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Room Temperature Magnetism in Layered Double Hydroxides due to Magnetic Nanoparticles

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Supporting Information

ABSTRACT: Some recent reports claiming room temperature spontaneous magnetization in layered double hydroxides (LDHs) have been published; however, the reported materials cause serious concern as to whether this cooperative magnetic behavior comes from extrinsic sources, such as spinel iron oxide nanoparticles. The syntheses of crystalline Fe^{3+}-based LDHs with and without impurities have been developed, highlighting the care that must be taken during the synthetic process in order to avoid misidentification of magnetic LDHs.

Numerous reports claiming ferromagnetic behavior exceeding room temperature in organic and metal−organic molecular magnets exist. However, for the most part, the source of magnetism is of extrinsic origin. A typical case is that of pure organic materials in which magnetism is often caused by the presence of metals, like iron, or metal oxide impurities.[1] The issue of intrinsic versus extrinsic sources of magnetism has also been pointed out more recently in some claims about room temperature magnetism in metal−organic Ni-TCNE charge-transfer salts.[2]

In the case of pure inorganic materials, this issue can also be present, although the intrinsic cooperative magnetism arising from the interacting metals often overcomes the extrinsic magnetism coming from impurities. Still, when intrinsic cooperative magnetism occurs at low temperatures, the presence of magnetic impurities can be dominant at high temperatures, thus leading to wrong claims. An illustrative example in this context is provided by the magnetic layered double hydroxides (LDHs), as we will show in this paper.

LDHs are a family of layered materials traditionally used in fields of utmost importance such as catalysis, absorbents, medicine, or industrial applications.[3] The structure of these anionic clays is related to that of the brucite, in which the partial substitution of divalent cations leads to an excess of positive charge, compensated for by the presence of interlamellar anions. The typical formula for these materials is $[M^{II}_{1-x}M^{III}_{x}(OH)_2](An^-)_{x/n}\cdot yH_2O$, thus offering the possibility of a wide tuning of the chemical composition.

Recently, these layered systems have been postulated both as functional hosts and as building blocks for the preparation of organic−inorganic hybrid magnetic materials.[4] In this sense, the introduction of magnetic metal cations within the layers can lead to ferro- or ferrimagnetic behavior, operating through superexchange interactions mediated by hydroxo bridges, in addition to the less intense dipolar interactions operating through the space between the magnetic layers. These magnetic properties are inherently designed to be manifested at low temperatures because of the low intensity of the involved exchange interactions. In fact, as a result of the structural features of these layers (MO_6 octahedra sharing edges), the M−O−M superexchange path is always close to orthogonality, leading to weak exchange interactions.[5]

Surprisingly, Wei and co-workers recently claimed in several works that iron-containing LDHs behave as magnets at room temperature.[6] In fact, they found that highly crystalline colloidal LDH suspensions obtained after the coprecipitation of nickel, cobalt, and iron nitrate or chloride salts, followed by a hydrothermal treatment at moderate temperatures, led to the synthesis of NiFe- or CoFe-LDHs, which were attracted by a conventional laboratory magnet. Although their applications as sensors are very appealing, this room temperature spontaneous magnetization is due to magnetic impurities, as we will demonstrate in this work.

Generally, the synthesis of highly crystalline non-Al^{3+}-based LDHs is very disfavored via a homogeneous precipitation route mainly because of the absence of a specific amphoteric behavior in transition-metal cations like Fe^{3+}. Recent work has developed novel synthetic strategies to address these problems, including the use of additional chelating reagents[7] or the smart topochemical approach developed by Sasaki and co-workers.[8] More concretely, the synthesis of iron-based LDHs has usually led to the presence of some amorphous phases like ferrihydrite (FeOOH), or even iron oxide nanoparticles (Fe_2O_3 or Fe_3O_4 maghemite and magnetite, respectively), that exhibit room temperature magnetism (see Figure 1).[8b,9] These impurities sometimes are not detectable through powder X-ray diffraction (PXRD). Thus, it is possible to obtain LDHs maintaining their chemical properties despite being decorated with spinel "nano impurities". As can be observed in Figure 1, highly crystalline NiFe-LDH phases with the highest iron content (i.e., Ni:Fe ratio equal to 2:1) can be prepared following a modified homogeneous precipitation method reported by our group using triethanolamine and urea as chelating and hydrolysis reagents, respectively, at 125 °C over 48 h (section SI-1 in the Supporting Information, SI).[7a,4i] The PXRD pattern shows the typical profile expected for a LDH. It presents sharp intense peaks at low θ values and less intense peaks at higher angular values, with no signature of contaminant phases. Despite the crystallinity exhibited by the apparently pure bulk sample, it is attracted by a conventional laboratory magnet.

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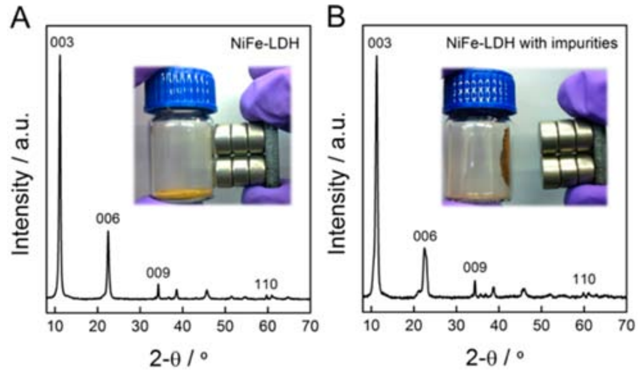

Figure 1. (A) PXRD of a NiFe-LDH (2:1 ratio) without room temperature magnetic impurities. (B) PXRD of a NiFe-LDH exhibiting a similar profile but decorated with nondetectable spinel impurities. The insets show digital photographs of the samples under an external magnetic field.

Sometimes these spinel peaks are seen as very weak signals of small intensity in the PXRD experiments. This can be observed in Figure 2A for samples of NiFe and CoFe prepared by the hydrothermal approach (sections SI-1−SI-3 in the SI). In this case, the broad peak at around a 2θ value ranging from 17 to 19° can be detected and is related to the presence of Co and Fe spinel impurities. In addition, a detailed inspection of the crystals through high-resolution transmission electron microscopy (HRTEM) shows the presence of very small nanoparticles of ca. 4 nm on the surface of the NiFe-LDH crystals (Figure 2B,C). Moreover, Rives et al.[10] reported that when CoFe-LDH is synthesized through a traditional coprecipitation method, Co^{II} can become partially oxidized to Co^{III}, being a possible source of spinel impurities (probably $Co^{II}Co^{III}{}_2O_4$, $Co^{II}Fe^{III}{}_2O_4$, or $Co^{II}Co^{III}Fe^{III}O_4$), which also exhibits room temperature magnetic properties (section SI-2 in the SI). In contrast, the nonaqueous method reported by Gardner et al.[11] leads to pure CoFe-LDHs (sections SI-2 and SI-4 in the SI).

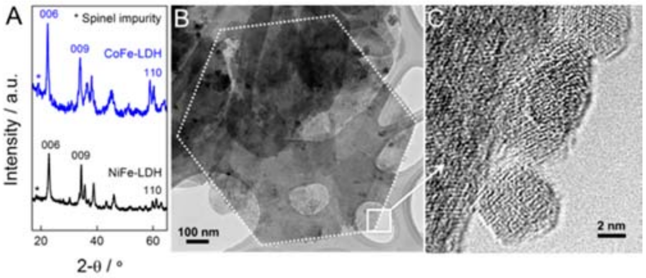

Figure 2. (A) PXRD patterns and peaks indexation of NiFe-LDH and CoFe-LDH at high angles highlighting the spinel impurities. (B) HRTEM image of a hexagonal crystal of the impure NiFe-LDH. (C) Magnified image showing some nanoparticles decorating the LDH surface.

These impure LDHs are immediately attracted to a magnet (as previously observed in the inset of Figure 1B). Moreover, the temperature-dependent magnetic susceptibility, χ, of NiFe and CoFe decorated with impurities reported as χT versus T shows an almost linear increase above ca. 25 K, suggesting a partial temperature-independent component that could be ferromagnetic or superparamagnetic in origin (Figure 3).[2b]

The drop observed in both the pure and "decorated" LDH phases in the χT plot below 20 K defining a maximum corresponds to the intrinsic cooperative magnetism in the LDH layers and is accompanied by steep jumps in the χ_M signals.[4] This intrinsic spontaneous magnetization at low temperature is confirmed by alternating-current (ac) dynamic susceptibility measurements (see Figure 4), which show the presence of defined peaks in both the in-phase (χ_M') and out-of-phase (χ_M'') signals (see the insets in Figure 4).[4] From the position of the χ_M'' signal, one can extract the critical temperature below which the spontaneous magnetization of the LDH material appears. In the case of NiFe, this temperature is about 16 K, while for CoFe, it is ca. 10 K.

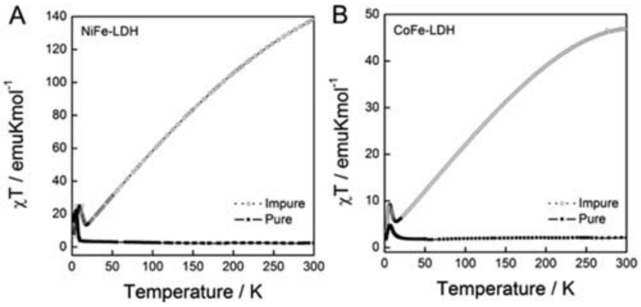

Figure 3. Temperature dependence of the $\chi_M T$ product for (A) impure NiFe-LDH (open symbols) and (B) impure CoFe-LDH. $\chi_M T$ values for pure NiFe- and CoFe-LDHs are shown for comparison (closed symbols).

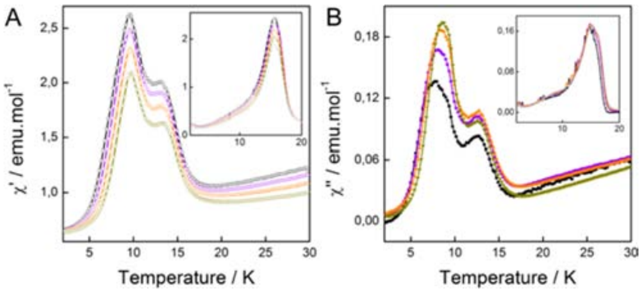

Figure 4. Measurements of ac susceptibility for the NiFe-LDH isolated compounds: (A) in-phase and (B) out-of-phase signals at 10, 100, 1000, and 10000 Hz (black, purple, orange, and green data points, respectively). The inset represents the signals of a pure LDH phase.

These dynamic experiments are strongly sensitive to the presence of magnetic impurities in the samples. In fact, in both NiFe and CoFe, these measurements show a peak at very low temperatures that is frequency-dependent and whose intensity increases with the amount of impurity. This peak is probably due to the presence of very small superparamagnetic nanoparticles anchored to the LDH surface, which undergo superparamagnetic blocking at these low temperatures. In fact, the blocking temperature for Fe_3O_4 nanoparticles of 4 nm in size is close to 8 K.[12] In the examples reported in the present paper (NiFe- and CoFe-LDHs with small intercalate anions such as $CO_3{}^{2-}$ or $NO_3{}^{-}$), one can notice that this low-T signal only appears when impurities are present. Still, we should remark that, in other pure LDH materials presenting a higher interlamellar space due to the intercalation of bulky anions, a similar frequency-dependent signal has also been observed at this temperature. In these cases, this signal is intrinsic and has been attributed to the movement of the domain walls in the ordered state[4a,b,f,g,i] or even to the presence of metallic disorder within the layers, which can give rise to spin-glass-like behavior or to superparamagnetism coming from metal clustering within the layers.[4f,i] The conclusion is that not always can this low-*T* and frequency-dependent χ_M'' signal be taken as proof of the presence of magnetic impurities. Other experiments, such as, for example, the presence of a hysteretic behavior in the magnetization versus field plot, can be more conclusive. In this context, we have plotted the *M* versus *H* curves at various temperatures for a pure NiFe-LDH (Figure 5). For the hysteresis cycle measured at 20 K, just above the critical temperature for the onset of the spontaneous magnetization, neither significant coercive field nor remnant magnetization can be measured.

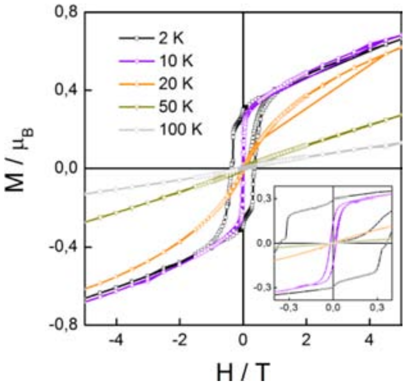

Figure 5. Field-dependent magnetization of pure NiFe-LDH at different temperatures ranging from 2 to 100 K. The inset shows enlarged partial hysteresis curves.

In addition, the *M* versus *H* curve for *T* > 50 K does not show any hysteresis, as expected. In turn, the impure sample exhibits hysteretic behavior, even at room temperature, as has already been observed.[6]

In conclusion, attention should be paid to the synthesis and characterization of iron-containing LDHs because of the possibility of having magnetic impurities that can induce wrong claims such as room temperature magnetism in LDHs. To date, there are no examples of spontaneous magnetization in LDHs exceeding ca. 20 K. Having said that, it is worth mentioning that the presence of ferromagnetic or superparamagnetic spinel nanoparticles in these kinds of layered materials could be of interest in the preparation of new hybrids combining the intrinsic properties of LDHs with the room temperature magnetic properties of metal oxide nanoparticles. This possibility opens the door for the use of LDHs as building blocks of new multifunctional materials, taking advantage of the flexibility and chemical versatility of these hosts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental information and additional PXRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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