Chapter 8
Magnetic Phase transition and Relaxation effects in LiFePO₄

8.1 Introduction

When two adjacent electronic magnetic moments (spins) in a paramagnetic crystalline lattice are spontaneously aligned parallel (↑↑) below a critical temperature, the Curie temperature Tc, there is a ferromagnetic order and the material is said to be ferromagnetic. When two such neighboring magnetic moments having same magnitude are anti-parallel (↑↓) aligned, and the net magnetic moment in the material is zero, the material is said to have attained an antiferromagnetic state/order. This ordered magnetic state is usually attained through a cooperative second-order phase transition. This transition is usually probed through a magnetic susceptibility measurement which shows a characteristic cusp at a temperature called Neel temperature (TN). The origin of (anti)ferromagnetism is quantum-mechanical and the most interesting experimental observation in magnetism is the gradual appearance of a spontaneous magnetization in a solid. This fascinating subject is treated in many textbooks [1–4]. The concept of a molecular field developed by Weiss sustains to this day and forms the basis of many important models for magnetism. The origin of magnetism in LiFePO₄ must be traced to the Fe²⁺ moments stabilized in the orthorhombic lattice and the highly temperature–sensitive microscopic crystalline environments in which they exist.

In this Chapter we describe and discuss our experimental efforts to understand the nature of magnetism and magnetic phase transitions and relaxation in LiFePO₄ through DC magnetization and Mossbauer spectroscopy. We begin with a brief theoretical background.

8.2 Molecular field theory of Antiferromagnetism

Let us assume an antiferromagnetic material with two sublattices A and B, with the A lattice consisting of the corner positions and the lattice B, the body-centre positions in a bcc lattice. An atom at an A site then has nearest neighbors that all lie on B sites and next nearest neighbors that all lie on A sites. A similar situation holds for an atom at a B site. The molecular field Hmₐ acting on an atom at an A site may be written as

\[ H_{mA} = -N_{AA}M_A - N_{AB}M_B \] (1)

where MA and MB are the magnetizations of the A and B sublattices, NAB is a molecular field constant for the nearest neighbor interaction, and NAA is a molecular field constant for the next nearest neighbor interaction. Similarly Hmₐ acting on an atom at a B site may be written as

\[ H_{mB} = -N_{BA}M_A - N_{BB}M_B \] (2)
Since the same type of atoms occupy the A and B lattice sites, \( N_{AA} = N_{BB} = N_{ii} \) and \( N_{AB} = N_{BA} \). Then, if a field \( H \) is also applied, the fields \( H_A \) and \( H_B \) at an atom on the A and B lattices, respectively, are given by

\[
H_A = H - N_{ii} M_A - N_{AB} M_B
\]

And

\[
H_B = H - N_{AB} M_A - N_{ii} M_B
\]

(3)

The interaction between nearest neighbors is antiferromagnetic and therefore the molecular field constant \( N_{AB} \) must be positive. On the other hand, it is conceivable that \( N_{ii} \) may be positive, negative or even zero, depending on the particular material.

At thermal equilibrium the magnetizations of the sublattices are given by

\[
M_A = \frac{1}{2} N g \mu_B S B_S(x_A)
\]

(5)

where

\[
x_A = \frac{S g \mu_B}{kT} H_A
\]

(6)

and

\[
B_S(x_A) = \frac{2S+1}{2S} \coth \frac{2S+1}{2S} x_A - \frac{1}{2S} \coth \frac{x_A}{2S}
\]

(7)

is the Brillouin function

Similarly

\[
B_S(x_B) = \frac{2S+1}{2S} \coth \frac{2S+1}{2S} x_B - \frac{1}{2S} \coth \frac{x_B}{2S}
\]

(8)

Here \( N \) is the total number of atoms (or ions) with a permanent dipole moment per unit volume, and \( J \) has been set equal to \( S \).

### 8.2.1 Behavior above the Néel temperature

The Néel temperature, \( T_N \), is the temperature at which an antiferromagnetic material becomes paramagnetic — that is, the thermal energy becomes large enough to destroy the macroscopic magnetic ordering within the material. Although there is no antiferromagnetic ordering above the Néel temperature, a small magnetization is induced by the applied field. For the usual values of applied field, saturation effects are negligible and the Brillouin function \([5]\) can be replaced by the first term of the series expansion in \( x \), namely, \( B_S(x) = [(S+1)/3S]x \). Then the above equations 5-8 become

\[
M_A = \frac{N g^2 \mu_B^2 S(S+1)}{6kT} H_A
\]

(9)

and
\[ M_B = \frac{N g^2 \mu_B^2 S(S+1)}{6kT} H_B \]  

(10)

Now

\[ H_A = \left| H - N_{\mu} M_A - N_{AB} M_B \right| \]

\[ \Rightarrow H_A = H - N_{\mu} M_A - N_{AB} M_B \]  

(11)

since \( H, M_A \) and \( M_B \) are parallel in the paramagnetic region. Similarly

\[ H_B = H - N_{\mu} M_B - N_{AB} M_A \]  

(12)

Substitution of these values of \( H_A \) and \( H_B \) into the foregoing equations for \( M_A \) and \( M_B \) gives

\[ M_A = \frac{N g^2 \mu_B^2 S(S+1)}{6kT} (H - N_{\mu} M_A - N_{AB} M_B) \]  

(13)

and

\[ M_B = \frac{N g^2 \mu_B^2 S(S+1)}{6kT} (H - N_{\mu} M_B - N_{AB} M_A) \]  

(14)

Addition of equations 13 and 14 gives

\[ M = M_A + M_B = \frac{N g^2 \mu_B^2 S(S+1)}{6kT} [2H - (N_{\mu} - N_{AB}) M] \]  

(15)

Hence the susceptibility \( \chi = \frac{M}{H} \) is given by

\[ \chi = \frac{C}{T + \Theta} \]  

(16)

Where

\[ C = \frac{N g^2 \mu_B^2 S(S+1)}{6kT} \]  

(17)

And

\[ \Theta = \frac{1}{2} C (N_{\mu} + N_{AB}) \]  

(18)

Since, generally, \( N_{AB} > N_{\mu} \), \( \Theta \) is positive. Equation (16) may be compared to \( \chi = \frac{C}{(T - \Theta)} \), the Curie-Weiss law.

### 8.2.2 The Néel temperature

Below the Néel temperature, both sublattices possess a spontaneous magnetization \((H=0)\) of equal magnitude but pointing in opposite directions. The critical temperature at which the spontaneous magnetization of one of these sublattices vanishes can be found from eq. 5-8.
Alternatively, the critical temperatures can be found by approaching from the high temperature side \((T > T_N)\). Equations \((13)\) and \((14)\) are valid in the vicinity of \(T_N\), for saturation effects are still unimportant. With \(H = 0\), these equations become

\[
M_A = C \left( -N_{ii} M_A - N_{AB} M_B \right)
\]  
\[
M_B = C \left( -N_{ii} M_B - N_{AB} M_A \right)
\]

For nonzero values of the magnetizations \(M_A\) and \(M_B\) the determinant of the coefficients of \(M_A\) and \(M_B\) must be zero. Application of this condition yields the Néel temperature, namely,

\[
T_N = \frac{1}{2} C (N_{AB} - N_{ii})
\]

Hence the Néel temperature is higher, the stronger the AB interaction and the weaker the AA or BB interaction, as is to be expected on physical grounds. Substitution for \(C\) from eq. \((16)\) then gives

\[
\frac{\Theta}{T_N} = \frac{N_{AB} + N_{ii}}{N_{AB} - N_{ii}}
\]

If \(N_{ii} = 0\), \(T_N = \Theta\), where as if \(N_{ii} > 0\), \(\Theta > T_N\). If \(N_{ii}\) is becomes too large in comparison to \(N_{AB}\), the two sublattice arrangement is assumed unstable.

### 8.2.3 Susceptibility below the Néel temperature

In the absence of any applied magnetic field the sublattice magnetizations \(M_A\) and \(M_B\) are antiparallel to one another below the Néel temperature. The crystalline anisotropy, assumed for simplicity to be uniaxial, determines the common direction of \(M_A\) and \(M_B\), since these sublattice magnetizations will be collinear with the easy direction. In general, the applied field may make any arbitrary angle with the easy axis. Now let us suppose the applied field \(H\) is parallel to \(H_{mA}\) and antiparallel to \(H_{mB}\). Then \(x_A\) and \(x_B\) equations may be written as

\[
x_A = \frac{g \mu_B S}{kT} (H - N_{ii} M_A + N_{AB} M_B)
\]

And

\[
x_B = \frac{g \mu_B S}{kT} (-H - N_{ii} M_B + N_{AB} M_A)
\]

On the other hand, when \(H = 0\), \(M_A = -M_B = M_0\), it follows from equations 5-8, that \(x_A = -x_B = x_0\), where

\[
x_0 = \frac{g \mu_B S}{kT} [(N_{AB} - N_{ii}) M_0]
\]
The Brillouin function may be expanded as a Taylor series in \( H \). If only the first-order term is retained, we have
\[
B_S(x_A) = B_S(x_0) + \frac{g\mu_B S}{kT} [H + N_{ii}(M_0 - M_A) + N_{AB}(M_B - M_0)] \times B_S^1(x_0)
\]
(26)

And
\[
B_S(x_B) = B_S(x_0) - \frac{g\mu_B S}{kT} [H + N_{ii}(M_B - M_0) + N_{AB}(M_0 - M_B)] \times B_S^1(x_0)
\]
(27)

where \( B_S^1(x_0) \) is the derivative of the Brillouin function with respect to its argument. The coefficient \( B_S^1(x_0) \) in eq. (26) is the difference of Eqs. (23) and (24). Multiplication of eqs. (26) and (27) by \( \frac{1}{2} g\mu_B S N \) yields the sublattice magnetizations \( M_A \) and \( M_B \), respectively. The magnetization \( M \) induced by the field is then \( M = M_A - M_B \). From this equation it is easy to show that the susceptibility \( \chi_{11}(T) = M / H \) is given by
\[
\chi_{11}(T) = \frac{n\mu_B^2 g^2 S^2 B_S^1(x_0)}{kT + \frac{1}{2}(N_{ii} + N_{AB})\mu_B^2 g^2 S^2 N B_S^1(x_0)}
\]
(28)

At absolute zero, this equation predicts \( \chi_{11} = 0 \). The physical reason is that in the approximation of the molecular field theory all the atomic moments are either parallel or antiparallel to the applied field at \( T = 0^\circ K \). Hence the field does not exert any torque on the moments and the induced magnetization is zero. As the temperature increases, the \( \chi_{11} \) also increases until at the Néel temperature \( \chi_{11}(T_N) \) becomes equal to the susceptibility \( \chi(T) \) given by eq. (16). For \( T > T_N \), eq. (28) reduces to eq. (16).

8.3 Paramagnetic – Antiferromagnetic Phase transition:

Although the magnetic moment of a body is zero both in paramagnetic and antiferromagnetic states, their magnetic characteristics are quite different. At high temperatures the magnetic susceptibility is governed by Curie-Weiss law, and at the Néel point it reaches maximum; as temperature is lowered further, the magnetic susceptibility diminishes. When temperature passes through the Néel point, the heat capacity of an antiferromagnetic undergoes a jump wise change; this
effect is typical of the phase transitions of the second order. Such a phase transition is a “disorder-to-order” transition when the Neel point is approached from above.

In this particular case, the ‘disorder’ is found in the absolute identity of all lattice sites in which magnetic atoms are located so that the mean magnetic moment is zero at each site. Beginning with the Neel point (at \( T \leq T_N \)), an ‘order’ appears and lattice sites grow to be different; in some of them the mean magnetic moment points in one direction, and in the others it points in the opposite direction. The transition is smooth (and it must be for any phase transition of the second order) because at the Neel temperature the mean magnetic moment in a lattice site is zero, and reaches its maximum possible value at \( T = 0 \) K. This behavior imparts more physical meaning to conclude that an antiferromagnetic is composed of two (or more in general) ferromagnetic sublattices inserted into each other. It is known that both in antiferromagnetics and ferromagnetics, the main role is played by the exchange interaction.

8.4 Antiferromagnetism in LiFePO₄

Even though LiFePO₄ was found to be electrochemically active material much later (in 1997) by Padhi et al [6], but its magnetic structure has been determined as early as in 1967 by Santoro and Newnham [7]. They have discovered that LiFePO₄ undergoes a magnetic structural transition from paramagnetic to antiferromagnetic state. They found that the reciprocal susceptibility of LiFePO₄ shows a minimum at \( 50 \pm 2^\circ\text{K} \), the Néel temperature. It is known that the magnetic properties are determined by the electronic states and may thus reflect the potential advantage of LiFePO₄. After Goodenough’s group [6] proposed the electrochemical nature of the material, the research on this material has shot up. Particularly, extensive work by Julien’s group [8–10] on magnetic measurements has given a picture of magnetic structure of LiFePO₄. Luo Zhi et al [11] have done the low temperature Mössbauer measurements of LiFePO₄ and evaluated the hyperfine parameters above and below the Néel temperature. Rousse et al [12] have solved the magnetic structures using neutron diffraction on polycrystalline samples of LiFePO₄. A comparison has been made between the magnetic structures of LiFePO₄ and FePO₄ and the difference in Néel temperatures have been discussed both in terms of super and super-super exchange interactions and anisotropy of Fe\(^{2+}\).
In 1969, Ok [13] had shown that the antiferromagnetic ferrous carbonate undergoes slow electron relaxation, that is spin-lattice relaxation phenomena, with Mössbauer spectra recorded at low temperatures. Also, electron-spin relaxation phenomena have been observed by many investigators [14–19]. However, most of these studies in iron compounds were restricted to the ferric (Fe³⁺) ions. Though, Luo Zhi et al [11] have done the Mössbauer studies of LiFePO₄, they were not aimed at the relaxation effects in it. And to the best of our knowledge, no relaxation effects in the Fe²⁺ ions in the antiferromagnetic LiFePO₄ have been discussed. Among all experimental probes, Mossbauer spectroscopy effectively combines and optimizes both electrical (electrostatic) and magnetic aspects of the magnetic response through isomer shift, quadrupole splitting and magnetic hyperfine interactions. In an Fe²⁺ system such as LiFePO₄ these parameters are all expected to be sensitive to temperature as mentioned earlier. Furthermore as a direct probe of low-temperature magnetism DC magnetization reveals in a sensitive manner the basic changes LiFePO₄ undergoes as it orders antiferromagnetically and enables the temperature-dependence of magnetic susceptibility to be accurately measured and used to test qualitatively the models for antiferromagnetism.

8.5 DC Magnetisation measurements

In the zero-field-cooled (ZFC) case, the sample was cooled in zero magnetic field to 5⁰K (T << T_N), and magnetisation, M(T), was measured as a function of temperature while heating the sample to temperatures above room temperature. While in the field-cooled (FC) case, a field of H = 100 Oe was applied on the sample and the sample was cooled to 5⁰K. Magnetisation M(T) of the sample was measured in the same field from 5⁰K to above room temperature. These measurements were carried out using SQUID magnetometer. All the above said measurements were carried out on 5.14 mg of C-LiFePO₄ sample.
Figure 2. Temperature variations of the zero-field-cooled (ZFC) and field-cooled (FC) magnetizations at an applied field of $H = 100$ Oe for C-LiFePO$_4$.

Figure 3. The DC magnetic susceptibility $\chi(T)$ of C-LiFePO$_4$.

Figure 4. The reciprocal magnetic susceptibility $\chi^{-1}(T)$ of C-LiFePO$_4$.

Figure 2 shows the zero-field-cooled (ZFC) and field-cooled (FC) magnetisation at an applied field of $H = 100$ Oe on C-LiFePO$_4$. While Figures 3 and 4 depicts the DC magnetic susceptibility $\chi(T)$ and reciprocal magnetic susceptibility $\chi^{-1}(T)$ with temperature. From figure 3, it is evident
that the magnetic susceptibility $\chi(T)$ increases down to 50°C, and suddenly undergoes a decrease. The temperature at which the fall in $\chi(T)$ was observed is identified as Néel temperature and is found to be 50.9°C. The magnetic susceptibility shows a deviation from the linear behavior at this temperature suggesting that the sample is well crystallized and neither structural defects nor the impurities can impede the propagation of long-range spin correlations that are responsible for the onset of the antiferromagnetic ordering. And also this spin correlation length is limited by thermal fluctuations. We note that the temperature dependence of the magnetic susceptibility does not follow the dependence predicted for the 2D square lattice of classical spins as it does not show a typical broad maximum [20].

Figure 5 shows the variation of reciprocal magnetic susceptibility $\chi^{-1}(T)$ down to temperature 50°C, the Néel temperature observed for C-LiFePO$_4$. As is evident, at temperatures above Néel temperature, the DC magnetic susceptibility obeys eq. (16), which may be compared to Curie-Weiss law $\chi = \frac{C}{(T - \Theta)}$. The reciprocal magnetic susceptibility $\chi^{-1}(T)$, shown as circles in the figure 5 is fitted to Curie-Weiss law and the thick line through the circles shows the fit. Due to the continuous variation of the slope of the curve shown in figure 5, Curie temperature could not be reported here and further investigations are under consideration.

![Graph](image_url)

*Figure 5. The reciprocal magnetic susceptibility $\chi^{-1}(T)$ of C-LiFePO$_4$ above Néel temperature.*
The variation of reciprocal susceptibility $\chi^{-1}(T)$ below the Néel temperature is shown in figure 6. An anomalous feature observed for the C-LiFePO$_4$ sample in question is that the $\chi^{-1}(T)$ curve at around 27°K is characterized by a sharp decrease in $\chi^{-1}(T)$ upon cooling through this temperature. This feature signals the onset of a spontaneous magnetisation at this temperature [10], which is the signature of the weak ferromagnetic component of Li$_3$Fe$_2$(PO$_4$)$_3$ at this temperature [21, 22]. This was proposed by showing a narrow doublet in the room temperature Mössbauer spectrum of Anderson et al [22]. This narrow doublet is conspicuously absent in the room temperature Mössbauer spectrum of LiFePO$_4$ shown in chapter 2 and also in the forthcoming sections of this chapter rules out the presence of Li$_3$Fe$_2$(PO$_4$)$_3$ in our sample demonstrating the power of Mossbauer spectroscopy. Thus the origin of the slight rise in the susceptibility around 27 K cannot possibly be traced to the existence of a ferromagnetic phase. More work is necessary to clarify this feature. The reciprocal magnetic susceptibility $\chi^{-1}(T)$ below Néel temperature has been fitted to a straight line. The thick line in figure 6 shows the fit. The fit has been extrapolated down to 0°K to obtain $\chi^{-1}(T)$ at absolute zero. The reciprocal susceptibility was found to be $1.26 \times 10^3$ gm Oe/emu and the magnetic susceptibility $\chi(T)$ of C-LiFePO$_4$ at absolute zero was determined to be $7.937 \times 10^{-4}$ emu/gm Oe.

8.6 Relaxation effects in Mössbauer spectroscopy:

Relaxation effects in Mössbauer line shape arise when the nucleus is subject to fluctuations in its surroundings occasioned by spin-lattice/spin-spin interaction, time-varying electric field gradients, and a host of other dynamical processes. Quite generally, the effect of relaxation is to cause shift, broadening, narrowing and sometimes collapse of the spectra. We shall present here, a qualitative picture of the relaxation phenomenon in Mössbauer studies with more emphasis on the physical concepts rather than mathematical details. Most theoretical treatments of relaxation effects in
Mössbauer spectra necessarily involve certain formal techniques which often obscure the essential physical insight.

While looking at Mössbauer line shape consider just a single nucleus which is part of a many body system consisting of the surrounding electrons and other elementary excitations including phonons, magnons. One of the features observed upon cooling the sample is the increase in width of the Mössbauer lines, due to Debye-Waller factor.

The basics of the relaxation phenomenon is shown in the following figure. It shows the nucleus in direct interaction with its surrounding electrons. The latter, in turn, interact with the other degrees of freedom which constitute the heat bath. Relaxation effects occur whenever there is time-fluctuation in the direct interaction between the nucleus and its surrounding electrons within the lifetime of the Mössbauer state. Thus relaxation phenomenon may arise from any of the following three events.

1. Fluctuations in the Isomer shift

A common example of this case is that of a point defect, e.g., an interstitial or vacancy which undergoes jump diffusion in the vicinity of the Mössbauer nucleus. As a result the electronic wave function is modulated abruptly leading to a fluctuating isomer shift. A case in point is the study of hydrogen diffusion in tantalum [23, 24]. From an analysis of the spectra, quantities such as the concentration and the diffusivity of hydrogen interstitials can be extracted.

2. Fluctuations in the Magnetic Hyperfine Interaction

There are innumerable instances of this case because the electronic component of the magnetic hyperfine coupling between the nucleus and its surrounding electrons is likely to interact with a host of other degrees of freedom e.g., the other electrons via the dipolar mechanism [25], phonons [26, 27], conduction electrons [28, 29], spin waves [30], etc. As a result of this interaction, the local field created by the electrons at the site of the nucleus fluctuates randomly. Denoting the local field by $H(t)$ the Hamiltonian for the nucleus may be written as

$$ H(t) = g\mu_N I_z H(t) $$

where $g$ is the g-factor, $\mu_N$ the nuclear magneton and $I_z$ the z-component of the nuclear spin. In view of this interaction, an isolated Mössbauer line (for $^{57}$Fe, say) with a natural line width, splits into a six-finger pattern if the local field is static. That is, during the lifetime of the Mössbauer state the local field remains almost constant in time. On the other hand, when the local field varies on a time-scale comparable to the lifetime one sees a relaxation pattern characterized by broadening and shift of the resonance line. From an analysis of the spectra the statistical properties of the internal field can be determined.
In writing down Eq. (29) two assumptions have been made. First, the field is taken to lie along the z-axis and second, the field is assumed to be a classical variable. One example of this simple-minded situation is that of a magnet consisting of various domains in which the internal field is pointed along positive (or negative) z-axis. If an oscillatory magnetic field is imposed on the system externally, the domains begin to move. A Mössbauer nucleus embedded inside the system will find the local field ‘switch’ between the ± z-axes at random.

\[
H(t) = AJ_zS_z(t)
\]

(30)

where \( A \) is the hyperfine constant. The time fluctuating electronic spin can be decomposed as

\[
S_z(t) = \bar{S}_z + \left( S_z(t) - \bar{S}_z \right)
\]

(31)

where the bar denotes a time average. If the system is ergodic (which means having zero probability that any of its states will never recur) as most systems are, \( \bar{S}_z \) may also be interpreted as the ensemble-averaged spin angular momentum of a many electron system which, in fact, is proportional to the magnetization of the specimen.

3. Fluctuations in the Electric Quadrupolar Interactions

The third important instance of relaxation effect occurs in the case of time varying electric field gradients (EFG) leading to a fluctuating quadrupolar interaction.

8.7 Low Temperature Mössbauer Experimental setup

A Mössbauer spectrometer with an electromechanical drive system manufactured by Elron Co. and stabilized up to ±0.001 mm/sec was used with 10-mCi Co\(^{57}\) source in rhodium matrix which
was kept at room temperature. Temperature measurement and control were carried out by a platinum resistance and a heater above 50K with an accuracy of 0.5K. A carbon resistance thermometer calibrated at liquid-nitrogen, liquid hydrogen and liquid-helium temperatures was used for temperature measurement and control below 50K with an accuracy of 0.1K. The temperature near the antiferromagnetic transition temperature was controlled manually with a stability of 0.01K using a highly sensitive galvanometer and a heater. The LiFePO$_4$ sample used for the Mössbauer measurements contained 10mg/cm$^2$ of the iron, and the uniformity was obtained by thoroughly grinding. The sample was sandwiched between the sheets of high-purity aluminium foil (~0.2 mm thick) and mounted in a variable temperature insert (for a helium cryostat), in which the sample temperature may be maintained as desired.

8.8 Analysis of Mössbauer Spectra

The Mössbauer spectra of LiFePO$_4$ at various temperatures are shown in figure 8 and these spectra are fitted to static full Hamiltonian and the fits are shown by thick line passing through the data. This static full Hamiltonian properly calculates the line positions and intensities for any combination of hyperfine magnetic field $B_{hf}$ and electric field gradient (EFG) tensor. Below 48 K, the spectra consists of six lines, which can be analysed by diagnolising the $4\times4$ magnetic hyperfine and quadrupole-interaction matrix [31] for the first excited state of Fe$^{57}$ to give magnetic hyperfine field and quadrupole splitting. And all the spectra at and below 45K are fitted with one doublet and a sextet.

On the basis of the temperature dependence of the magnetic hyperfine field $B_{hf}$, the transition point of antiferromagnetic phase may be determined. The temperature dependence of the hyperfine field is shown in figure 9. From the figure, it is evident that, the spectra did not change as the temperature is increased from 20 to 45 K. The magnetic hyperfine field of the sample at 20K was found to be 12.32(1) Tesla, and found to decrease to two-third value (of 12.32 T) at 45 K. And it showed a sudden fall at 48 K and reaches the minimum value (roughly 0.1 T) as the temperature approaches to 50K. So, the transition temperature for antiferromagnetic to paramagnetic transition is less than 48 K, the Néel temperature. While the hyperfine field observed by Zhi et al [11] at the Neel temperature 50K (their claim) was around 53kOe, little less than the half of the hyperfine field (115kOe) observed at 20 K.
Figure 8. The Mössbauer spectra recorded at temperatures 300, 50, 48, 45 and 20 K, from top to bottom. The thick line being the fit obtained from Static full Hamiltonian.

Another interesting point evident from the fits shown in figure 8 is that as the temperature is increased above 20°K towards T_N the highest-energy line (the extreme right line) broadens much more.
than the other lines. To begin with note that this asymmetric broadening does not come from a non uniform temperature distribution across the sample or from any other instrumental effects. This has been proved by mounting an iron foil in the same place as the LiFePO$_4$ sample, which did not show any instrumental effects on the line broadening.

Another noteworthy point is the asymmetric line broadening of the doublet in the paramagnetic state above $T_N$, as shown in figure 8. This kind of asymmetric line broadening of a doublet has been observed for paramagnetic Fe$^{3+}$ ions in some materials [32], and was interpreted as evidence of slow electron-spin relaxation as compared to the nuclear–precession frequency.

The angle between the magnetic hyperfine field $B_{hf}$ and the direction of the maximum electric field gradient is defined as $\theta$, and $\eta$ is defined to be asymmetry parameter of the electric field gradient (EFG). The line positions and relative intensities shown in the figure 8 are calculated for $\theta = 0$ i.e., the hyperfine field $B_{hf}$ is along the principal axis of the electric field gradient. This is due to the fact that the EFG axis must be perpendicular to the mirror symmetry plane, so are the magnetic moments. The asymmetry parameter $\eta$ is found to be 0.766(6). Since this value is in the range of 0 to 1, it means that the fitted angles between x-y-z of the electric field gradient (EFG) tensor and the hyperfine magnetic field $B_{hf}$ are corrected (not necessarily to reorder the axis system of the EFG).

![Figure 10. Temperature dependence of quadrupole splitting $\Delta$.](image)

The temperature dependence of the quadrupole splitting $\Delta$ is shown in figure 10. The change in $\Delta$ is caused by the influence of hyperfine field. Under the first-order perturbation, the quadrupole splitting may be expressed as

$$\Delta(T < T_N) = \frac{eQV}{2} (3 \cos^2 \theta)$$

(32)