Charge and magnetic ordering in a ladder system: the Fe-Ludwigite

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Recibido el 30 de noviembre de 2006; aceptado el 8 de octubre de 2007

Oxyborates exhibit a large variety of magnetic and transport properties resulting from strong correlations and low-dimensional effects. Among these compounds, the Fe-ludwigite \( \text{Fe}_2\text{O}_2\text{BO}_3 \) shows interesting magnetic and charge ordering properties believed to be related to the presence of three-leg ladders in its structure. In particular, it presents a structural and charge ordering transition at \( T_c = 283K \), such that long and short bonds alternate along the ladder axis. These ladders consist of \( \text{Fe}^{3+} \) localized high-spin \( (d^5) \) with an extra electron for each rung. We will emphasize the role of the interaction of the conduction electrons with the localized spin similarly to the double-exchange (DE) mechanism and the interplay of the lattice instability with the magnetic structure. The Fe-ludwigite may provide a good example of the specific magnetic structures arising from the competition between DE and antiferromagnetic superexchange (SE) interactions among the localized spins, as was found previously in one or two dimensions \cite{1, 2}. In addition to a ferromagnetic phase, we find (i) a phase with ferromagnetic rungs ordered antiferromagnetically and (ii) a zigzag canted spin ordering along the legs presenting the same symmetry as the low temperature distorted structure. Similar magnetic structures have been obtained recently with neutron experiments \cite{3}. The charge distribution among the rungs is a key issue and will be determined within the different phases. Our model is discussed in connection with the structural transition showing the important role of the magnetic structure.

Keywords: Charge-density-wave systems; Classical spin models; Oxyborates.

Los sistemas conocidos como oxiboratos presentan una gran variedad de propiedades magnéticas y de transporte que son el resultado de los efectos de la baja dimensionalidad de estos sistemas así como de la presencia de fuertes correlaciones. Entre estos sistemas está el compuesto ludwigita a base de hierro-Fe \( \text{Fe}_2\text{O}_2\text{BO}_3 \), el cual muestra interesantes propiedades magnéticas y de orden de carga que al parecer están relacionadas con la presencia de estructuras en forma de escaleras con tres pies. Particularmente este sistema presenta una transición estructural y de orden de carga a la temperatura de \( T_c = 283K \). La transición estructural es tal que se alternan enlaces largos y cortos a lo largo del eje de la escalera. Esas escaleras están constituidas de iones de hierro localizados \( \text{Fe}^{3+} \) \((d^5)\) que presentan una configuración de espín alto \( S = 5/2 \), además, estas escaleras tienen un electrón extra dentro de cada travesaño. En este articulo se hará hincapié en el papel de la interacción de los electrones de conducción con los espines localizados como en el mecanismo de doble intercambio (DE) de sus siglas en inglés, así como también en la relación entre la estructura magnética y la inestabilidad de la red. Este sistema Ludwigita a base de hierro puede ser un buen ejemplo de estructuras magnéticas que son obtenidas a partir de la competencia entre el mecanismo de doble intercambio y las interacciones antiferromagnéticas de super intercambio (SE) entre los espines localizados, como fue encontrado previamente en una y dos dimensiones \cite{1, 2}. Con respecto a las fases magnéticas, además de una fase ferromagnética se encontró, (i) una fase magnética con peldaños ferromagnéticos ordenados antiferromagnéticamente entre ellos y (ii) una fase con una estructura zigzag de espines a lo largo de la escalera que presenta la misma simetría que la estructura con distorsión a baja temperatura. Recientemente se obtuvieron estructuras magnéticas similares utilizando experimentos de difracción de neutrones \cite{3}. La distribución de carga dentro de los peldaños es un resultado clave y será calculada para las distintas fases. Nuestro modelo será discutido en conexión con la transición estructural donde se mostrará la importancia del papel de la estructura magnética.

Descriptores: Sistemas de onda de densidad de carga; Modelos de espín clásico; Oxiboratos.

PACS: 75.10.Hk; 71.45.Lr

1. Introduction

The homometallic oxyborate Fe-ludwigite system \( \text{Fe}_2\text{O}_2\text{BO}_3 \) presents exciting physical properties associated with the presence of low dimensional structural units and strong correlation effects \cite{4, 5}. The transport measurements show an unusual behavior on the derivative of the resistivity close to the structural transition at \( T_c \approx 283K \). These transport properties could be described by activated behavior with two characteristic energies, \( \Delta_1/k_B = 60K \) and \( \Delta_2/k_B = 1300K \) below and above \( T_c \), respectively \cite{5}. The magnetic measurements show three magnetic transitions. The first one is an antiferromagnetic (AF) transition and has been observed at \( 112K \) which involves paramagnetic (P) Fe ions and essentially antiferromagnetic \( \text{Fe}^{3+} \) ions. The second transition at \( 74K \) presents a weak ferromagnetism, mostly of \( \text{Fe}^{2+} \) ions. The third transition shows a reentrant antiferromagnetic state at \( 50K \) \cite{5}. The specific heat measurements of the ludwigite system \( \text{Fe}_2\text{O}_2\text{BO}_3 \) can be described at low temperature \( T < 60K \) by two-dimensional antiferromagnetic magnons and at high temperature \( T > 112K \) by a Wigner glass \cite{6}. The ludwigites have the general formula...
$M^{2+}_3 M'^{3+}_3 O_2 BO_3$, where $M$ and $M'$ are transition metal atoms. For $M = M' = Fe$, the system is known as homometalllic Fe-ludwigite. The Fe-ludwigite system is formed by an assembly of subunits in the form of zigzag walls of edge-sharing FeO$_6$ octahedra, connected by BO$_3$ triangular groups [3]. The charge distribution along the octahedral sites given by the Mössbauer study of Guimarães et al. [5] suggested that Fe$_3$O$_2$BO$_3$ has two spin sublattices and these sublattices are decoupled to a first approximation [7]. The first sublattice is formed by the Fe(3)-Fe(2)-Fe(3) groups [3]. The charge distribution along the octahedral sites resulting from the competition between DE and SE. Our model will be discussed in association with the lattice dimerization transition at $T_c \approx 283K$, such that the deformations on the rungs alternate along the ladder axis [4]. These ladders consist of Fe$^{3+}$ (d$^3$) localized high-spin $S = 5/2$ with an extra electron for each rung. The second sublattice is formed by Fe(4)-Fe(1)-Fe(4) corner-sharing triads. Sites 1 and 4 are basically occupied by Fe$^{3+}$ ($S = 2$).

In this paper, spin and charge ordering and the interplay with lattice instability will be studied in the Fe(3)-Fe(2)-Fe(3) 3LL. We will show the existence of simultaneous spin and charge ordering and its connection with the lattice instability resulting from the competition between DE and SE. Our model will be discussed in association with the lattice dimerization transition at $T_c \approx 283K$ observed in the Fe-ludwigite system, emphasizing the role of the magnetic structure. In Sec. 2 we give a brief description of the Hamiltonian; in this section, the magnetic phase diagram and the charge distribution will be studied in connection with the lattice structural instability. Finally, in Sec. 3 we summarize our results.

\section{Magnetic phase diagram and charge distribution}

To describe the magnetic structure and the charge distribution, we use general double exchange [9] and superexchange interactions between the localized spins $S_i$. In the Fe$^{3+}$ (d$^3$) configuration of the 3-2-3 ladders, all orbitals are occupied in one spin channel. This means that itinerant electrons can hop to a site $i$ only if its spin is antiparallel to the local spin $S_i$, or that also means an infinite antiferromagnetic Hund’s energy $J_H \rightarrow -\infty$. The itinerant electrons are indeed spinless electrons. The general DE interactions favoring a ferromagnetic (F) background of local spins will be thwarted by antiferromagnetic SE interactions leading to interesting and unusual magnetic states.

\subsection{Without lattice structural distortion}

We use this tight-binding Hamiltonian together with SE interactions among the local spins to describe the magnetic structure without lattice distortion of the 3LL-ludwigite (see Fig. 6a),

\begin{equation}
H = -\sum_{\langle i,j \rangle} (t^e_{i,j} c_i^+ c_j + H.c.) + \sum_{\langle i,j \rangle} J_{ij} \vec{S}_i \cdot \vec{S}_j,
\end{equation}

where $\langle i,j \rangle$ represents nearest-neighbor (NN) sites. $t^e_{i,j}$ represents the effective hopping resulting from the interaction with the background of localized spins, and $c_i^+$ ($c_i$) are the creation (annihilation) operators at sites $i$. The local spins $\vec{S}_i$ being fairly large $S = 5/2$, we will treat them as classical spins $S \rightarrow \infty$, specified by their polar and azimuth angles $\theta_i$ and $\varphi_i$ ($0 < \theta_i < \pi, 0 < \varphi_i < 2\pi$). The constraint imposed on the hopping may be studied by rotating the itinerant electron quantization axis on each site to make it parallel to $\vec{S}_i$ using the spin-1/2 rotation matrix. One gets the effective hopping between electrons antiparallel to local spins at sites $i$ and $j$ as

\begin{equation}
t^e_{i,j} = t_v \left( \cos \frac{\theta_i}{2} \cos \frac{\theta_j}{2} + e^{-i(\varphi_i - \varphi_j)} \sin \frac{\theta_i}{2} \sin \frac{\theta_j}{2} \right).
\end{equation}

$t_v = t_a$, $t_c$ are the NN hopping integrals on the rungs and along the axis of the ladder. $J_{ij} = J_a$, $J_c$ are SE interactions in the two directions. We further assume that this band is non-degenerate; therefore, the band filling is $n = 1/3$. We take the simple situation in which all the spins are in the same plane. This simplification is consistent with neutron scattering results [3, 10]. All coplanar phases being degenerate, we choose the plane of the ladder, taking $\theta_i = \pi/2$ and the hopping terms simply becomes

\begin{equation}
t^e_{i,j} = t_v e^{-\frac{i}{2}(\varphi_i - \varphi_j)} \cos \frac{1}{2}(\varphi_i - \varphi_j).
\end{equation}

Guided by the periodicity 2$c$ of the low temperature distorted phase [4], we consider a unit-cell containing two rungs. We define the magnetic structure by the five angles $\alpha, \beta, \gamma, \delta, \varepsilon$, giving the orientation of the spins on the six sites $i = 1 - 6$ unit cell as shown in Fig. 1a.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1}
\caption{(a) Magnetic structure of the 3-leg ladder Ludwigite. The five angles $\alpha, \beta, \gamma, \delta, \varepsilon$ give the orientation of the spins on the six sites $i = 1 - 6$ unit cell. (b) Magnetic structure of the $I_a$ phase. This structure can present a zigzag modulation of the angles $\theta_1$ and $\theta_2$.}
\end{figure}
The dispersion of the conduction electrons is obtained from the following tight-binding matrix,

\[
\begin{pmatrix}
0 & t_{12} & 0 & 0 & 0 & t_{16} \\
0 & t_{23} & 0 & t_{25} & 0 & 0 \\
0 & t_{32} & t_{34} & 0 & 0 & 0 \\
0 & 0 & t_{43} & 0 & t_{45} & 0 \\
0 & t_{52} & 0 & t_{54} & 0 & t_{56} \\
t_{61} & 0 & 0 & 0 & t_{65} & 0
\end{pmatrix}
\]  \quad (3)

The hopping terms are,

\[
t_{12} = -t_a \exp \left( -i \frac{(\alpha + \beta + \gamma)}{2} \right) \cos \left( \frac{\alpha + \beta + \gamma}{2} \right),
\]

\[
t_{16} = -2t_c \exp \left( -i \frac{\alpha}{2} \right) \cos \left( \frac{\alpha}{2} \right) \exp \left( \frac{k_c}{2} \right) \cos \left( \frac{k_c}{2} \right),
\]

\[
t_{23} = -t_a \exp \left( -i \frac{\delta}{2} \right) \cos \left( \frac{\delta}{2} \right),
\]

\[
t_{25} = -2t_c \exp \left( -i \frac{\gamma}{2} \right) \cos \left( \frac{\gamma}{2} \right) \exp \left( \frac{k_c}{2} \right) \cos \left( \frac{k_c}{2} \right),
\]

\[
t_{34} = -2t_c \exp \left( -i \frac{\epsilon}{2} \right) \cos \left( \frac{\epsilon}{2} \right) \exp \left( \frac{k_c}{2} \right) \cos \left( \frac{k_c}{2} \right),
\]

\[
t_{45} = -t_a \exp \left( i \frac{(\gamma + \delta + \epsilon)}{2} \right) \cos \left( \frac{\gamma + \delta + \epsilon}{2} \right),
\]

\[
t_{56} = -t_a \exp \left( i \frac{\delta}{2} \right) \cos \left( \frac{\delta}{2} \right),
\]

\[-\pi \leq k_c = 2kc \leq \pi.
\]

(4)

The dispersion consists of six bands \(Z_{i=1-6}(k)\), the values \(Z_i(k)\) increase from \(i = 1\) to \(6\). For the band-filling \(n = 1/3\), only the two lowest bands \(Z_{i=1,2}\) are occupied. We minimize the total energy with respect to the five angles \(\{\alpha, \beta, \gamma, \delta, \epsilon\}\). Figure 2 shows the phase diagram as a function of \(J_aS^2/t_c\) and \(J_cS^2/t_c\) for a typical value \(t = t_a/t_c = 1.2\), roughly estimated from the different Fe-Fe distances in the triad and along the legs.

Besides the fully \(F\) state characterized by the uniform angles \(\alpha = \beta = \gamma = \delta = \epsilon = 0\), when \(J_a\) and \(J_c\) are not too large \(J_aS^2/t_c \lesssim 0.07\) and \(J_aS^2/t_c \lesssim 0.13\), we find two other phases: (i) at larger \(J_a\), a phase \(A\) which is antiferromagnetic in the \(c\)-direction \((\alpha = \gamma = \epsilon = \pi)\) with two different angles in the rung; (ii) a phase \(I\), with different angles \((\alpha, \beta, \gamma, \delta, \epsilon)\), which is the stable one in a large part of the phase diagram for lower \(J_c\). These phases are further described below. Except for the ferromagnetic phase, there is a gap between the two lowest bands and the middle ones. At 1/3-filling, the Fermi energy is located in this gap, so that all these phases are insulating. Due to a symmetry reason, the same also occurs at 2/3-filling. This gap depends on the values of the different angles and can be direct or indirect.

In phase \(A\), the hopping is totally suppressed in the \(c\)-direction, and the dispersion reduces to three energy levels. The particular phase \(A\) with fully ferromagnetic rungs \((\beta = \delta = 0)\) is encountered at lower \(J_a\). This phase is in qualitative agreement with the magnetic structure recently proposed from neutron experiments at 82\(K\) [3]. At larger \(J_a\), canting occurs within the rungs with two different angles \(\beta, \delta\); we call this phase \(A_{11}\).

Phase \(I\) presents very interesting simple structures such as, the phase \(I_a\) \((\alpha, \beta, \gamma, \delta, \epsilon = \pi, -\beta, -\varepsilon = -\alpha)\) which can be defined in terms of only two angles \(\theta_1\) and \(\theta_2\) \((\beta = \theta_1, \alpha = \pi - \theta_1 - \theta_2)\). It is AF along the central leg, so that no hopping is taking place along this leg. This structure presents a zigzag modulation of the angles \(\theta_1\) and \(\theta_2\), and consequently, of the hopping \(t_{1}, t_{2}\), as shown in Fig. 1b. A phase called \(I_{\beta}\) tends toward a ferromagnetic behavior along the \(c\)-direction with \(\gamma < \pi\).

\[
\begin{align*}
\text{Figure 2.} & \quad \text{Phase diagram as a function of } J_aS^2/t_c \text{ and } J_cS^2/t_c, \text{ for a typical value of } t = t_a/t_c = 1.2. \text{ The different phases are described in the text.} \\
\text{The dispersion consists of six bands } Z_{i=1-6}(k), \text{ the values } Z_i(k) \text{ increase from } i = 1 \text{ to } 6. \text{ For the band-filling } n = 1/3, \text{ only the two lowest bands } Z_{i=1,2} \text{ are occupied. We minimize the total energy with respect to the five angles } \{\alpha, \beta, \gamma, \delta, \epsilon\}. \text{ Figure 2 shows the phase diagram as a function of } J_aS^2/t_c \text{ and } J_cS^2/t_c \text{ for a typical value } t = t_a/t_c = 1.2, \text{ roughly estimated from the different Fe-Fe distances in the triad and along the legs.}
\end{align*}
\]

\[
\begin{align*}
\text{Phase } I \text{ presents very interesting simple structures such as, the phase } I_a(\alpha, \beta, \gamma, \delta, \epsilon = \pi, -\beta, -\varepsilon = -\alpha) \text{ which can be defined in terms of only two angles } \theta_1 \text{ and } \theta_2 \text{ (} \beta = \theta_1, \alpha = \pi - \theta_1 - \theta_2 \text{)}. \text{ It is AF along the central leg, so that no hopping is taking place along this leg. This structure presents a zigzag modulation of the angles } \theta_1 \text{ and } \theta_2, \text{ and consequently, of the hopping } t_{1}, t_{2}, \text{ as shown in Fig. 1b. A phase called } I_{\beta} \text{ tends toward a ferromagnetic behavior along the } c\text{-direction with } \gamma < \pi.
\end{align*}
\]
As soon as the central leg is AF (γ = π) the bands are two-fold degenerate with gaps at k = ±π/2c. The dispersion of the bands are Z(k) = 0 and

\[
Z(k) = \pm [1 + t^2 + \frac{1}{2} t^2 (\cos \theta_1 + \cos \theta_2) - \cos(\theta_1 + \theta_2)] + (1 - \cos(\theta_1 + \theta_2)) \cos 2k_c \frac{1}{2}.
\]  

(5)

The dispersion for three different values of angles can be seen in Fig. 3. As can be seen in the same Fig. 3c, the lower band of \( I_a \)-phase is filled precisely for \( n = 1/3 \), lowering the kinetic energy to stabilize this phase.

The total energy per rung \( E \) for this \( I_a \)-phase can be expressed as:

\[
\frac{E}{t_c} = -\frac{2}{\pi} [2 + t^2 + \frac{1}{2} t^2 (\cos \theta_1 + \cos \theta_2) + 2 \cos(\theta_1 + \theta_2)]^\frac{1}{2} \mathcal{E}(q) - 2 J_c \frac{S^2}{t_c} [\frac{1}{2} + \cos(\theta_1 + \theta_2)] + \frac{J_a S^2}{t_c} (\cos \theta_1 + \cos \theta_2),
\]

(6)

\( \mathcal{E}(q) \) being the complete Elliptic Integral of second kind with parameter

\[
q = \frac{2(1 - \cos(\theta_1 + \theta_2))}{2 + t^2 + \frac{1}{2} t^2 (\cos \theta_1 + \cos \theta_2) - 2 \cos(\theta_1 + \theta_2)}.
\]

The angle \( \gamma \) varies discontinuously between phase \( I_a \) (\( \gamma = \pi \)) and phases \( F \) (\( \gamma = 0 \)) and \( I_b \) (\( \gamma < \pi \)), so these transitions are first order. All other transitions are second order. In the \( I_b \) phase, close to \( F \), we find a canted ferromagnetic phase with canting within the rungs, one angle only \( \beta \) (or equivalently \( \delta \)) being different from zero; at the transition \( \beta \to 0 \) giving the second order boundary line

\[
\frac{J_a S^2}{t_c} = \frac{\arccos(-t/2\sqrt{2})}{4\pi \sqrt{2}}.
\]

Between the \( F \) and \( A_1 \) phases, the \( I_a \) phase has essentially \( \theta_1 = \theta_2 = \theta \); this can be seen, for example, close to \( A_1 \), in Fig. 4 for \( J_c S^2/t_c = 0.14 \). Therefore, the transition line between \( I_a \) and \( A_1 \) (\( \theta_1, \theta_2 \to 0 \)) is also second order corresponding to

\[
\frac{J_c S^2}{t_c} = \frac{\sqrt{2}(4 - t^2)}{32t} + \frac{J_a S^2}{4t_c}.
\]

For larger values of \( J_a S^2/t_c \), the phase evolves towards the more general zigzag structure \( \theta_1 \neq \theta_2 \) (see Fig. 4).

**Figure 4.** Cut of the phase diagram along the line \( J_c S^2/t_c = 0.14 \), showing the angles between the spins and the resulting charges.

**Figure 5.** Electronic distribution \( n_i \) of the homogeneous magnetic phase as a function of \( t \).

Charge distribution is crucial in the Fe-ludwigite ladder, so it will be examined in detail. It is clear that bond ordering is linked to the spin ordering through the modulation of the hopping amplitudes. The ferromagnetic bonds tend to localize the extra electron. This in turn may induce different types of charge ordering on the non-equivalent Fe-sites in the rung. Experimentally [8, 11], two charge regimes are identified (i) above \( T_c \), the side sites 1 and 3 are identical \( n_1 = n_3 \approx 0.25 \) and the central site 2 has more electrons \( n_2 \approx 0.5 \) (ii) below \( T_c \) down to \( 74K \), the charge on site 3 (the site which gets closer to site 2) increases close to the charge of site 2 which remains stable, \( n_2 \approx n_3 \approx 0.5 \), and at the same time the charge of site 1 decreases to \( n_1 \approx 0.15 \). Of course these values [3] indicate only the tendencies, since one should have \( n_1 + n_2 + n_3 = 1 \). However, below \( 74K \), two contradictory behaviours have been reported [8, 12]. Douvalis et al. [12] found that the low temperature ordering below \( T_c \) persists down to \( T = 0 \), while Larrea et al. [8] recover the same charge ordering as above \( T_c \).

Let us begin the charge distribution study with homogeneous magnetic phases, i.e. magnetic phases without modu-
lation of the hopping amplitude; in this sense, ferromagnetic and paramagnetic phases are equivalent, only the effective hoppings are different in the two cases. The electronic distribution is shown in Fig. 5 as a function of $t$.

We see that the high temperature behaviour can be reproduced only if $t$ is large $t \geq 2.5 - 3$, in particular for $t \geq 2\sqrt{2}$ one gets $n_1 = n_3 = 1/4$ and $n_2 = 1/2$, but such $t$ values are far too large in the Fe-ludwigite ladder. But we see that the same regime can be reached in the $A_I$ phase as well since, in this case, the effective hopping is zero in the $c$-direction, which is equivalent to taking $t_c = 0$ (see Fig. 4), and the problem reduces to three sites. The $I_a$ phase close to $A_I$ with $\theta_1 = \theta_2$ could also give quite well the high temperature charge distribution as seen in Fig. 4 for $J_a S^2 / t_c \lesssim 0.2$. However, as can be seen in Fig. 4, an interesting point resulting from our analysis is the existence of the $I_a$ structure with $\theta_1 \neq \theta_2$, as in Fig. 1b. This produces a zigzag bond alternation which, in turn, will give rise to a lattice instability of the same type. Due to the magnetic structure, the two border sites of a rung have different electronic charges leading to the formation of a zigzag charge ordering, $n_2 \approx n_3 \gg n_1$, similar to the one observed experimentally below $T_c$. Note that a phase of type $(\theta_1 = 0, \theta_2 = \pi/2)$, \(\uparrow\downarrow\uparrow\uparrow\) on the rung has been proposed at $10K$ [3], in contrast with the antiferromagnetic ordering \(\uparrow\downarrow\uparrow\uparrow\) inside the triad obtained from earlier neutron experiments [13]. Except asymptotically, i.e. $J_a \rightarrow \infty$, we do not find phases with AF arrangement of the triads.

### 2.2. With lattice structural distortion

We study the effect of the lattice distortion by considering the hopping $t_a(1 \pm \delta)$ alternating along the $c$-direction, as can be seen in Fig. 6b, and we introduce an elastic energy term $(1/2)B\delta^2$ per rung.

For a homogeneous magnetic state, the model reduces to the simple Peierls model considered by Latgé and Continentino [14] and is unlikely to reproduce the experimental behaviour for reasonable values of $t$, even in the undimerized state as shown in Fig. 5. As discussed above, the zigzag $I_a$ phase strongly favors the related rung distortion and, as expected, it occupies an important part of the phase diagram, as shown in Fig. 7 for a value $B/t_c = 6$.

Here we do not consider the more complicated $I_b$ phase appearing at lower $J_a$. Phase $I_a$ shows two distinct regions, an undistorted one with $\theta_1 = \theta_2$ and a wide distorted one. A phase $I_{aa}$ with fully dimerized hoppings $(\theta_1 = 0, \theta_2 = \pi)$, one ferromagnetic and one antiferromagnetic bond in each rung, is now stabilized by the distortion (Fig. 7, below the dashed line). The distortion $\delta$ for the $F$, $A_I$ and $I_{aa}$ phases is shown in Fig. 8a as a function of $B/t_c$. The existence of hopping distortion $\delta \neq 0$ in $A_I$ requires small values of the elastic term $B/t_c \lesssim \sqrt{2}$. This is easily obtained from the total energy per rung $E$ which reduces to

$$
\frac{E}{t_c} = -t\sqrt{2(1+\delta^2)} + \frac{1}{2} \frac{B}{t_c} \delta^2
$$

![Figure 6](image1.png)

**Figure 6.** (a) Ludwigite Fe(3)-Fe(2)-Fe(3) 3LL without lattice distortion (b) The same ladder with structural distortion. Hopping is indicated in the figures.
in the 3-site problem. The $I_{aa}$ phase presents the largest distortion among these phases, clearly showing the bond order related to the ferromagnetic character of the bonds. The corresponding charges on the Fe sites in phases $A_I$ and $I_{aa}$ are shown in Fig. 8b.

We see that the phase $A_I$ represents better than others the experimental charges both above ($\delta = 0$) and below ($\delta \neq 0$) the structural transition $T_c$, i.e. $n_2$ remains constant equal to 1/2, while $n_1 = n_3 = 1/4$ in the undistorted phase and $n_3$ approaches 1/2, whereas $n_1$ decreases in the distorted phase. In the $I_{aa}$ phase, it is site-3 which has the largest electronic charge $n_3 = 0.5$, contrary to experimental estimate both above $T_c$ and below for $74K<T_c$.

### 3. Conclusions

Our results are consistent with the existence of an $A$-type phase as proposed at 82 K [3], but imply that it persists above $T_c$. On the other hand, the $I$-type structure proposed at 10 K [3] should present charge ordering and lattice distortion, in contradiction with the recent Mössbauer results of Larrea et al. [8]. We have shown that simultaneous spin and charge ordering in qualitative agreement with the experimental behaviour for $T>74K$ occurs from the competition between DE and SE interactions. The bonding is strongly reinforced by the ferromagnetic correlations; therefore, this may induce a lattice instability as observed. Below 74 K, the experimental results [3, 8, 12] are contradicting and further experiments are required to clarify the low temperature situation. Our approach has emphasized the importance of the magnetic structure and bring to light the interplay between spin ordering, charge ordering and lattice distortion.

### Acknowledgement

We are grateful to J. Dumas, M.A. Continentino and P. Bordet for helpful discussions. E.V. acknowledge CONACyT for financial support.

3. P. Bordet et al., private communication.