Iron Clustering and The Magnetic Properties in α-Al_2O_3 Crystals after Iron Implantation to High Doses

N. Hayashi[A], I. Sakamoto[B], H. Tanoue[B], H. Wakabayashi[C], and T. Toriyama[C]

[A] Research Center of Ion Beam Technology, Hosei University, 3-7-2 Kajinochou, Koganei-shi, Tokyo 184-8584, Japan

[B] Electrotechnical Laboratory, 1-1-4Umezono, Tsukuba-shi, Ibaraki 305-0075, Japan

[C] Musashi Institute of Technology, 1-28-1, Tamazutsumi, Setagaya-ku, Tokyo 158-8557, Japan

（Abstract）

Magnetization and magnetoresistance were studied in iron-ion-implanted aluminum oxide crystals. The implantation was done up to a total dose of 3.5×10^{17} ions/cm^2 into Al_2O_3 substrates with projectile energy of 100 keV. Using conversion electron Mössbauer spectroscopy, it is shown that most of the implanted ions precipitate as α-Fe clusters and that the nano-size clusters exhibit a transition from superparamagnetic to ferromagnetic state at the dose range of $(1.5 – 2.0) \times 10^{17}$ ions/cm^2. A maximum magnetoresistance ratio of 7.5 % was observed around a dose of 1.5×10^{17} ions/cm^2 at a field of H = 1.2 T.

1. Introduction

Ion implantation in insulating refractory oxides induces very complex structural changes due to high-density cascades and special chemical effects due to low solubility of impurities. This leads to formation of impurity-point defect complexes at low doses and nano-sized composites of metallic phase clusters at higher doses [1]. Thus, the production of magnetic-buried-granular layers can be achieved through the implantation of magnetic ions. We have found that the surface layer of α-Al_2O_3 crystals implanted with Fe ions to a dose of 1.0×10^{17}ions/cm^2 exhibits giant magnetoresistance (GMR)

properties and suggested that the eminent magnetic properties in the implanted layer are induced by superparamagnetic precipitates of implanted ions [2].

In this study the magnetic properties of the nano-clusters were investigated in the Fe/Al_2O_3 granular system formed by implantation to higher doses such as 3.5×10^{17} ions/cm^2. Conversion electron Mössbauer spectroscopy (CEMS) shows that ferromagnetic lines appear at a dose of 1.5×10^{17} ions/cm^2, indicating an increase in the clusters' size and the start of the blocking of superparamagnetic relaxation at room temperature.

2.Experimental

Implantation into R-cut α-Al_2O_3, tilted 5^o with respect to the ion beam, was performed at room temperature with 100 keV ^{56}Fe and/or ^{57}Fe ions up to dose of 3.5×10^{17} ions/cm^2. The projected range of implanted ions was estimated as 50 nm by TRIM code. The magnetization curves were measured with a vibrating sample magnetometer (VSM) and magnetoresistance (MR) was measured using a DC method at room temperature. CEMS was measured with a He—4%CH_4 gas flow proportional counter, using 740 MBq ^{57}Co source in Rh matrix. The spectra were analyzed by least-squares fitting with overlapping Lorentzians.

3.Results and Discussions

Fig. 1 shows CEM spectra taken from the granular samples with Fe doses of 1.5×10^{17}, 2.5×10^{17} and 3.5×10^{17} ions/cm^2. A trace of ferromagnetic lines appears in the spectra for a dose of 1.5×10^{17} ions/cm^2, whose evolution suggests an indication of superparamgnetic blocking in some Fe clusters due to the size increase [3]. The central line component located near zero velocity has slightly negative isomer shift (IS) when it was fitted with one singlet. Therefore, as it is sure that the main central component arises from superparamagnetic α-Fe cluster (Fe^0 state), we decomposed the central line to two singlets, i.e. one for Fe^0 with IS = 0 mm/s and another for γ-like Fe clusters with IS = – 0.10 mm/s [4]. Then, the spectra were fitted with the assumption of overlapping Lorenzians which are assumed to

consist of two singlets, two ferromagnetic sextets, and two doublets. The doublets are assigned to two forms of ferrous irons ($Fe^{2+}_{1,\ 2}$), which are supposed to come from iron oxides in the complex form [1]. A distribution in the internal field was postulated for the analysis of one of the sextets, taking account of the size distribution of the Fe clusters. Another magnetic sextet appears in the spectra at higher doses and the proportion in the spectra is small. The small magnetic sextet appears in the spectra with an internal field B_{hf} of about 37 T and IS = 0.4 mm/s. Thus, the states can be assumed to be Fe-Al-oxides phase with the form of $Fe_{2-x}Al_xO_3$, judging from the observation in the Fe-implanted and annealed Al_2O_3 [1].

Fig. 2 shows the changes in B_{hf} of the main α-Fe sextet and relative intensity for main spectral components plotted against doses. It is clearly shown that the spectral parameters change drastically between the implantation of 1.5×10^{17} and 2.0×10^{17} ions/cm^2, e.g., the ferromagnetic phase grows at the expense of superparamagnetic Fe^0 clusters at the dose range. At a dose of 1.5×10^{17} ions/cm^2 the distribution of the α-Fe clusters' size has been estimated by analysis of CEMS spectra measured with applied external magnetic fields, and the two most probable values obtained are 3-4 nm and 5-6 nm in diameter [4]. The former size is supposed to be near the threshold for the particles to be superparamagnetic.

Fig.3 shows the magnetization curves measured for the Fe ion implanted to three doses of 1.5×10^{17}, 2.0×10^{17}, and 3.0×10^{17} ions/cm^2, where the solid and broken curves denote the magnetization when applying in-plane and perpendicular fields, respectively. At a dose of 1.5×10^{17} ions/cm^2 we can see ferromagnetic characteristics in the loop of magnetization curves, especially for in-plane fields, which are consistent with the CEMS measurement: that is, the ferromagnetic characteristics superpose superparamagnetic magnetization with the loop of nonhysteresis and unsaturation. At higher doses, where superparamagnetic relaxation is blocked at room temperature, the characteristics of ferromagnetism in the loop are clearer. The difference between the curves for in-plane and perpendicular

fields becomes more eminent for higher implantation doses, and the anisotropy is considered to be caused by shape anisotropy since the formation of platelets elongated in the implanted plane has been observed with TEM observations by McHargue et al. [1]. However, at a dose of 3.0×10^{17} ions/cm^2, we can see a hysteresis for the magnetization for perpendicular field suggesting that the clusters increase in size and results in some changes to their shapes with increasing doses.

Fig. 4 shows MR curves for doses of 1.5×10^{17} to 3.0×10^{17} ions/cm^2, measured with external fields H parallel to the sample face, i.e. to the implantation layers. The MR ratio is defined by relative changes of resistivity with H [2]. It should be noted that the MR ratio obtained for the samples implanted to a dose of 1.5×10^{17} ions/cm^2 is as high as 7.5 %. In the granular layer the GMR effect is considered to be induced by the spin dependent tunneling between the nano-size clusters. It is remarkable that even after the formation of ferromagnetic clusters the Fe/Al_2O_3 granules show a rather high MR ratio at 3.0×10^{17} ions/cm^2. This suggests that tunneling conduction still works in ferromagnetic clusters. It should be noted that granular films by sputtering co-deposition showed MR ratio of 3 - 5 % at most [5, 6], indicating the superiority of the ion implantation techniques.

4. Conclusion

CEMS has shown that most of the implanted Fe ions precipitate as nano-size clusters in α- Al_2O_3 matrices and that the clusters exhibit a transition from superparamagnetic to ferromagnetic state at a dose range of $(1.5 – 2.0) \times 10^{17}$ ions/cm^2. The change in magnetization and magnetoresistance in the granular layers were observed to be accompanied by transition, i.e., the blocking of superparamagnetic relaxation. A high MR ratio of 7.5 % for H = 1.2 T is observed at around a dose of 1.5×10^{17} ions/cm^2.

References

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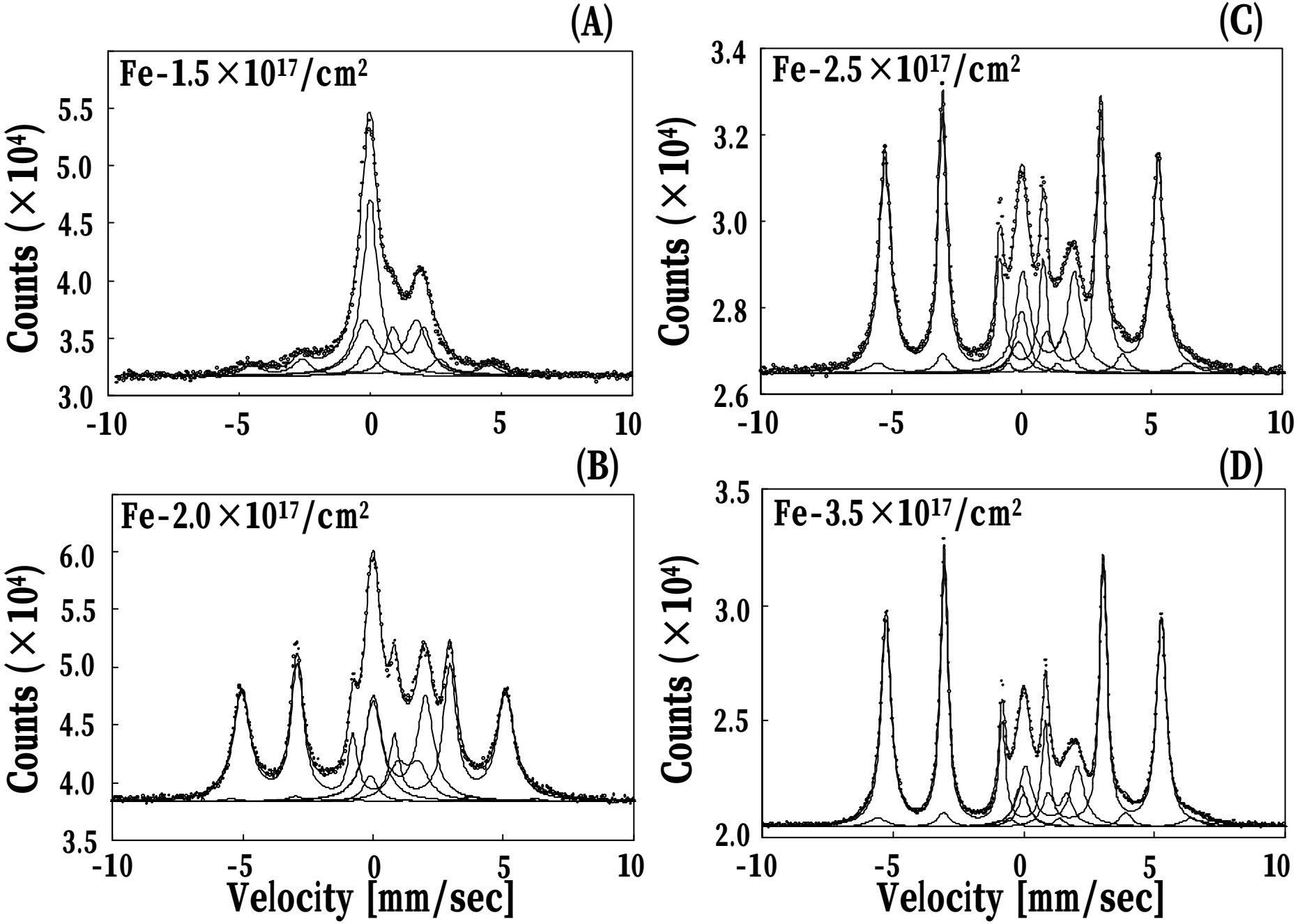
Figure Captions

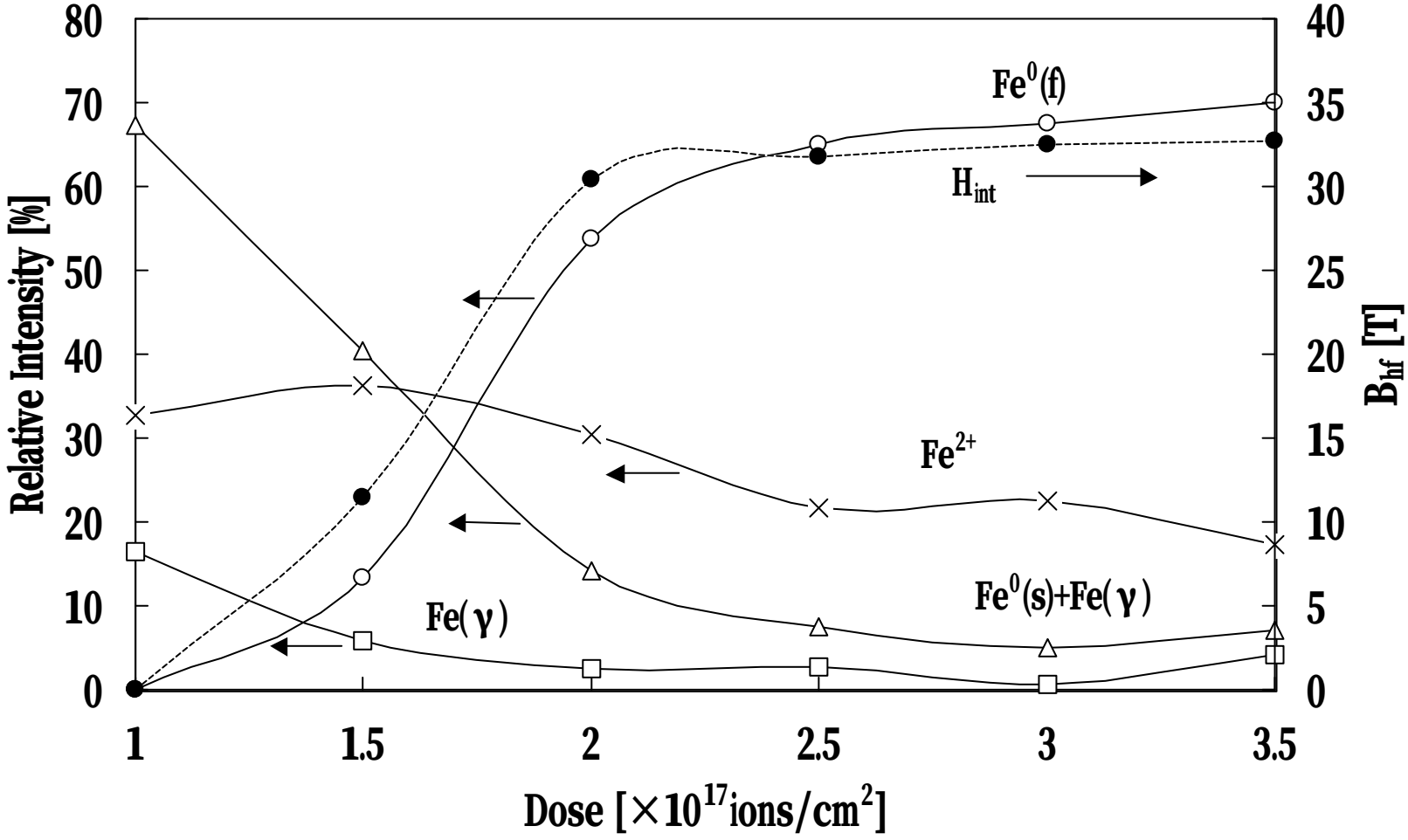
Fig. 1 : CEM spectra for Fe-ions implanted α-Al_2O_3 to doses of (A) 1.5×10^{17}, (B) 2.0×10^{17}, (C) 2.5×10^{17} , and (D) 3.5×10^{17} ions/cm^2.

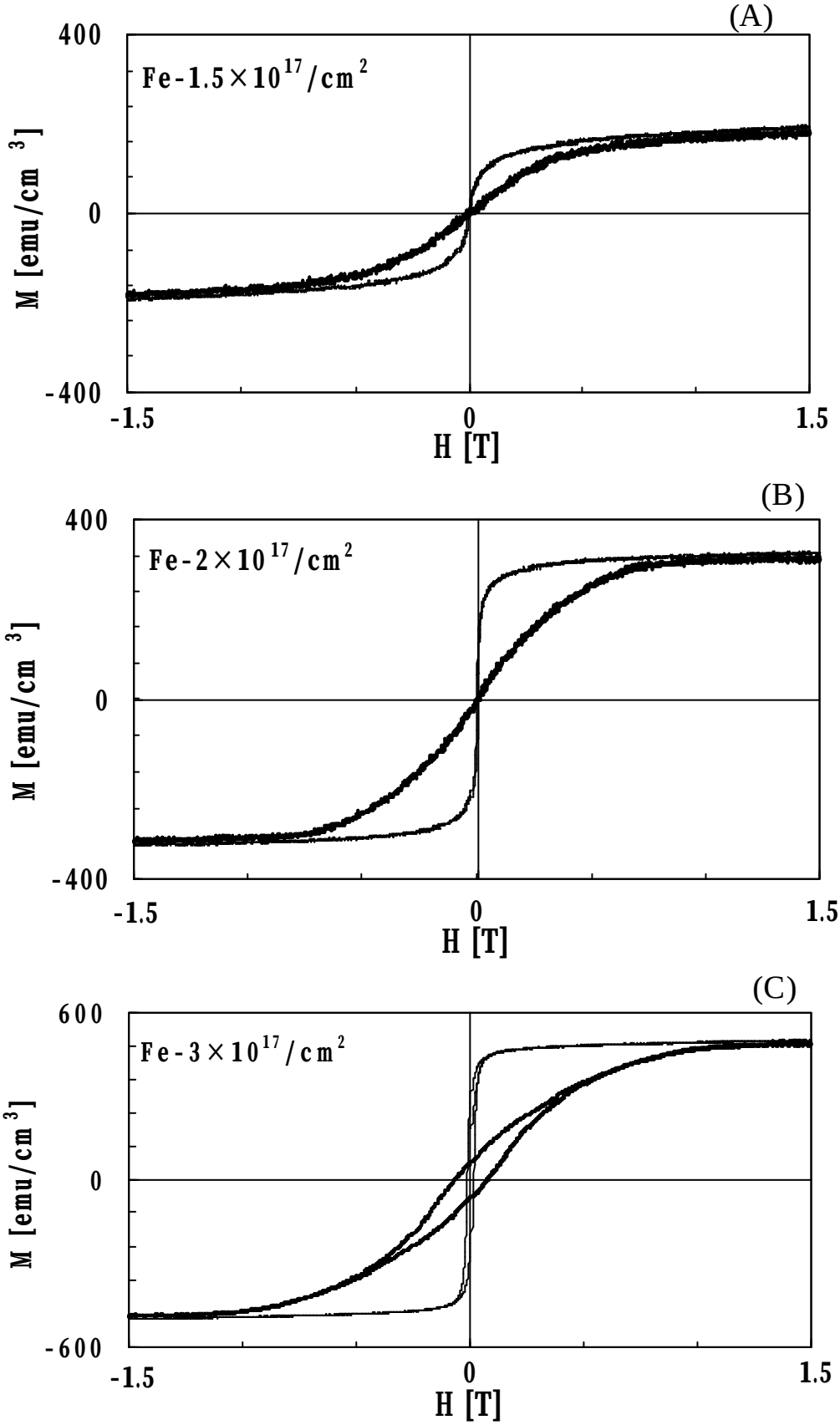
Fig. 2 : Changes of B_{hf} for α-Fe sextet and relative intensity for the main spectral components plotted against Fe-ion doses.

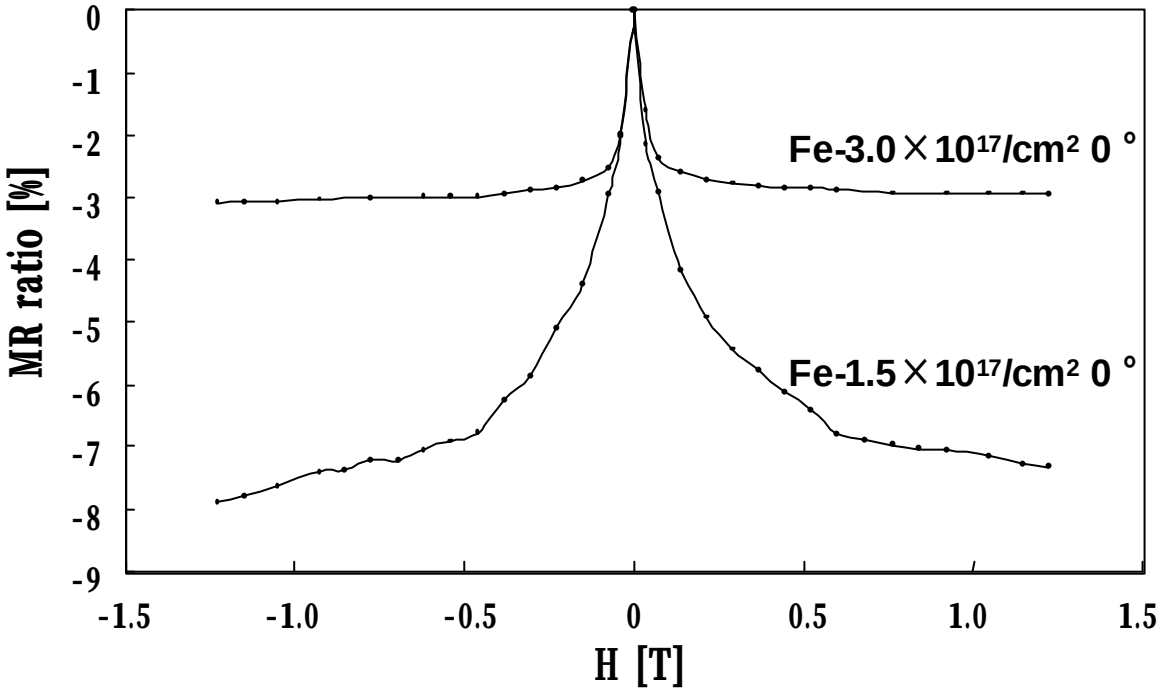
Fig. 3 : Magnetization curves for Fe implanted α-Al_2O_3 to (A) 1.5×10^{17}, (B) 2.0×10^{17}, and (C) 3.0×10^{17} ions/cm^2.

Fig. 4 : Magnetoresistance curves for Fe implanted α-Al_2O_3 to two doses of $1.5 \times 10^{17}$and 3.0×10^{17} ions/cm^2.


(A)
Fe-1.5×10^17/cm^2
Counts (×10^4)
5.5
5.0
4.5
4.0
3.5
3.0
-10
-5
0
5
10
(C)
Fe-2.5×10^17/cm^2
Counts (×10^4)
3.4
3.2
3.0
2.8
2.6
(B)
Fe-2.0×10^17/cm^2
Counts (×10^4)
6.0
5.5
5.0
4.5
4.0
3.5
Velocity [mm/sec]
(D)
Fe-3.5×10^17/cm^2
Counts (×10^4)
3.5
3.0
2.5
2.0
Velocity [mm/sec]


80
70
60
50
40
30
20
10
0
Relative Intensity [%]
40
35
30
25
20
15
10
5
0
B_{hf} [T]
1
1.5
2
2.5
3
3.5
Dose [×10^{17}ions/cm^2]
Fe^0(f)
H_{int}
Fe^{2+}
Fe^0(s)+Fe(γ)
Fe(γ)


(A)
400
Fe-1.5×10^17/cm^2
0
-400
M [emu/cm^3]
-1.5
0
1.5
H [T]
(B)
400
Fe-2×10^17/cm^2
0
-400
M [emu/cm^3]
-1.5
0
1.5
H [T]
(C)
600
Fe-3×10^17/cm^2
0
-600
M [emu/cm^3]
-1.5
0
1.5
H [T]


0
-1
-2
-3
-4
-5
-6
-7
-8
-9
MR ratio [%]
-1.5
-1.0
-0.5
0
0.5
1.0
1.5
H [T]
Fe-3.0×10¹⁷/cm² 0 °
Fe-1.5×10¹⁷/cm² 0 °