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LETTER TO THE EDITOR

Magnetic Studies of Orthotitanate $Ln_{1-x}Nd_xTiO_3$ (Ln = Ce and Pr; $0 \leq x \leq 1$)

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It was found that solid solutions $Ln_{1-x}Nd_xTiO_3$ (Ln = Ce and Pr) with an orthorhombic perovskite structure exhibited a characteristic suspectibility peak phenomenon in their susceptibility–temperature (χ–T) curves, similar to that for $La_{1-x}Sm_xTiO_3$ reported previously. However, it was observed only in a region in which x was higher ($0.5 \leq x$) than in the latter system ($0 < x < 0.3$). Only in $PrTiO_3$ and $Pr_{0.75}Nd_{0.25}TiO_3$ were remarkably asymmetric magnetization–field (M–H) curves observed at low temperatures. This suggests the existence of metamagnetic or spin-flop type extremely slow relaxation processes in $Pr_{1-x}Nd_xTiO_3$. © 1998 Academic Press

The lanthanide titanates $LnTiO_3$ form an isostructural orthorhombic phase ($GdFeO_3$ type) for Ln = La to Tm and show remarkable variation in physical properties (1–6). The compounds containing early lanthanides (Ln = La, Ce, Pr, and Nd) are known to exhibit so-called canted antiferromagnetism below ~100 K, whereas those containing later lanthanides (Ln = Gd, Tb, Dy, Ho, Er, and Tm) exhibit ferrimagnetism (6).

Of particular interest is what further variations in electronic properties are brought about in these isostructural compounds. In view of our limited knowledge of the properties of mixed lanthanide orthotitanates $LnLn'TiO_3$ (Ln and Ln': lanthanides), the present authors have initiated a systematic study and have found in $La_{1-x}Sm_xTiO_3$ a characteristic peak in susceptibility–temperature (χ–T) curves (7). In this paper we report results for similar systems $Ln_{1-x}Nd_xTiO_3$ (Ln = Ce and Pr), revealing some new magnetic features of mixed lanthanide orthotitanates.

All the samples were prepared by the conventional ceramic method using the starting materials dried CeO_2 (4N), Nd_2O_3 (4N), Pr_2O_3 (3N), and as-cast Ti_2O_3 (3N) and TiO (3N) (Soekawa Chemical). The reaction for Ln = Ce is

$$(1-x)CeO_2 + (x/2)Nd_2O_3 + (1-x)TiO + (x/2)Ti_2O_3 \rightarrow Ce_{1-x}Nd_xTiO_3 \ (x = 0, 0.25, 0.5, 0.75, \text{and } 1.0)$$

and the reaction for Ln = Pr is

$$((1-x)/2)Pr_2O_3 + (x/2)Nd_2O_3 + (1/2)Ti_2O_3 \rightarrow Pr_{1-x}Nd_xTiO_3 \ (x = 0, 0.25, 0.5, 0.667, 0.75, \text{and } 1.0).$$

The firing was done at 1550°C in a vacuum better than 10^{-5} Torr and was repeated two to three times. Some samples were prepared twice in a seperate run and were verified to show reproducibility in their structural and magnetic properties.

Oxygen contents were determined by the TGA (thermogravimetric analysis) method from the weight gain when the samples were heated to 1000°C in air. The actual oxygen content (y) was 3.03–3.04 ± 0.02 for $Ce_{1-x}Nd_xTiO_y$ and 3.02 ± 0.02 for $Pr_{1-x}Nd_xTiO_y$. This result shows the slight oxidation of the Ti ions during the heating process. Hereafter the samples are denoted as $Ln_{1-x}Nd_xTiO_3$ for convenience.

Powder XRD (X-ray diffraction) measurements using Cu$K\alpha$ radiation (Rigaku Geigerflex) revealed the formation of a single orthorhombic perovskite phase ($GdFeO_3$ type) in the whole $0 \leq x \leq 1$ composition region for both $Ce_{1-x}Nd_xTiO_3$ and $Pr_{1-x}Nd_xTiO_3$. Their lattice parameters calculated by least-squares fitting are shown in Fig. 1 as a function of the Nd content (x). For the end compounds $CeTiO_3$ ($x = 0.0$) and $NdTiO_3$ ($x = 1.0$), good agreement was obtained with those previously reported (1, 5). To the authors' knowledge, lattice parameters of $PrTiO_3$ have not been reported. The values obtained here are $a = 5.518$ Å, $b = 5.607$ Å, and $c = 7.799$ Å.

DC magnetization measurements were performed using a SQUID magnetometer (Quantum Design MPMS) with an applied field (H) of 100 G. Details of the magnetization measurements were given in Ref. (7). Figures 2a and 3a show susceptibility–temperature (χ–T) curves for $Ce_{1-x}Nd_xTiO_3$ and $Pr_{1-x}Nd_xTiO_3$, respectively. For most of the samples which showed no susceptibility peak, the ZFC (zero-field

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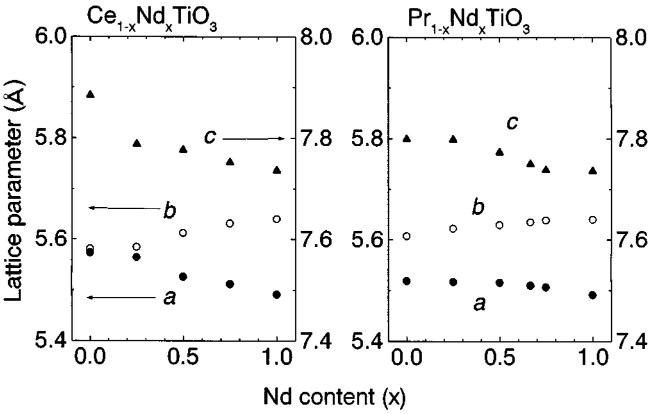

FIG. 1. Unit cell parameters plotted as a function of Nd content (x).

cooled) susceptibilities were larger by $\sim$20% than the FC (field-cooled) susceptibilities. Therefore only the ZFC curves were displayed in the figures.

It is obvious that both systems exhibit a systematic variation in their χ–T curves with the Nd content (x). The χ–T curves of $CeTiO_3$ and $PrTiO_3$ are quite analogous to those previously reported for these compounds with two-step-like magnetic transition around $T_N \sim 120$ K and $T_{N'} \sim 60$ K (1, 3). The transitions at T_N and $T_{N'}$ were assigned as the ordering of the Ti^{3+} and Ln^{3+} (Ln = Ce or Pr) moments, respectively (2, 4). This behavior is different from $LaTiO_3$ containing nonmagnetic $La^{3+}(4f^0)$ ions, which have a single magnetic transition at $T_N \sim 130$ K. Also, the χ–T curve of $NdTiO_3$ is similar to that reported previously with $T_N \sim 90$ K (5). The most striking feature of the figures is that the χ–T curves for $x \sim 0.5$ are remarkably different from those for the end compounds and exhibit susceptibility peaks at $\sim$40 K ($Ce_{0.5}Nd_{0.5}TiO_3$) and $\sim$20 K ($Pr_{0.5}Nd_{0.5}TiO_3$ and $Pr_{0.333}Nd_{0.667}TiO_3$). Figures 2b and 3b show susceptibility data in extended scales for other samples in both ZFC and FC runs. It is seen that the FC curves exhibit more pronounced susceptibility peaks than the ZFC curves. This is just reverse to the behavior of the samples having no peak phenomenon as mentioned above. In $Pr_{1-x}Nd_xTiO_3$, a more significant variation in magnetic properties occurs with the Nd substitution, as is apparent in Fig. 3b. That is, for $x = 0.75$, another upturn of the susceptibilities occurs below $T \sim 20$ K, suggesting the onset of some other magnetic structure.

In $La_{1-x}Sm_xTiO_3$, the susceptibility peak was observed only for $x < 0.3$, where the slight modification of crystal structure from $LaTiO_3$ occurred (7). For the present systems, however, this seems not to be true, and the susceptibility peaks appear in a larger x region, i.e., $0.5 \le x \le 0.75$. This different composition range between $La_{1-x}Sm_xTiO_3$ and the present systems implies that the susceptibility peaks in the present systems have additional different origins, i.e.,

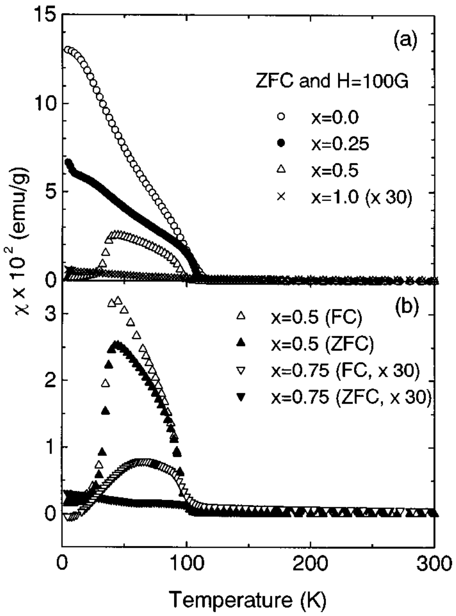

FIG. 2. χ–T curves for $Ce_{1-x}Nd_xTiO_3$ with (a) $x = 0.0, 0.25, 0.5$, and 1.0 and (b) $x = 0.5$ and 0.75. The susceptibilities of $NdTiO_3$ and $Ce_{0.25}Nd_{0.75}TiO_3$ were multiplied by a factor of 30.

commitment of magnetic ions $Ce^{3+}(4f^1)$. $Pr^{3+}(4f^2)$, and $Nd^{3+}(4f^3)$ in addition to Ti^{3+}.

Also, magnetization–field (M–H) curves are measured at several temperatures. One result is presented in Fig. 4a for $Ce_{0.5}Nd_{0.5}TiO_3$, where a susceptibility peak was observed

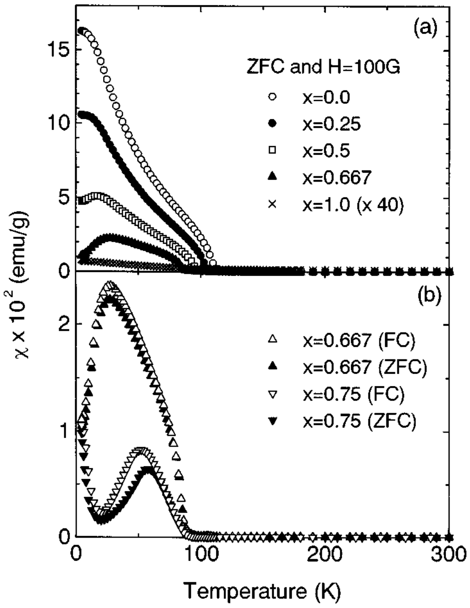

FIG. 3. χ–T curves for $Pr_{1-x}Nd_xTiO_3$ with (a) $x = 0.0, 0.25, 0.5, 0.667$, and 1.0 and (b) $x = 0.667$ and 0.75. The susceptibilities of $NdTiO_3$ were multiplied by a factor of 40.

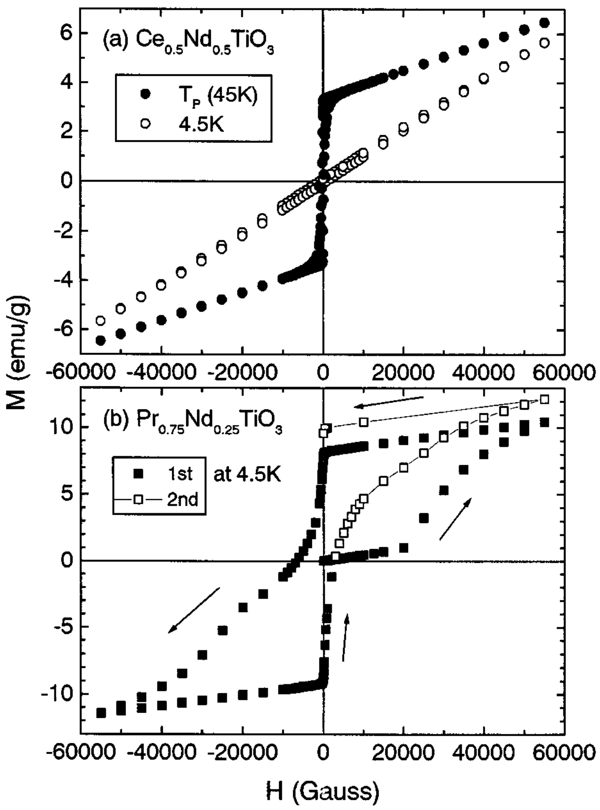

FIG. 4. *M–H* curves of (a) $Ce_{0.5}Nd_{0.5}TiO_3$ and (b) $Pr_{0.75}Nd_{0.25}TiO_3$. T_P means the temperature of the susceptibility peak.

(Fig. 2a). At the susceptibility peak temperature ($T_P \sim$ 45 K), the largest and quite pronounced residual moment was found, compared to that below T_P. This is a similar trend to that for $La_{1-x}Sm_xTiO_3$ and is also true for $Pr_{0.333}Nd_{0.667}TiO_3$, where a single T_P ($\sim$30 K) was obtained (Fig. 3b).

Distinctly different *M–H* curves were obtained at low temperatures for $PrTiO_3$ and $Pr_{0.75}Nd_{0.25}TiO_3$, for which no peak phenomenon was found, and for $La_{1-x}Sm_xTiO_3$ and $Ce_{1-x}Nd_xTiO_3$. This is shown in Fig. 4b for $Pr_{0.75}Nd_{0.25}TiO_3$. The curves were measured in two sequential cycles at 4.5 K. It took 5–6 h to measure one *M–H* curve. The first cycle curve (filled rectangle) shows a transition around $H = 20{,}000$ G, where the magnetization (M) suddenly increases. The profile of the curve is remarkably asymmetric. The second cycle curve (open rectangle) deviates from the first curve. Its profile is comparably symmetric, and the curve itself shifts upward. This result suggests the existence of a metamagnetic or spin-flop transition with an extremely long relaxation time. The spin-flop-like behavior was observed only for $PrTiO_3$ and $Pr_{0.75}Nd_{0.25}TiO_3$ having no peak. In a larger x region where the peak appears, this behavior almost disappeared. The *M–H* curves were somewhat analogous to those of $La_{1-x}Sm_xTiO_3$ and $Ce_{1-x}Nd_xTiO_3$, which showed no such behavior. At present, time dependence measurement of the *M–H* curve has been performed only for $Pr_{0.75}Nd_{0.25}TiO_3$. Thus the correlation between the behavior mentioned above and the susceptibility phenomenon is not clear; however, slow magnetic relaxation implies the formation of a spin-glass state (8). All of these results reveal a wide variety of magnetic properties in these mixed lanthanide orthotitanates, depending on both the individual lanthanide ions and their combinations.

In summary, solid solutions $Ln_{1-x}Nd_xTiO_3$ (Ln = Ce and Pr) are found to exhibit a characteristic susceptibility peak in their χ–T curves, similar to that for $La_{1-x}Sm_xTiO_3$. However, it was observed only in a higher x region ($0.5 \le x$) than in the latter system ($0 < x < 0.3$). Furthermore, for $PrTiO_3$ and $Pr_{0.75}Nd_{0.25}TiO_3$, remarkably asymmetric *M–H* curves were observed at low temperatures, which clearly demonstrates the existence of a metamagnetic or spin-flop type extremely slow relaxation.

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