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Characterization of the metastable magnetic phase of $Li_xNi_{1-x}O$ using non-linear susceptibility

A Bajpai and A Banerjee

Inter-University Consortium for DAE facilities, University Campus, Khandwa Road, Indore 452017, India

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Abstract

Metastable magnetism is observed in two important compounds (those with $x = 0.35$ and $x = 0.5$) of the $Li_xNi_{1-x}O$ series, with similar experimental features found in bulk susceptibility measurements. For each of these two compositions, a frequency dependence in the first-order alternating-current (ac) susceptibility (χ_1), a negative peak in the third-order ac susceptibility (χ_3), and a field-cooled/zero-field-cooled bifurcation in the direct-current magnetization were seen. We have used χ_3 to discern the nature of the metastability for these samples. We find that for $x = 0.35$, χ_3 becomes critical as a function of field (h), frequency (f), and temperature (T), confirming the existence of a spin-glass-like phase. However, χ_3 for $x = 0.5$ does not become critical as a function of h and f, and shows a $-T^{-3}$-dependence as predicted by Wohlfarth's model of superparamagnetism. Thus $Li_xNi_{1-x}O$ shows magnetic phases of different types in two important composition ranges which are identified using χ_3. The results also indicate the importance of non-linear susceptibility for distinguishing the two metastable phases by means of bulk susceptibility measurements.

1. Introduction

Substitution of Li at the Ni site of NiO has produced interesting magnetic properties and their exact nature has remained intriguing for a long time [1–8]. Since a reasonable understanding of the complexity of the structure of Li–Ni–O has developed in the last decade [3–7], it is important that the natures of the magnetic phases are identified as unambiguously as possible. Subsequently, one could look for the microscopic origin of the respective magnetic phases. In this series, two compositions are of particular importance, namely, those with $x = 0.3$ and $x = 0.5$. It has been shown for this series of compounds that Li replaces Ni randomly in the composition range $x < 0.3$ while retaining the cubic rock-salt lattice of NiO, represented by the formula unit $Li_xNi_{1-x}O$. However, for $x \geqslant 0.3$, a rhombohedral distortion together with cationic ordering takes place, leading to the doubling of the unit cell as Li and Ni order in individual cationic planes perpendicular to the $\langle 111 \rangle$ direction of cubic NiO [2]. This is conveniently represented by the formula unit $Li_{2x}Ni_{2-2x}O_2$. This rhombohedral distortion and

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the cationic ordering are also marked by the occurrence of a different magnetic phase, which can be interpreted in a number of ways, as is evident from the literature. It is important to note that the samples with $0.3 \leqslant x < 0.5$ represent the compositions in which rhombohedral distortion, cationic ordering, and magnetic anomaly are observed, in addition to which both interlayer and intralayer Ni–Ni interactions occur for this composition range. On the other hand, the $x = 0.5$ composition shows rhombohedral distortions along with the cationic ordering, and in an ideal case it has pure Ni and Li layers and hence the interlayer Ni–Ni interactions are substantially reduced. Though the $x = 0.5$ composition has been very widely studied because of its technological application in insertion electrodes used in making rechargeable batteries [9], perfect cationic ordering is very difficult to achieve [6, 7].

One crucial point in connection with the interpretation of the magnetic phase is that in general all of the samples with compositions with $0.3 \leqslant x \leqslant 0.5$ show typical signatures of metastable magnetic phases in low-field susceptibility measurements. At this point we emphasize that the typical signatures of metastability, i.e. time and history dependence of bulk susceptibility measurements, have been interpreted as indicating a spin glass [4, 6] or superparamagnetic phase [1, 7, 8], even for the same composition, for this series of compounds on the basis of the history dependence of the dc magnetization, which is not fully conclusive for the reasons given below.

It is worth recalling that frequency dependence of the ac susceptibility, history dependence of the dc magnetization, and time dependence of the remnant magnetization are exhibited by various magnetically disordered systems such as spin glasses, cluster glasses, superparamagnets, and even inhomogeneous ferromagnets, etc [10, 11]. In these systems the bulk magnetization is considered to be in a metastable state and the relaxation times of the magnetic entity fall in the range of the probe times of bulk susceptibility experiments. This manifests itself in qualitatively similar time and history effects, as mentioned above—though they may have completely different physical origins. For instance, the origin of metastability in a spin-glass-like system is the 'frustration effects' leading to freezing of the spin system on a typical timescale. The 'magnetic frustration effect' can arise from either bond or site disorder. The frustration phenomenon is also observed in the long-range triangular antiferromagnetic lattice [10]. On the other hand, superparamagnets consist of small magnetic particles (which are small enough to be single domain) and exhibit the phenomenon of 'blocking' over the experimental timescale. The 'blocking' is a purely dynamic phenomenon arising out of competition between the thermal energy and anisotropy energy of the individual magnetic particles composing the superparamagnetic system [10, 11]. For the above-mentioned reasons, ambiguous conclusions can be derived from conventional bulk susceptibility measurements for all of these metastable systems which exhibit similar experimental features originating from entirely different physics. It is also difficult to differentiate between the magnetic metastable systems using microscopic tools. In such a situation the non-linear susceptibility can be used as a probe to discern the cause of the metastability, guided by theories and experiments [10, 12–15]. Distinguishing between these systems, particularly spin glasses (SG) and superparamagnets (SPM), using non-linear susceptibility is also non-trivial; both SG and SPM phases show a negative peak in the real part of the third-order susceptibility (χ_3) around the transition temperature.

Non-linear susceptibility was introduced as a direct probe of the Edwards–Anderson order parameter fluctuation in spin glasses [10]. Later a Landau-type phenomenological theory for spin glasses was proposed, where the magnetization (m) is expanded as an odd-power series in the magnetic field (h); it finally showed negative divergence of χ_3 at T_g, the glass transition temperature. This is given as $\chi_3 = \tau\varepsilon^{-\gamma_3}$. Here ε is the reduced temperature $(T - T_g)/T_g$ and the experimental values of γ_3 are found to be between 1 and 3 (3 for Heisenberg and 1–2

for Ising spin glasses) [12, 13]. χ_3 for SG also diverges as the frequency (f) and amplitude of the applied field (h) tend to zero in the ac χ measurements. This behaviour has been observed experimentally for many spin glasses [3, 10, 14, 15]. It is interesting to note that the f- and h-dependent peak in χ_1 is non-critical for SG. In contrast, SPM is understood as a progressive blocking of moments on the experimental timescale and does not show criticality either in χ_1 or χ_3 with h, f, or T. The higher-order terms have normal field and temperature dependences [11]. For instance, using Wohlfarth's superparamagnetic blocking model it can be shown that χ_1 above T_B follows the Curie–Weiss law ($\chi_1 = \phi M_S^2 V/3k_BT$). χ_3 follows a $-T^{-3}$-dependence above T_B, and is given by $\chi_3 = -(1/45)(\phi M_S)(M_S V/k_BT)^3$. Here ϕ is the volume fraction occupied by the magnetic particles, T is the temperature, K is the total anisotropy constant, M_S is the saturation magnetization of the particles, k_B is the Boltzmann constant, and V is the volume of the magnetic particles [14, 15].

The main theme of the present work is related to the point that qualitatively similar history and time dependences arising in bulk susceptibility may have entirely different origins. However, many reports on these compounds have inferred the existence of metastable phases merely from a bifurcation of the FC and ZFC magnetization cycles, which is interpreted either as indicating a spin-glass phase or as indicating a superparamagnetic phase. The present work attempts to probe the nature of the magnetic phase of $Li_xNi_{1-x}O$ in two important composition ranges. We have used the non-linear ac χ to unambiguously assign a spin-glass phase for $x = 0.3$ and 0.35 by showing the criticality of χ_3 as a function of h, f, and T. We have also found the associated critical exponents. Further, it is shown that χ_3 for the $x = 0.5$ sample is non-critical as a function of h, f, and T, and shows a $-T^{-3}$-dependence as predicted by Wohlfarth's model of superparamagnetism. The possible origins of these two types of metastability are also discussed. To the best of our knowledge this study is the first of its kind for this series of compounds. More significantly, this study deals with the issue of determining whether the metastable magnetism is arising out of purely dynamic effects (superparamagnetism) or because of a cooperative phenomenon (a spin-glass phase) for any general magnetic system.

2. Sample preparation and characterization

The series was prepared by a solid-state route and characterized by Rietveld profile refinement of x-ray diffraction (XRD) data [3]. The samples crystallize in the rhombohedral ($R\bar{3}m$) symmetry. The structure analysis reveals that for all compounds for which $0.3 \leqslant x \leqslant 0.5$, cationic ordering takes place; however, there is always some disorder as regards cationic sites. The degree of disorder, i.e. the intermixing of Li and Ni sites, in any sample is quantified, as it crystallizes in a rhombohedral structure in which Li and Ni share a common cationic site with formula unit $Li_xNi_{1-x}O$. This is referred to as the random phase. A phase in which cationic ordering has taken place also crystallizes in a rhombohedral structure with the formula unit $Li_{2x}Ni_{2-2x}O_2$, and this has distinct cationic sites for Li and Ni and therefore a double unit cell. This is referred to as the ordered phase. We have prepared certain compositions in different batches under similar preparation conditions and we find that the magnetic and structural properties are reproducible as long as the percentages of ordered and random phases are similar for that particular composition. In the present work, we report susceptibility measurements for: an $x = 0.3$ sample that contained 18% ordered phase; an $x = 0.35$ sample with 36% ordered phase; an $x = 0.5$ sample prepared in two batches with 80% and 70% ordered phase. We also briefly discuss one $x = 0.3^*$ sample which we were able to prepare in such a way that it had rhombohedral distortion but no cationic ordering. The details of the sample preparation and structural analysis are given in references [3] and [18].

3. Alternating-current χ-measurements

The magnetization (m) can be written as a power series in terms of an oscillating magnetic field h:

$$m = m_0 + \chi_1 h + \chi_2 h^2 + \chi_3 h^3 + \cdots \tag{1}$$

where χ_1, χ_3 are defined as the linear and non-linear susceptibilities, respectively, which can be directly measured using a mutual inductance bridge. Since m has inversion symmetry with respect to the sign of h, χ_2 and other even-order terms are zero in the absence of any superimposed dc field.

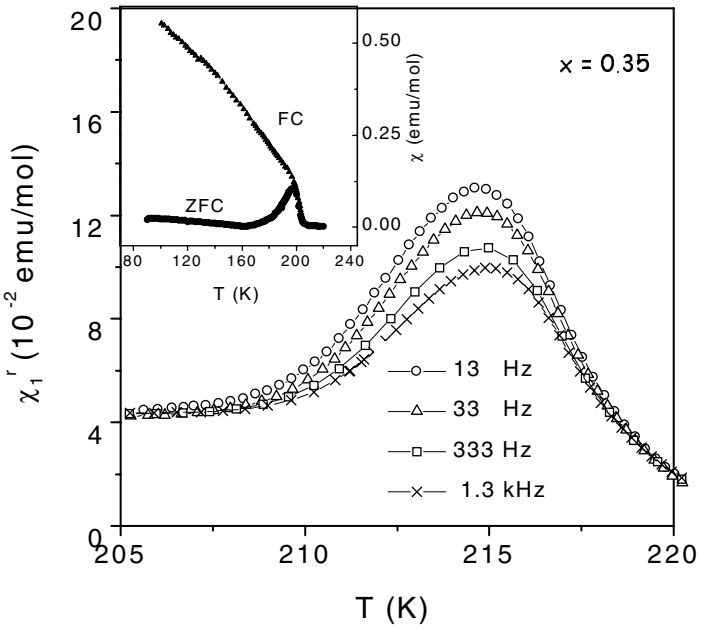
The measurements as functions of h (up to 50 Oe), f (up to 1.5 kHz), and T (77–300 K) were made using a home-made ac susceptometer. With this set-up, the phase-resolved higher-harmonic susceptibility is directly measured [16]. Direct-current magnetization measurements were also carried out using a home-made vibrating-sample magnetometer [17].

4. Results and discussion

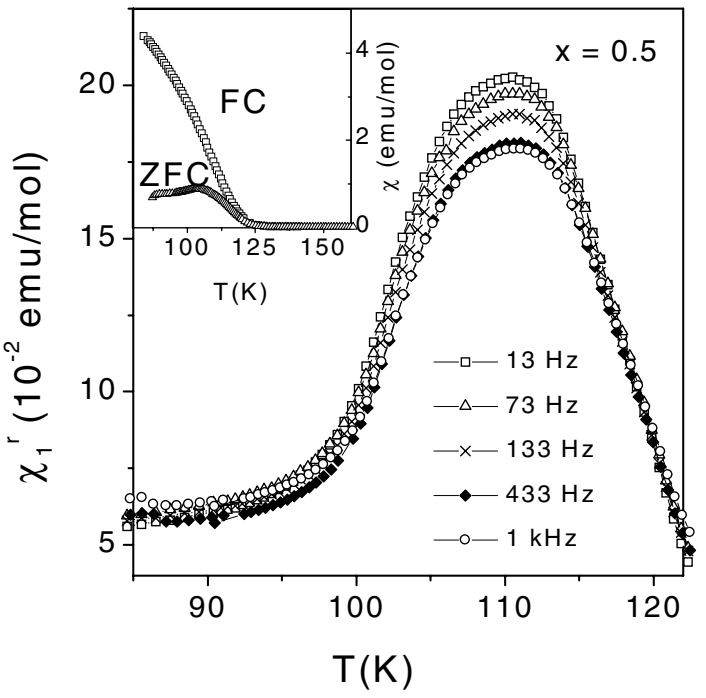
Figures 1(a) and 1(b) show the frequency dependence of the first-order ac χ as a function of temperature for the $x = 0.35$ and $x = 0.5$ samples. The insets of figure 1(a) and figure 1(b) show the history dependence of the dc magnetization for the samples with $x = 0.35$ and $x = 0.5$ respectively. Figures 2(a) and 2(b) show the third-order susceptibility as a function of temperature, showing a negative peak around the transition for the samples with $x = 0.35$ and $x = 0.5$ respectively. The insets of figure 2(a) and figure 2(b) show the same for the samples with $x = 0.3$ and $x = 0.5$—samples having different ratios of ordered and random phases. Thus figures 1 and 2 display qualitatively similar time and history effects as well as qualitatively similar third-order susceptibilities for samples with $x = 0.3$, $x = 0.35$, and $x = 0.5$ (prepared in different batches). However, further experiments on the third-order susceptibility revealed some interesting features using which we could group the samples with $x = 0.3$ and $x = 0.35$ together, whereas the sample with $x = 0.5$ emerged as distinct.

Theoretically, the non-linear susceptibilities of spin glasses are expected to diverge in the limits where $h \to 0$ and $f \to 0$ [12]. We have already shown that the magnitude of the peak value of χ_3 ($|\chi_3|^{max}$) as a function of the oscillating field and frequency diverges in the limits $h \to 0$ and $f \to 0$ for the samples with $x = 0.3$ and $x = 0.35$ [3]. In this report, the divergence in χ_3 in the limits $h \to 0$ and $f \to 0$ is further substantiated by log–log plots of χ_3 against h and f in figures 3(a) and 3(b), respectively. The negative slopes of the straight lines as obtained from the log–log plots are taken as associated critical exponents. The field exponent is -1.1 (± 0.04) and the frequency exponent is -0.36 (± 0.005). In the absence of any experimental value of this exponent, to our knowledge, we are unable to compare it with the values for canonical spin glasses. It is rather difficult to extract these values from the theoretical work where the divergence is predicted in these limits. These result conclusively show the existence of a spin-glass-like phase in our samples with $x = 0.35$.

The temperature variation of χ_3 showed a negative peak at a temperature T_g for the samples with $x = 0.3$ and 0.35 (figure 2(a)). Here T_g is defined as the glass transition temperature. In figure 4 we provide a log–log plot for χ_3 against the reduced temperature $(T - T_g)/T_g$ at 433 Hz and 1.3 kHz. The inset of figure 4 shows the same at 333 Hz. This shows the criticality of χ_3 as a function of temperature. From measurements at various frequencies we find that the exponent associated with the third harmonic remains close to that of the random-bond Ising spin glass ($\gamma_3 = 1.18 \pm 0.04$). This divergent behaviour of χ_3 distinguishes the spin-glass transition from other transitions.

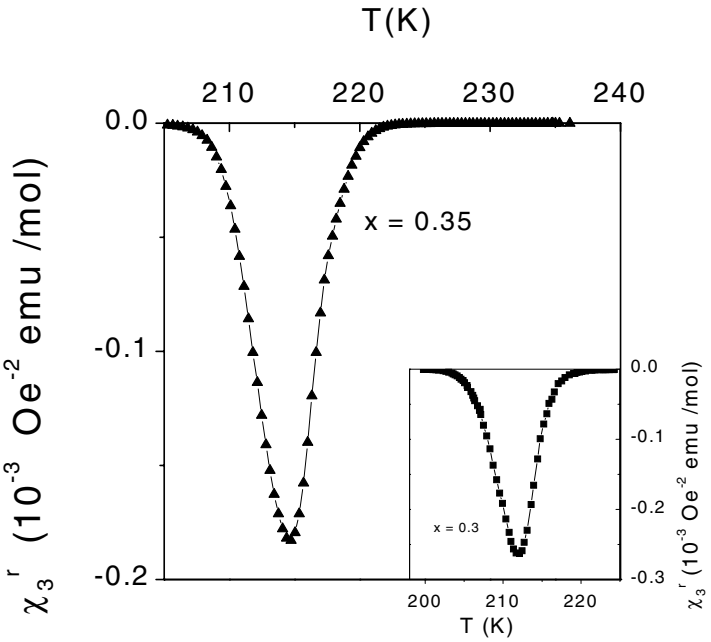


(a)

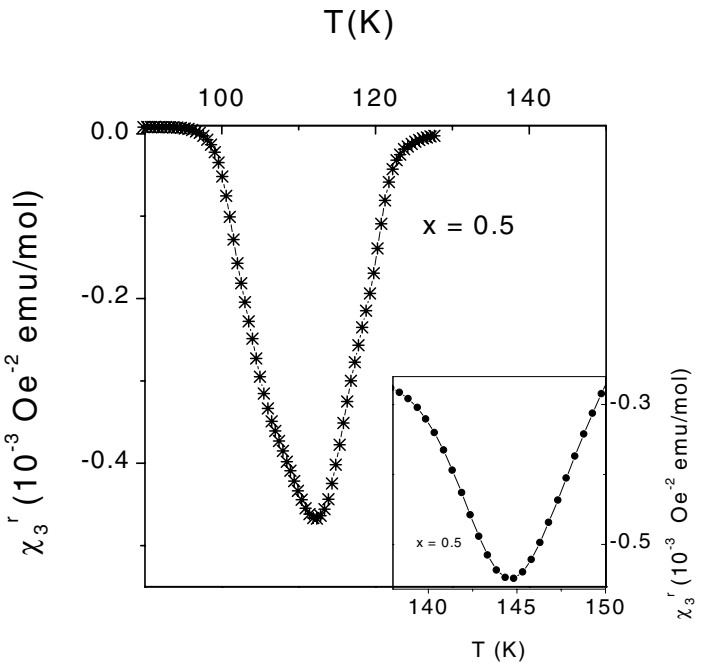


(b)

Figure 1. Typical signatures of metastable magnetic phases for (a) an $x = 0.35$ sample and (b) an $x = 0.5$ sample. The real part of the ac χ (χ_1^r), at various frequencies measured at a constant ac field of 1 Oe, is plotted against temperature. The inset shows the dc susceptibility measured in FC and ZFC cycles. The dc field is 20 Oe for the $x = 3.5$ sample and 12 Oe for the $x = 0.5$ sample.



(a)



(b)

Figure 2. The negative peak in the real part of the third-order susceptibility (χ_3^r) as a function of temperature for (a) a sample with $x = 0.35$ (the inset shows the same for a sample with $x = 0.3$) and (b) a sample with $x = 0.5$ (the inset shows the same for an $x = 0.5$ sample prepared in a different batch having a different ratio of ordered and random phases). Please note that the patterns for χ_3 displayed by these samples are all qualitatively similar.

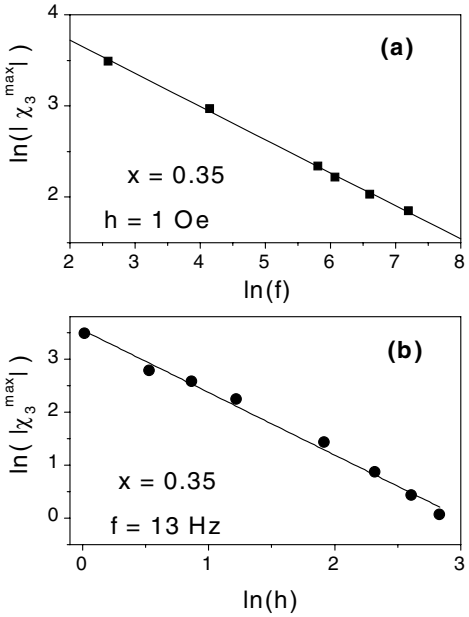


Figure 3. A log–log plot of χ_3^{max} against field and frequency for an $x = 0.35$ sample. (a) $|\chi_3^{max}|$ against frequency at 1 Oe. (b) $|\chi_3^{max}|$ against field at 13 Hz. This shows the divergent nature of χ_3 in the limits $f \to 0$ and $h \to 0$, as expected for a spin-glass-like magnetic phase.

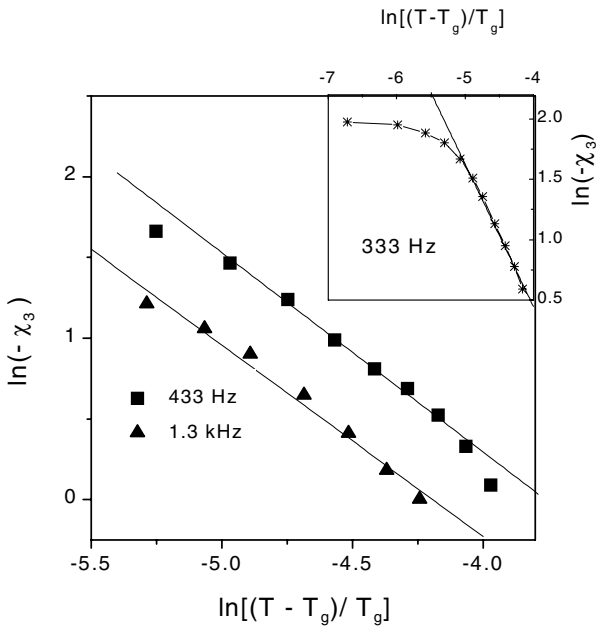


Figure 4. A log–log plot of χ_3 against reduced temperature $\varepsilon = (T - T_g)/T_g$ for an $x = 0.35$ sample at 433 Hz (squares) and 1.3 kHz (triangles). The inset shows the same at 333 Hz.

As is evident from figure 2(b), the sample with $x = 0.5$ showed a similar peak in the third-order susceptibility and therefore it was tempting to conclude that there was a spin-glass phase for this sample as well. However, when the same set of measurements were performed for this sample, we found striking differences. Unlike the previous samples, the $x = 0.5$

sample did not show any divergence in χ_3. Figures 5(a) and 5(b) show that the peak value of χ_3 does not diverge in the limits of $f \to 0$ and $h \to 0$. For the same frequency and field range, the change in χ_3 as $f \to 0$ and $h \to 0$ for the samples with $x = 0.3$ and 0.35 is by a factor of nearly 35, as has already been reported by us in reference [3]. However, under similar conditions the 0.5 sample shows a much smaller change, by about a factor of 2. Moreover, as one approaches the limit $h \to 0$, χ_3 starts decreasing, and in the limit $f \to 0$, χ_3 shows a tendency to saturate. This clearly indicates the basic difference in third-order susceptibility between the sample with $x = 0.5$ and those with $x = 0.3$ and 0.35. χ_3 does not become critical as a function of temperature either. More significantly, figure 6 shows that χ_3 has a $-T^{-3}$-dependence as predicted by Wohlfarth's model for superparamagnetic particles [14]. A detailed proof of existence of superparamagnetism in the $x = 0.5$ sample based on other measurements has been published elsewhere [18].

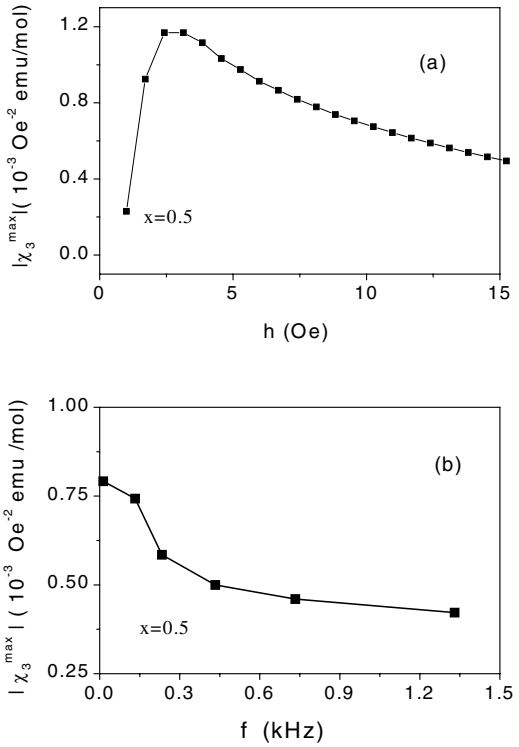


Figure 5. $|\chi_3^{max}|$ for a sample with $x = 0.5$ as a function of (a) h and (b) f. This shows that χ_3 does not diverge in the limits $h \to 0$ and $f \to 0$.

It is also interesting to note that the number of magnetic atoms in the $x = 0.5$ sample is far less than the numbers in the $x = 0.3$ and 0.35 samples, yet the magnetic susceptibility of the $x = 0.5$ sample is larger than those of the $x = 0.3$ and 0.35 samples. This also shows that the nature of the magnetic coupling is drastically different in the sample with $x = 0.5$ as compared to those with $x = 0.3$ or $x = 0.35$. It is interesting to explore the physical mechanisms that may give rise to these apparently similar yet distinct features within the same series of compounds. The magnetic interactions in this series of compounds are basically indirect exchange between two Ni atoms mediated by the oxygen atom. The insertion of Li in place of Ni dilutes these interactions and leads to various magnetic orders as a function of

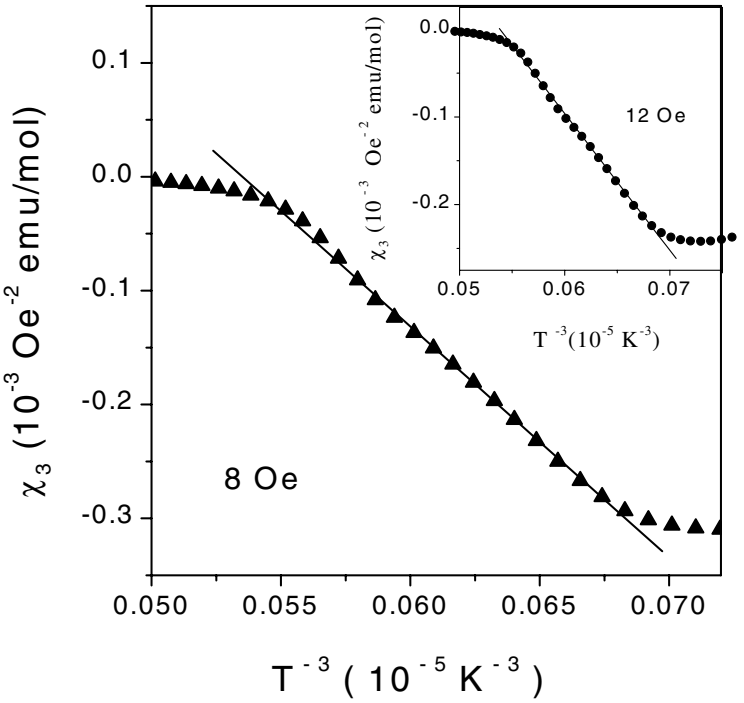


Figure 6. χ_3 shows a T^{-3}-dependence above the blocking temperature for the sample with $x = 0.5$. The inset shows the same for a different measurement field.

composition. At present, we are able to make the following three points regarding the origin of the observed magnetic phases for $x = 0.3$ and 0.35 samples which is different from that for the $x = 0.5$ sample.

(a) It is obvious that for all three compounds both random and ordered phases exist. As shown in reference [3], the $x = 0.3$ composition is the critical composition where the rhombohedral distortion as well as cationic ordering starts taking place. For this composition we were able to prepare a sample (referred to as $x = 0.3^*$) for which rhombohedral distortion appeared but no ordered phase could develop. It showed a broad hump in the first-order ac χ—as opposed to a sharp peak followed by a broad hump as found for another $x = 0.3$ sample in which 18% ordered phase developed. The magnitudes of the broad humps for the $x = 0.3$ and $x = 0.3^*$ samples were nearly the same; therefore, it appears that the broad hump probably originates from the random phase for all of the samples, including the $x = 0.3^*$, $x = 0.3$, $x = 0.35$, $x = 0.5$ ones. Figure 7 shows χ_1' as a function of temperature for the $x = 0.3^*$, $x = 0.3$, and $x = 0.5$ samples.

(b) Now, decoupling the effect of the random phase, it is possible that the sharp peak is related to the ordered phase for $x = 0.3$, 0.35, and 0.5. Again, the samples with $x = 0.3$ and 0.35, and, for that matter, all the samples with $0.3 \leqslant x < 0.5$, can be grouped together in the sense that in the ordered phase the effective arrangement of cations is that where there is a pure Ni layer followed by a Ni + Li layer where the percentage of Li varies depending on the composition. With increasing amount of dopant, the percentage of Ni in the Ni + Li layer reduces, and for the $x = 0.5$ sample there are effectively alternating Li and Ni layers. It is clear that in the $x = 0.3$ and 0.35 samples interlayer Ni–O–Ni

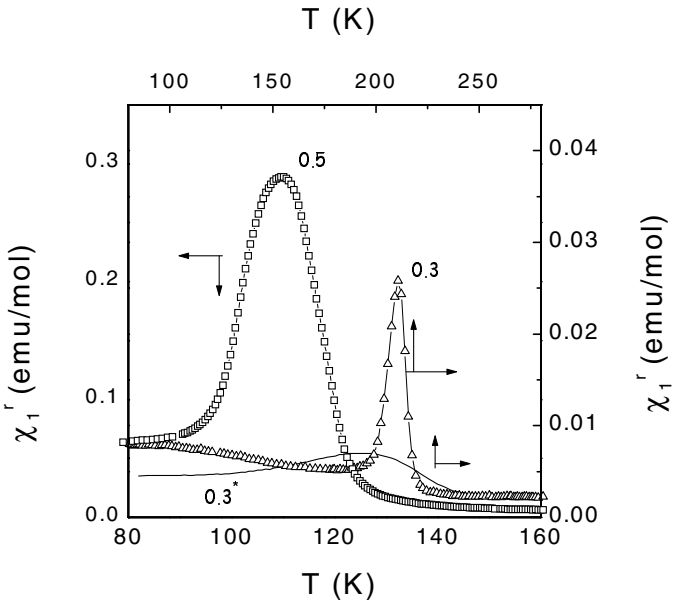


Figure 7. χ_1^r plotted against temperature for samples with $x = 0.3^*$ (line), $x = 0.3$ (triangles), $x = 0.5$ (squares) for a measuring field of 12 Oe at 173 Hz. The axes for the samples with $x = 0.3$ and $x = 0.3^*$ are top and right, whereas the axes for the sample with $x = 0.5$ are bottom and left.

(antiferromagnetic) and intralayer Ni–O–Ni (ferromagnetic) interactions coexist. These interactions are responsible for the observed frustration effects in the samples with $x = 0.3$ and 0.35.

(c) For the $x = 0.5$ sample, interlayer Ni–Ni interactions are reduced due to the insertion of an intervening Li layer. Thus the effective magnetic exchange interactions remain within the Ni planes. This planar interaction together with the small Ni–Ni clusters present in the random phase are likely to give rise to the observed superparamagnetic phase.

5. Conclusions

Samples with $x = 0.35$ and $x = 0.5$ from the $Li_xNi_{1-x}O$ series have shown similar time and history effects in susceptibility measurements. The ac susceptibility showed a frequency- and field-dependent peak and the dc magnetization showed FC/ZFC bifurcation (history dependence). Thus the qualitative features shown for these two important compositions are similar. We also show that the temperature dependences of χ_3 are qualitatively similar for all of these samples. However, χ_3 becomes critical for $x = 0.35$ samples whereas it does not show such criticality for $x = 0.5$ samples. We have determined the associated critical exponents for field, frequency, and temperature for $x = 0.35$. We have shown that the temperature dependence of χ_3 for $x = 0.5$ samples fits well within the framework of superparamagnetism. Thus the third-order susceptibility can be used to distinguish between the metastable magnetic phases in these samples. The microscopic reasons for the presence of a SG phase for $x = 0.35$ samples and a SPM phase for $x = 0.5$ samples are discussed briefly.

Acknowledgments

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