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# Generic properties of Mn spinels with an immiscibility induced by a Jahn–Teller distortion

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## Abstract

The generic properties are scrutinized in Mn spinels with an immiscibility induced by a Jahn–Teller distortion through the  $\text{CoFe}_{2-x}\text{Mn}_x\text{O}_4$  system. The x-ray diffraction experiment reveals that the immiscibility occurs at  $1.1 < x < 2.0$  and the relevant kinetics becomes faster with  $x$ . The temperature of the Jahn–Teller transition, which accompanies a sharp resistivity anomaly and matches the immiscibility gap boundary, increases with increasing  $x$ . The evolution of the magnetic and structural properties with various thermal treatments is studied carefully in this paper. Based on our comprehensive results, we have constructed a phase diagram of  $\text{CoFe}_{2-x}\text{Mn}_x\text{O}_4$ .

(Some figures in this article are in colour only in the electronic version)

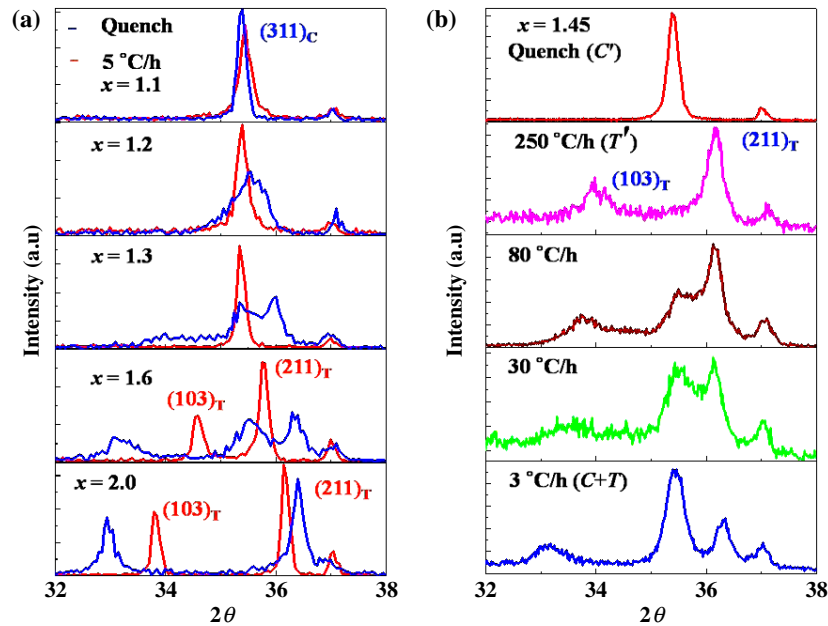
## 1. Introduction

Spinel oxides have attracted interest due to their various physical phenomena such as their multiferroicity [1], geometric frustration [2], and Verwey transition [3]. The chemical formula of spinel oxides can be described by  $\text{AB}_2\text{O}_4$  where the A and B sites form tetrahedral and octahedral cages, respectively. A and B sites can be occupied by alkali, alkali earth and transition metals so that spinels are one of the most abundant materials in the world. Recently, it has been reported that spinel oxides can generate an ordered heterogeneous nano-bar array by minimizing a stress that results from a Jahn–Teller distortion [4–6]. Generally, a Jahn–Teller distortion can lower the electronic energy of systems by lifting the orbital degeneracy of ions and the prominent Jahn–Teller effect occurs in the systems with an octahedral cage in which a Jahn–Teller ion such as  $\text{Mn}^{3+}$  and  $\text{Cu}^{2+}$  resides. (For example, colossal magneto-resistance in perovskite manganite [7], high temperature superconductivity in layered cuprate [8] and etc.) Likewise, a heterogeneous nano-bar array occurs in the spinels which have an octahedral cage.

When the octahedral B sites are occupied by Jahn–Teller ions and non-Jahn–Teller ions, both ions tend to gather the same kind of ions into clusters: an immiscibility takes places.

A theory [9, 10] proposed that the immiscibility separates the high and low Jahn–Teller ion concentration regions spatially. In a proper condition, this immiscibility produces a unique nanostructure where two different nano-bars corresponding to two different concentrations are stacked alternatively in such a way that checkerboard and herring bone patterns are observed in the cross-sectional and side view, respectively [4]. Since it is possible to produce a mixed array of magnetic and nonmagnetic nano-bars whose size is  $\sim 4 \text{ nm} \times 4 \text{ nm} \times 70 \text{ nm}$ , this nanostructure can be applied to a perpendicular magnetic recording media with an ultra-high areal density. Since there are abundant ferrimagnetic spinels at room temperature, various ferrimagnetic spinels have been studied by regulating the cooling rate and annealing time [4–6]. Interestingly, there seems to be a common route to achieve a nanostructure. Furthermore, the magnetic properties changed by the heat treatment also display some generic behavior in the miscibility gap. In this paper, we present the generic properties of Mn spinels with an immiscibility induced by a Jahn–Teller distortion through the  $\text{CoFe}_{2-x}\text{Mn}_x\text{O}_4$  system.

$\text{CoFe}_2\text{O}_4$  [11, 12] and  $\text{CoMn}_2\text{O}_4$  [13] are ferrimagnetic spinels whose transition temperatures are about 800 K and 100 K, respectively. For  $\text{CoMn}_2\text{O}_4$ , the Jahn–Teller ion,  $\text{Mn}^{3+}$ , occupies the B site so that the cooperative Jahn–Teller



**Figure 1.** (a) X-ray diffraction data for  $\text{CoFe}_{2-x}\text{Mn}_x\text{O}_4$ . The magnification of the  $2\theta$  angle from  $32^\circ$  to  $38^\circ$  clearly reveals the miscibility gap of  $\text{CoFe}_{2-x}\text{Mn}_x\text{O}_4$ . For  $1.1 < x < 2.0$ , the quenching displays a clean phase while the slow cooling shows a two phase coexistence. (b) The structural change by the cooling rates for  $x = 1.45$ . The evolution of the structure by the cooling rate follows a common route,  $C' \rightarrow T' \rightarrow C + T$ .

distortion leads to a tetragonal structure ( $I4_1/amd$ ,  $a \sim 8.1 \text{ \AA}$ ,  $c \sim 9.3 \text{ \AA}$ ) at room temperature. In contrast,  $\text{CoFe}_2\text{O}_4$  has a cubic structure ( $Fd3m$ ) whose lattice parameter is  $\sim 8.3 \text{ \AA}$ . Although some Mn doping studies on  $\text{CoFe}_2\text{O}_4$  have confirmed the immiscibility of  $\text{CoFe}_{2-x}\text{Mn}_x\text{O}_4$  [14, 15], they have not scrutinized the origin of the immiscibility nor systematically studied the immiscibility by a Jahn–Teller distortion. As a matter of fact, a systematic study on the immiscibility of spinels is very rare [16]. In this paper, we present an intensity study on the immiscibility by the Jahn–Teller distortion.

## 2. Experiment

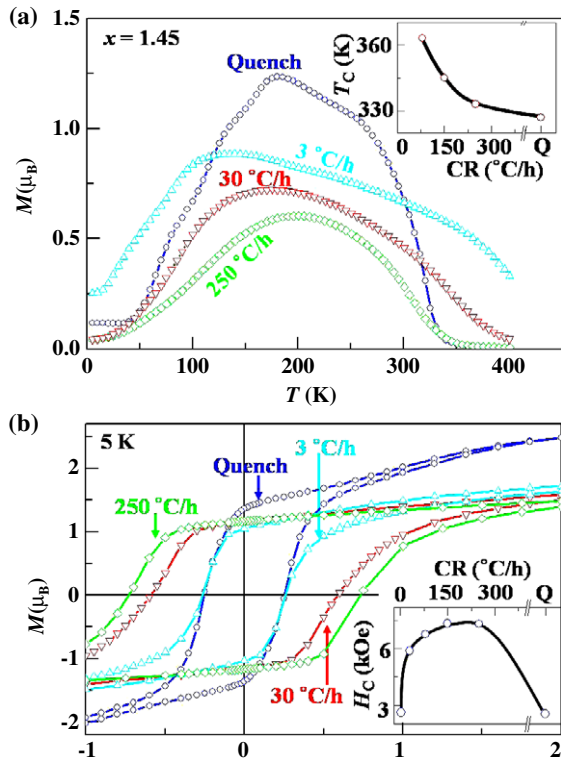
$\text{CoFe}_{2-x}\text{Mn}_x\text{O}_4$  specimens were prepared by the conventional solid state reaction method using high purity starting materials,  $\text{Co}_3\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  powder. Well mixed stoichiometric amounts of the starting materials were fired three times at  $950$ ,  $1050$ , and  $1150^\circ\text{C}$ , respectively. After the final sintering, the specimens were cooled down to room temperature with various cooling rates. Water was used to quench the specimens. We used a Rigaku x-ray diffractometer to examine the crystal structures of the various cooled samples at room temperature. The magnetization data was obtained with a SQUID magnetometer from  $400$  to  $5 \text{ K}$  and the high temperature resistivity data with a standard four-probe technique.

## 3. Result and discussion

The x-ray diffraction data for different concentrations clearly shows the miscibility gap of the system, as shown in figure 1(a). In order to detect a subtle structural change,

we concentrated on the  $2\theta$  angle from  $32^\circ$  to  $38^\circ$  where the highest intensity appears. For  $x = 1.1$ , the quenched and  $5^\circ\text{C h}^{-1}$  cooled specimens display a sharp (311) peak from the cubic phase suggestive of no phase separation. For  $x = 1.2$ , however, the (311) peak of the  $5^\circ\text{C h}^{-1}$  cooled specimen starts to collapse though that of the quenched specimen is sharp. Thus, one can suggest that the immiscibility starts between  $x = 1.1$  and  $1.2$ . The  $5^\circ\text{C h}^{-1}$  cooled specimen of  $x = 1.3$  displays a cubic and a tetragonal phase simultaneously while the quenched one shows only a cubic phase. This indicates that for low Mn concentrations the quenching is faster than the process to change the structure by a cooperative Jahn–Teller distortion. For a high Mn concentration, however, a cooperative Jahn–Teller distortion takes place in the entire quenched specimen so that a x-ray diffraction reveals a tetragonal phase. In fact, this kinetics happens ubiquitously in spinels with the immiscibility due to the Jahn–Teller distortion such as  $\text{ZnGa}_{2-x}\text{Mn}_x\text{O}_4$  and  $\text{MgFe}_{2-x}\text{Mn}_x\text{O}_4$  [4, 5]. For the  $\text{CoFe}_{2-x}\text{Mn}_x\text{O}_4$  system, the quenched specimen for  $x \geq 1.6$  displays a clean tetragonal phase. The immiscibility causes a two phase coexistence for the  $5^\circ\text{C h}^{-1}$  cooled specimen of  $x = 1.6$ . In contrast, for  $x = 2.0$ , the  $5^\circ\text{C h}^{-1}$  cooled one does not show any immiscibility behavior but a larger tetragonality than the quenched one. The quenching process causes the Mn ions to distribute randomly in the A and B sites. However, a slow cooling tends to make the Mn ions migrate from the A site to the B site so that a slow cooling may have a larger tetragonality.

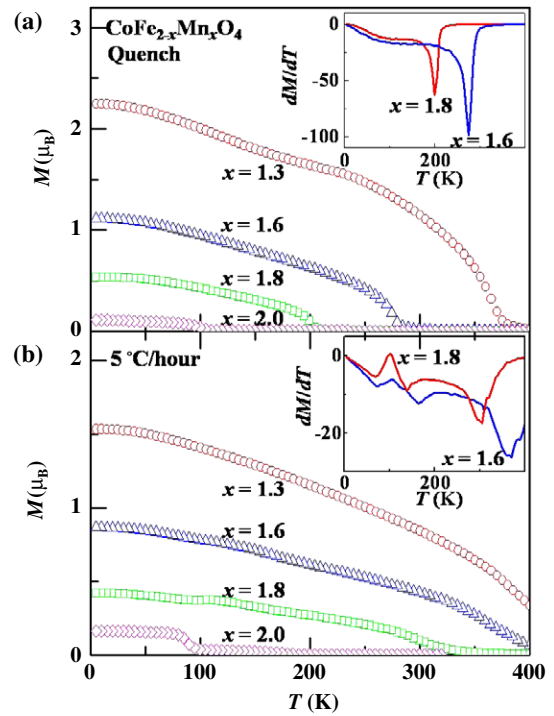
It is interesting to investigate how the structure is transformed by the cooling rates for a fixed concentration such as  $x = 1.45$  which is in an approximately middle concentration range with an immiscibility. For the convenience of discussing a structural change, we introduce four notations,



**Figure 2.** (a) The temperature dependence of the magnetization for  $x = 1.45$ . The inset displays the ferromagnetic transition temperature as a function of the cooling rates. (b) The magnetic field dependence of the magnetization for  $x = 1.45$ . The 250 °C h<sup>-1</sup> cooled specimen ( $T'$ ) shows the largest coercivity due to the magneto-crystalline anisotropy. All the lines are guides to the eyes.

$C'$ ,  $T'$ ,  $C$ , and  $T$ .  $C'$  and  $T'$  are a metastable phase of the quenched specimen and an intermediate metastable tetragonal phase for the 250 °C h<sup>-1</sup> cooled specimen, respectively.  $C$  and  $T$  denote a Fe rich cubic phase and a Mn rich tetragonal phase, respectively. Slower cooling than 250 °C h<sup>-1</sup> causes a mixture of  $C$  and  $T$  so that the structure evolution can be described schematically by  $C' \rightarrow T' \rightarrow C + T$ . This structural evolution can be achieved by controlling the annealing time, indicating that this structural evolution is generic for a spinel with an immiscibility [6]. It has been reported that the transformation for  $C' \rightarrow T'$  is a martensitic transformation and that for  $T' \rightarrow C + T$  is due to a spinodal decomposition [6]. In other words,  $C'$  transforms to a metastable tetragonal state  $T'$  without any diffusion and  $T'$  separates into distinct regions with high and low Mn concentrations. Note that the heterogeneous nano-bar array can be formed during a spinodal decomposition,  $T' \rightarrow C + T$ . This discussion can be applied to all spinels with an immiscibility.

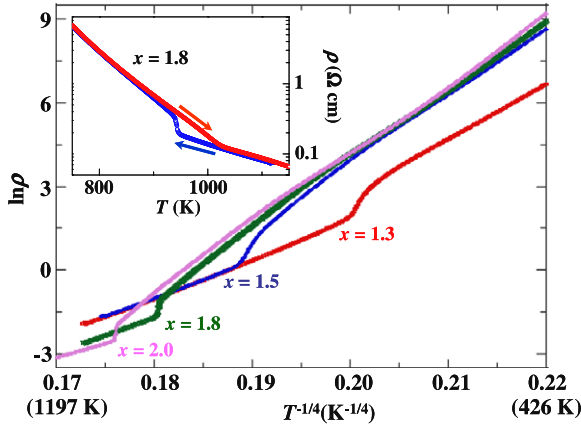
The magnetization for  $x = 1.45$  is dramatically affected by the cooling rates. The temperature dependence of the magnetization is measured under a zero field cooling condition, shown in figure 2(a). The transition temperature is decided by the peak temperature of the first derivative of the magnetization with respect to the temperature,  $dM/dT$ . The transition temperature increases with decreasing cooling rates, shown in the inset of figure 2(a). The transition temperature increases



**Figure 3.** (a) The temperature dependence of the magnetization for the quenched specimen. The transition temperature decreases with increasing Mn concentration. The inset displays  $dM/dT$  for  $x = 1.6$  and 1.8, where the peak indicates a ferromagnetic transition. (b) The temperature dependence of the magnetization for the 5 °C h<sup>-1</sup> cooled specimen. Compared to the quenched specimen of the same concentration, one can easily notice the increase of the transition temperature. The inset shows more than one transition for the 5 °C h<sup>-1</sup> cooled specimen because of the immiscibility.

drastically with a cooling rate below 250 °C h<sup>-1</sup> ( $T'$ ). Since a slower cooling than 250 °C h<sup>-1</sup> develops  $C + T$  where the  $C$  phase is close to  $\text{CoFe}_{0.9}\text{Mn}_{1.1}\text{O}_4$ , it is natural that the transition temperature increases. This behavior is also found in other ferrimagnetic spinels such as  $\text{MgFe}_{2-x}\text{Mn}_x\text{O}_4$  [5]. Furthermore, the field dependence of the magnetization also displays a common property for a spinel with an immiscibility by a Jahn–Teller distortion. Figure 2(b) plots the magnetization as a function of the magnetic field at 5 K. The quenched one has the largest saturation moment and the smallest coercivity. The inset of figure 2(b) shows the coercivity versus the cooling rates. The 250 °C h<sup>-1</sup> cooled specimen has a maximum coercivity which is about three times larger than the coercivity of the quenched one. Coercivity can be enhanced by impeding a magnetization reversal by a rotation process [17]. There are several ways to impede a magnetization reversal; for example, the nucleation or the growth of a reverse domain and an increasing magnetic anisotropy such as a crystal or shape anisotropy. Among them, a crystal anisotropy is one of the most effective means of impeding a magnetization reversal so that  $T'$  has the largest crystal anisotropy. The  $\text{MgFe}_{2-x}\text{Mn}_x\text{O}_4$  system also displays a maximum anisotropy at  $T'$  indicating that the maximum anisotropy of  $T'$  is a generic property.

Figure 3 shows the temperature dependence of the magnetization for the quenched and 5 °C h<sup>-1</sup> cooled specimens

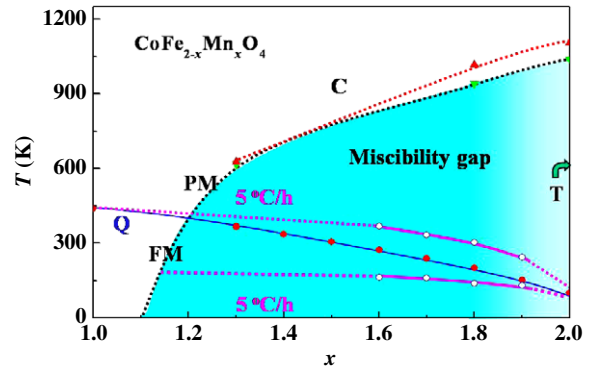


**Figure 4.** Variable range hopping analysis for  $\text{CoFe}_{2-x}\text{Mn}_x\text{O}_4$ . The inset represents an example of the high temperature resistivity. The high temperature resistivity clearly shows the Jahn–Teller transition on a heating and a cooling where a huge hysteresis occurs.

of  $\text{CoFe}_{2-x}\text{Mn}_x\text{O}_4$  under the field cooling condition. For the quenched specimen as shown in figure 3(a), the ferrimagnetic transition temperature decreases systematically with increasing Mn concentration. The transition temperatures of the  $5^\circ\text{C h}^{-1}$  cooled specimens are higher than that of the quenched one, as shown in figure 3(b). Furthermore, as shown in the inset of figure 3(b),  $dM/dT$  shows another peak at low temperatures which is totally different from the quenched specimen. Since the x-ray data of the quenched specimen displays a single phase, it is natural that  $dM/dT$  has only one sharp peak at the ferrimagnetic transition temperature, as shown in the inset of figure 3(a). However, the x-ray data of the  $5^\circ\text{C h}^{-1}$  cooled specimens reveals C + T where the concentrations of C and T are close to  $\text{CoFe}_{0.9}\text{Mn}_{1.1}\text{O}_4$  and  $\text{CoMn}_2\text{O}_4$ , respectively. Since both the C and T phases are ferrimagnetic, the  $5^\circ\text{C h}^{-1}$  cooled specimens have more than one transition temperature. This is further evidence of the immiscibility.

Figure 4 displays a variable range hopping analysis by plotting  $\ln \rho$  as a function of  $T^{-1/4}$  where  $\rho$  and  $T$  are the resistivity and temperature, respectively. The resistivity shown in figure 4 is measured during cooling. The kink represents the Jahn–Teller transition temperature which increases with increasing Mn concentration. Since  $\text{CoFe}_{2-x}\text{Mn}_x\text{O}_4$  is a bulk system, the exponent of  $-1/4$  is chosen. Over the Jahn–Teller transition temperature, straight lines appear suggesting a variable range hopping is clearly observed. Below the Jahn–Teller transition temperature, however, these lines are slightly bent, though a variable range hopping is usually applicable at low temperatures. The inset of figure 4 represents an example of the high temperature resistivity for  $x = 1.8$ . The resistivity shows a large hysteresis around the Jahn–Teller transition temperature, indicative of a first order transition.

In figure 5, the phase diagram of the  $\text{CoFe}_{2-x}\text{Mn}_x\text{O}_4$  system shows an immiscibility at  $1.1 < x < 2.0$  which is decided by an x-ray diffraction analysis. The Jahn–Teller transition temperature increases with increasing Mn concentration. The Jahn–Teller transition temperature for a heating (red triangles) is different from that of a cooling (green reverse triangles), indicative of a first order transition.



**Figure 5.** The phase diagram of  $\text{CoFe}_{2-x}\text{Mn}_x\text{O}_4$ . Solid and open circles stand for the ferrimagnetic transition temperatures of the quenched and  $5^\circ\text{C h}^{-1}$  cooled specimens, respectively. Triangles and reversed triangles represent the Jahn–Teller transition temperature for a heating and a cooling, respectively. All the lines are guides to the eyes.

Above the Jahn–Teller transition temperature, the structure of the system remains a cubic structure. At a low temperature, however, the structure changes drastically with the cooling rates for  $1.1 < x < 2.0$ . The ferrimagnetic transition temperature of the quenched sample (solid circles) decreases with increasing Mn concentration, while that of the slow cooled sample (open circles) reveals two transitions due to the immiscibility.

#### 4. Conclusion

We have investigated the structural, magnetic, and resistivity properties of  $\text{CoFe}_{2-x}\text{Mn}_x\text{O}_4$  which has an immiscibility induced by a Jahn–Teller distortion. The structure of the specimens is highly affected by the cooling rates and Mn concentration. At a fixed Mn concentration such as  $x = 0.45$ , the structure evolved by the cooling rates observes a rule,  $C' \rightarrow T' \rightarrow C + T$ , which is generic for a spinel system with an immiscibility. A structural change by a heat treatment drastically affects the magnetic properties, such as the coercivity and transition temperatures. The coercivity change by the cooling rates for  $x = 0.45$  is associated with a structural change so that the largest coercivity appears at  $T'$  which has the largest magneto-crystalline anisotropy. For  $x \geq 1.6$ , the slow cooled specimen has two ferrimagnetic transitions due to the spinodal decomposition while the quenched one displays only one transition. The high temperature resistivity displays a clear Jahn–Teller transition whose temperature increases with increasing Mn concentration. Based on all the data, we constructed a phase diagram of the  $\text{CoFe}_{2-x}\text{Mn}_x\text{O}_4$  system. We expect the phase diagram will be useful to synthesize a nanostructure as well as to understand the physical properties of a spinel system with the immiscibility induced by a Jahn–Teller distortion.

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