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Superparamagnetism in polycrystalline $Li_{0.5}Ni_{0.5}O$ samples: Low-field susceptibility measurements

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A frequency-dependent sharp peak in ac susceptibility (χ_{ac}) was found in $Li_{0.5}Ni_{0.5}O$ around 110 K having an unusual magnetic-field (H) dependence. Temperature variation of first- and third-order χ_{ac} have shown good agreement with Wohlfarth's model (WM) for superparamagnetism (SP) but with an unusually low value of anisotropy constant to saturation magnetization ratio ($2K/M_S$). A simple model is proposed using Néel's relaxation approach to explain the unusual field dependence of χ_{ac}. The data fit well to this model and gives a similar $2K/M_S$ value found from WM. This model can be used to quantitatively explain the field and temperature dependence as well as to extract various important physical parameters of other SP systems from a simple experiment. Existence of dipolar interactions among the superparamagnetic particles is concluded from history and time dependence of dc magnetization measurements. The correlation of ac and dc susceptibility also brings out some interesting features.

I. INTRODUCTION

NiO is still considered to be the prime example to define the problem of ''band concept'' in presence of large electron-electron correlations in transition-metal oxides.[1] In fact, despite a few decades of intense experimental and theoretical investigations, it is still debated whether NiO is a Mott Hubbard or a charge-transfer-type insulator.[2] The substitution of Li in an Ni site was initially done to tailor the band gap so as to modify the conductivity properties as well as to explore the much sought after problem concerning the nature of the band gap.[3,4] However, this substitution not only added many dimensions to the basic problem of NiO with some exotic experimental results and their interpretations,[3–14] but also provided a material of technological importance.[5]

In short, the problem in the entire series of compound $Li_xNi_{1-x}O$ is threefold. (i) First is its structural aspect, in relation to the cationic arrangements in the sample which, in turn, is a crucial function of sample preparation conditions.[3,6–10] (ii) The second and probably the most interesting problem is that of the magnetic phase. The antiferromagnetic character of the parent compound NiO is understood to be driven through the indirect superexchange interactions. The dilution of the magnetic entity (i.e., Ni) through Li substitution invokes a variety of magnetic phases that remain controversial despite a few decades of research.[3–14] For instance, this was also considered to be one of the rare compounds in which $S=\frac{1}{2}$ two-dimensional triangular antiferromagnetic lattice leading to quantum liquid ground state could be realized.[11] (iii) The third problem inherited from NiO is with the nature and the location of the hole that is introduced, when monovalent Li replaces divalent Ni. Ideally, the Li substitution on an Ni site is believed to create a hole in Ni $3d$ level and almost all magnetic and transport measurements either confirm it or their interpretation is based on this conjecture. On the contrary spectroscopy results predict that holes are of primarily oxygen $2p$ character.[4] There is also some indication that these holes carry magnetic moment.[15]

The composition $x=0.5$ of $Li_xNi_{1-x}O$ series crystallizes in a layer-type structure and is suitable for use as an insertion electrode in low cost, high-energy density rechargeable batteries.[5] For this reason the $x=0.5$ composition in the above-mentioned series is most widely studied. Different groups have attributed diverse magnetic properties such as ferrimagnetism,[3,6] enhanced antiferromagnetism,[4] two-dimensional (2D) Ising ferromagnet,[11] 2D Heisenberg ferromagnet,[12] spin glass (SG),[8] and orbital frustration effects,[9] from the measurements of dc magnetization, electron paramagnetic resonance (EPR) and photoelectron spectroscopy, etc. The $x=0.5$ composition crystallizes in rhombohedral structure in which Ni and Li order into individual layers normal to one of the four $\langle 111\rangle$ directions in the cubic NiO lattice. However, it is found that this ordering is never perfect and that some Ni ions occupy Li sites. The clear understanding about the nature of cationic ordering has emerged in the 1990s when serious efforts were made to analyze x-ray diffraction (XRD) and the neutron-diffraction data by Rietveld profile refinement analysis.[6–10,13] This is an important point which correlates the above-mentioned problems (i) and (ii) and is the root cause for the unresolved problems of the magnetic phases in the entire series of compounds. This was highlighted in our previous study where we reported the structural properties of the $Li_xNi_{1-x}O$ series from $0.1\leqslant x\leqslant 0.5$ and showed the role of underlying cationic arrangement in the magnetic properties of $x=0.3$ and 0.35 compositions.[10]

Our aim was to probe the magnetic phase of $x=0.5$ sample from bulk susceptibility measurements and we concentrated on a few aspects which we feel are important but lacking in literature. First, there are plenty of reports in literature on dc magnetization studies which essentially show a time- and history-dependent magnetization[7–9] which is often attributed to the spin-glass phase. However, it is widely accepted now that a mere bifurcation in field-cooled/zero-field-cooled (FC/ZFC) magnetization is not enough proof and a more careful susceptibility analysis is needed before metastability is attributed to any cause. For such cases, ac χ and its harmonic study is often the best and easiest way to probe

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metastability[16] and this coupled with dc magnetization is likely to give a complete picture as we show in the present study. The second motive was to identify the magnetic phase of $Li_{0.5}Ni_{0.5}O$, that results from even a slight variation of the preparation conditions. Instead of making various samples in order to achieve perfect layering of Li and Ni in individual planes (i.e., no interlayer mixing of cations), we concentrated on the relationship between the nature of cationic ordering and the corresponding magnetic phase. To the best of our knowledge, the sample with perfect ordering of Li and Ni planes is so far not prepared, although samples close to this have been reported.[7,8,13]

A frequency and field-dependent sharp peak is observed in χ_{ac} around 110 K indicating metastable magnetism in the sample with $x=0.5$. The bifurcation in field-cooled (FC) and zero-field-cooled (ZFC) magnetization as well as time dependence of magnetization in low dc fields further indicate metastability. These experimental features are typically found in spin-glass (SG), cluster glass or superparamagnets (SP) and even in inhomogeneous ferromagnets, etc. However, we observed some unusual features. For instance, the real part of χ_{ac} increases with increasing ac field upto some critical field, beyond which it falls with the applied field, but the dc susceptibility (χ_{dc}) shows a monotonic decrease with the applied field in the same field range. Thus the field dependence of ac and dc susceptibilities is opposite in nature. The field dependence of χ_{ac} is unlike other conventional long-range-order (LRO) systems as well. For instance in ferromagnetic samples it has been shown using the static scaling law, that magnitude of χ decreases as the field is increased.[16] For weak ferromagnets that have shown signatures of metastability arising from domain-wall dynamics, the χ falls with increasing field.[17] A similar behavior, i.e., χ_{ac} decreasing with increasing ac field is also observed in SG-like systems.[18] Even for conventional SP as well as SG systems that are analyzed following the SP theories, the increasing trend with the increase in field is not observed,[19,20] although, studies on uniaxial ferromagnets and recording media have shown a peak in the reversible transverse ac χ (RTS) as a function of superimposed, high dc field which is applied perpendicular to the constant ac field.[21] The above-mentioned anomalous field dependence is not observed in χ_{ac} even in these recording media as a function of ac field only.[21] Apart from the anomalous field dependence of ac susceptibility there were also some other interesting features such as the χ_{ac} in zero-frequency limit does not extrapolate to χ_{dc}. At the same field the ZFC χ_{dc} is nearly three times larger than its low-frequency ac counterpart, which has not been observed previously. The system does not exhibit any decay in thermoremanent magnetization (TRM) at fields of the order of 300 Oe but in relatively low fields of a few Oe, a decay in magnetization is observed with a slow dynamics. The FC χ_{dc} shows a monotonic increase with decreasing temperature below the peak temperature of ZFC χ_{dc}. These effects in FC χ_{dc} were also observed by some of the earlier works.[7–9] We attribute this feature to a different effect with a justification.

Thus we present a rich variety of experimental data which needs to be interpreted addressing the following important points: (i) the identification of nature of metastability and (ii) the explanation of the unusual features. We have briefly discussed the first problem in a recent paper where we have ruled out the possibility of SG and LRO in this sample.[22] In this paper we first present a detailed proof of the SP phase using the Wohlfarth's model. Then we propose a model which is based on Néel's relaxation approach for a system of SP particles, to explain the unusual χ_{ac} behavior. We have used this model to extract various important physical parameters of the system and authenticated them using other measurements. This model can be applied to conventional SP systems such as ferrofluids, recording media, and various other small magnetic particle systems which are of immense academic and technological interest. One can obtain important physical parameters for different types of superparamagnetic systems from a very simple experiment and this model. In a preliminary study we have shown the possibility to calculate both ac and dc susceptibility using the above-mentioned model and its general applicability to one system.[23]

This paper is organized as follows: The experimental details concerning sample preparation and susceptibility measurements are given in Sec. II. The experimental results of ac χ, its harmonics, and the interpretation using relevant models are discussed in Secs. III A and III B. Some of the dc magnetization results together with their correlation with ac susceptibility are discussed in Sec. III C.

II. EXPERIMENTAL DETAILS

A. Sample preparation and characterization

Samples are prepared by solid-state route and characterized by Rietveld refinement of powder XRD data. The details of the sample preparation and refinement procedure along with the XRD pattern are given in Ref. 10. As mentioned earlier, the nature of cationic ordering in this series of compounds plays a vital role, therefore we would like to restate a few important points in this connection.

The sample with $x=0.5$ crystallizes in rhombohedral structure ($R\bar{3}m$) with cationic arrangement in which Li and Ni order in individual planes perpendicular to the $\langle 111\rangle$ of the cubic rock-salt structure of the parent NiO compound.[3,6–10] This is evident from the appearance of the superlattice peaks in the XRD pattern. However, this ordering is never perfect and some of the Ni ions occupy Li sites.[7,8,10] In other words, there is a disorder in terms of cationic sites. The Rietveld refinement of XRD provides a way to model this disorder. There are two approaches to model this disorder using the Rietveld profile refinement.[6,8] Our approach is similar to that adopted by Azzoni *et al.*[6] in which two phases are assumed which are crystallographically similar (rhombohedral) but possess different cationic arrangement.[10] This apparently results in the following two phases. (i) Random phase: In this phase, both Li and Ni share the same cationic site (0,0,0) and the anionic (oxygen) site is $(0,0,\frac{1}{2})$. This will be referred to as the random phase (as Li replaces Ni randomly). This corresponds to formula unit $Li_xNi_{1-x}O$, Fig. 1(a). (ii) Ordered phase: Here the first cationic site is (0,0,0) for Ni, second cationic site $(0,0,\frac{1}{2})$ for Li or Ni and anionic site $(0,0,z)$ with $z=\frac{1}{4}$. This will be referred to as the ordered phase, usually quoted as $LiNiO_2$ with doubled *c* axis. This corresponds to the formula unit

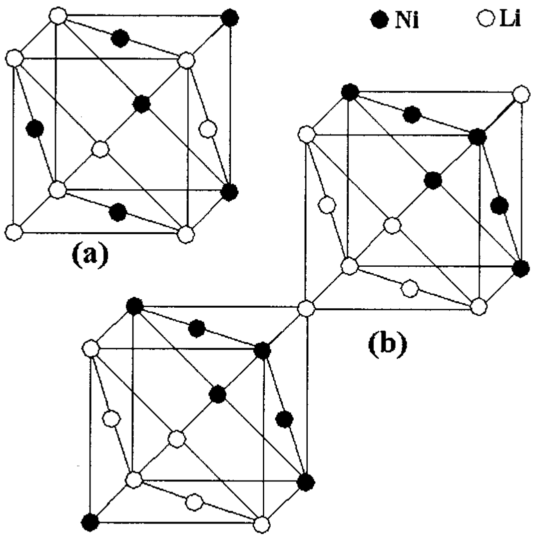

FIG. 1. Schematic representation of the cation distribution in Li-Ni-O unit cell. (a) Random phase in which both the atoms (i.e., Li and Ni) share a unique cationic site. (b) Ordered phase in which Li and Ni are distributed in alternate layers perpendicular to one of the cubic ⟨111⟩ direction of NiO.

$Li_{2x}Ni_{2-2x}O_2$. This phase is in accordance with the perfect ordering of Li and Ni in alternate set of planes as is described in the literature, Fig. 1(b).

We prepared two batches of $x=0.5$ sample, referred to as sample A and sample B, respectively, and characterized them through Rietveld x-ray pattern analysis. Sample A contains nearly 80% ordered and 20% random phase and sample B has 70% of ordered phase and 30% of random phase as estimated from the Rietveld profile refinement.[10] Here we emphasize that these two phases (i.e., the random and the ordered phase) are not two distinct crystallographic phases but differ only in terms of the cationic arrangement. In this paper we report the quantitative study made on sample A. We also give some representative results on sample B to show the similar qualitative features.

B. Susceptibility measurements

The magnetization (M) can be written as a power series with respect to an oscillating magnetic field H as

$$M=M_0+\chi_1 H+\chi_2 H^2+\chi_3 H^3+\ldots,$$

where χ_1,χ_3 are defined as the first- and third-order susceptibilities, respectively, which can directly be measured using a mutual inductance bridge. The phase resolved linear and nonlinear susceptibility are measured as a function of field (H), frequency (f), and temperature (T) using a home made setup.[24] dc magnetization measurements were made using a indigenously developed vibrating sample magnetometer.[25] Both ac and dc measurements were done on the same pellet of typical dimension 10×3×2 mm^3. Measurements were repeated on the same pieces of samples, prepared in different batches.

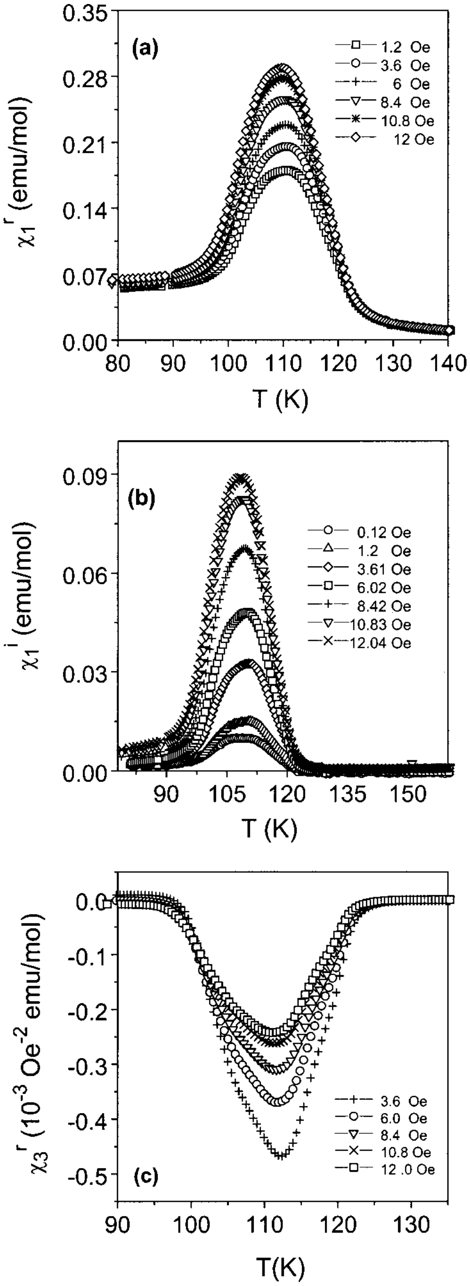

FIG. 2. Temperature dependence of ac susceptibility measured at different fields for $x=0.5$, referred to as sample A, with 80% of ordered phase. (a) Real part of first-order susceptibility (χ_1^r). (b) Imaginary part of first-order susceptibility (χ_1^I). (c) Real part of the third-order susceptibility (χ_3^r).

III. RESULTS AND DISCUSSION

First we list all the important observations from the ac susceptibility and its harmonics measurements for sample A containing 80% of ordered phase and sample B containing 70% of ordered phase.

- A peak is observed in both the real and imaginary parts of ac χ as a function of temperature, at about 110 K having a transition width of about 30 K. A little below the peak, the real part of the susceptibility is nearly independent of temperature. The imaginary part of the susceptibility is practically zero in this region. Figures 2(a) and (b) show the

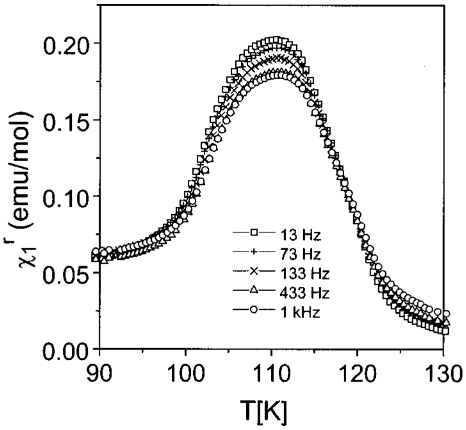

FIG. 3. Temperature dependence of the real part of χ_1 at various frequencies for sample A.

real (χ_1^r) and imaginary (χ_1^i) parts of first-order ac χ as a function of temperature measured at different fields, respectively. Figure 2(c) shows the real part of the third-order susceptibility (χ_3^r) plotted against temperature at different fields.

- The peak shows frequency dependence in the range of a few Hz to 1.5 kHz in both the real and imaginary parts of first-order susceptibility.[22] Beyond 733 Hz, there is hardly any frequency dependence, as shown in Fig. 3.
- The real and imaginary parts of the first-order ac χ increase with increasing ac field upto some critical field. Beyond this critical field, the susceptibility is seen to fall with the applied field. This is shown in Fig. 4 where χ_1^r is plotted as a function of field at various temperatures around the peak.
- Similar qualitative features are found in sample B with 70% of ordered phase. Only the peak is shifted to the higher temperature by a few K. This is compatible with the earlier observations where it is found that decreasing cationic order shifts the peak temperature to the higher side.[8] Figure 5 shows a representative plot showing the temperature dependence at various fields for sample B.

The frequency-dependent susceptibilities (Fig. 3) suggest that this is a metastable magnetic phase. One may be tempted to conclude that the transition is spin-glass-like, as seen for $x=0.3$ and 0.35 samples.[10] In spin glasses the field dependence of susceptibility maximum is given by Edwards Anderson order parameter ($q \propto H^{2/\delta}$ with $\delta \approx 4$).[18] This turns out to be unphysical for our sample. We have checked the $x=0.5$ sample for the same and found that no dramatic divergence is observed in the higher harmonics. The possible existence of LRO and frustration is ruled out from the temperature and field dependence of χ_1, χ_2, and χ_3.[22] In Ref. 22 we have shown that the nature of third-order susceptibility is a very good probe to distinguish spin-glass and superparamagnetic samples. Here we show the existence of superparamagnetic phase from the temperature dependence of χ_1 and χ_3.

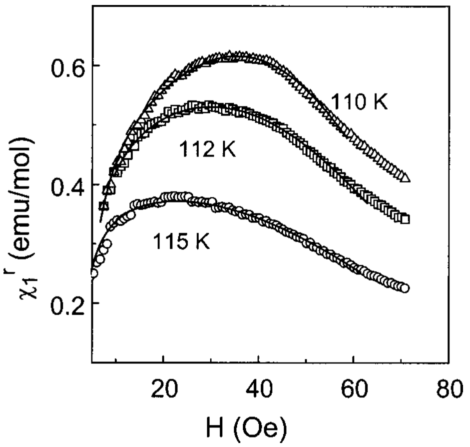

FIG. 4. ac field dependence of χ_1 at different temperatures for sample A. The solid lines are fit of Eq. (4) to the experimental data.

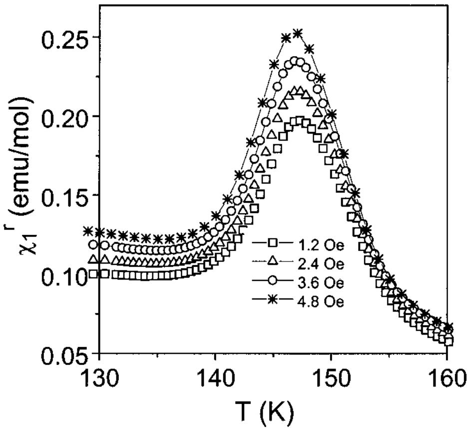

FIG. 5. The $x=0.5$ sample with 70% ordered phase referred to as sample B, showed the similar qualitative features as of sample A. This figure shows the typical field dependence of the real part of first-order ac susceptibility.

A. Temperature variation of ac χ

The overall experimental signatures suggest a superparamagnetic phase which is also a very probable magnetic state for this particular sample from crystallographic considerations. Hence we fit the temperature variation of first- and third-order susceptibility to Wohlfarth's model of superparamagnetism.

According to Wohlfarth's superparamagnetic blocking model,[26,27] the first order of susceptibility (χ_1^{SP}) above blocking temperature (T_B) should follow Curie-Weiss law, whereas it remains independent of temperature (χ_1^{BL}) below T_B. The third order (χ_3^{SP}) follows a negative $1/T^3$ dependence above T_B and again it is independent of temperature in the blocked state (χ_3^{BL}) given by

$$\chi_1^{\mathrm{SP}} = \varepsilon M_S^2 V/3k_B T = P_1/T; \quad \chi_1^{\mathrm{BL}} = \varepsilon M_S^2/3K, \tag{1}$$

$$\chi_3^{\mathrm{SP}} = -(1/45)(\varepsilon M_S)(M_S V/k_B T)^3 = -P_3/T^3;$$

$$\chi_3^{\mathrm{BI}} = \varepsilon M_S^4/60K^3. \tag{2}$$

Here ε is the volume fraction occupied by the magnetic particles, T is temperature, K is total anisotropy constant, M_S is the saturation magnetization of the particles, k_B is Boltzmann

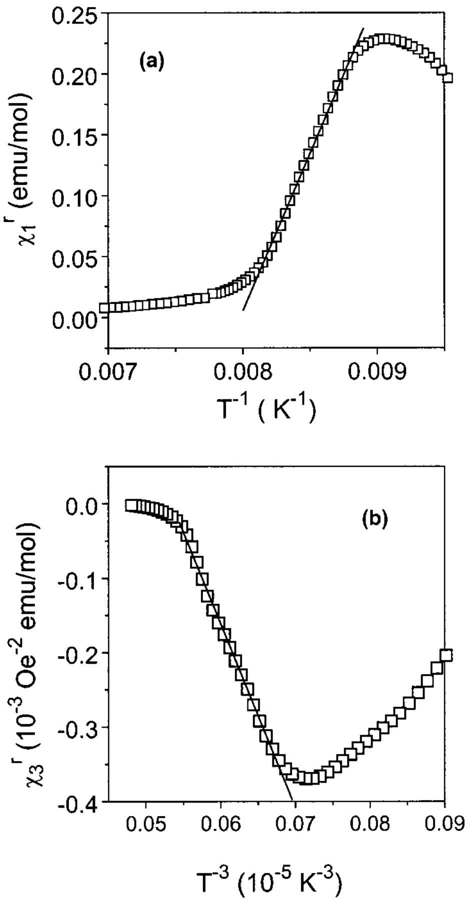

FIG. 6. First- and third-order ac susceptibility are fitted to Wohlfarth's model above the blocking temperature for sample A. (a) The solid line shows T^{-1} fit to χ_1 and (b) T^{-3} fit to χ_3, respectively.

constant, and V is the volume of the magnetic particles. P_1 and P_3 are temperature-independent constants in the first approximation.

Figures 6(a) and (b) show the first- (χ_1) and third-order (χ_3) susceptibilities as a function of T^{-1} and T^{-3}, respectively. The solid lines are fits of Eqs. (1) and (2) to the experimental data. The ratio of parameters P_3 and P_1 derived from fitting directly gives an estimation of $M_S V$. The $M_S V$ comes out to be $\approx 10^{-15}\,\mathrm{G\,cm^3}$ for the measured field range up to 12 Oe. We note that χ_1 and χ_3 practically do not have any temperature and field dependence in the blocked state as shown in Figs. 2(a) and (c) and hence from Eqs. (1) and (2) we calculate the $2K/M_S$ ratio which turns out to be nearly 40. This is a surprisingly low value and is probably responsible for many unusual features exhibited in susceptibility measurements. For conventional[27] SP systems this ratio is of the order of 10^2-10^3.

In the above-mentioned fitting procedure, the range of fit is about 10 K above T_B, beyond which the spin correlation within a particle goes away. Here the blocking temperature and the spin-correlation temperature are quite near. This can be seen from the plot of $1/\chi_{\mathrm{ac}}$ vs T having two distinct slopes, Fig. 7. In other conventional SP systems, the particle's spin-correlation temperature is much higher than T_{B}. For instance, in the superparamagnetic assembly of magnetite, Fe_3O_4, the Curie temperature of bulk magnetite is 850 K whereas the blocking is observed around 20 K.[28] Hence one can measure the superparamagnetic tail above T_B, covering a much larger temperature range.

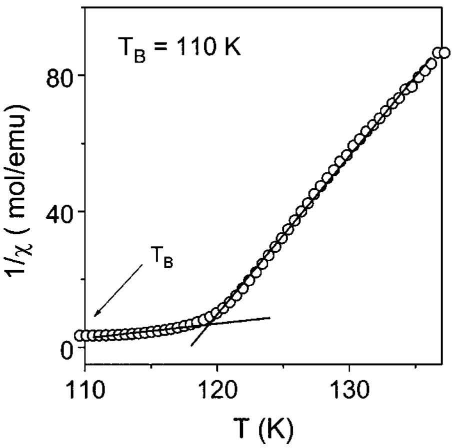

FIG. 7. The inverse of first-order ac χ plotted against temperature showing two distinct slopes corresponding to paramagnetic and superparamagnetic regions.

B. Field variation of ac χ

Having shown the system to be SP-like, we now make an attempt to explain the unusual features, the anomalous field dependence of χ_{ac} as shown in Fig. 4. It is found that χ_{ac} increases with the field up to a certain field beyond which a monotonic fall is observed.

To explain this unusual field dependence we propose a model based on Néel's relaxation approach[29] for an assembly of superparamagnetic particles. Here one considers a system of magnetic particles with a volume V and saturation magnetization M_S which are magnetized in $+Z$ direction. Subsequently, the external field (H) is reversed in the $-Z$ direction. The process of reversing the magnetization requires the rotation of magnetization through the energy maximum ($E_B = M_S^2 H^2 V/4K$). Now the height of the potential barrier relative to the energy maximum is given by $E_\pm = (VM_S^2/4K)[H \mp 2K/M_S]^2$. Here $E_{-(+)}$ is the energy difference between the $-Z$ ($+Z$) state and the energy maximum. Thus the rate of increase in the number of particles magnetized in the field ($-Z$) direction is given by[30,31]

$$dN_-/dt = (1/\tau_o)[N_+ \exp(-\beta E_+) - N_- \exp(-\beta E_-)], \tag{3}$$

where $\beta = 1/k_B T$, $1/\tau_o$ is the attempt frequency from the $\pm Z$ state to $\mp Z$ state, and $N_\pm$ are the numbers of particles in $\pm Z$ state. The above equation basically describes the dynamics of the single domain magnetic particles. We note that dN_-/dt is directly proportional to the rate change of magnetization (dM/dt). For ac field ($H = H_o \sin \omega t$), dM/dt is proportional to χH_o. Therefore the total magnetization is $M = M_o + \chi H_o$ in the field direction, with M_o as the residual magnetization. Hence we can write the measured χ_{ac} (M/H_o) as

$$\chi_{\mathrm{ac}} = (M_o/H_o) + (1/H_o)[C_1 \exp(-\beta E_+) - C_2 \exp(-\beta E_-)], \tag{4}$$

where C_1 and C_2 are constants. We measured χ_{ac} as a function of H_o at different temperatures and fitted it to Eq. (4). The solid lines in Fig. 4 show a very good fit of Eq. (4) to the experimental data of the field-dependent susceptibility. It is noteworthy that there is no adjustable input fitting parameter in the above-mentioned fitting procedure. From the constants of fitting we get $2K/M_S \approx 55$. This ratio remains same for different temperatures around the peak, as shown in Fig. 4. This confirms our conjecture of a low $2K/M_S$ ratio for this system. Significantly, the $2K/M_S$ ratio is similar to that obtained from the temperature variation of χ_{ac} using Wohlfarth's model (WM). The $M_S V$ value derived from this fitting differs from that derived from WM, within 10%. Two independent models using two different measurements (i.e., for χ vs H and χ vs T) yielding the consistent value of physical parameters also imply that there is no artifact in the fitting procedure. The physical origin of residual magnetization M_o in Eq. (4) may be related to the time-independent or almost instantaneous response of some particles within the experimental time window. We found that M_o has a monotonic increase with temperature suggesting that it may originate from smaller particles having much faster time scale than the blocked ones.

For a more general case to calculate both ac and dc χ, Eq. (3) can be integrated over the experimental probe time. In general, the second term in Eq. (3) is sufficiently small compared to the first term. Therefore neglecting the second term we integrate Eq. (3) over the whole cycle and get $N_- = N_o - \exp[-t/\tau]$, since total number of particles is constant $(N_+ + N_-)$. Here, we have defined $\tau = \tau_o \exp(\beta E_+)$ and N_o is a constant. N_- is the total number of particles magnetized in the field direction within the experimental time window, hence it is proportional to the measured magnetization. Therefore we can write

$$\chi_{\mathrm{ac}} = (M_o/H_o) - (1/H_o) C_3 \exp\{C_4 \exp[-(V\beta M_S^2/4K) \times (H_o - 2K/M_S)^2]\}. \tag{5}$$

Here C_3 and C_4 are some constants. Our experimental data fit quite well to Eq. (5) and the fitting is as good as it is shown in Fig. 4. The $2K/M_S$ ratio remains the same whereas other parameters vary within 10% compared to the values obtained through the fitting of data to Eq. (4).

In the above-mentioned fitting procedures, some important approximations involved are as follows. (i) M_S is considered to be independent of T and H. This can be justified from the similar $2K/M_S$ value derived from the fitting of χ vs H at different temperatures, as shown in Fig. 4. (ii) K is defined as total anisotropy constant and it may have contributions from shape and stress anisotropy in addition to the magnetocrystalline anisotropy. In this assembly of superparamagnetic particles the dynamics of the particles K is governed by the total anisotropy constant. Moreover, in the polycrystalline sample, it is not possible to estimate the individual contributions of shape and size anisotropy as the dimensions of the ''magnetic units'' that form the superparamagnetic phase are not known. In fact, in this case the various contribution to anisotropy may have comparable values and this may be one of the physical reasons for the observed low $2K/M_S$ ratio for this system. K is justified to be temperature and field independent. (iii) The volume distribution of the superparamagnetic particles is found to be independent of field. This is checked using WM[26] (not shown).

In a polycrystalline sample it is not possible to estimate K, M_S, and V independently. However, if either of these three parameters is known, the remaining two can be estimated directly from a simple experiment. In our case we could determine the ratio $2K/M_S$ as we did not have any idea about V of the magnetic unit that formed the superparamagnetic assembly. In conventionally grown superparamagnetic systems, the volume of the particle is known and K and M_S are assumed to be the bulk value of the corresponding magnetic material. For small particle systems this assumption may not be valid due to the size effects. Therefore if V is known then other parameters can be directly estimated using this model.

This fitting procedure also indicated that a particular combination of a set of parameters leads to a variety of features observed in susceptibility measurements. For instance, we speculated that the unusually low $2K/M_S$ ratio was responsible for the unusual behavior in the field dependence of ac susceptibility. To further confirm this we analytically calculated ac susceptibility using the above-mentioned model and applied it on a general superparamagentic system with quoted set of physical parameters. For the $\mathrm{Cu}_{97}\mathrm{Co}_3$ superparamagnetic system the quoted values for M_S, K, and V are 1.46 kOe, 5.8×10^5 erg/cm^3 and 5.6×10^{-20} cm^3, respectively.[27] Using these values we calculated ac susceptibility, through numerical simulation, and showed that unlike this LiNiO system, it falls monotonically with the increase in the field as usually observed. However, keeping the rest of the parameters the same when $2K/M_S$ was changed to the value close to our LiNiO sample, the field dependence of susceptibility showed the similar anomalous features observed by us. This is discussed in Ref. 23.

Thus in this section we not only explain the unusual behavior of χ_{ac} but also show the importance of $2K/M_S$ ratio and its determination from a simple experiment using this model. The $2K/M_S$ value determined from other methods, for example, RTS, needs a relatively complicated experimentation. The physical origin of the superparamagnetic phase in this sample ($\mathrm{Li}_{0.5}\mathrm{Ni}_{0.5}\mathrm{O}$) can be understood as follows. In ordered phase, the addition of one Li plane between two Ni planes effectively results in Ni-O-Li-O-Ni arrangement of the ionic planes, Fig. 1(b). It is easy to visualize that the intraplanar Ni-Ni interaction would be significant whereas interplane Ni-Ni interactions will come down drastically. The loss of magnetic connectivity (in terms of indirect exchange) between two planes can finally result in superparamagnetic clusters for a polycrystalline sample which may have a very large volume distribution owing to different shape and orientation of planes. In random phase, 50% of magnetic ions have been replaced randomly by Li so it is difficult to assume a long-range order although the formation of small magnetic clusters is highly probable, Fig. 1(a). This again indicates the presence of superparamagnetic phase in this sample. In this context it is noteworthy that a recent report also indicates the formation of magnetic clusters at around 120 K.[7]

C. dc magnetization studies

In this section we discuss the dc magnetization measurements together with their correlation with ac susceptibility results. Some of the significant results are as follows.

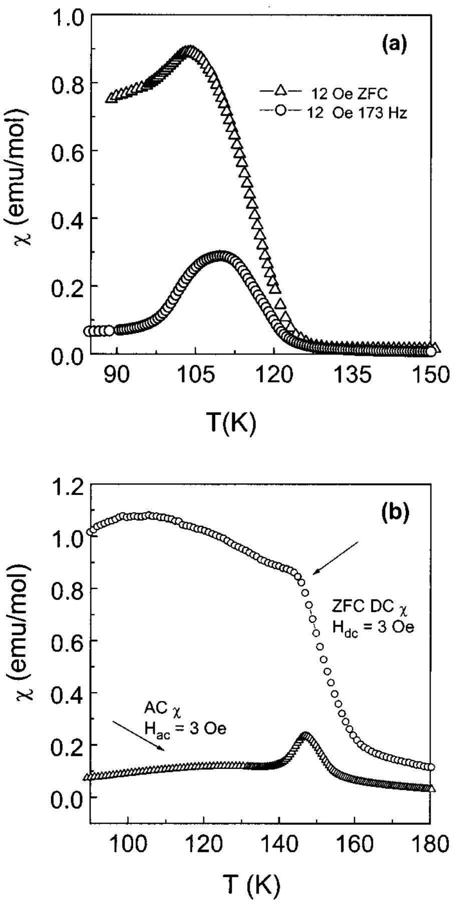

FIG. 8. dc susceptibility is much higher than its ac counterpart at the same field. (a) Sample A with 80% ordered phase measured at 12 Oe, (b) sample B with 70% ordered phase measured at 3 Oe.

- The dc susceptibility does not match with the low-frequency ac susceptibility. Instead, at the same field dc susceptibility is much larger than its ac counterpart, Fig. 8(a).
- The frequency-dependent peak of χ_{ac} in zero-frequency limit does not extrapolate to the observed χ_{dc} value. Blocking is observed at around 103 K in dc susceptibility and at 110 K in ac susceptibility, when measured at 12 Oe. Similar features are also observed for sample B which contains 70% ordered phase, Fig. 8(b).
- Bifurcation of FC and ZFC cycles and a monotonic increase below the blocking temperature is observed in FC cycle, Fig. 9(a).
- The difference between FC and ZFC data decreases with increasing fields and at relatively higher fields (>300 Oe) the ZFC and FC curves merge as shown in Fig. 9(b).
- TRM showed a nonexponential time decay as well as slow dynamics at small (a few Oe) fields. The TRM did not decay with time for the observation time of more than a day, if field cooled in fields of the order of 300 Oe, Fig. 10.

First observation is that the low-frequency ac and dc susceptibilities do not match at the same applied field. The typical probe time (τ_{probe}) of dc measurement is 10–100 sec and the inverse of applied frequency defines the probe time in an ac measurement. We see that over three decades of frequency from 13 Hz to 1.3 kHz, the change is 10% whereas in the three decades of lower frequency (i.e., 13–0.1 Hz) it is about 300%. Therefore the relaxation times of the system (τ_{sys}) seem to have a very broad range from a few milliseconds to a few seconds. Obviously, the particles with the larger relaxation time do not contribute in ac χ experiment therefore dc susceptibility is higher than its ac counterpart. In

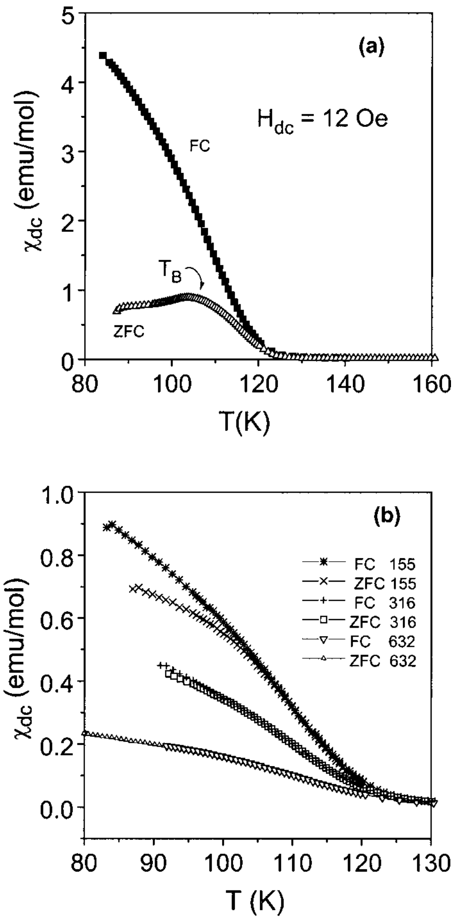

FIG. 9. dc susceptibility shows bifurcation in ZFC and FC cycles for sample A. (a) Bifurcation is large at lower fields. (b) The bifurcation reduces with increasing field and FC and ZFC cycles merge at about 300 Oe.

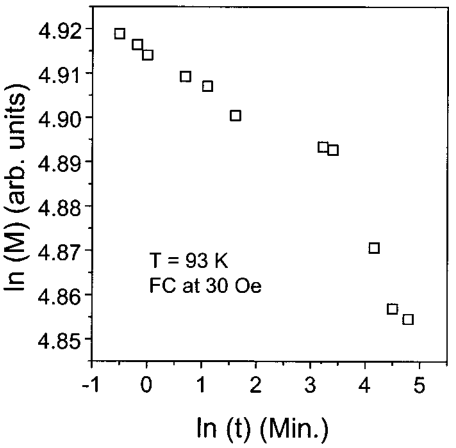

FIG. 10. The log-log plot of thermoremnant magnetization (TRM) as a function of time for sample A.

other words, dc measurements cover the entire range of volume/relaxation time distribution whereas ac measurements cover a small time window in which only small particles contribute resulting in the larger difference in these two measurements. It is not possible to guess the upper limit for the relaxation time but one can roughly estimate the lower limit from the experimental observation that there is no detectable frequency dependence above 500 Hz as shown in Fig. 3.

The fact that the zero-frequency ac susceptibility (as extrapolated from the frequency dependence of ac susceptibility data) does not extrapolate to the dc susceptibility leads to several implications. If the relaxation time distribution is smoothly varying from millisecond to second range then zero-frequency ac susceptibility should have been close to that of the dc measurement. This implies that the volume/relaxation time distribution function is not a smoothly varying one. This also indicates that the function might have two peaks corresponding to two distinct average relaxation times. The large shift in the blocking temperature in ac and dc measurements also support this argument. Here one can note that the shift in the blocking temperature in ac susceptibility over three decades of frequency change is limited to a few 100 mK whereas for the dc measurement it is shifted by 7–8 K. The TRM measurement showed a sudden decrease up to 20% of its initial value (as soon as the field was switched off after field cooling), then a nonexponential time decay was observed, Fig. 10. This result also indicates that the volume distribution function may not be smoothly varying. The physical mechanism that gives rise to this peculiar relaxation time pattern is not very clear but the cationic arrangement in this sample supports very small Ni-Ni clusters[7] originating from random phase and fairly large cluster originating from the ordered phase, as explained in the previous section.

The difference in FC-ZFC cycle keeps on reducing with the increasing field, Figs. 9(a) and (b). This suggests that at high enough fields, M_SHV becomes comparable to KV (and at some fields it may exceed KV) so even in the ZFC state the field is able to move the particle in its direction so the difference between FC and ZFC keeps on reducing. On the contrary, for low applied fields most particles are blocked in a direction that is defined by their anisotropy axis and they are distributed over the angle $0–2\pi$. This amounts to the large bifurcation at lower fields. Such merging of FC and ZFC magnetization is also observed in conventional superparamagnets, but at fields which are order of magnitude higher. This result also shows the importance of low-field susceptibility measurements for this series of compounds since the bifurcation is smeared out at moderately low fields. No decay is observed in TRM at fields of the order of 300 Oe indicating that even such small field can pin the particle crossing the anisotropy barrier and does not allow the magnetization decay. The merging of FC and ZFC cycles at such low fields, along with the fact that there is no TRM above 300 Oe further strengthen our conjecture that the system has a low $2K/M_S$ value.

The FC value does not saturate and a monotonic increase in FC susceptibility is observed with reducing temperature, much below the peak temperature of ZFC cycle. Such behavior in FC data is usually observed in superparamagnetic particles with dipolar interactions among them.[28,32–33] For ZFC measurement where the system is cooled through the transition in the absence of the dc field, the various clusters or particles are blocked in the direction that is defined by the easy axis and the applied field direction. The total dipolar contribution to magnetization therefore could average out to zero. However for FC measurement the particles are oriented towards the magnetic field (or at an angle decided by their anisotropy axis and the applied field) before they are blocked and their magnetic dipolar contribution $(\mu_1 \cdot \mu_2)$ in the direction of the magnetic field becomes large. In this particular system with a small $2K/M_S$ value it is possible that magnetic particles give a significant dipolar contribution even when they are field cooled in small fields. Here the problem is to determine the average particle moment and average distance between the particles so that the effect of such an interaction can be quantified around the transition.[33] This effect is not picked up in ac χ even after application of dc field since the relaxation time for such interacting particles is larger. Also the ac χ response comes from only the smaller particles for which the individual moment may not be large enough to make a significant dipolar contribution. The experimental observation that at relatively higher fields no decay is observed in TRM, along with the nonexponential decay at lower fields is a very strong evidence for the existence of dipolar interactions among the magnetic clusters.[31] These results along with the opposite nature of the field dependence of ac and dc susceptibility will be discussed in a forthcoming publication.

There are a few difficulties that one faces in order to handle SP phase in polycrystalline samples. First we want to mention that canonical superparamagnetic systems are relatively dilute (in terms of the concentration of the magnetic particles) where size and shape of the particles are kept quite identical. Inter particle distance can also be roughly fixed and care is taken that particles are not in intimate contact to avoid the exchange coupling among them. In fact, often magnetic particles are coated with nonmagnetic layer[28] so that the picture of ideally noninteracting SP particles can be achieved. This makes the system relatively clean and easy for analysis. In the case of polycrystalline magnetic sample one does not have much control (and information) about certain parameters. Despite such complications the present work assures the existence of superparamagnetic phase in the sample using bulk susceptibility measurements.

IV. CONCLUSION

The metastable magnetism found in $Li_{0.5}Ni_{0.5}O$ is unambiguously attributed to superparamagnetism from detailed analysis of ac and dc susceptibility measurements performed on two batches of the same composition with different percentage of ordered phase. The temperature variation of first- and third-order ac χ is fitting well to Wohlfarth's model of superparamagnetism. This allows us to determine important physical parameters like $2K/M_S$ ratio and M_SV for the superparamagnetic system. A model based on Néel's relaxation approach is proposed for SP particles to explain the unusual field dependence of χ_{ac}. This model not only explains the unusual field dependence of χ_{ac} but also provides consistent $2K/M_S$ and M_SV values. Significantly, this model has a general applicability for SP systems and has potential to determine the important physical parameters from a simple experiment. A wide distribution of relaxation times is envisaged for this system which was also justified using microscopic considerations. The experimental signatures of dipolar interactions are found in the system which needs to be considered to explain some of the equilibrium and nonequilibrium properties of the SP system.

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