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Preparation and Magnetic Properties of the FeV_2O_4–Fe_3O_4 System

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A series of spinels having stoichiometric composition in the Fe_3O_4–FeV_2O_4 system has been prepared at 1500°K under controlled CO_2–H_2 atmospheres. The relationship between lattice parameter and composition of the spinel solid solution system showed a significant deviation from Vegard's law, and the Curie temperature varied with composition almost linearly except for the composition in the vicinity of FeV_2O_4. A minimum value of saturation moment, approximately 0.04 μ_B per formula unit, was observed at the composition $Fe_{1.8}V_{1.2}O_4$. Saturation magnetization was reasonably explained by assuming the cation distribution as $Fe^{3+}(Fe^{2+}Fe_{\mu}^{3+}V_{1-\mu}^{3+})O_4$ for the Fe_2VO_4–Fe_3O_4 solid solution, and $Fe_{\lambda}^{3+}Fe_{1-\lambda}^{2+}(Fe_{\lambda}^{2+}V_{2-\lambda}^{3+})O_4$ for the FeV_2O_4–Fe_2VO_4, where both μ and λ change from 0 to 1.

Introduction

The solid solution system of FeV_2O_4–Fe_3O_4 has been studied by several investigators (*1–3*). Since FeV_2O_4 and Fe_3O_4 have a normal (*4*) and an inverse (*5*) spinel structure, respectively, the FeV_2O_4–Fe_3O_4 system might show interesting magnetic properties. The magnetic properties of FeV_2O_4 and Fe_2VO_4 were studied by Wold et al. (*6*). They reported a Curie point for FeV_2O_4 of 190°K and a saturation moment at 4.2°K of 1.95 μ_B per formula unit; those for Fe_2VO_4 are 440°K and 0.72 μ_B, respectively. Recently, the ionic configuration in Fe_2VO_4 was proposed to be $Fe^{3+}(Fe^{2+}V^{3+})O_4$ by Bernier and Poix (*7*) on the basis of their anion–cation distance calculation method and studies of various magnetic properties. Magnetic and electric properties of the spinel solid solution $Fe_{1+\lambda}V_{2-\lambda}O_4$ ($0 \leqq \lambda \leqq 1$) were studied by Rogers et al. (*8*). The Mössbauer spectra of this solid solution were measured by Rossiter (*9*) and cation distributions of $Fe^{2+}(Fe_{\lambda}^{3+}V_{2-\lambda}^{3+})O_4$ ($0 \leqq \lambda \leqq 1$) were proposed for this system.

The purpose of the present study was to prepare the stoichiometric spinel solid solution of FeV_2O_4–Fe_3O_4 system under controlled CO_2–H_2 atmospheres at 1500°K and to investigate the lattice parameters and magnetic properties of the system for the temperature range from 77°K (liquid nitrogen temperature) to 860°K.

Experimental

Sample Preparation

Fe_2O_3 and V_2O_5 were used for preparing the solid solution $Fe_{1+2x}V_{2-2x}O_4$ ($0 \leqq x \leqq 1$). V_2O_5 was obtained by decomposition of ammonium meta vanadate in air at 450°C. V_2O_5 and Fe_2O_3, predried at 700°C, were thoroughly mixed in a desired proportion, loosely pressed into a small-size platinum crucible, and heated at 650°C in an atmosphere of a mixed gas of $CO_2/H_2 = 1$ for 20 min. An error in the atomic ratio of V/Fe in a mixture was estimated to be within $\pm 0.1\%$. The prepared sample was a mixture of reduced forms of vanadium and iron oxides. The grinding, pressing, and heating were repeated to obtain an uniform mixture. The mixed oxide sample was removed from the crucible and suspended in a vertical tube-quenching furnace with a thin, platinum–40% rhodium wire; here it was heated for 10–18 hr at 1500 ± 3°K in a desired ratio of CO_2/H_2 until equilibrium was attained between the gas and the solid phases. The equilibrated sample was quenched to the temperature of cold water. The detailed techniques are just the same as those described previously (*10*).

Total composition of the quenched sample were determined by means of the gravimetric weight-gain method. The sample was completely oxidized to a mixture of V_2O_5 and Fe_2O_3 at 800°C in air for 24–48 hr; vaporization of V_2O_5 was insignificant during heating within the present accuracy.

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The CO_2/H_2 gas mixtures were prepared by proportioning the two gas components in a desired ratio by means of the method similar to that used by Darken and Gurry (*11*). The actual partial pressure of oxygen was measured by the solid electrolyte cell composed of $(ZrO_2)_{0.85}(CaO)_{0.15}$. The principle and design of the cell used in the present study are the same as those described by Katsura and Hasegawa (*12*) and Wakihara and Katsura (*13*).

A thermogravimetric method was used to determine the rate of approach to an equilibrium state and to determine ranges of oxygen partial pressure and composition in which the spinel solid solution exists in equilibrium. The method was described in previous studies (*12, 13*).

The phases present in the quenched sample were identified by an X-ray diffraction method using Fe K_α radiation. Silicon powder was used as the standard in determining *d* values.

Magnetic Measurements

The magnetization of samples was determined by the Faraday method. The force, the emf of the thermocouple attached on the specimen, and the current intensity of the applied field were automatically recorded by a suitable recording device. The maximum value of the field was approximately 7000 Oe.

Calibration of the magnetization was carried out by using nickel powder with a purity of 99.99%, which has the value of 0.5714 μ_B per atom (*14*) at 293°K. The error of measured magnetization for each specimen was estimated to be within ±3%. The experimental formula, $M_h = M_s(1 - \text{const}\cdot H^{-1})$ was used to correct the observed magnetization at 77°K to the saturation magnetization at 77°K. M_h and M_s indicate a moment at any value of H (magnetic field) at 77°K and the saturation moment at 77°K, respectively. A value of M_s for each specimen was graphically taken as the intercept on the M_h axis by extrapolating a value of H^{-1} to zero (or by choosing a value of H as infinity). No extrapolation to the saturation moment at 0°K was carried out because magnetization curves of FeV_2O_4, or those close to that composition, and $Fe_{1.8}V_{1.2}O_4$ were uncertain in the temperature range from 77° to 0°K, as will be shown in Fig. 3b and Fig. 3c.

Pt–13%Rh and Au·2%Co–Cu thermocouples were used to measure temperatures above and below room temperature, respectively. The variation of temperatures between 77 and 860°K was achieved by use of suitable Dewar vessel and noninductive electric furnace. Temperature calibration was carried out at liquid N_2 temperature and at the freezing point of water for the Au·2%Co–Cu thermocouple; at the Curie temperatures of pure nickel (546°K) and stoichiometric magnetite (851°K) for the Pt–13%Rh·Pt thermocouple. The temperature is correct within an accuracy of ±5°K.

Results and Discussion

The Area of the Spinel Solid Solution in the V_2O_3–Fe_2O_3–FeO System at 1500°K

The area of the spinel solid solution at 1500°K in the V_2O_3–Fe_2O_3–FeO system is given together with the isobaric lines of the oxygen partial pressure in Fig. 1. The figure illustrates the relationship between atomic ratio of 4(Fe + V)/O and compositional parameter x for the general formula of the spinel $Fe_{1+2x}V_{2-2x}O_4$ $(0 \leqq x \leqq 1)$. The variation of 4(Fe + V)/O, which is a measure of defect structure of the present spinel, is seen to depend on the value of x. For example, the spinel with $x = 0.5$ varied its composition from $(Fe_{2/3}V_{1/3})_3O_4$ to $(Fe_{2/3}V_{1/3})_{2.965}O_4$, while FeV_2O_4 was stoichiometric within experimental error.

The isobaric lines of oxygen were concentrated near the stoichiometric spinel solid solution when the partial pressure of oxygen became lower, and a spinel with a stoichiometric composition was decomposed to more reduced phases below a certain oxygen partial pressure. The spinel with a greater metal to oxygen ratio than 3/4 was not found in the present study. These situations are similar to the cases of the spinel solid solutions Fe_2TiO_4–Fe_3O_4 (*15*) and $FeCr_2O_4$–Fe_3O_4 (*16*). The detailed study will be published elsewhere in the near future.

Specimens were prepared in the most suitable oxygen partial pressure under which the spinel

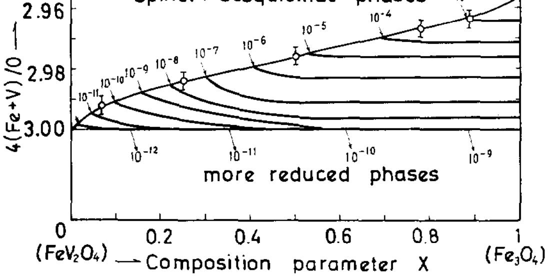

FIG. 1. Area of the spinel solid solution with composition parameter x for the $Fe_{1+2x}V_{2-2x}O_4$ $(0 \leqq x \leqq 1)$ at 1500°K. Some curved lines in the area indicate the isobaric lines of oxygen partial pressures.

TABLE I

VALUES OF CONSTANTS FOR SOME MEMBERS OF THE FeV_2O_4–Fe_3O_4 SYSTEM

$Fe_{1+2x}V_{2-2x}O_4$ Value of x	$Fe_{1+2x}V_{2-2x}O_4$ Compound	Atmospheric condition ($-\log P_{O_2} \pm 0.05$)	Lattice parameter (a_0(Å))	Saturation magnetization in μ_B per formula unit (77°K)	Curie temp. ((°K) ± 5°)
0	FeV_2O_4	13.08	8.452 ± 0.001	1.54	127
0.0625	$Fe_{1.125}V_{1.875}O_4$	12.03	8.450 ± 0.002	1.49	121
0.1	$Fe_{1.2}V_{1.8}O_4$	11.90	8.450 ± 0.002	1.39	132
0.175	$Fe_{1.35}V_{1.65}O_4$	11.90	8.450 ± 0.002	1.08	170
0.25	$Fe_{1.5}V_{1.5}O_4$	10.90	8.446 ± 0.002	0.72	222
0.325	$Fe_{1.65}V_{1.35}O_4$	10.90	8.441 ± 0.002	0.294	295
0.3625	$Fe_{1.725}V_{1.275}O_4$	10.90	—	0.142	333
0.4	$Fe_{1.8}V_{1.2}O_4$	10.45	8.426 ± 0.002	0.044	358
0.4375	$Fe_{1.875}V_{1.125}O_4$	10.45	—	0.253	—
0.475	$Fe_{1.95}V_{1.05}O_4$	10.15	—	0.50	432
0.5	Fe_2VO_4	9.72	8.418 ± 0.002	0.73	454
0.55	$Fe_{2.1}V_{0.9}O_4$	9.72	—	0.98	516
0.625	$Fe_{2.25}VO_{3.75}O_4$	9.72	8.408 ± 0.002	1.40	566
0.7	$Fe_{2.4}V_{0.6}O_4$	9.17	8.407 ± 0.002	2.02	621
0.775	$Fe_{2.55}V_{0.45}O_4$	8.89	8.401 ± 0.001	2.34	698
0.8125	$Fe_{2.625}V_{0.375}O_4$	8.89	—	2.85	—
0.85	$Fe_{2.7}V_{0.3}O_4$	8.89	8.399 ± 0.002	3.05	738
0.8875	$Fe_{2.775}V_{0.225}O_4$	8.89	8.396 ± 0.001	3.19	—
0.925	$Fe_{2.85}V_{0.15}O_4$	8.50	8.395 ± 0.002	3.42	814
1.0	Fe_3O_4	8.10	8.394 ± 0.002	4.03	851

existed in the stoichiometric composition in equilibrium state at 1500°K. The values of oxygen partial pressure are listed in Table I.

Lattice Parameters

Lattice parameters for the present spinels are given in Table I and shown in Fig. 2. The relation between lattice parameters and compositions deviates considerably from Vegard's law. In the range $0 \leqq x \leqq 0.5$, they are in good agreement with those of Rogers et al. (*8*) and Rossiter (*9*). In the range $0.5 \leqq x \leqq 1$, however, the parameter decreases with a gentler slope than in the range $0 \leqq x \leqq 0.5$, and the results are slightly different from the work by Vorob'ev et al. (*2*).

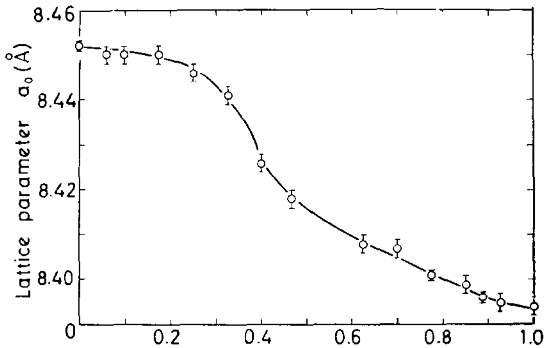

FIG. 2. Relationship between lattice parameter and composition parameter x for the system $Fe_{1+2x}V_{2-2x}O_4$ ($0 \leqq x \leqq 1$).

Magnetic Properties

The magnetizations of a number of spinels were measured between 77°K and their Curie temperatures. Typical examples of magnetization versus temperature are shown in Fig. 3a,b,c. In Fig. 3a, the magnetizations decrease smoothly with increase of temperature. Similar temperature dependence of magnetization was observed for the compositional range $0.44 \leqq x \leqq 1$. In the Fe_2VO_4 ($x = 0.5$), the curve agrees well with that examined by Bernier and Poix (*7*) in a field of 26 000 Oe and down to 40°K. The magnetization for the specimen of $Fe_{1.8}V_{1.2}O_4$ ($x = 0.4$) is shown in Fig. 3b. The curve shows complex behavior. This composition, $Fe_{1.8}V_{1.2}O_4$, also corresponds to the minimum value of the magnetic moment (0.044 μ_B) at 77°K, as will be illustrated in Fig. 5 and tabulated in Table I.

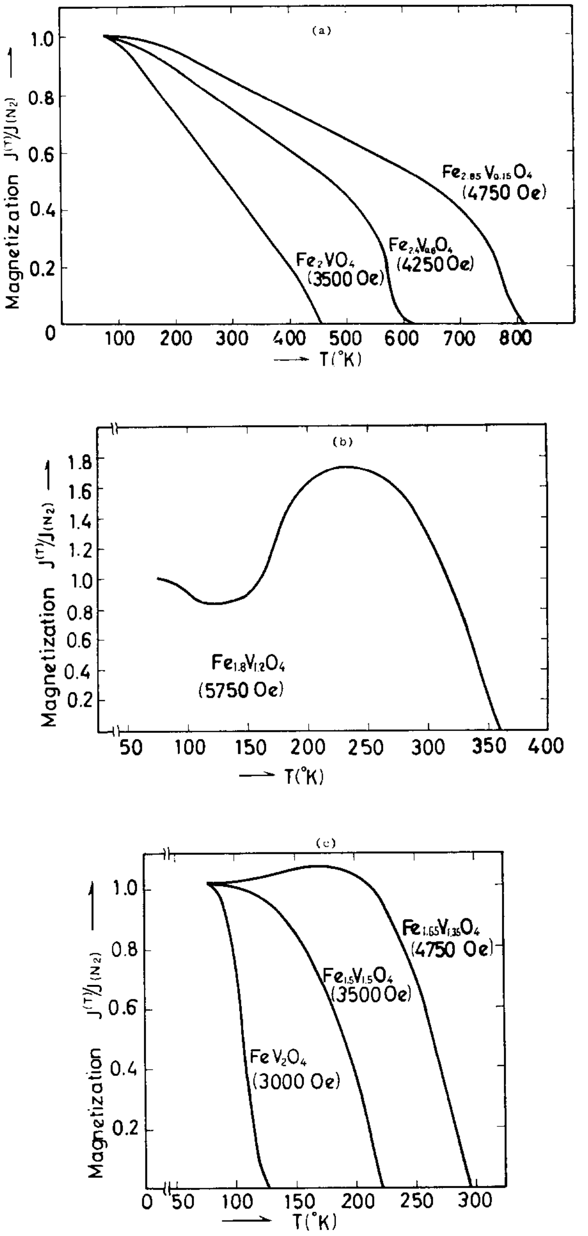

FIG. 3a, b, c. Magnetization curves with temperature for several compositions of spinels taken the magnetization at 77°K as a reference.

Similar $J(T)$ curves were observed in the specimens within $0.33 \leqq x \leqq 0.4$. One of the curves, $Fe_{1.65}V_{1.35}O_4$ ($x = 0.325$), is shown in Fig. 3c. In the specimens within $0 \leqq x \leqq 0.25$, the variations of magnetization are similar to those of examples, $Fe_{1.5}V_{1.5}O_4$ ($x = 0.25$) and FeV_2O_4 ($x = 0$), shown in Fig. 3c. In those specimens, the Curie temperatures are too low to evaluate the value of the saturation magnetization at 0°K from the data obtained above 77°K. Therefore, in these compositional ranges, the measurement of magnetization between liquid helium temperature and the Curie temperature seems to be necessary to ensure the saturation magnetization.

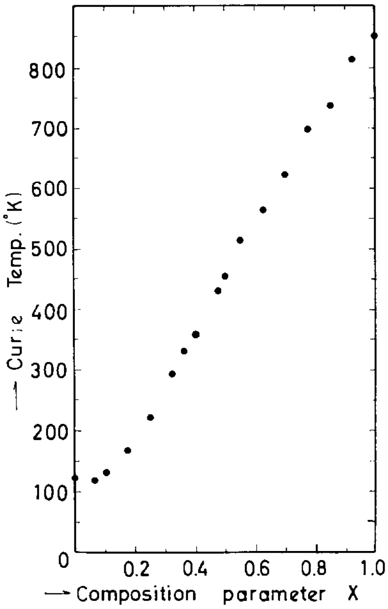

FIG. 4. The Curie temperature vs composition parameter x for the system $Fe_{1+2x}V_{2-2x}O_4$.

The Curie points for the present solid solution are illustrated in Fig. 4 and Table I. As seen in Fig. 4, the Curie points increase almost linearly with x for the system $Fe_{1+2x}V_{2-2x}O_4$ in the range from 0.1 to 1, while they are almost constant in the vicinity of FeV_2O_4. The Curie points of FeV_2O_4 and Fe_2VO_4 are 127 and 454°K, respectively. These values are slightly higher than the data obtained by Wold et al. (6).

Figure 5 illustrates the relationship between the corrected saturation moment in μ_B per formula unit at 77°K and x ($0 \leqq x \leqq 1$) for the system $Fe_{1+2x}V_{2-2x}O_4$. The values of saturation moments are also tabulated in Table I. The magnetic moment decreases almost linearly with decrease of x and becomes almost zero at the composition, $Fe_{1.8}V_{1.2}O_4$; it then increases again toward FeV_2O_4.

In order to consider the cation distributions and the magnetic structure of the system $Fe_{1+2x}V_{2-2x}O_4$ without difficulty, let us divide it into two parts, the subsystems Fe_2VO_4–Fe_3O_4 and FeV_2O_4–Fe_2VO_4.

Magnetite, Fe_3O_4, is well known to be an inverse spinel with ferrous iron in octahedral sites (5). Five

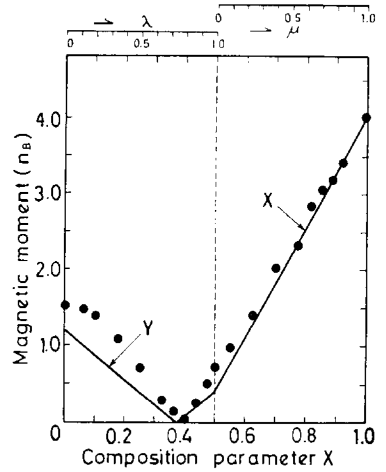

FIG. 5. Relationship between corrected saturation moments in μ_B (Bohr magnetons) per molecule at 77°K and composition parameter μ ($0 \leqq \mu \leqq 1$) and λ ($0 \leqq \lambda \leqq 1$) according to the models of $Fe^{3+}(Fe^{2+}Fe^{3+}_{\mu}V^{3+}_{1-\mu})O_4$ and $Fe^{3+}_{\lambda}Fe^{2+}_{1-\lambda}(Fe^{2+}_{\lambda}V^{3+}_{1-\lambda})O_4$, respectively. ($n_B$ reads μ_B)

models of cation distributions for Fe_2VO_4–Fe_3O_4 solid solution series may be possible as illustrated in Table II, where outside and inside ions of the parenthesis denote ions occupying A (tetrahedral) and B (octahedral) sites, respectively. Mu is the composition parameter, and varies from 0 to 1. The values of magnetic moment Fe^{2+}, Fe^{3+}, and V^{4+} ions are, assuming spin only values, 4.0, 5.0, and 1.0 μ_B per ion, respectively. Goodenough (*17*) has given 1.40 μ_B per ion for the magnetic moment of V^{3+} ions at B site. An equation to calculate magnetic moments for the solid solution Fe_2VO_4–Fe_3O_4 is easily derived from the difference of the moments between A and B sites by assuming antiparallel coupling of sublattice moments between A and B sites and by using the moments for each ion as described above. Equations of magnetic moments for each of five models are also illustrated in Table II, where S_a and S_b represent magnetic moments of A site and B site, respectively. The calculated moments using models of 1, 4, and 5 markedly deviate from the measured moments. On the other hand, the calculated moments using equations for models of 2 and 3 are in reasonable agreement with observed ones.

TABLE II

POSSIBLE CATION DISTRIBUTIONS FOR THE FeV_2O_4–Fe_3O_4 AND EQUATIONS TO CALCULATE MAGNETIC MOMENTS PER MOLECULE WHEN Fe^{3+}, Fe^{2+}, V^{4+} AND V^{3+} ARE GIVEN 5.0, 4.0, 1.0, AND 1.4 μ_B, RESPECTIVELY; μ CHANGES IN THE RANGE $0 \leqq \mu \leqq 1$ AND S_a AND S_b INDICATE THE MOMENTS FOR A SITE AND B SITE RESPECTIVELY

Model	
1	$V^{4+}_{1-\mu}Fe^{3+}_{\mu}(Fe^{2+}Fe^{2+}_{1-\mu}Fe^{3+}_{\mu})O_4$ $X = S_b - S_a = -3.0 \times \mu + 7.0$
2	$Fe^{2+}_{1-\mu}Fe^{3+}_{\mu}(Fe^{2+}Fe^{3+}_{\mu}V^{4+}_{1-\mu})O_4$ $X = S_b - S_a = 3.0 \times \mu + 1.0$
3	$Fe^{3+}(Fe^{2+}Fe^{3+}_{\mu}V^{3+}_{1-\mu})O_4$ $X = S_b - S_a = 3.6 \times \mu + 0.4$
4	$Fe^{3+}_{\mu}V^{3+}_{1-\mu}(Fe^{2+}Fe^{3+})O_4$ $X = S_b - S_a = -3.6 \times \mu + 7.6$
5	$Fe^{2+}_{1-\mu}Fe^{3+}_{\mu}(Fe^{3+}Fe^{2+}_{\mu}V^{3+}_{1-\mu})O_4$ $X = S_b - S_a = 1.6 \times \mu + 2.4$

FeV_2O_4 is known from X-ray diffraction results to be normal with ferrous iron in tetrahedral sites (*4*). Hence, two cation distributions for FeV_2O_4–Fe_2VO_4 solid solution are possible as the results of the above suitable models, 2 and 3.

$$Fe^{2+}(V^{3+}V^{3+})O_4\text{—}Fe^{2+}(Fe^{2+}V^{4+})O_4, \quad \text{(a)}$$

$$Fe^{2+}(V^{3+}V^{3+})O_4\text{—}Fe^{3+}(Fe^{2+}V^{3+})O_4. \quad \text{(b)}$$

The general formula for the cation distribution of (a) can be written as $Fe^{2+}(V^{3+}_{2-2\lambda}Fe^{2+}_{\lambda}V^{4+}_{\lambda})O_4$ ($0 \leqq \lambda \leqq 1$). The equation of magnetic moments on this model is evaluated from the following equation;

$$Y = |S_b - S_a| = |2.2\lambda - 1.2|; \quad (0 \leqq \lambda \leqq 1), \quad (1)$$

where S_a and S_b represent magnetic moments on A and B sites, respectively. Lambda is the compositional parameter varying from 0 to 1. Similarly, the model for cation distributions of (b) can be written as $Fe^{3+}_{\lambda}Fe^{2+}_{1-\lambda}(Fe^{2+}_{\lambda}V^{3+}_{2-\lambda})O_4$. The equation to calculate moments on this model is given by follows;

$$Y = |S_b - S_a| = |1.6\lambda - 1.2|; \quad (0 \leqq \lambda \leqq 1). \quad (2)$$

Equation (2) agrees better with the observed moments than Eq. (1) as shown in Fig. 5 where the data points are taken from Table I. In the vicinity of Fe_2VO_4, lattice parameters, the Curie points and magnetic moments vary continuously with x as shown in Figs. 2, 4, and 5. Therefore, we can not consider remarkedly different cation distributions on either side of Fe_2VO_4. Also, the lattice parameters begin to increase rapidly when compositional parameter x becomes smaller than 0.5. This may be consistent with the assumption of model (b) that Fe^{2+} ions replace Fe^{3+} in A sites. Thus, we may conclude that the cation distributions of $Fe^{3+}(Fe^{2+}Fe^{3+}_{\mu}V^{3+}_{1-\mu})O_4$ and $Fe^{3+}_{\lambda}Fe^{2+}_{1-\lambda}(Fe^{2+}_{\lambda}V^{3+}_{2-\lambda})O_4$ are suitable for Fe_2VO_4–Fe_3O_4 and FeV_2O_4–Fe_2VO_4 subsystems, respectively. As a result, it should be noted that both Fe^{2+} and V^{3+} ions prefer B sites to A sites through all the system of $Fe_{1+2x}V_{2-2x}O_4$ ($0 \leqq x \leqq 1$). The equation of model 2 in Table II and Eq. (2) are indicated by a solid line X and a folded line Y, respectively, in Fig. 5. The measured saturation moments for the FeV_2O_4–Fe_2VO_4 solid solution indicate a significant deviation from the folded line Y in the compositional range FeV_2O_4–$Fe_{1.5}V_{1.5}O_4$. The disagreement between the observed and the calculated saturation moments may be partly due to a noncollinear spin configuration in the FeV_2O_4–Fe_2VO_4 spinel solid solution series and partly due to uncertainty of the corrected saturation moment in the vicinity of FeV_2O_4. Indeed, Menyuk et al. (*18*) and Dwight et al. (*19*) studied the magnetic properties of the normal cubic spinels MnV_2O_4 and CoV_2O_4, and recognized that these spinels have not a Néel type configuration at low temperature (4.2°K). They also mentioned that the effect is attributed to the importance of orbital degeneracy and spin-orbit coupling in connection with V^{3+} ions.

Rossiter (*9*) proposed the model $Fe^{2+}(Fe^{3+}_{\lambda}V^{3+}_{2-\lambda})O_4$ ($0 \leqq \lambda \leqq 1$) for the FeV_2O_4–Fe_2VO_4 solid solution series based on his Mössbauer spectra study. However, the corresponding equation, $Y = |S_b - S_a| = |3.6\lambda - 1.2|$, which assumes ferrimagnetic coupling, deviates extremely from our data. Bernier and Poix (*7*) proposed $Fe^{3+}(Fe^{2+}V^{3+})O_4$ for the Fe_2VO_4 based on the structural and magnetic properties of this compound. Their conclusion is consistent with our study in the composition of Fe_2VO_4.

Thus, it seems that in the FeV_2O_4–Fe_3O_4 solid solution system, Néel's ferrimagnetic AB coupling is sufficiently large to keep linear spin configuration if Fe^{2+} ions occupy half of the B site, but the AB coupling becomes weak and in turn BB coupling becomes compatible with it if V^{3+} ions occupy more than half of the B sites.

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