Cation-mediated interaction and weak ferromagnetism in $Fe_3O_2BO_3$

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The oxyborates show a variety of interesting physical behavior associated with the existence of low dimensional units in their crystalline structure. In this paper we present transport, x-ray, magnetic, and Mössbauer spectroscopy measurements in homometallic ludwigites. These results give evidence of charge localization and reveal an unusual magnetic behavior. We observe the existence of a reentrant weak ferromagnetism as well as the coexistence of paramagnetic and antiferromagnetic spins in $Fe_3O_2BO_3$. [S0163-1829(99)09533-8]

I. INTRODUCTION

A renewed interest in transition-metal insulating oxides has arisen after the discovery of properties like high-temperature superconductivity[1] and colossal magneto-resistance,[2] which appear in some of these systems if conveniently doped. These exciting properties and the interesting physics of these oxides have led us to start an investigation of certain families of oxyborates that present a combination of strong correlations and low dimensional effects.[3–7]

In this paper we present structural, transport, and magnetic properties in a class of oxyborates known as *ludwigites*.[6] These materials, with chemical formula $2MO \cdot M'BO_3$, have a crystalline structure that consists of an assembling of subunits in the form of *zigzag walls*, with four nonequivalent octahedral sites that are preferentially occupied by divalent or trivalent metallic ions, M and M', respectively (see Fig. 1). We focus here on homometallic ludwigites with $M=M'=$Fe,Co. In contrast with the heterometallic ones ($M \neq M'$), they do not present positional disorder and the electrons may delocalize within the two-dimensional structures (the walls). In fact, the conductivity of the present materials is much higher than that of the mixed ludwigites we studied earlier ($M'=$Fe, $M=$Cu,Ni).[6,7] In spite of the higher conductivity of the present samples, we do not find evidence for ferromagnetic interactions that could arise from double exchange between the metallic ions, all located in octahedral sites.

Previous investigations of the homometallic Fe ludwigite dealt essentially with its structural properties and the magnetic properties at high temperatures, i.e., above the appearance of long-range magnetic order at T_N.[9] Here we extend these investigations to lower temperatures using ac-susceptibility, dc-magnetization measurements, and Mössbauer spectroscopy to reveal a variety of interesting behavior. ac-susceptibility results are also presented for the homometallic Co ludwigite. These results, together with transport and structural measurements allow for a consistent description of the physical properties of these materials. We find that, as for the FeNi and FeCu systems, the homometallic Fe ludwigite can be viewed as consisting of two independent magnetic subsystems. Differently from the former materials we observe an unusual weak ferromagnetism in $Fe_3O_2BO_3$.

II. EXPERIMENT

A. Sample preparation

The Fe sample was prepared by heating at $1120\,°C$ a stoichiometric mixture of FeO, Fe_2O_3, and B_2O_3 in borax under an argon atmosphere. The Co sample was prepared according to Norrestam *et al.*[10] In both, small impurity phases were formed. In the case of Co, Co_3O_4. In the case of the Fe material, the spurious magnetite phase, $FeO \cdot Fe_2O_3$, was magnetically separated from the main ludwigite phase. The x-ray spectra of the $Fe_3O_2BO_3$ samples used in the present experiments indicate a single phase material with the characteristic peaks of the ludwigites.
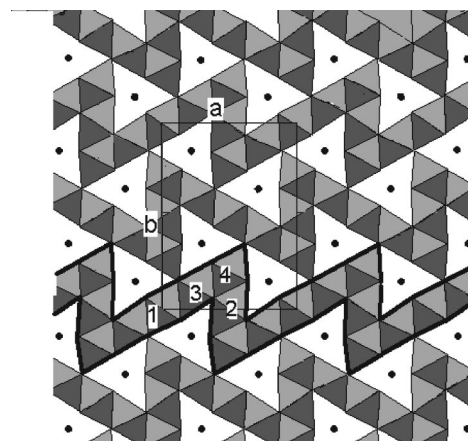

FIG. 1. Structure of the ludwigites showing the *ab* plane, perpendicular to the *c* axis. Notice the subunits in the form of *zigzag walls* that assemble to form the $3d$ structure. The four different crystallographic sites occupied by metals are indicated.
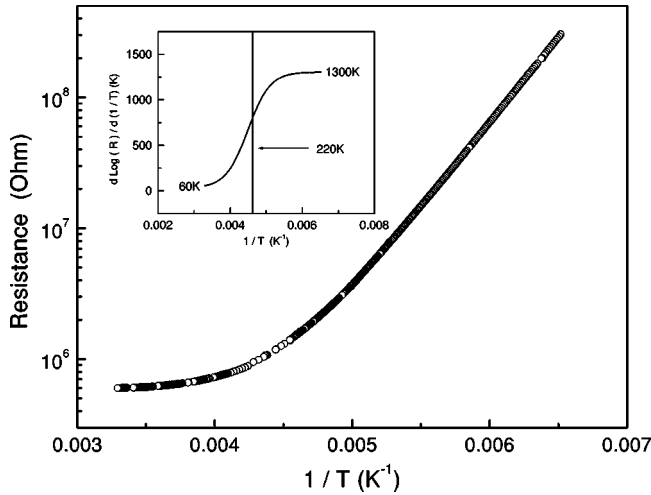
FIG. 2. Resistance of $2FeO \cdot FeBO_3$ measured below room temperature. Below 150 K the resistance is too large to be measured. In the inset the derivative of the curve is plotted, showing the two activation energies, Δ_1, Δ_2, and the crossover regime around T_{co}.

B. Transport measurements

The electrical resistance of a needle-shaped Fe ludwigite single-crystal 4 mm long was measured between 4.2 and 300 K. Due to the high room-temperature resistance of the sample (600 kΩ), we measured the resistance with two contacts only, using the resistance scale of a Keithley multimeter. The electrical contacts were made with silver paint. The resistance versus temperature curve, shown in Fig. 2, can be described by activated behavior, with two characteristic energies, $\Delta_1/k_B = 60$ K and $\Delta_2/k_B = 1300$ K, below and above $T_{co} \approx 220$ K, respectively. Below 150 K, the resistance was too high to be measured ($R > 300$ MΩ, the maximum scale of the multimeter). The crossover at T_{co} is associated with charge localization, as the barrier for electron hopping rises by two order of magnitude close to this temperature. This is probably due to short-range magnetic order that in low dimensional systems occurs at temperatures much above the magnetic ordering transition.

C. X-ray measurements

The x-ray measurements were performed at room temperature and at 93 K using the Cu $K\alpha$ radiation and with the sweeping speed of $0.25°$ per minute. There is no significant difference between both spectra, in particular the same space group, $Pbam$, fits the data at both temperatures. No sign of spurious phase was found. Table I gives the orthorhombic cell parameters at room temperature and at 93 K. The room-temperature parameters are in agreement with those in Ref. 9. The x-ray results rule out the possibility that the charge

TABLE I. Orthorhombic unit-cell parameters of $Fe_3O_2BO_3$ at room temperature (RT) and at 93 K.

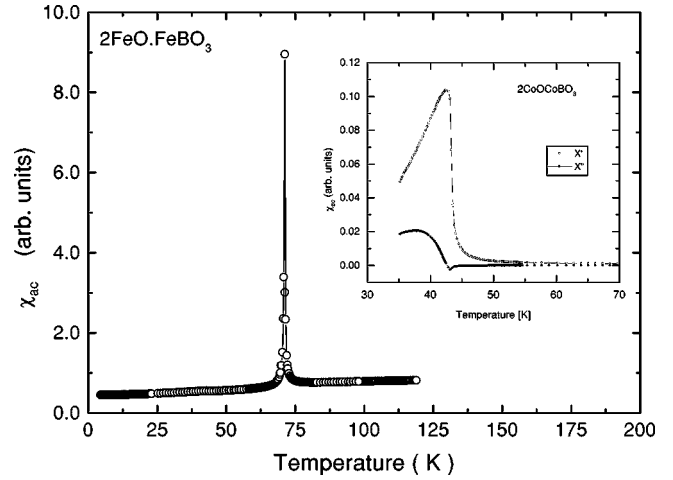| T (K)	a (Å)	b (Å)	c (Å)
RT	9.453	12.296	3.072
93	9.434	12.266	3.072

FIG. 3. ac-susceptibility measurements of the Fe and Co (inset) ludwigites at a frequency of 125 Hz. The ac field is 20 Oe.

localization seen in the transport properties close to $T_{co} = 220$ K is associated with some change in the crystalline structure.

D. Magnetic measurements

The magnetic ac-susceptibilities, χ_{ac}, were measured on powder samples using a commercial Lake-Shore apparatus, from 4.2 K to room temperature in an ac field of 20 Oe at a frequency of 125 Hz. The susceptibilities, shown in Fig. 3, are in strong contrast with those obtained in our previous studies of heterometallic ludwigites.[6,7] In the present case they have a steep increase at a critical temperature T_c ($T_c^{Co} \approx 40$ K, $T_c^{Fe} \approx 70$ K) instead of rising monotonously.[6,7] As temperature decreases, the rise of the ac signal at T_c is equally sharp for both homometallic ludwigites. This is a well-known feature of weak ferromagnets.[8] Below T_c the ac signal falls sharply for the Fe system. The maximum of χ_{ac} close to T_c has a negligible frequency dependence implying that, in spite of some competition, this is indeed a magnetic phase transition and not a progressive freezing of the magnetic moments. dc-magnetization measurements were performed in a powder sample of the Fe ludwigite using a Quantum Design SQUID magnetometer (where SQUID is a superconducting quantum interference device). Magnetization as a function of temperature was measured for different magnetic fields (500 and 1000 Oe) in field-cooled and zero-field–cooled procedures. In Fig. 4 we show the magnetization curve for an applied field of 1000 Oe. For the Fe ludwigite, the measurements are sufficiently sensitive to detect the Verwey transition,[11] at 119 K, of a remaining trace of the spurious magnetite phase and which manifests as a small anomaly at the magnetization curve at this temperature. At $T_c \approx 70$ K, which coincides with the temperature of the peak in χ_{ac}, the magnetization rises sharply, reaches a maximum, and then slowly drops with decreasing temperature reaching the values before the transition for the fields used in the experiments ($h \leq 0.1$ T). Below T_c the magnetization is clearly history dependent.

Several magnetization versus field isotherms for the Fe ludwigite are shown in Fig. 5, some of them extending up to 5 T. We note the appearance of a spontaneous magnetization
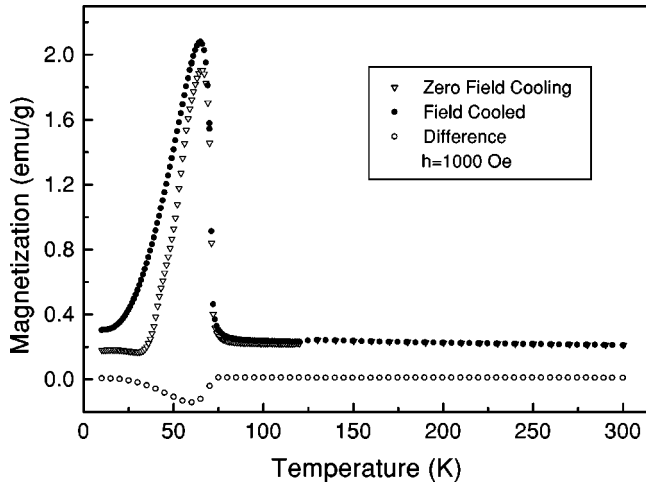
FIG. 4. dc-magnetization measurements of $2FeO \cdot FeBO_3$, under field-cooled and zero-field–cooled conditions. The difference between the two curves is also shown.

and a hysteresis loop at $T_c \approx 70$ K. The total magnetic moment at 70 K is small and corresponds to $\sim 0.1 \mu_B$ per chemical formula. The hysteresis loop vanishes again at approximately 40 K, in agreement with the reentrant behavior observed in the magnetization versus temperature curve. In fact, the magnetization curves $m(h)$ at 20 K and above $T_c \approx 70$ K are very similar, except for different inclinations associated with a weakly temperature dependent susceptibility. Note that even at 20 K a field of 5 T does not saturate the $m(h)$ curves. The magnetization curves at low fields have a temperature-independent feature, associated with the small traces of magnetite, which, however, does not affect the main behavior of these curves.

Mössbauer (ME) spectroscopy of ^{57}Fe gives additional information on the magnetic behavior. The spectra were taken with the sample in a variable-temperature helium cryostat and the ^{57}Co:Rh source at room temperature, moving in a sinusoidal mode outside the cryostat. Figure 6 shows the spectra at some selected temperatures, above and below the Néel temperature $T_N \approx 112$ K determined by the temperature dependence of the ^{57}Fe ME spectra. More detailed analysis of the Mössbauer data will be published elsewhere.[12] We are interested here in the information that can be obtained from a simple inspection of the spectra shown in Fig. 6, namely, the occurrence of magnetic order for the Fe^{3+} ions at $T_N \approx 112$ K. This progressively leads to the magnetically split spectra at 80 K where *part of the Fe^{2+} still remains paramagnetic*. The weak ferromagnetic transition at $T_c \approx 70$ K can also be seen in the ^{57}Fe ME spectra, as the temperature at which the lines associated with these remaining paramagnetic Fe^{2+} become split. It is striking that in the ac and dc magnetic measurements, there is no indication of the magnetic transition seen in the Mössbauer experiments at T_N.

III. DISCUSSION

In order to understand the magnetic and transport behavior of the homometallic ludwigites, it is helpful to consider the various distances between the Fe ions in different sites of the ludwigite structure and which are given in Table II.[9] They give rise to a hierarchy of interactions and influence the charge states that determine the magnetic moments of the ions in a particular site.

The important information on the charge distribution along the octahedral sites is given by the Mössbauer study.[9] The characteristic lines of the paramagnetic spectrum, above T_N, can be understood assuming that sites 1 and 4, in Fig. 1,
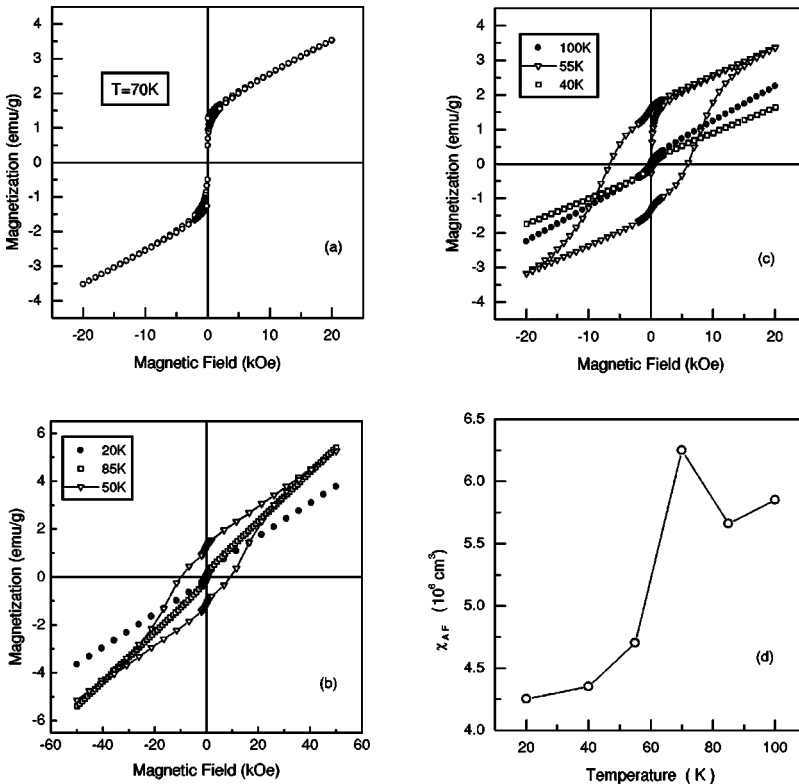

FIG. 5. Magnetization versus magnetic-field isotherms, both above and below the weak ferromagnetic transition of $2FeO \cdot FeBO_3$. In (b) the magnetic field extends up to 5 T. In (d), the antiferromagnetic susceptibility χ_{AF} that is given by the inclination of the magnetization curve in the linear region of the isotherm is shown.
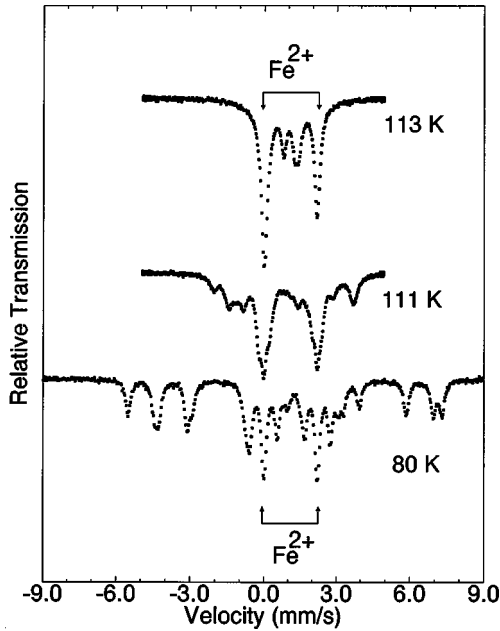
FIG. 6. Mössbauer spectra of $2FeO \cdot FeBO_3$ at selected temperatures, above and below T_N.

are basically occupied by Fe^{2+} ($S=2$), whereas the group of sites 3-2-3, have two trivalents ($S=5/2$) and one divalent ion.[9] The distance between the latter is very short, $d_{23} = 2.787$ Å,[9] which gives rise to strong d-d overlap and, consequently, direct exchange. On the other hand, the distance between ions along the c axis of the orthorhombic unit cell is 3.05 Å,[9] which is just at the limit for direct d-d overlap.

Recently, a structurally related material, an homometallic Fe *warwickite*, has been investigated using magnetic and structural probes.[13] This oxyborate has subunits in the form of *ribbons* instead of walls as in ludwigites.[3–5] These studies have shown the occurrence of a charge ordering transition within the ribbons, at a temperature $T_{co} \approx 320$ K, much higher than the antiferromagnetic ordering of this warwickite at $T_N \approx 150$ K.[13] Since the low dimensionality of the ribbons is detrimental to magnetism, the charge ordering transition at T_{co} occurs above the Néel temperature. This is quite different from another Fe oxide, the magnetite $FeO \cdot Fe_2O_3$,[14] where the ions Fe^{2+} and Fe^{3+} in octahedral sites align ferromagnetically due to double exchange. Ferrimagnetism, due to antiferromagnetic coupling between the Fe ions in tetrahedral and octahedral sites, occurs at $T_F \approx 850$ K. Between this temperature and the charge ordering transition (the Verwey transition) at $T_V \approx 120$ K the system is metallic.

The phenomenology of the above materials, which in turn has many similarities with that of the manganites,[2] is clearly relevant to understand some of the present results. This is

TABLE II. Distances between ions in the Fe ludwigite according to Ref. 9. See Fig. 1 for the specification of the sites. d_{AA} ($\bar{c}$) means the c axis of the orthorhombic unit cell.

d_{31}	d_{32}	d_{34}	d_{41}	d_{AA} ($\bar{c}$)
3.101	2.787	3.192	3.374	3.073

TABLE III. The ordering temperatures T_N of Fe^{3+} in sites 3 of ludwigites, as functions of the nature and spin of the divalent cations. Except for the MgFe ludwigite, the critical temperatures T_N have been obtained by Mössbauer spectroscopy.

Cation	Mg^{2+}	Cu^{2+}	Ni^{2+}	Fe^{2+}
S	0	1/2	1	2
T_N (K)	10	60	106	112
Ref.	20	7	6	This work

essentially a competition between a charge ordering transition leading to an insulating state, generally accompanied by antiferromagnetic (AF) ordering and double exchange, which couples the spin ferromagnetically, if the system is sufficiently metallic. In our Fe system there is no charge ordering transition but a crossover to a much more resistive state close to $T_{co} \approx 220$ K as indicated by the transport measurements. This is probably, due to the larger number of inequivalent sites, 4 instead of 2 as in warwickite. This crossover occurs at a temperature lower than the charge ordering transition of the Fe warwickite. In both Fe oxyborates however, charge localization takes place above the magnetic transitions and no ferromagnetic interactions are present, as would be expected if electronic transitions between Fe^{2+} and Fe^{3+} in distinct octahedral sites could occur.

The antiferromagnetic transition in the Fe ludwigite, at $T_N = 112$ K, as seen in the Mössbauer experiments does not show up in the macroscopic magnetic measurements as we pointed out previously. We have encountered this phenomenon before in our studies of the FeNi (Ref. 6) and FeCu (Ref. 7) ludwigites. There, the appearance of the Mössbauer splitting, associated with the set in of magnetic order, gave rise to hardly noticeable anomalies in the χ_{ac} susceptibility curves. The evidence for the antiferromagnetic nature of the transition in the Fe ludwigite, at $T_N \approx 112$ K, is given by the magnetization measurements that yield a zero net magnetization below T_N ($T_N > T > T_c = 70$ K). Note that the charge distribution along the ab planes, as obtained from the Mössbauer experiments, implies an antiferromagnetic alignment between spins in different planes in order to produce a state with zero net magnetization. The Mössbauer spectra in Fig. 6 also reveals the interesting feature that part of the Fe^{2+} remains paramagnetic at 80 K below T_N. These results together with our previous studies of ludwigites shows that $Fe_3O_2BO_3$ can be viewed as formed of two magnetic subsystems. One subsystem consists of the strongly interacting triads of mostly trivalent Fe ions in sites 3-2-3, which orders antiferromagnetically at T_N. The other subsystem contains Fe^{2+} ions in sites 1 and 4. In Table III we give the Néel temperature T_N of the Fe^{3+} for different Fe ludwigites. These ordering temperatures clearly depend on the nature and spin of the divalent cations, suggesting that these cations intermediate the interactions among the triads. This is the case of triads in the same wall that interact along the ab plane, through the divalent cations in sites 1. Note that since the atomic distances are all very similar in these materials,[15] the spin of the cation is the relevant feature determining the strength of the interaction. In the simple case of two Ising spins, coupled by an interaction J to a paramagnetic ion with

$2S+1$ states, a *decoration transformation* yields an effective, temperature-dependent, coupling between the Ising spins.[16] If we add to this interaction, that which arises in the case of a nonmagnetic cation as Mg, we may obtain within a temperature range, an effective antiferromagnetic interaction that is stronger the larger the spin of the mediating cation.

As temperature decreases further the susceptibility rises abruptly at $T_c \approx 70$ K with the concomitant appearance of a spontaneous magnetization. This is confirmed by the $m(h)$ isotherms and the opening of a hysteresis cycle. The small moment of $0.03\mu_B$ per Fe, which appears at T_c, indicates weak ferromagnetism in the present material. On further cooling, the magnetization decreases, vanishes at approximately 40 K and does not reappear down to the lowest temperature (10 K). Weak ferromagnetism has been observed previously in hematite,[17] αFe_2O_3. This material presents, below a critical temperature $T_N = 950$ K, a small spontaneous magnetization that disappears below the Morin point ($T_M \approx 260$ K) where it becomes purely antiferromagnetic.[18,19] The established mechanism for weak ferromagnetism in this system is a canting of antiferromagnetically aligned spins in the basal plane towards each other giving rise to a small net moment.[19] The underlying microscopic interaction is the Dzyaloshinski-Moriya coupling that favors the canted state. We propose that the same mechanism is present in the Fe ludwigite and involves in this case the subsystem of Fe^{2+}. In fact, the common features of $Fe_3O_2BO_3$ with hematite supports the idea that canting of the moments antiferromagnetically aligned below $T_c \approx 70$ K is responsible for the weak ferromagnetism of this material. Among these features we point out the highly distorted octahedra containing the Fe^{2+} ions,[9] a magnetization that rises linearly with field at high fields and a large coercive field in the weak ferromagnetic region (40 K$<T<$70 K) of about 9 kOe at 50 K (see Fig. 5). Also the antiferromagnetic susceptibility χ_{AF}, defined by $m_T = m_0 + \chi_{AF}h$, where m_T and m_0 are the total and the spontaneous magnetization respectively, see Fig. 5, behaves similarly as in hematite.[18] On the other hand, distinctively from hematite, the weak ferromagnetic component rises very sharply at T_c and the weak ferromagnetic region is small. This may be a consequence of the low dimensionality of the walls within which the spins are located. It is interesting to point out that the weak moment is largest just below the ordering temperature T_c. As temperature decreases the weak ferromagnetic moment decreases and the equivalent of the Morin point, where m_0 vanishes, is close to 40 K. Below this temperature we have antiferromagnetic ordering within the two subsystems.[21]

In conclusion we have shown the existence of weak ferromagnetism in homometallic ludwigites. Different from the Fe warwickite, there is no true charge ordering transition in Fe ludwigite but a steep crossover to a more localized state. This crossover occurs above the magnetic transition and precludes the possibility of ferromagnetic interactions due to double exchange in these systems. The low magnetic ordering temperatures in these materials are due to the low dimensionality of these systems with subunits in the form of ribbons and walls.

The existence of a weak ferromagnetic component is a distinguishing feature of homometallic ludwigites. In the FeNi and FeCu ludwigites straightforward antiferromagnetism or spin-glass ordering occurs due to positional disorder in these systems.

The magnetic ludwigites can be viewed as formed of two subsystems, consisting of divalent and trivalent ions, respectively. These subsystems interact and interfere with each other giving rise to an interesting magnetic behavior. In particular the paramagnetic divalent cations mediate an interaction between the Fe^{3+} ions remaining paramagnetic much below the ordering temperature of the latter at T_N.

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