Heat Capacity Measurements of Mn$_x$Fe$_{3-x}$O$_4$

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Heat capacities of Mn$_x$Fe$_{3-x}$O$_4$ with the composition x = 1.0, 1.5, and 2.0 were measured from 200 to 740 K. λ-type heat capacity anomalies due to the ferri-paramagnetic transition were observed for all the compositions. The transition temperatures were 577, 471, and 385 K for the composition x = 1.0, 1.5 and 2.0, respectively, which are in good agreement with the results of magnetic measurements. The difference in heat capacities between the different samples was small except for the temperature range of the transition. The magnetic contribution to the observed heat capacity was obtained by assuming that the heat capacity can be expressed by the sum of the lattice heat capacity C_V (l), the dilation contribution $C(d)$, and the magnetic contribution $C(m)$. Entropy changes due to the transition were obtained from $C(m)$ as 55.5, 50.7 and 49.2 J K^{-1} mole^{-1} for the composition x = 1.0, 1.5, and 2.0, respectively. The entropy changes were also calculated by assuming the randomization of unpaired electron spins on each ion, but they were from 6 to 10 J K^{-1} mole^{-1} smaller than the observed ones. The difference between the experimental and the calculated values is roughly explained by taking into account the cation exchange reaction between the tetrahedral and the octahedral sites in the spinel structure.

I. Introduction

Manganese ferrites, Mn$_x$Fe$_{3-x}$O$_4$, have been known to have the spinel structure, in which the metal ions partially occupy the tetrahedral (A site) and octahedral (B site) interstices of the closed-packed oxygen lattice. Various physical properties of Mn$_x$Fe$_{3-x}$O$_4$ such as the lattice constant *(1, 2)*, magnetic saturation moment *(3–5)*, Curie temperature *(3, 5–7)*, electrical conductivity *(8–10)*, and Seebeck coefficient *(10, 11)* have been measured as a function of composition x, and discussed in terms of the cation distribution among these sites.

In the mixed oxides such as Mn$_x$Fe$_{3-x}$O$_4$, the change in heat capacity due to the compositional change is usually small, as the Kopp–Neumann law predicts

as long as the classical lattice vibration is the predominant contribution to the heat capacity *(12)*. However, when phase transition occurs, as in the case of TiO$_x$ *(13)*, Ni$_{1-x}$Se$_x$ *(14)*, U$_4$O$_{9-y}$ *(15)*, and Fe$_{1-x}$Co$_x$S$_2$ *(16)*, the heat capacity and resulting enthalpy and entropy changes due to the transition depend on the composition, which would give useful information for understanding the mechanism of the transition. Since manganese ferrites, Mn$_x$Fe$_{3-x}$O$_4$, have a ferri–paramagnetic transition, it is expected that the heat capacity anomaly due to the transition depends strongly on the composition x.

The heat capacities of Mn$_x$Fe$_{3-x}$O$_4$ in the temperature region of the transition have been measured by Grønvold and Sveen *(17)* for the composition x = 0 : Fe$_3$O$_4$, and by

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Nielsen ([18]) and Reznitskii ([19]) for x = 1.0 : MnFe$_2$O$_4$. Each study, however, was restricted to one composition, and no discussion on the composition dependence of the heat capacity has been reported.

II. Experimental

II. 1. Sample Preparation

Samples of Mn$_x$Fe$_{3-x}$O$_4$ with the composition x = 1.0, 1.5, and 2.0 were prepared as follows. The mixture of α-Fe$_2$O$_3$ and MnCO$_3$ in an appropriate metal composition was prefired for 3 hr at 600°C and then sintered for 100 hr at 1200°C in air. After that, the samples were kept in an argon gas stream for 100 hr at 1050°C in order to adjust the metal–oxygen ratio and then they were quenched to room temperature. The diffraction patterns obtained from X-ray powder photographs of the samples showed the cubic spinel phase for the composition x = 1.0 and 1.5, and the tetragonal spinel phase for x = 2.0. The obtained lattice constants were 8.512 ± 0.002 Å for x = 1.0, 8.521 ± 0.002 Å for x = 1.5, and a = 8.34 ± 0.03 Å and c = 8.79 ± 0.03 Å (c/a = 1.05) for x = 2.0.

II. 2. Heat Capacity Measurement

Heat capacities of Mn$_x$Fe$_{3-x}$O$_4$ were measured by the adiabatic scanning calorimeter ([20]); in this calorimeter the power supplied to the sample was measured continuously, and the heating rate was maintained constant regardless of the kind and amount of the sample.

The heating rate chosen was 2 K min^{-1}, and the measurement was carried out between 200 and 740 K under nitrogen gas of about 1 Torr. The heating rate control and adiabatic control were usually maintained within ±0.01 K min^{-1} and ±0.03 K, respectively. The powder sample Mn$_x$Fe$_{3-x}$O$_4$ was sealed in a Pyrex glass vessel filled with helium gas of about 200 Torr. The

TABLE I

HEAT CAPACITY OF Mn$_x$Fe$_{3-x}$O$_4$

	C_p/J K^{-1} mole^{-1}		
T (K)	x = 1.0 (MW; 230.63)	x = 1.5 (MW; 230.18)	x = 2.0 (MW; 229.72)
200	124.4	123.4	123.6
210	128.9	127.9	129.8
220	134.2	132.2	133.7
230	139.5	138.9	137.7
240	143.4	141.6	144.1
250	146.7	146.4	147.8
260	150.9	151.4	151.3
270	153.1	153.7	155.4
280	158.4	157.9	160.0
290	161.2	159.8	161.9
300	164.4	163.0	165.0
310	167.1	166.9	168.4
320	169.4	169.9	172.6
330	172.0	172.8	175.4
340	174.1	175.2	177.5
350	176.4	177.6	179.7
360	178.8	179.3	182.0
370	180.9	182.1	185.5
380	184.7	184.7	189.8
390	187.3	185.8	188.0
400	187.1	188.9	182.9
410	189.6	191.8	181.0
420	193.9	196.1	181.5
430	195.6	200.4	181.6
440	196.6	204.0	182.9
450	201.1	208.4	183.7
460	203.7	212.8	183.6
470	206.0	217.4	184.4
480	208.0	215.1	184.6
490	210.0	203.8	185.0
500	211.8	195.4	185.4
510	215.2	191.2	185.8
520	217.0	191.6	184.6
530	219.7	190.3	186.9
540	222.0	188.7	186.1
550	225.2	188.4	187.0
560	229.1	188.7	187.8
570	232.8	189.2	188.7
580	236.3	189.1	189.0
590	230.8	188.5	188.2
600	217.4	188.8	188.6
610	208.3	189.1	188.6
620	202.6	189.2	187.1
630	199.5	189.4	188.0
640	198.3	189.6	189.4
650	197.9	190.0	189.5
660	197.0	190.3	189.9
670	196.2	190.6	189.8

TABLE I—*continued*

	$C_p/\text{J K}^{-1} \text{ mole}^{-1}$		
T (K)	$x = 1.0$ $(MW; 230.63)$	$x = 1.5$ $(MW; 230.18)$	$x = 2.0$ $(MW; 229.72)$
680	195.7	190.8	190.2
690	195.5	191.2	190.7
700	194.3	191.6	189.8
710	194.0	191.8	190.4
720	194.3	192.2	192.1
730	193.1	192.5	192.7
740	193.3	192.9	192.5

sample amount used for the measurement was 10.174 g for the composition $x = 1.0$, 9.928 g for $x = 1.5$, and 10.628 g for $x = 2.0$.

III. Results and Discussion

III. 1. Heat Capacity and Curie Temperature

The results of the heat capacity measurement on $Mn_xFe_{3-x}O_4$ for the composition $x = 1.0$, 1.5, and 2.0 are listed in Table I and are shown in Fig. 1, where the results for $MnFe_2O_4$ by Nielsen (*18*) and Reznitskii (*19*) are also shown for comparison. The precision of the heat capacity measurement of the present study was within ± 1%. As seen in Fig. 1, the λ-type heat capacity anomaly due to the ferri-paramagnetic transition is largely dependent on the composition. The difference in heat capacities due to different composition is small except for the temperature range of the transition, as the Kopp–Neumann law predicts. The difference in the transition temperatures between our data and those by the previous studies may come from the difference in the cation distribution in the sample which would be caused by the process of making the sample, as will be discussed later.

In the dynamic calorimeter, a temperature difference is produced in the sample

and a so-called scanning error is produced, as discussed in previous papers (*15, 20*). The scanning error was corrected by shifting the sample temperature by about 3 K in this study according to the earlier method (*15, 20*). In order to determine the exact peak temperature of heat capacity anomaly, the peak temperature was measured at various heating rates, from which the transition temperature was determined by extrapolating the heating rate to zero. The obtained Curie temperatures are plotted against composition in Fig. 2, where previous results reported in the literatures are also shown for comparison. In Fig. 2, the Curie temperature data are considerably scattered, which may be ascribed to the difference in the cation distribution of the samples.

The cation distribution of $Mn_xFe_{3-x}O_4$ has been measured by means of neutron diffraction (*21–23*), X-ray diffraction (*24*), and Mössbauer effect (*25, 26*). According to Lotgering (*8*) and Lotgering and Diepen (*26*), the cation distribution of
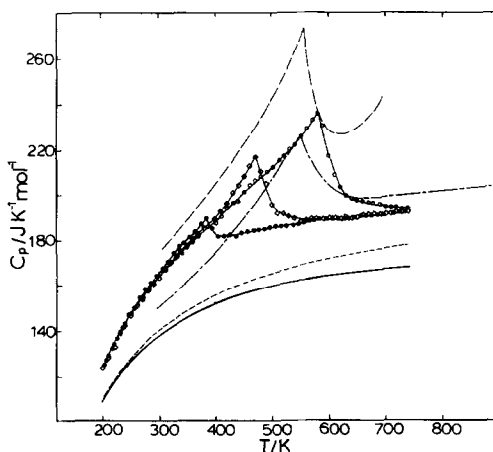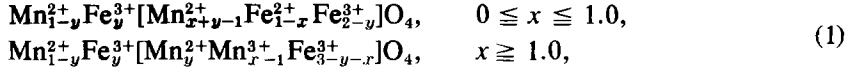

Fig. 1. Heat capacity of $Mn_xFe_{3-x}O_4$: ○, present experimental result of $x = 1.0$; ◇, $x = 1.5$; ●, $x = 2.0$; — — —, result of $x = 1.0$ by Nielsen (*18*); — — —, result of $x = 1.0$ by Reznitskii (*19*); ———, estimated lattice heat capacity $C_v(l)$ for $x = 1.0$; ———, estimated $C_v(l) + C(d)$ for $x = 1.0$.

$Mn_xFe_{3-x}O_4$ can be represented by the formula:

$$Mn_{1-y}^{2+}Fe_y^{3+}[Mn_{x+y-1}^{2+}Fe_{1-x}^{2+}Fe_{2-y}^{3+}]O_4, \qquad 0 \leqq x \leqq 1.0,$$

$$Mn_{1-y}^{2+}Fe_y^{3+}[Mn_y^{2+}Mn_{x-1}^{3+}Fe_{3-y-x}^{3+}]O_4, \qquad x \geqq 1.0, \qquad (1)$$

where the cations before the brackets occupy tetrahedral (A) sites, and those in the brackets the octahedral (B) sites, and y denotes the degree of inversion. Šimša and Brabers (27) studied the relationship between Curie temperature and the degree of inversion y for $MnFe_2O_4$ and found that Curie temperature increases with y. By using their data and the Curie temperature obtained in this study, y was determined to be 0.2 for $MnFe_2O_4$. This value is in good agreement with that measured by means of neutron diffraction (21).

III. 2. Entropy Change Due to the Ferri–Paramagnetic Transition

In order to estimate the entropy change (ΔS_m) due to the ferri–paramagnetic transition of $MnFe_{3-x}O_4$, the observed heat capacity (C_p) is considered to the sum

$$C_p = C_v(l) + C(d) + C(m), \qquad (2)$$

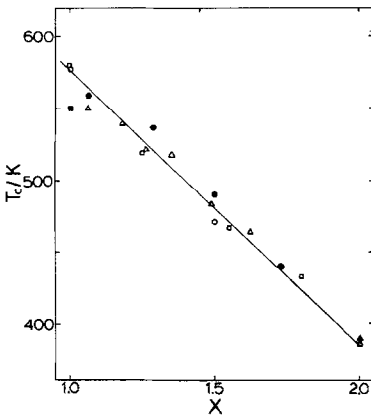FIG. 2. Curie temperature of $Mn_xFe_{3-x}O_4$ against composition x: ○, present study; △, Harrison et al. (3); □, Moruzzi (5); ▲, Buhl (6); ●, Gerber et al. (7); ■, Reznitskii (19).

where $C_v(l)$ is the lattice heat capacity at constant volume, $C(d)$ the dilation contribution, and $C(m)$ the magnetic contribution.

(A) The lattice heat capacity $C_v(l)$ was calculated by the same method applied to $MgAl_2O_4$ (28), $CoFe_2O_4$ (29), and $NiFe_2O_4$ (29) by Grimes. The lattice heat capacity is expressed by a linear combination of Debye and Einstein functions and each characteristic frequency of the phonon is determined from the four fundamental infrared absorption bands ν_1, ν_2, ν_3, and ν_4, as follows (30):

$$C_v(l) = 2E\left(\frac{\theta_1}{T}\right) + 2D\left(\frac{\theta_2}{T}\right)$$
$$+ 2E\left(\frac{\theta_3}{T}\right) + D\left(\frac{\theta_4}{T}\right), \quad (3)$$

$$\theta_n = \frac{hc}{k}\nu_n = 1.438\nu_n, \qquad (4)$$

where $E(x)$ and $D(x)$ are the Einstein and Debye functions, respectively, θ_n the characteristic temperature, h Planck's constant, k Blotzmann's constant, c the light velocity, and ν_n the infrared absorption frequency in cm^{-1}.

The infrared-absorption spectrum of $Mn_xFe_{3-x}O_4$ has been reported by Waldron (30), Brabers (31), Brabers and Klerk (32) and Ishii et al. (33). In this study the results of Ishii et al. were used to determine θ_n (Table II), because only their data covered the necessary compositions. The obtained lattice heat capacity is shown in Fig. 1 for $MnFe_2O_4$ as an example.

(B) The dilation contribution $C(d)$ is usually expressed by

$$C(d) = C_p - C_v = \alpha^2 VT/\kappa \qquad (5)$$

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TABLE II

CHARACTERISTIC TEMPERATURE FOR THE
CALCULATION OF LATTICE HEAT CAPACITY OF
$Mn_xFe_{3-x}O_4$

x	θ_1 (K)	θ_2 (K)	θ_3 (K)	θ_4 (K)
1.0	777	532	467	245
1.5	798	559	467	245
2.0	820	565	467	245

$$\simeq \alpha\Gamma C_v T, \qquad (6)$$

where α is the expansivity, V the molar volume, κ the compressibility, and Γ is the Grüneisen constant (34) which is defined as $\Gamma = \alpha V/\kappa C_v$ and does not strongly depend on temperature. However, since neither expansivity nor compressibility of $Mn_xFe_{3-x}O_4$ with composition $x = 1.0, 1.5,$ and 2.0 has been reported (in the temperature range of the present study), the Grüneisen constant Γ and expansivity α of $Mn_xFe_{3-x}O_4$ with $x = 1.0, 1.5,$ and 2.0 are assumed to be equal to those of magnetite Fe_3O_4 in order to calculate $C(d)$ in Eq. (6). The expansivity of magnetite was reported by Gorton et al. (35) and the Grüneisen constant for magnetite was determined as 1.75 by Grønvold and Sveen (17). The results of the calculation of $C(d)$ are shown in Fig. 1 for the composition $x = 1.0$.

(C) The magnetic contribution $C(m)$ was obtained by subtracting $C_v(l)$ and $C(d)$ from the observed heat capacity C_p according to Eq. (2). The resulting $C(m)$ for $MnFe_2O_4$ is shown in Fig. 3 as an example, showing a usual λ-type curve.

In Fig. 3, a broken line below 200 K represents the magnetic heat capacity calculated from the equation derived by Grimes (29). Grimes' equation for magnetic heat capacity is based on the spin wave theory on the spinel ferrites discussed by Kaplan (36), and Glasser and Milford (37), and expressed as follows:

$$C(m) = F_1 + F_2$$
$$+ E\left(\frac{12 J_{AB} S_A}{kT}\right) + \tfrac{1}{3} E\left(\frac{24 J_{AB} S_B}{kT}\right), \qquad (7)$$

where F_1 and F_2 are the contributions of the heat capacity due to an acoustic and an optical branch of spin wave, respectively, using a long-wavelength approximation and the last two terms represent the Einstein function due to optical branches of spin wave. All these terms in Eq. (7) include the parameters: J_{AB}, the exchange interaction energy between A and B sites, and S_A and S_B, the average spin values at each site. The magnetic heat capacity can be calculated from the equation by determining the three parameters; J_{AB}, S_A, and S_B. In this study S_A and S_B are derived on the basis of $S = \frac{5}{2}$ for Mn^{2+} and Fe^{3+} and $S = 2$ for Mn^{3+} and Fe^{2+}, and assuming that the cation distribution of $Mn_xFe_{3-x}O_4$ can be expressed by Eq. (1), and J_{AB} was determined by fitting the data of $C(m)$ between 200 and 250 K, and then $C(m)$ below 200 K was calculated. The obtained parameters are given in Table III. J_{AB} for $MnFe_2O_4$, 1.58 meV, obtained in this study is in good agreement with that of
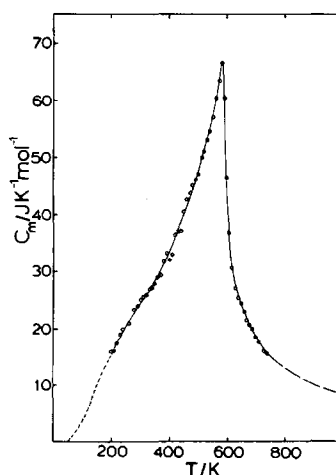

FIG. 3. Magnetic heat capacity of $x = 1.0$, $MnFe_2O_4$: $\bigcirc$, magnetic heat capacity obtained from Eq. (2); ---, magnetic heat capacity calculated by spin wave theory; — — —, extrapolated magnetic heat capacity.

TABLE III

EXCHANGE INTERACTION ENERGY AND AVERAGE
SPIN VALUES OF $Mn_xFe_{3-x}O_4$

x	J_{AB} (meV)	S_A	S_B
1.0	1.58	2.5	2.5
1.5	1.48	2.5	2.38
2.0	1.38	2.5	2.25

Wegner et al. (38), 1.52 meV, determined by means of inelastic neutron scattering.

Since the heat capacity measurement in the present study was carried out between 200 and 740 K, the magnetic heat capacity $C(m)$ above 740 K was estimated by extrapolation, assuming that the magnetic heat capacity obeys the relationship $C(m)T^2 =$ const. (39) sufficiently far above the transition temperature. The extrapolation is shown by a dashed line in Fig. 3. From Fig. 3 the entropy change due to the transition $\Delta S_m(exp)$ was calculated numerically for $MnFe_2O_4$ by integrating up to an infinite temperature, and similar calculations were also carried out for the composition $x = 1.5$ and 2.0. The results are obtained as 55.5, 50.7, and 49.2 J K^{-1} $mole^{-1}$ for the composition $x = 1.0$, 1.5, and 2.0, respectively, and they are plotted against composition in Fig. 4 where the result of Fe_3O_4 by Grønvold and Sveen (17) is also shown.

The origin of the ferri–paramagnetic transition is thought to be the randomization of unpaired electron spins of each ion, and the entropy change due to the transition can be described, assuming that the cation distribution can be expressed by Eq. (1), as follows:

$$\Delta S_m \text{ (calc.)} = R \{(2 \ln 6 + \ln 5) + (\ln 6 - \ln 5)x\}, \qquad 0 \leq x \leq 1.0,$$
$$= R \{(4 \ln 6 - \ln 5) - (\ln 6 - \ln 5)x\}, \qquad x \geq 1.0, \tag{8}$$

where R is the gas constant. It is noted from Eq. (8) that $\Delta S_m(calc.)$ is independent of the degree of inversion y. $\Delta S_m(calc.)$ by Eq.
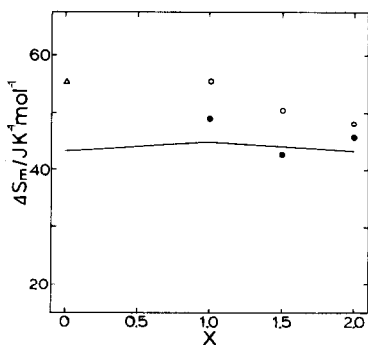

FIG. 4. Entropy change due to ferri–paramagnetic transition against composition x: O, present experimental results before subtracting the term due to the exchange reaction; ●, results after subtracting the term due to the exchange reaction; △, the result of Fe_3O_4 by Grønvold and Sveen (17); ——, calculated entropy change from Eq. (8).

(8) is shown in Fig. 4. As seen in the figure, the experimental values are from 6 to 10 J K^{-1} $mole^{-1}$ larger than the calculated ones. This difference may suggest that there is another contribution to the observed heat capacity C_p of $Mn_xFe_{3-x}O_4$ in addition to those of Eq. (2).

Grønvold and Sveen (17) explained the difference between the experimental and the theoretical entropy changes for Fe_3O_4 by taking into account the orbital heat capacity contributions for the Fe^{2+} ion in octahedral site. $Mn_xFe_{3-x}O_4$ with the composition more than $x = 1.0$, however, has no Fe^{2+} ion in the present temperature region according to Eq. (1). Therefore, it is not reasonable to consider such a contribution in the present study.

An additional contribution to the observed entropy change $\Delta S_m(exp.)$ may come from the cation exchange reaction

between the tetrahedral and octahedral sites of the spinel structure. An anomaly in the thermal expansion has been observed by Bravers (40) at 400°C besides the anomaly due to the magnetic transition in the sample of $MnFe_2O_4$, quenched from 600°C, which was interpreted in terms of the temperature dependent cation distribution between the octahedral and tetrahedral sites of the 2–3 spinel AB_2O_4:

$$AB_2O_4 \rightleftharpoons A_{1-y}B_y[A_yB_{2-y}]O_4, \quad (9)$$

where y and bracket have the same meaning as Eq. (1). A similar anomaly in the electrical conductivity has also been found (41) around 725 K in the sample of $MnFe_2O_4$, quenched from 1050°C at the oxygen pressure of 6.0×10^{-5} atm, which can be ascribed to the same origin.

Jirák and Vratislav (42) have reported that the reaction of Eq. (9) for $MnFe_2O_4$ is extremely slow below 300°C and becomes faster as temperature increases. According to Šimšová and Šimša (43), the time constant to attain the equilibrium of the reaction for $MnFe_2O_4$ varies from 1 min at 400°C to 0.1 sec at 600°C. In this study, the heat capacity measurement was carried out at a heating rate of 2 K min⁻¹ and up to 740 K. Therefore, cation exchange reaction is thought to be equilibrium at 740 K according to the data of Šimšová and Šimša (43), and the contribution due to the exchange reaction above 740 K is rather small, because the electrical conductivity measurement (41) showed that the cation exchange reaction almost ends around this temperature. Thus one can assume that the magnetic heat capacity $C(m)$ obtained from Eq. (2) includes the contribution of the cation exchange reaction at higher temperatures, although this contribution becomes very small above 740 K. Then, the T^{-2} dependence of $C(m)$ above 740 K approximately holds and the observed entropy change $\Delta S_m(exp.)$ is regarded to be the sum of $\Delta S_m(calc.)$ and the entropy change due to the cation exchange $\Delta S(exchange)$:

$$\Delta S_m(exp.)$$
$$= \Delta S_m(calc.) + \Delta S(exchange). \quad (10)$$

According to Navrotsky and Kleppa (44), the entropy change due to the exchange reaction (Eq. (9)) is considered to be mainly a configurational one, which is expressed by

$$\Delta S(exchange)$$
$$= -R[y \ln y + (1 - y) \ln (1 - y)$$
$$+ y \ln (y/2) + (2 - y) \ln (2 - y)/2] \quad (11)$$

The configurational entropy by Eq. (11) has a maximum at $y = \frac{2}{3}$, which corresponds to the random distribution of cations on both sites.

The additional entropy change due to cation exchange can be estimated by Eq. (11) assuming that the degree of inversion at room temperature for the $MnFe_2O_4$ sample used in this study is 0.2 as discussed in section III. 1 and the reaction Eq. (9) takes place until random distribution of the cations is attained. The additional entropy increment obtained by Eq. (11) for $MnFe_2O_4$ is 6.3 J K⁻¹ mole⁻¹. This value is subtracted from the observed entropy change $\Delta S_m(exp.)$ to compare with $\Delta S_m(calc.)$ and is shown in Fig. 4. The similar calculations have been done for composition $x = 1.5$ and 2.0, respectively, using the degree of inversion data reported by Yamzin et al. (23) for $x = 1.5$ and Tanaka et al. (45) for $x = 2.0$. The results are also shown in Fig. 4. As can be seen in Fig. 4, $\Delta S_m(exp.) - \Delta S(exchange)$ is roughly in agreement with $\Delta S_m(calc.)$. The small differences between them may mainly be caused by the uncertainty of the parameters used in these calculations.

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