimensional chains of edge sharing CuO_4 squares or one dimensional chains of Cu^{+2} spins (s=1/2) along one crystallographic axes [127,163]. For this system, there is a competition between nearest neighbor (NN) and next nearest neighbor (NNN) exchange interaction of Cu^{+2} ions through the Cu-O-Cu exchange paths. Scheme of intrachain and interchain exchange interactions are given below figure [Fig.1.10].

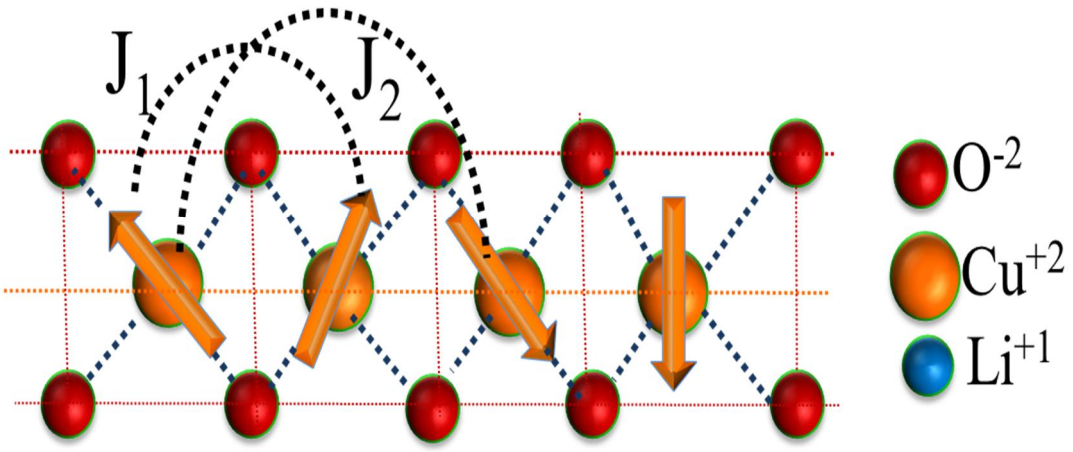


Fig.1.10: *Schematic diagram of (a) intrachain interaction path between Cu^{2+} in CuO_4 unit of $LiCuVO_4$.*

The investigation of the magnetism in $LiVCuO_4$ was focused on the quasi-one dimensionality of the Cu^{+2} ($3d^9$ configuration, S=1/2) spin system at elevated temperatures, where three dimensional correlations can be neglected. This system also behaves as multiferroic material at very low temperature (T=2.3 K) [164] because spontaneous electric polarization occurs due to the flop of collinear spin ordering (sinusoidal) to non-collinear spin ordering (spiral) at 2.3 K and exhibits magnetoelectric coupling and also behave as frustrated magnet. Actually we are interested in the spin interaction of nearest neighbor and next nearest neighbor interaction in one dimensional CuO_2 chain because that competition explain the magnetic behavior and energy of the system.

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