

A Study on Crystallographic and Mössbauer Spectroscopic Properties of Magnetic Oxide

Seung-Han Choi

Faculty of Natural Science, Kyungsan University, Kyungsan 712-240, Korea

산화물 자성체의 결정학적 및 뫼스바우어 분광학적 특성 연구

최 승 한

경산대학교 자연과학대학 자연과학부

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초 록 산화물 자성체 $(\text{Fe}_2\text{O}_3)_x(\text{Al}_2\text{O}_3)_{1-x}(\text{Ga}_2\text{O}_3)_y\text{SiO}$ 계에 대한 결정구조 및 자기적 특성을 X-선 회절법과 Mössbauer 분광법을 이용하여 연구하였다. Mössbauer 분광법을 통해 Ga 이온의 치환량과 온도변화에 따른 자기구조의 변화를 조사하고 초전도 양자간섭장치(SQUID)에 의한 거시적 자성정보와 비교하였다. X-선 회절법에 의한 결정구조는 Ga 이온의 치환량에 따라 입방정 스피넬 구조에서 사방정 구조로의 결정학적 전이가 관측되었으며 양이온 빈자리가 상당수 포함된 새로운 형태의 페라이트임을 알았다. 비자성 Ga 이온의 치환량 증가로 초상자성 군집체(cluster)가 형성되어 치환전의 준강자성체 질서가 점차로 초상자성 군집체와 공존하는 초상자성체 특성을 보였다. $x > 0.2$ 경우 상온이하 온도영역에서 Mössbauer 스펙트럼은 다양하고 복잡한 형태를 보이는데 이것은 초상자성 군집체의 동결에 의한 것으로 설명된다. 또한 SQUID 측정에서 나타난 50K 이하에서의 급격한 자화값의 감소는 스핀 canting의 효과로 설명된다.

Abstract The crystal structure and magnetic properties of magnetic oxide system $(\text{Fe}_2\text{O}_3)_x(\text{Al}_2\text{O}_3)_{1-x}(\text{Ga}_2\text{O}_3)_y\text{SiO}$ has been studied using X-ray diffraction and Mössbauer spectroscopy. The changes of magnetic structure by the Ga ion substitution and the temperature variation have been investigated using Mössbauer spectroscopy, and the results are compared with those of the SQUID measurements. Results of X-ray diffraction indicated that the crystal structures of the system change from a cubic spinel type to an orthorhombic via the intermediate region. This magnetic oxide system seems to be new kind of spinel type ferrites containing high concentration of cation vacancies. Various and complicated Mössbauer spectra were observed in the samples ($x > 0.2$) at temperatures lower than room temperature. This result could be explained by freezing of the superparamagnetic clusters. On cooling and substitution, magnetic states of the system show various and multicritical properties. Unexpected dip in magnetization curves below 50K was observed in SQUID measurements. It was interpreted as an effect of spin canting including spin freezing or collective spin behavior.

1. Introduction

Spinel ferrites (magnetic oxides) are suitable for studying the various types of magnetic orderings occurring in solids. The interest in these materials stems from their wide industrial applications.¹⁻³⁾ Relatively easy preparation and low cost make these materials widely usable for cores of intermediate- and high-frequency transformers, inductors, loudspeakers and other electromagnetic devices. Their crystal structure consists of an FCC frame of oxygen ions containing two interstitial sites which have tetrahedral (A-site) and octahedral sites (B-site) oxygen coordinations. The interesting physical and chemical properties of spinel ferrites, including their magnetic structure, strongly depend on

the type of cations and the nature of their distribution present in the lattice. Spinel ferrites can have various types of magnetic structure. The main factors responsible for the realization of a particular spin configuration in a two sublattice ferrite are the exchange interactions between the nearest cations. These are the exchange integrals, J_{AA} , J_{AB} , J_{BB} , where A and B denote the tetrahedral and octahedral sites. The strength of three competitive exchange interactions can be individually controlled by a proper choice of constituent cations. Generally all those three exchange interactions are negative with $J_{AB} > J_{BB} > J_{AA}$. When $J_{AB} \gg J_{BB}$ and J_{AA} , the A- and B-site moments align themselves ferromagnetically but remain antiparallel to each other (Neel's collinear model).

Recently Lee et al.⁴⁾ synthesized a spinel type magnetic oxide $(\text{Fe}_2\text{O}_3)_5(\text{Al}_2\text{O}_3)_4(\text{SiO})$ which is non-stoichiometric spinel ferrite and also strongly deviates from the cation-anion number ratio. This solid solution forms a spinel-like structure and shows well-defined Zeeman sextets. The results can be compared to the magnetic behavior of the mixed ferrites even though it contains a lot of cation vacancies, compared with the prototype spinel ferrites. To author's knowledge, this seems to be another kind of spinel type ferrites. Thus, one may expect an interesting variation in magnetic properties if one substitutes some constituent cations by any other proper cations. In particular it is known that ferrites⁵⁾ which have been sufficiently substituted with non-magnetic ions show significant departures from the Neel's collinear model. Disordered magnetic materials are of great interest due to the multicritical behavior they exhibit. It is because that Ga_2O_3 has the same crystal structure as that of $\alpha\text{-Fe}_2\text{O}_3$, Al_2O_3 (i.e. rhombohedral) and their ions are in the same charge state, Ga_2O_3 is very interesting substituent in $(\text{Fe}_2\text{O}_3)_5(\text{Al}_2\text{O}_3)_4(\text{SiO})$. The Ga^{3+} and Al^{3+} cations have similar property but occupy different crystallographic sites. Various changes are also expected by substituting Ga_2O_3 because Ga is nonmagnetic ion.

In this work $(\text{Fe}_2\text{O}_3)_5(\text{Al}_2\text{O}_3)_{4-x}(\text{Ga}_2\text{O}_3)_x\text{SiO}$ ($x = 0.2 \sim 4.0$) has been prepared and the structure and magnetic properties have been investigated by X-ray diffractometry, Mössbauer spectroscopy and SQUID.

2. Experimental

The $(\text{Fe}_2\text{O}_3)_5(\text{Al}_2\text{O}_3)_{4-x}(\text{Ga}_2\text{O}_3)_x\text{SiO}$ ($x = 0.2 \sim 4.0$) powder samples were prepared by a direct reaction method as shown in Fig. 1. The purity of $\alpha\text{-Fe}_2\text{O}_3$, Al_2O_3 , Ga_2O_3 , and SiO were more than 99.99%. They were dried and thoroughly mixed in agate mortar with varying Ga_2O_3 amounts ($0.2 \leq x \leq 4.0$). To increase the reaction rate, the mixtures were pressed into the form of pellets using a hydraulic press at 11 tons/cm². These pellets were sealed into evacuated quartz tubes, heated at 1100 °C for 48 hours and then quenched in liquid nitrogen.

To obtain a homogeneous material, it was necessary to grind the samples after the first firing and to press the powder into a pellet before the second firing. This procedure was repeated two times and then the samples were used for X-ray analysis and Mössbauer experiments in powder form.

Crystal structure of the sintered samples was investigated by the X-ray diffraction at room temperature

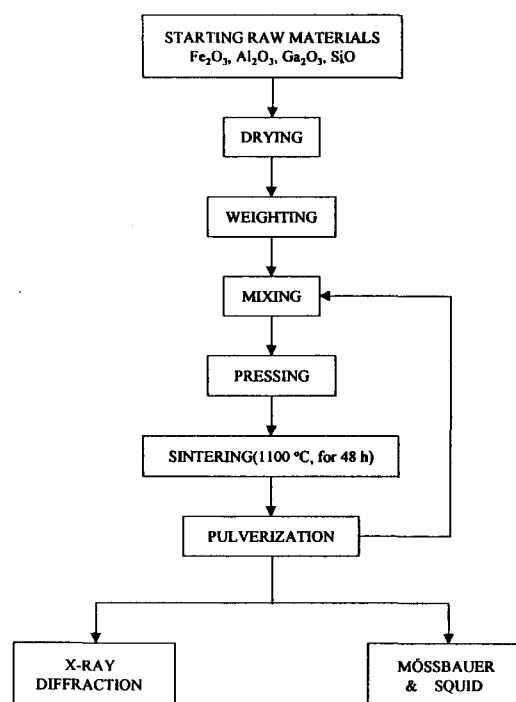


Fig. 1. Block diagram of $(\text{Fe}_2\text{O}_3)_5(\text{Al}_2\text{O}_3)_{4-x}(\text{Ga}_2\text{O}_3)_x\text{SiO}$ ($x = 0.2 \sim 4.0$) powder sample preparation procedure.

using Geiger-flex (M-3A) diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$), $\text{CoK}\alpha$ ($\lambda = 1.7903 \text{ \AA}$) radiation.

Mössbauer spectra were obtained using a conventional constant acceleration spectrometer (A-1 model, ASA Inc., Austin, U.S.A.). The spectrometer was calibrated using iron foil. A 5mCi ^{57}Co in a palladium matrix and a 10mCi ^{57}Co in a rhodium matrix at room temperature (R.T.) were used as γ -ray source.

Magnetization curves were obtained in a zero-field cooled (ZFC) specimens by applying a magnetic field of 1000e and monitoring the magnetic moment using a commercial SQUID magnetometer.

A least-square fit computer program with Lorentzian components was used to determine the Mössbauer parameters and the Zeeman patterns could be fitted assuming each pattern consists of six Lorentzian lines.

3. Results and Discussion

Figure 2 shows X-ray diffraction patterns of $(\text{Fe}_2\text{O}_3)_5(\text{Al}_2\text{O}_3)_{4-x}(\text{Ga}_2\text{O}_3)_x\text{SiO}$ ($x = 0.2 \sim 4.0$) powder samples. They show that the crystal structure is transformed from a cubic spinel type ($x = 0.2 \sim 2.0$) to an orthorhombic phase ($x = 4.0$) via the intervening region ($x = 3.0$). JCPDS (Joint Committee on Powder Diffraction Standards) cards and Hull-Davey charts were used to determine the Miller indices and crystal structure. The lattice constants have been found by extrapolation

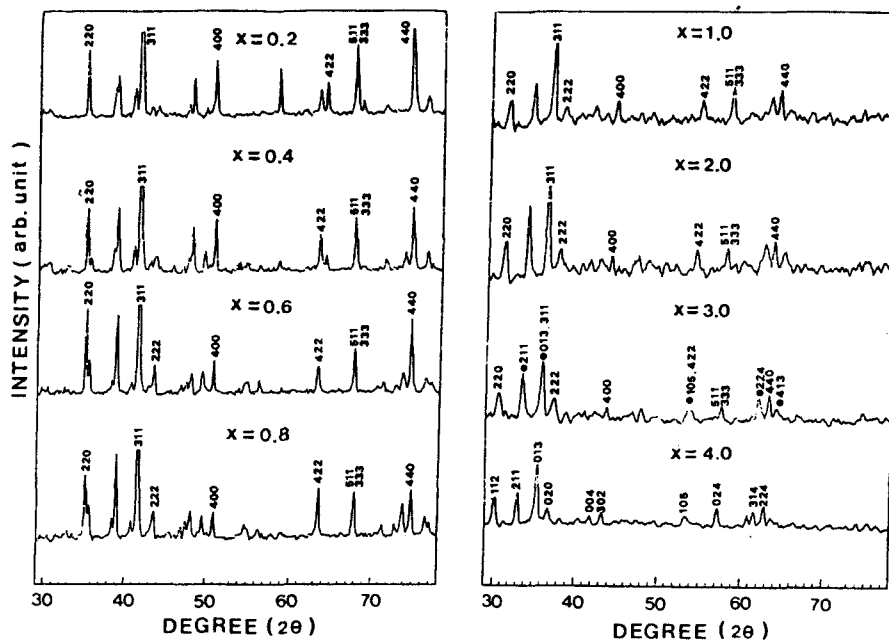


Fig. 2. X-ray diffraction patterns of $(\text{Fe}_2\text{O}_3)_x(\text{Al}_2\text{O}_3)_{4-x}(\text{Ga}_2\text{O}_3)_x\text{SiO}$ for $0.2 \leq x \leq 0.8$ ($\text{CoK}\alpha$) and $1.0 \leq x \leq 4.0$ ($\text{CuK}\alpha$). (● denotes orthorhombic phase) The samples were sintered at 1100°C for 48 hours and then quenched in liquid nitrogen.

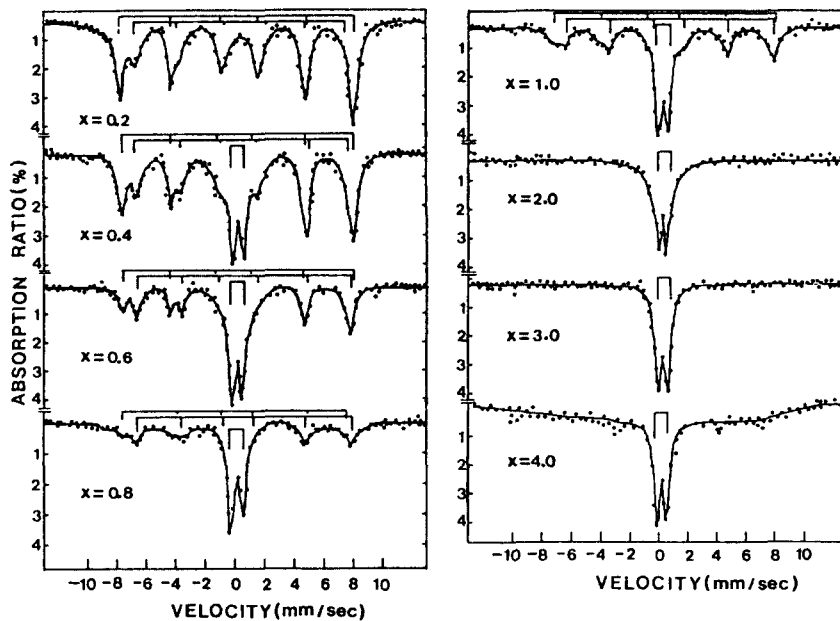


Fig. 3. Zero-field Mössbauer spectra of $(\text{Fe}_2\text{O}_3)_x(\text{Al}_2\text{O}_3)_{4-x}(\text{Ga}_2\text{O}_3)_x\text{SiO}$ ($x = 0.2 \sim 4.0$) at room temperature.

using Nelson-Riley function and then they decrease slightly with increasing Ga concentration although the Ga^{3+} ionic radii are larger than those of Al^{3+} ions. This can be attributed to a higher degree of covalency in Ga-O bonds than in Al-O and Fe-O bonds, which can also be explained with the help of the observed Mössbauer parameters.

The zero-field Mössbauer spectra of the samples ($x = 0.2 \sim 4.0$) have been obtained at R.T. as shown in Fig. 3. Various and anomalous lineshapes show slight nar-

rowing in line-widths of Zeeman sextets. This line-narrowing, as shown Fig. 4, seems to be attributed to the change⁶⁾ in the mean lifetime of the excited state.

Only the spectrum of $x = 0.2$ is consists of a superposition of two Zeeman sextets which are identified to arise from Fe^{3+} ions at tetrahedral(A-) sites and octahedral(B-) sites. A strong doublet with two sextets appears for $x = 0.4 \sim 1.0$ and consequently varies into a doublet for $x \geq 2.0$ without sextets.

To elucidate the origin of the doublet, the peak area

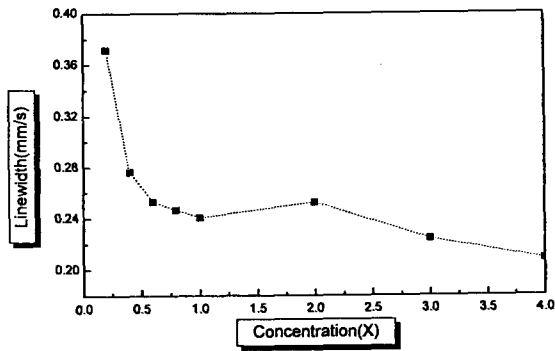


Fig. 4. The variations of line-width by Ga concentration in $(\text{Fe}_2\text{O}_3)_x(\text{Al}_2\text{O}_3)_{1-x}(\text{Ga}_2\text{O}_3)_x\text{SiO}$.

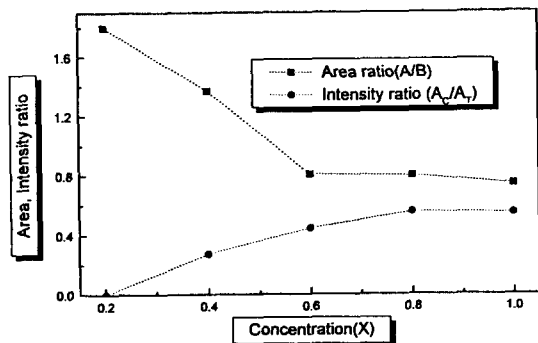


Fig. 5. The peak area ratio of A-, B-sites and intensity ratio of central line (A_c), total spectral line (A_T) in $(\text{Fe}_2\text{O}_3)_x(\text{Al}_2\text{O}_3)_{1-x}(\text{Ga}_2\text{O}_3)_x\text{SiO}$ ($x=0.2\sim 1.0$).

ratio of the doublet to the total lines (A_c/A_T) has been calculated as a function of x and also the temperature behavior of A_c/A_T has been considered. This is important since a large increase in A_c/A_T could mean the presence of a large number of superparamagnetic clusters. Figure 5 shows the changes of A_c/A_T with Ga concentration and then increases considerably in the range of $x \geq 0.2$. They show the existence of superparamagnetic clusters, as proposed by Ishikawa,⁷⁾ which exist simultaneously with ferrimagnetic regions in the material. It means that there are ferrimagnetic regions separated magnetically from matrix since the region is surrounded by nonmagnetic Ga ions. And also area ratio (A/B), as shown in Fig. 5, gives further evidence of the rapid evolution of the frustration with selective sublattice dilution. Other possible explanations for central line like the presence of any impurity, entropic spin⁸⁾ and domain wall oscillation or relaxation effect⁹⁾ were ruled out considering A_c/A_T nature.

Above mentioned results are explained in terms of the magnetic disorder and insufficient magnetic linkages resulting from the presence of nonmagnetic Ga^{3+} ions. Those clusters are not from ferrimagnetic fine particles but ferrimagnetic regions separated magnetically

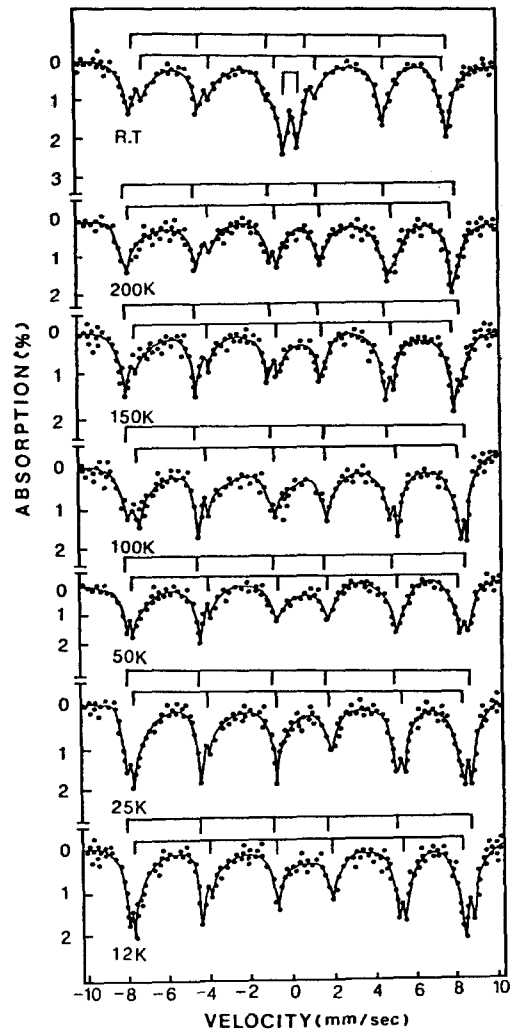


Fig. 6. Mössbauer spectra (12K~R.T) for $x=0.4$ in $(\text{Fe}_2\text{O}_3)_x(\text{Al}_2\text{O}_3)_{1-x}(\text{Ga}_2\text{O}_3)_x\text{SiO}$ by zero-field.

from the matrix since the region is surrounded by nonmagnetic Ga ions. One of the characteristics of superparamagnetic behavior of this sort is the existence of an interaction between the clusters. It shows diluted ferrite properties due to the observation of superparamagnetic behavior which is closely related to semi-spin-glass-like behavior resulting from frustration and cation or bond disorder arise owing to the presence of nonmagnetic ions.

The Mössbauer measurements have shown that the Fe^{3+} ions occupy both sites and also have confirmed the strong existence of Ga^{3+} ions on A-sites because of changing B-sites peak area with respect to assuming constant A-sites area as shown Fig. 5.

Figures 6, 7 and 8 show interesting Mössbauer spectra of samples ($x=0.4, 0.6$ and 0.8 , respectively), which show the temperature dependence of magnetic behavior from the low temperature (12K) to the room temperature. There are interesting common features to

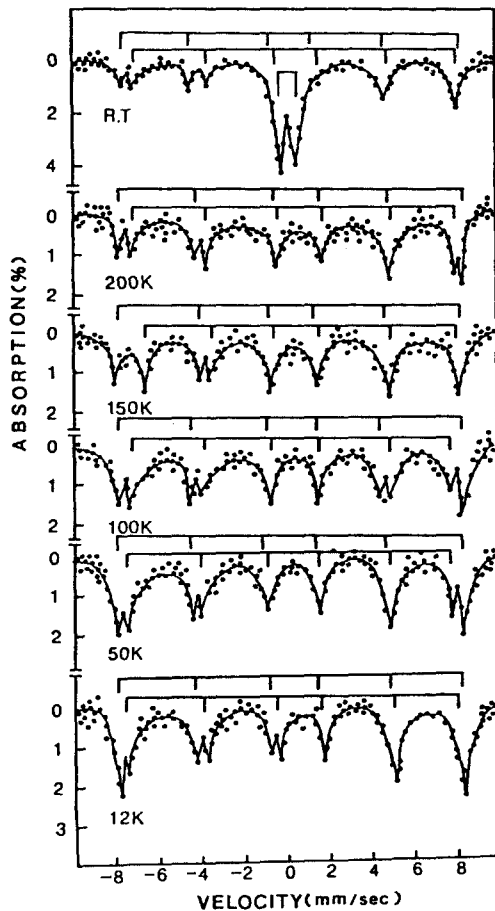


Fig. 7. Mössbauer spectra (12K~R.T) for $x=0.6$ in $(\text{Fe}_2\text{O}_3)_5(\text{Al}_2\text{O}_3)_4-(\text{Ga}_2\text{O}_3)_3\text{SiO}$ by zero-field.

be considered: (1) the cause of the line broadening of the magnetic component, (2) the behavior of the clusters is clearly distinctive between low and high temperature variation (3) the disappearance of a strong doublet at low temperature.

On cooling, these superparamagnetic clusters would block into a state referred to as "a complicated structure" by Ishikawa mode.⁷⁾ This is because the clusters are inevitably coupled with each other through the exchange interaction, so that at sufficiently low temperatures the magnetic moments of the superparamagnetic clusters arrange in some order. This result also suggests that the aligned spins in the clusters are not thermally agitated to a large extent up to high temperature above room temperature. These clusters may not have the collinear spin configuration within as the near-neighbours are at random. When the intercluster interaction becomes comparable to the thermal energy there is a rapid increase in the magnetic viscosity resulting in the freezing of the clusters. They cause to increase magnetization.

The magnetically ordered phase at low temperatures

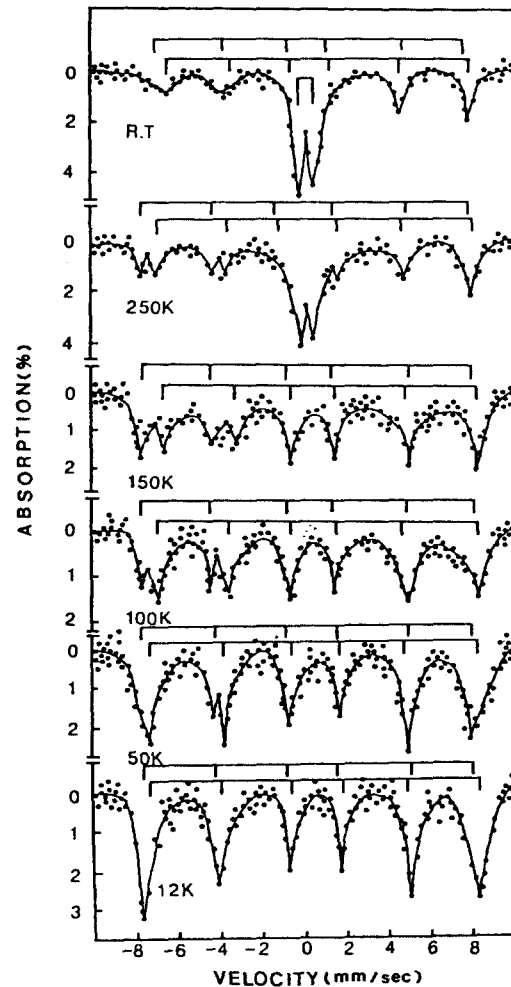


Fig. 8. Mössbauer spectra (12K~R.T) for $x=0.8$ in $(\text{Fe}_2\text{O}_3)_5(\text{Al}_2\text{O}_3)_4-(\text{Ga}_2\text{O}_3)_3\text{SiO}$ by zero-field.

except for 12K seems to be a semi-spin-glass^{10,11)} or a mictomagnet in which Fe^{3+} moments are frozen, coupled by long range exchange interactions in addition to the nearest neighbor superexchange interactions i.e. a mixture of frozen spins and frozen clusters. The well resolved hyperfine splittings characteristic of the magnetically ordered phase except some regions are observed in the samples at extremely low temperatures (12K).

To understand the properties of the magnetic behavior at low temperature, SQUID measurements were performed in the temperature range of R.T.~4.2K under the $H_{ext}=1000\text{Oe}$ for $x=0.2, 0.4,$ and 1.0 as shown in Fig. 9. Magnetization values rapidly decrease at temperatures below 50K for all samples. It was interpreted as an effect of spin canting including spin freezing¹²⁻¹⁴⁾ or superparamagnetic effect (collective spin behavior). The nonlinear increasing behavior of magnetization with the increase of Ga ions is well interpreted as the existence of superparamagnetic clusters.⁵⁾ Above mentioned

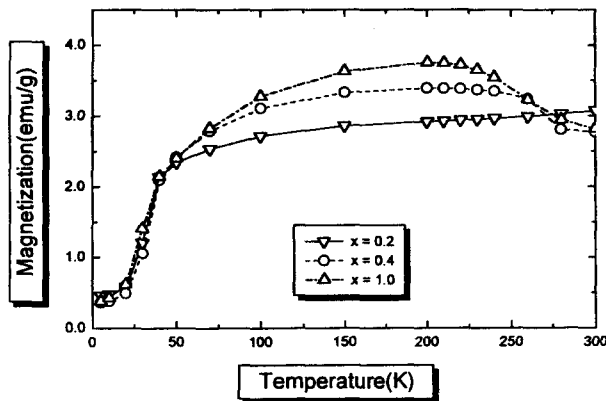


Fig. 9. Magnetization curves by SQUID for $x=0.2, 0.4, 1.0$ in $(\text{Fe}_2\text{O}_3)_5(\text{Al}_2\text{O}_3)_{4-x}(\text{Ga}_2\text{O}_3)_x\text{SiO}$ ($4.2\text{K}\sim\text{R.T}$), which were obtained in a zero-field cooled (ZFC) by applying a magnetic field of 100Oe.

anomalous dip behavior of magnetization may be due to a more complex exchange process which leads to development of canted spin structure and thus they are strong evidence for a canted structure. However it is difficult to distinguish between a Local Canted Spin or a Yafet-Kittel-type structure. The canting is strongly temperature dependent owing to the excitation of surface spin waves. Eventually magnetization results could be understood in terms of the temperature evolution of the spin-spin correlation within and between groups of spins or clusters.

4. Conclusions

The crystal structure and magnetic properties of magnetic oxide system $(\text{Fe}_2\text{O}_3)_5(\text{Al}_2\text{O}_3)_{4-x}(\text{Ga}_2\text{O}_3)_x\text{SiO}$ has been studied using X-ray diffraction and Mössbauer spectroscopy. Results of X-ray diffraction indicated that the crystal structures are transformed from a cubic spinel type ($x=0.2\sim 2.0$) to an orthorhombic phase ($x=4.0$) via the intervening region ($x=3.0$).

A strong doublet with two sextets appears for $x=0.4\sim 1.0$. They shows the existence of superparamagnetic clusters. Various and complicated Mössbauer spectra were observed in the samples for $x>0.2$ at temperatures lower than room temperature. This result could be explained by freezing of the superparamagnetic clus-

ters. On cooling and substitution, magnetic states of the system show various and multicritical properties. This magnetic oxide system seems to be new kind of spinel type ferrites containing high concentration of cation vacancies.

Unexpected dip in magnetization curves below 50K was observed in SQUID measurements. It was interpreted as an effect of spin canting including spin freezing or collective spin behavior.

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