DC and AC Magnetization Study of Complex Ilmenite Oxides (Ni$_{1-x}$Co$_x$)TiO$_3$
$(0.05 \leq x \leq 0.8)$

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Abstract
Ilmenite solid-solutions, (Ni$_{1-x}$Co$_x$)TiO$_3$ $(0.05 \leq x \leq 0.8)$, were synthesized at ambient atmosphere through solid-state reaction and were studied by energy dispersive spectroscopy of X-rays, X-ray diffraction, and DC and AC magnetometry. Temperature dependent DC magnetic measurements revealed two transitions. The first took place at around 27 K and the second at 63 K. The low-temperature phase was antiferromagnetic. The phase observed between 27 and 63 K is characteristic to the solid-solution and is not found in either of the constituent members. A fit of the data to the Curie-Weiss law gave magnetic moment values which were significantly larger than the values based on the quenched orbital momentum assumption. Zero-field-cooled magnetization measurements with weak magnetic field revealed unexpected negative magnetization at low temperatures. Below 63 K the DC magnetization exhibited time dependent behavior. Frequency and magnetic field dependent AC magnetization is also addressed.

1 Introduction
NiTiO$_3$ (NTO) and CoTiO$_3$ (CTO) are both antiferromagnetic below Néel temperatures 23 K[1] and 38 K[2], respectively. They crystallize in ilmenite-type structure with the space group $R3$. Planes formed of double sheets of triangular network of Ni (or Co) and Ti cations are altered along the hexagonal $c$-axis and each cation is coordinated by six oxygen atoms which form a distorted octahedron. The magnetic moments of NTO and CTO order in the same way. Ni$^{2+}$ (Co$^{2+}$) moments, parallel to the planes (the easy axis being perpendicular to the $c$-axis), are ferromagnetically coupled within each plane while the inter-plane coupling is antiferromagnetic[2][3].

When ilmenite oxides form a solid-solution, complex and interesting magnetic properties emerge. An example is (Fe$_y$Co$_{1-y}$)TiO$_3$ (FCT), where the spin

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arrangement of FeTiO$_3$ (FTO) is the same as that of NTO except for the spin direction. FCT is known to be a mixed Ising-XY antiferromagnet. The phase diagram of the concentration ($x$) versus temperature ($T$) given in Ref. 4 shows that there are three magnetically ordered phases with respect to the composition: two antiferromagnetic phases with different spin directions for Co- and Fe-rich areas and a 'mixed ordering', or oblique antiferromagnetic, phase in the vicinity of the Fe$_{0.5}$Co$_{0.5}$TiO$_3$ composition.

The motivation for the present study is to look a solid-solution system closely related to FCT but in which the two constituents have identical magnetic ordering. The study is dedicated on polycrystalline (Ni$_{1-x}$Co$_x$)TiO$_3$ (NCT) solid solutions. Our experiments reveal that, despite identical spin structures of the constituents, magnetic properties of NCT behave in a complicated manner.

2 Material and methods

Polycrystalline stoichiometric (Ni$_{1-x}$Co$_x$)TiO$_3$ ($0.05 \leq x \leq 0.8$) were prepared through the conventional solid-state technique. Samples are referred to as NC$a/b$ indicating $a\%$ of Ni and $b\%$ of Co. NiO (99 %, Aldrich), CoO ($\geq 99.99 \%$, Aldrich) and TiO$_2$ (99 - 100.5 %, Riedel-de Haën) powders were mixed in the desired molar ratio, then pressed into a pellet and sintered in air at 1373 K. Phase quality was inspected by X-ray diffraction using Cu Kα radiation.

Composition analysis were carried out by energy dispersive spectroscopy of X-rays (EDS) employing JEOL JSM-7500FA analytical field-emission scanning electron microscope (SEM).

Magnetization measurements were performed by a superconducting quantum interference device (SQUID) magnetometer (Quantum Design XL7). DC magnetization in zero-field-cooled (ZFC) and field-cooled (FC) runs were carried out over the temperature range down to 5 K under various magnetic fields between 1 and 1000 Oe. Field-dependent magnetization data as a function of applied field were collected at various temperatures. AC magnetization measurements were performed with the heating rate of 0.8 K/min with 1 Oe AC field amplitude. Prior to measurements, sample was carefully centered with respect to pick-up coils and the centering was regularly monitored. Residual magnetic field was estimated using a paramagnetic material prior to and after each measurement so that the real applied field is given.

3 Results and Discussion

3.1 Characterization

Because of the similarity in the crystal structure and chemical character between NTO and CTO, one can expect solid solution with no miscibility gap for whole composition range. In fact, all solid-solutions in the tested composition range were obtained as single phase. Figure 1 shows X-ray diffraction patterns of selected NCT powders. The NCT sample with lowest Co content was light green in color and became dark with increasing Co content. $h0l$ ($l$ is odd) reflections, such as 003 and 101, indicative to the ilmenite phase $R\bar{3}$. Disappearance of these reflections implies a higher symmetry $R\bar{3}c$. For NTO and CTO, however, the $h0l$ peaks are usually rather weak and the degree of ordering could not be
determined from the XRD data alone. The room-temperature X-ray diffraction also show that lattice parameters were increasing with increasing Co-content, suggesting that Co$^{2+}$ and Ni$^{2+}$ were in a high-spin state (their ionic radii are 0.745 Å and 0.690 Å, respectively[7], in contrast, the low-spin ionic radii of Co$^{2+}$ is 0.65 Å[7]). However, as the antiferromagnetic ordering temperatures of CoTiO$_3$ and NiTiO$_3$ demonstrate, the consideration of bond-lengths alone is insufficient for understanding the composition dependent magnetic transition temperatures.

Homogeneity of the compounds were also inspected by SEM-EDS. No spatial composition variation was evidenced. Compositions determined by SEM-EDS, listed in Table 1 show that the starting molar ratio was preserved well.

3.2 Magnetic properties

Overview of DC magnetization results. Figures 2 and 3 show the temperature dependence of DC magnetization [$M(T)$] at various applied fields. Overall the magnetic properties of NCT samples were quite similar: there are two magnetic transitions at around 23 and 67 K. The higher temperature transition is only characteristic to the solid-solutions. Above this temperature, NCTs were paramagnetic: the inverse susceptibility was linearly decreasing with decreasing temperature down to the transition temperature.

In the paramagnetic phase, susceptibility obeys the Curie-Weiss law. Correspondingly, effective magnetic moments $\mu_e$ were estimated from the paramagnetic region data, as shown in Table 1. For comparison, the magnetic moment values were estimated from the equation based on the assumption of quenched orbital moments: $\mu_{e,q} = 2\{(1-x)\sqrt{S_{Ni^{2+}}(S_{Ni^{2+}} + 1)} + x\sqrt{S_{Co^{2+}}(S_{Co^{2+}} + 1)}\}$, where $S_{Ni^{2+}}$ and $S_{Co^{2+}}$ are total electron spin moment values of Ni and Co ions in their high-spin states, respectively. The difference between the magnetic moments estimated from the susceptibility data and the quenched orbital moment values became larger with increasing Co content, suggesting that the orbital moments of Co-ions were not entirely quenched. Interestingly, the magnetic moment values of NiTiO$_3$ [1] and notably of CoTiO$_3$ [2] were larger than the values expected for quenched orbital moments. For comparison, also values based on the Hund’s rules are given in Table 1. Also the Co$^{2+}$ ions in LaMn$_{0.5}$Co$_{0.5}$O$_3$ were found to possess a large orbital moment, which was predicted to result in a nontrivial temperature dependence of the magnetic susceptibility [8].

The low temperature transition was close to the $T_N$ of NTO. With increasing field, the cusp at around 27 K became sharper. The cusp is characteristic signal to a transition to an antiferromagnetic phase. The peak temperature of the cusp is referred to as $T_{AFM}$. Antiferromagnetic order is consistent with the negative values of asymptotic Curie point $\theta_a$/K and the results of field dependent magnetization [$M(H)$], as given in Figs. 4 and 5. Magnetization was almost linearly dependent of the applied field, except for the small hysteresis loop which diminished significantly at 40 K and vanished above the high temperature transition. The opening was largest at around $x = 0.50$ composition, and decreased for small and large values of $x$. With increasing Co content up to 0.8, $T_{AFM}$ almost linearly increased to 32 K. The linear increase of $T_{AFM}$ with increasing $x$ parallels with the linear increase of magnetic moment $\mu_e$, see Table 1. Despite the fact that the solid solution has larger number of magnetic interactions (Ni-Ni, Ni-Co and Co-Co interactions in simplest terms) than the
parent compounds, it seems that the exchange integrals $J$ of different magnetic atom pairs are roughly the same, in contrast to $(\text{Fe}_y\text{Co}_{1-y})\text{TiO}_3$ or other spin glass compounds. For a typical spin glass material, glass transition temperature declines when the composition approaches the intermediate region[6]. This behavior is explained by random distribution of $J$ over magnetic ion pairs.

We estimated the temperature at which the inverse DC susceptibility versus temperature curve starts to depart from the extrapolation of Curie-Weiss relation, the onset of a transition. Hereafter this temperature is referred to as irreversible point $T_{irr}$. $T_{irr}$ exhibited composition dependence: increasing Co content pushed the transition temperature down. The decrease was not linear as a function of Co content but was faster at highest Co content so that $T_{irr}$ decreased to 57 K for NC20/80 sample. $T_{irr}$ was sensitive to an applied field: with increasing applied field $T_{irr}$ was shifted to lower temperature.

**DC and AC magnetization measurements of NC50/50 and NC60/40.**

To look closer to the nature of the transitions, frequency dependence of AC magnetization with various applied fields were measured for NC50/50 and NC60/40. In both cases, real and imaginary AC magnetization showed sharp peaks at the point corresponding to the high temperature transitions, see Figs. 6 and 8. $T_{AFM}$ also corresponds to the low temperature cusp of real part of AC magnetization curves. Next we focus on the result of NC50/50, although the discussion is valid to all NCT solid-solutions.

With increasing field, the difference between ZFC and FC curves [panels (a), (b), and (c) in Fig. 6] became smaller and the higher temperature transition slightly shifted to lower temperature, as was commonly observed in all other NCTs. The higher temperature transition at which both the real and imaginary parts of AC magnetization curves show a peak is labeled as $T_p$. We note that $T_p$ is slightly lower than $T_{irr}$, though they indicate the same magnetic transition. Except for the peak at $T_p$, the imaginary part of magnetization was close to zero. A sharp peak in imaginary part generally indicates that magnetic domain structure with switchable magnetization is formed. On the contrary, clear yet small hysteresis loop was observed only at low temperature: the net magnetization was largest at lowest temperature. Thus, the dissipation peak at $T_p$ and the ferromagnetic hysteresis seem to be unrelated phenomena suggesting the different nature of the two phases. The small hysteresis loop can be explained by canting the antiferromagnetically ordered spins so that there is a small net magnetization. Both DC and AC magnetization results of the low-temperature phase are consistent with the canted antiferromagnetic order. The difference in magnetic ordering was also reflected by the different shape of the magnetization versus applied field: whereas the lowest temperature curve had an s-shape, above $T_{AFM}$ the curve was practically a straight line.

The dissipation peak at $T_p$ suggests a formation of domains which are sufficiently large to show no frequency dependent response. Consistently with the DC magnetization results, the $T_p$, determined through the AC-measurements, was slightly shifted with increasing applied field. This suggests that the origin of the phenomena is on the collective spin ordering on the layers perpendicular to the hexagonal $c$-axis rather than magnetic nanodomains. Specifically the high $T_p$ and the sensitivity to an applied field further implies that the magnetic phase transitions can be related to the in-plane spin order.
The magnetization of the NC50/50 samples in ZFC curve measured with weak field was negative up to $T_p$, see panel (a) in Fig. 6. Negative magnetization was also observed in the NC80/20 and NC60/40. The temperature at which the sign of magnetization changes varied by the heating rate. To verify the time dependence of the magnetization, data were collected keeping the temperature constant at 12 and 40 K for 100 min in ZFC run with weak external field, as shown in Fig. 7(a). Magnetization curve in Fig. 7(a) crosses zero at much lower temperature comparing to Fig. 6(a), still the peak temperatures matched to $T_{AFM}$ and $T_p$. With increasing time, magnetization at 12 and 40 K gradually increased though the change at 40 K was larger than 12 K. Similar time-dependent magnetization can be seen in a spin glass. However, AC magnetization data (the right column of Fig. 6) contradict the characteristic feature of spin glass which displays a clear frequency dependence when a small field is applied: neither real or imaginary part of AC magnetization curves exhibited frequency dependence. The construction of a detailed picture of the magnetic and possible cation ordering requires neutron and synchrotron diffraction studies.

4 Conclusions
In conclusion, solid-solution of NiTiO$_3$ and CoTiO$_3$, (Ni$_{1-x}$Co$_x$)TiO$_3$ (0.05 $\leq$ $x$ $\leq$ 0.80), were successfully prepared through the solid-state reaction at ambient atmosphere. DC and AC magnetization revealed that below the room temperature NCT solid solution has two magnetic transitions: to an antiferromagnetic phase, which took place $T_{AFM}$ = 27 K and another transition which occurred around $T_p$ = 63 K, being significantly higher than $T_{AFM}$. Small net magnetization was observed at the lowest temperatures, which was probably due to the canted spins. Negative magnetization was observed at weak fields for samples with $x$ = 0.2, 0.4 and 0.5. Unlike in most 3$d$ transition metal oxides, the orbital moments of Ni and Co in NCT were not entirely quenched. Though the time dependence of magnetization was observed, there was no evidence for a spin glass transition. In summary, we have shown that peculiar magnetic properties emerge in NCT system.

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Figure 1: Room-temperature XRD patterns collected on NCT powders. Samples are, from bottom to top, NC95/5, NC90/10, NC80/20, NC50/50, NC40/60, and NC20/80. Tick marks indicate reflections from the $R\bar{3}$ phase. Inset shows the $2\theta$ region where the characteristic peaks of the $R\bar{3}$ phase are seen.

Table 1: Compositions, Néel point $T_{\text{AFM}}$/K, irreversible point $T_{\text{irr}}$/K, effective moment $\mu_e$ in Bohr magneton unit $\mu_B$ and asymptotic Curie point $\theta_a$/K estimated from Curie-Weiss law and effective moment $\mu_{e,q}$ in Bohr magneton unit assuming orbital quenching of $(\text{Ni}_{1-x}\text{Co}_x)\text{TiO}_3$ ($0.05 \leq x \leq 0.8$). Also moments $\mu_{e,J} = g_J \sqrt{J(J+1)}$, where $J$ is the total orbital angular momentum and $g_J$ is the Landé g-value (based on Hund’s rules expectations) are given. Compositions indicate cation ratio (oxygen content was not determined).

| Compound | Composition | $T_{\text{AFM}}$ | $T_{\text{irr}}$ | $\mu_e$ | $\theta_a$ | $\mu_{e,q}$ | $\mu_{e,J}$ |
|----------|-------------|------------------|------------------|---------|------------|-------------|-------------|
| NiTiO$_3$ [1] | 23 | 71 | 3.00 | -17 | 2.88 | 5.64 |
| NC95/5 | (Ni$_{0.95}$Co$_{0.05}$)Ti$_{1.00}$O$_3$ | 23 | 71 | 3.00 | -17 | 2.88 | 5.64 |
| NC90/10 | (Ni$_{0.90}$Co$_{0.11}$)Ti$_{0.99}$O$_3$ | 23 | 70 | 3.58 | -19 | 2.97 | 5.69 |
| NC80/20 | (Ni$_{0.77}$Co$_{0.23}$)Ti$_{1.00}$O$_3$ | 24 | 69 | 3.80 | -19 | 3.07 | 5.80 |
| NC70/30 | (Ni$_{0.68}$Co$_{0.33}$)Ti$_{0.99}$O$_3$ | 24 | 71 | 4.32 | -18 | 3.20 | 5.90 |
| NC60/40 | (Ni$_{0.62}$Co$_{0.40}$)Ti$_{0.97}$O$_3$ | 25 | 69 | 4.03 | -16 | 3.30 | 6.01 |
| NC50/50 | (Ni$_{0.53}$Co$_{0.47}$)Ti$_{0.99}$O$_3$ | 26 | 66 | 4.21 | -15 | 3.32 | 6.11 |
| NC40/60 | (Ni$_{0.42}$Co$_{0.58}$)Ti$_{0.99}$O$_3$ | 28 | 66 | 4.73 | -14 | 3.51 | 6.22 |
| NC20/80 | (Ni$_{0.15}$Co$_{0.85}$)Ti$_{0.99}$O$_3$ | 32 | 57 | 5.77 | -11 | 3.67 | 6.42 |
| CoTiO$_3$ [2] | 38 | – | 5.3 | -15 | 3.87 | 6.63 |
Figure 2: Temperature and weak field dependent magnetization. Co concentration increases from top to bottom. Panel pairs at the same row show data from the same sample. Filled and open marks indicate ZFC and FC data, respectively.
Figure 3: Temperature and field-dependent magnetization. Co concentration increases from top to bottom. Panel pairs at the same row show data from the same sample. Filled and open marks indicate ZFC and FC data, respectively.
Figure 4: Field-dependent magnetization at constant temperature of the samples with $x \leq 0.3$. (a) NC95/5, (b) NC90/10, (c) NC80/20, (d) NC70/30.

Figure 5: Field-dependent magnetization at constant temperature of the samples with $0.4 \leq x \leq 0.8$. (e) NC60/40, (f) NC50/50, (g) NC40/60, (h) NC20/80.
Figure 6: Left column shows temperature dependent DC magnetization of the NC50/50 sample. Right column shows field and frequency dependent AC magnetization. For AC imaginary part, phase difference in degrees is given in the second vertical axis. Peak temperatures of AC magnetization curves are indicated by dashed lines. It is worth to note that the data measured with different frequencies overlap, in contrast to spin glass systems.
Figure 7: (a) DC magnetization collected continuously on zero-field-cool cycle with the magnetic field of 3 Oe from the NC50/50 sample. At 12 and 40 K (indicated by arrows), temperature was kept constant for 100 min. (b) Time dependent magnetization at 12 and 40 K.

Figure 8: Temperature dependent DC and AC magnetization of the NC60/40 sample. In panel (a), closer look around zero magnetization is given in inset. AC data (d) was measured using a DC field 1.5 Oe, AC-field amplitude 1 Oe and frequency 10 Hz.