Bull. Inst. Chem. Res., Kyoto Univ., Vol. 61, No. 4, 1983

Magnetic and Dielectric Relaxations in Ferrites

Kozo Iwauchi

Received July 26, 1983

Dielectric relaxations are observed near 30 K for $Mn_xZn_yFe_zO_4$, (x, y, z)=(0.47, 0.48, 2.05), (0.63, 0.31, 2.06), (0.53, 0.43, 2.04) and (0.4, 0, 2.6) powder samples precipitated from aqueous solution. These relaxations are considered to be caused by electron hopping between ferrous and ferric ions. All these MnZn ferrites show no magnetic relaxation in the temperature range from 4.2 K to room temperature though $Mn_{0.4}Fe_{2.6}O_4$ powder shows magnetic relaxation at about 30 K. Superparamagnetic particles coexisting in MnZn ferrite powder prevent the observation of magnetic relaxation.

KEY WORDS: Magnetic relaxation/ Dielectric relaxation/ Ferrite/

1 INTRODUCTION

Magnetic and dielectric relaxations have been reported in Fe_3O_4 and several ferrites which contain ferrous ions[1),2)]. Electron hopping between ferrous and ferric ions was considered to be the origin of these relaxations.[3,4)] In Fe_3O_4 sintered sample magnetic and dielectric relaxations were observed at about 50 K. In the powder sample of Fe_3O_4 precipitated from aqueous solution containing ferrous ions dielectric and magnetic relaxations were observed at about 30 K, with the distribution of relaxation times of these relaxations being in a skewed arc type. In magnetic and dielectric relaxations of the sintered compacts of MnZn ferrites skewed arc type of relaxation times was obtained and the magnetic relaxation was observed at lower (20 K) temperature than dielectric one (35–60 K). However, the sintered sample and single crystal of these ferrites have very large electrical conductivity, and therefore dielectric measurement is very difficult above 77 K. In this paper I present the result of dielectric and magnetic measurements of MnZn ferrite and Mn ferrite powder in the temperature range from 4.2 K to 300 K. Magnetic and dielectric relaxations are observed at about 30 K for Mn ferrite powder. MnZn ferrite powders show no magnetic relaxation in the temperature range of 4.2 K to 300 K, though dielectric relaxations are observed for all these powder samples at about 30 K. Mössbauer spectra of these powder precipitates indicate the existence of paramagnetic component which prevents observation of the magnetic relaxations.

2 EXPERIMENTALS

Powder samples MZ1, MZ2, MZ3 and MZ4, the composition of which is listed in Table I, were obtained as the precipitates from aqueous solution containing Fe^{++}, Mn^{++}, Zn^{++} ions by adding NaOH solution.[5,6)] X-ray diffraction of MnZn ferrites showed broad background around the Bragg peaks which indicates the existence of small particle with superparamagnetic character. Mössbauer spectra of these MnZn

岩内幸蔵：Laboratory of Dielectrics, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

Table I. Composition of samples

Sample	Composition
MZ1	$Mn_{0.47}Zn_{0.48}Fe_{2.05}O_4$
MZ2	$Mn_{0.63}Zn_{0.31}Fe_{2.06}O_4$
MZ3	$Mn_{0.53}Zn_{0.43}Fe_{2.04}O_4$
MZ4	$Mn_{0.4}Fe_{2.6}O_4$

ferrites showed ferrimagnetic sextet spectrum superposed on paramagnetic spectrum, while $Mn_{0.4}Fe_{2.6}O_4$ (MZ4 which is called Mn ferrite hereafter) powder showed only sextet Mössbauer spectrum. For dielectric measurement powder samples were compressed under the pressure of 1500 kg/cm^2 in a powder cell produced by an Ando Electric Co.. In order to remove the effect of water on dielectric constant, powder samples were evacuated for several hours in the dielectric cell. For magnetic susceptibility measurement samples with troidal shape were prepared by compressing precipitate powders and solidification with Araldite resin. Dielectric constant and magnetic susceptibility were measured by use of an Ando Electric TR-1C bridge and YHP model 4741A LCR meter.

3 RESULTS AND DISCUSSIONS

MnZn ferrites used in this experiment had iron concentration of 50–55 mol% which is the most useful concentration as commercial soft magnetic MnZn ferrites because of high permeability. MnZn ferrites obtained by the precipitation from aqueous solution have homogeneous ion distribution compared with those by the dry method which makes ferrites by calcination of α-Fe_2O_3, $MnCO_3$ and ZnO. MnZn ferrites obtained by the calcination of these precipitates have uniform ion distribution and therefore good quality. These MnZn ferrites contain some concentration of ferrous ions. Figure 1 shows the temperature dependence of the dielectric constant of MZ1 powder sample. Two dielectric relaxations are seen in this figure at 30 and 300 K. Dielectric relaxations near 30 K is more clearly shown

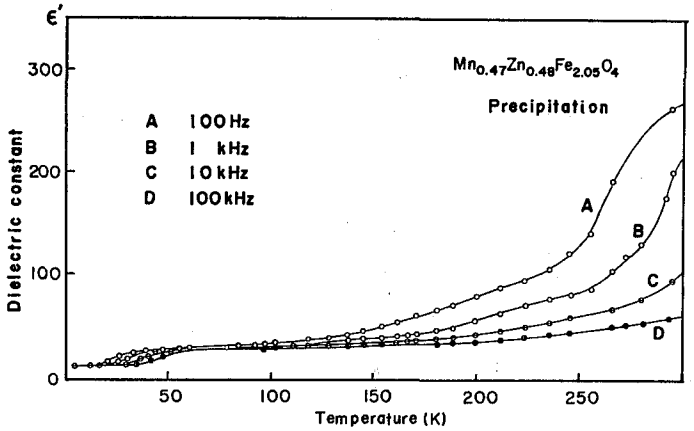

Fig. 1. Temperature dependence of dielectric constant of MZ1.

in Fig. 2. Dielectric dispersion of this ferrite was measured at 37 K as shown in Fig. 3. The Cole-Cole type distribution of relaxation times was found for this dispersion. Dielectric constant is 23 at lower frequency and 10 at higher frequency. Electrical conductivity changes greately from 10^{-11} at 20 Hz to 10^{-7} at 1 MHz. Figure 4 shows the dielectric dispersion of MZ2 powder sample at 32.7 K. Relaxation intensity is about 12 which is nearly equal to that of MZ1 powder sample. Conductivity of MZ2 showed about the same change as that of MZ1 in the frequency range from 20 Hz to 1 MHz. The same kind of dielectric dispersion was observed for MZ3 powder sample. In these three MnZn ferrite powder samples dielectric relaxation intensity is about 20 and conductivity is very low (10^{-11} S/cm) at lower frequencies, while sintered samples of these ferrites had very large dielectric constant and conductivity as shown in Fig. 5. In Fig. 5 a dielectric relaxation is found near 60 K. The sintered ferrites exhibited the skewed arc type of distribution of relaxation times in the dielectric relaxation. Since these dielectric relaxations were not found for α-Fe_2O_3 and ferrites without ferrous ions,[2] electron hopping between ferrous and ferric ions had been considered to be the origin of the relaxation. However, sintered ferrites

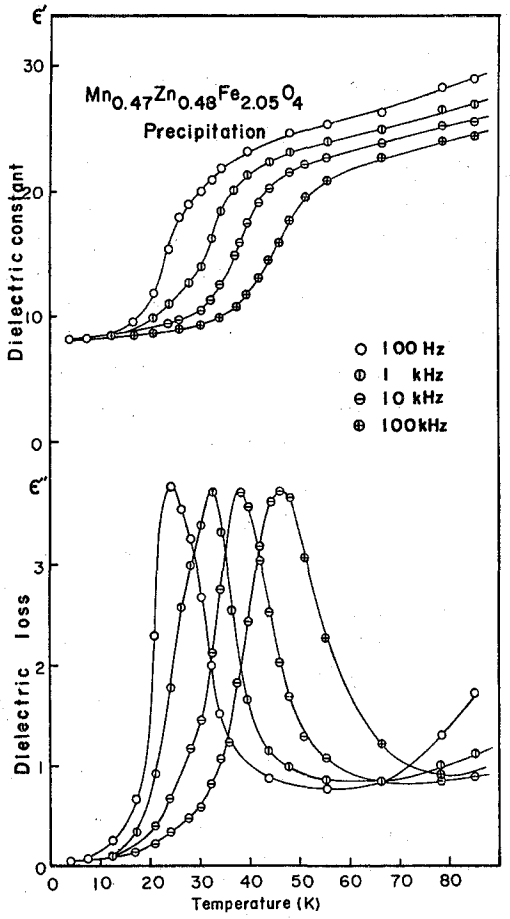

Fig. 2. Temperature dependence of dielectric constant and loss of MZ1 below 80 K.

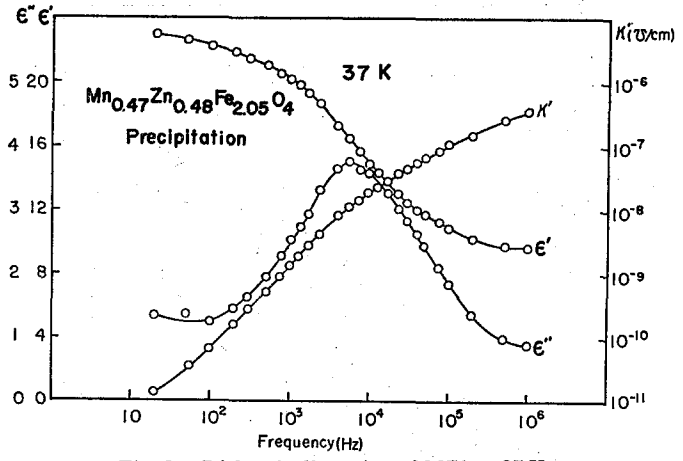

Fig. 3. Dielectric dispersion of MZ1 at 37 K.

have different situation from that of the powder ones. There is great difference in dielectric constant between powder and sintered samples. Powder samples have dielectric constant of 10–100 and sintered ones 10^5. Relaxation temperatures of the dielectric relaxation are 30 K for powder samples and 60 K for sintered samples. Relaxation temperatures are different between powder and sintered samples in spite of these relaxation being considered to be caused by electron hopping between ferrous and ferric ions, namely intrinsic property of material. It is well known that dielectric constant is very sensitive to the structure of material. The dielectric relaxation seen at 300 K in Fig. 1 is considered to be the relaxation arising from the Maxwell-Wagner interfacial polarization which suggests the heterogeneous structure of the sample. In the other two MnZn ferrites this kind of relaxation was not observed near room temperature. The heterogeneous structure will be different in different samples.

Figure 6 shows temperature dependence of dielectric constant of MZ4 powder samples. In the figure dielectric relaxations are found at 30 and 90 K. The relax-

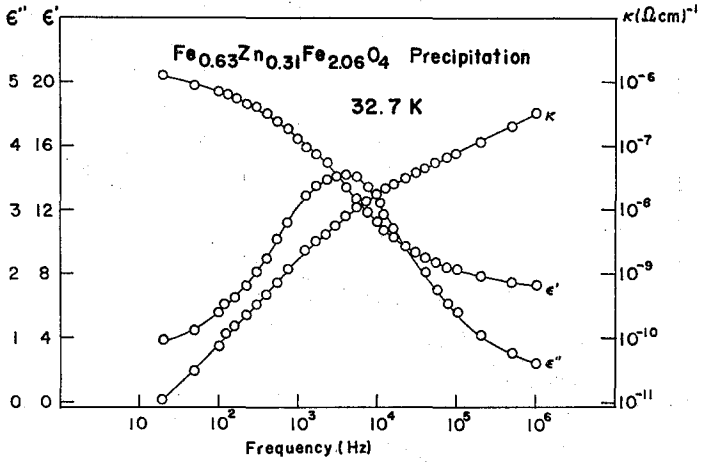

Fig. 4. Dielectric dispersion of MZ2 at 32.7 K.

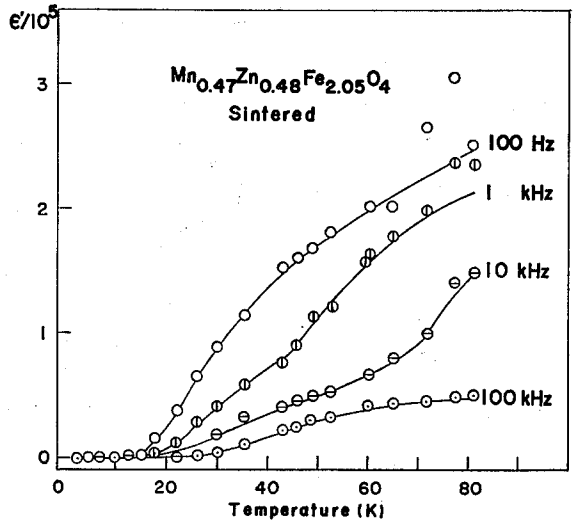

Fig. 5. Temperature dependence of dielectric constant for a sintered sample of MZ1.

ation at 30 K is due to the same mechanism as that of MnZn ferrites near 30 K, namely electron hopping between ferrous and ferric ionss. Dielectric dispersion of this Mn ferrite powder sample is shown in Fig. 7. Figure 8 is the complex plane plots of this dielectric dispersion of Mn ferrite. Figure 9 shows dielectric dispersion of the Mn ferrite at 88 K. Relaxation times of dielectric relaxation in the Maxwell-Wagner interfacial polarization is proportional to ε/κ, where ε is dielectric constant and κ is conductivity. The larger the conductivity of a sample, the smaller the relaxation

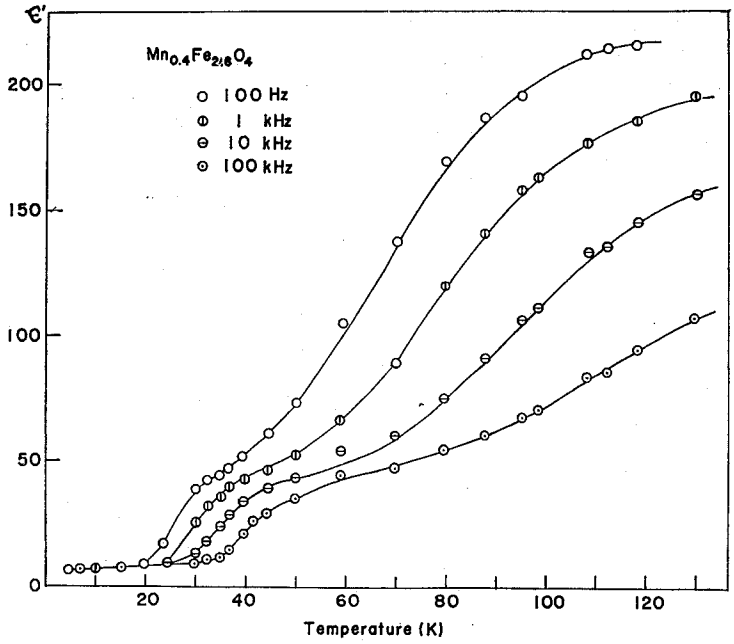

Fig. 6. Temperature dependence of dielectric constant of MZ4.

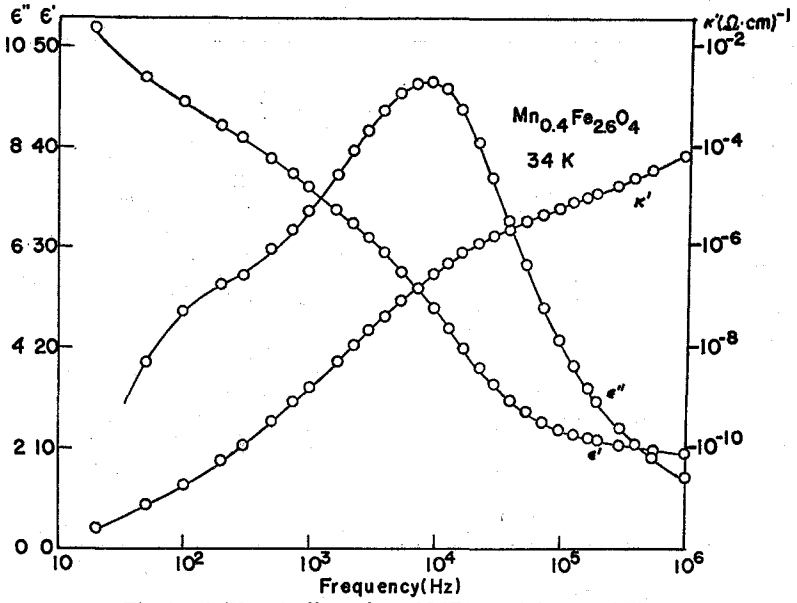

Fig. 7. Dielectric dispersion of MZ4 precipitate at 34 K.

time of dielectric relaxation. Therefore the sample with larger conductivity exhibits dielectric relaxation at lower temperature. The sample of Mn ferrite (MZ4) contains higher ferrous ions than the sample of MZ1 and hence conductivity of MZ4 is much higher than that of MZ1. Therefore dielectric relaxation due to the Maxwell-Wagner interfacial polarization in the sample of MZ4 should be observed at lower temperature than that in the sample of MZ1. Then the dielectric relaxation of the sample of MZ4 at 88 K is considered to be due to the Maxwell-Wagner interfacial polarization arising from the heterogeneity of a sample, though the relaxation temperature 88 K seems to be rather low for Mn ferrite (MZ4) in comparison with that of magnetite (113 K).[5] Since dielectric relaxation due to electron hopping is observed at 30 K in the sample of MZ4, magnetic relaxation due to electron hopping between ferrous and ferric ions is expected to be observed at about the same temperature. In fact the sample of MZ4 shows a magnetic relaxation at about 30 K as shown in Fig. 10. Magnetic and dielectric relaxations have the Cole-Cole type distribution of relaxation times and have activation energy of .033 and .045 eV respectively. The same kind of magnetic and dielectric relaxations has been found at about 30 K for magnetite powder samples.

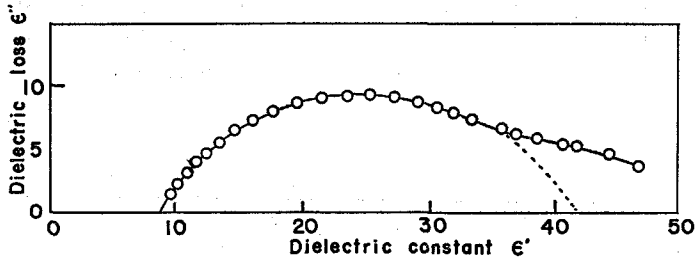

Fig. 8. Complex plane plots of Fig. 7.

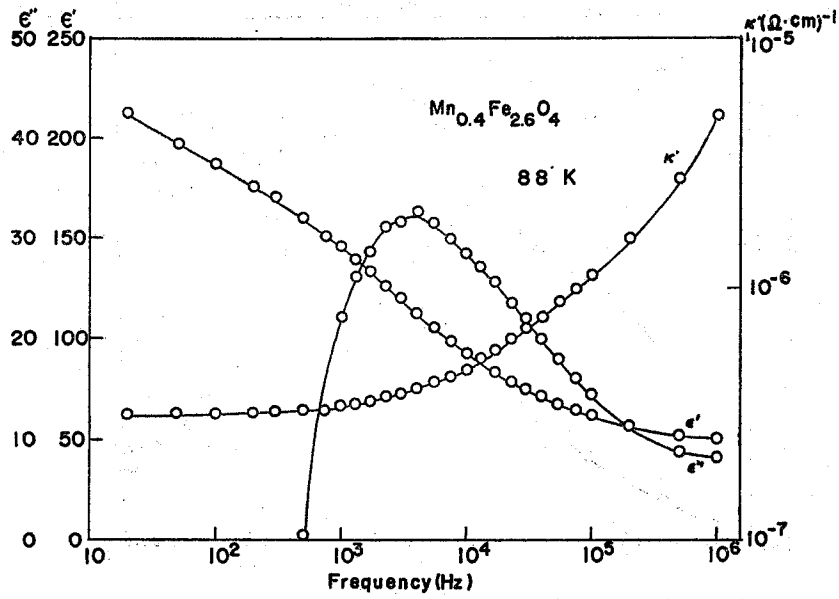

Fig. 9. Dielectric dispersion of MZ4 precipitate at 88 K.

On the other hand the powder samples of MnZn ferrite MZ1, MZ2 and MZ3 showed no magnetic relaxation in the temperature range from 4.2 to 300 K as shown in Figs. 11, 12, 13 and 14 although these MnZn ferrites exhibited the dielectric relaxation due to electron hopping (Figs. 1–4). Sintered samples of these MnZn ferrites showed sharp peaks of μ'' near 20 K which means the magnetic relaxation. The powder samples of MnZn ferrite and Mn ferrite have very low permeability.

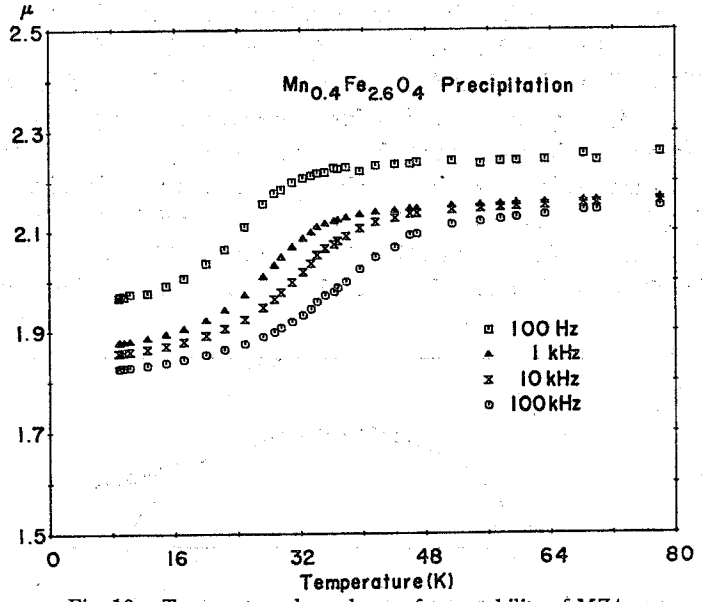

Fig. 10. Temperature dependence of permeability of MZ4.

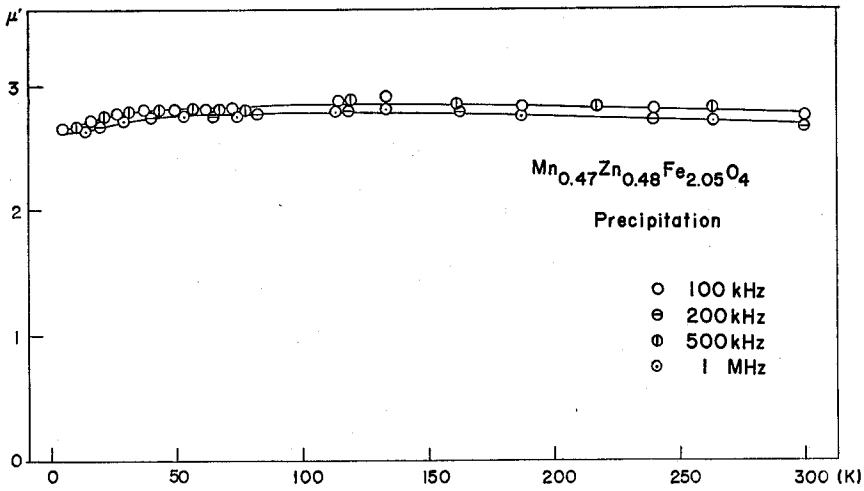

Fig. 11. Temperature dependence of permeability of MZ1.

The permeability of Mn ferrite shows frequency dependent increase near 30 K, while the permeability of MnZn ferrite shows no frequency dependent increase in the temperature range from 4.2 K to 300 K.

Figure 15 shows the Mössbauer spectrum of MZ2 precipitate sample. In this figure we see the existence of paramagnetic component. The paramagnetic component was found for the other two MnZn ferrite MZ1 and MZ3 precipitates. Figure 16 is the Mössbauer spectrum of Mn ferrite precipitate sample MZ4. MZ4 shows the sextet Mössbauer spectrum without the paramagnetic peak. The difference in the Mössbauer spectrum between Mn ferrite and MnZn ferrites will be the reason why the magnetic relaxation is not found in these MnZn ferrite precipitate samples in spite of magnetic and dielectric relaxations being found for Mn ferrite MZ4. X-ray diffraction of these MnZn ferrites showed sharp Bragg peaks with

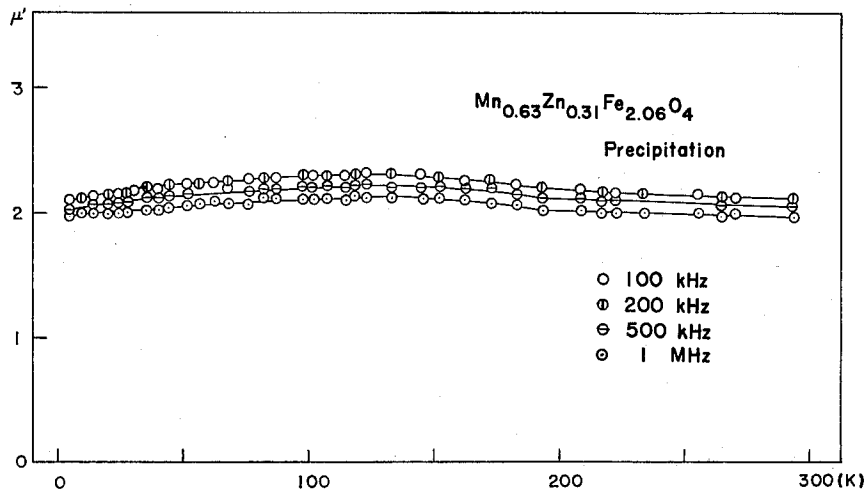

Fig. 12. Temperature dependence of permeability of MZ2.

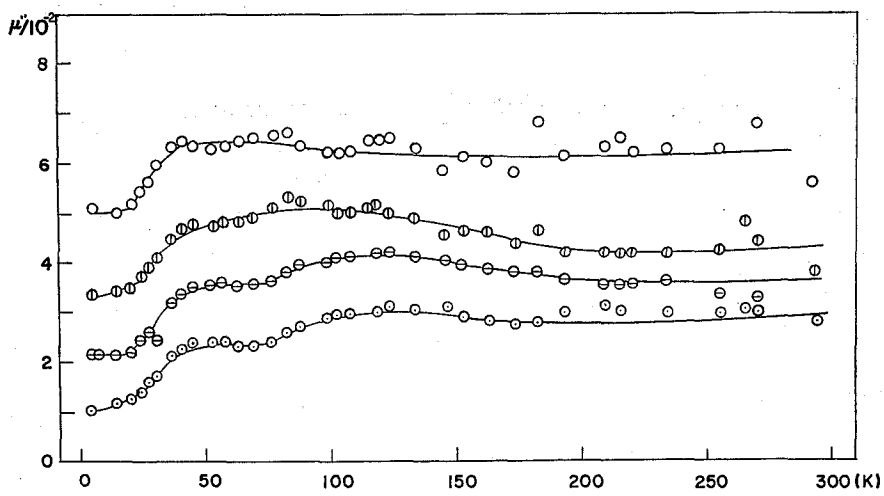

Fig. 13. Temperature dependence of imaginary part μ'' of MZ2.

broad background around them, which mean that there are fine particles of MnZn ferrite. If there is paramagnetic $ZnFe_2O_4$ with spinel structure, the Bragg diffraction peak itself becomes broader. Therefore the paramagnetic component shown in the Mossbauer spectrum is not due to $ZnFe_2O_4$. Fine particles of MnZn ferrite become superparamagnetic particle which is represented as paramagnetic component in the Mössbauer spectrum. Superparamagnetic particles make blocking at some low temperature and susceptibility owing to these superparamagnetic particles becomes zero. Therefore total susceptibility of a sample decreases at some low temperature with decreasing temperature. However, in Figs. 11 and 12 we can see no decrease of permeability with decreasing temperature. Of course ferrimagnetic particles exist in powder samples. These ferrimagnetic particles, however, do not show the magnetic relaxation mentioned above. This means that the superparamagnetic

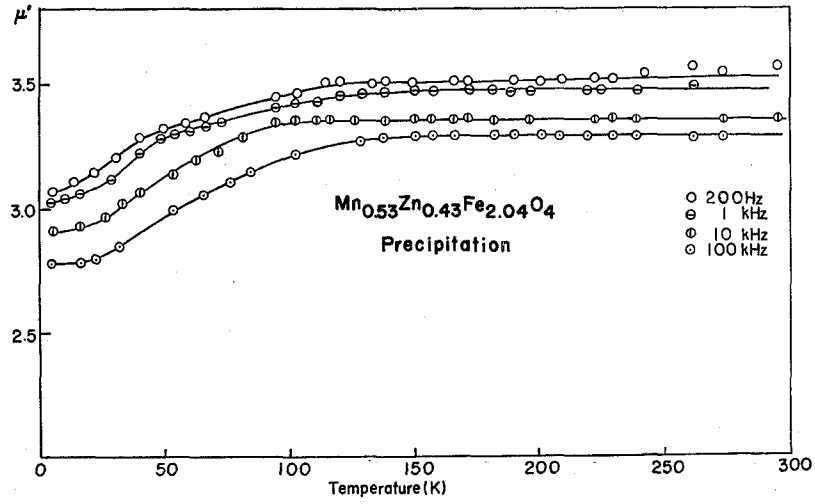

Fig. 14. Temperature dependence of permeability of MZ3.

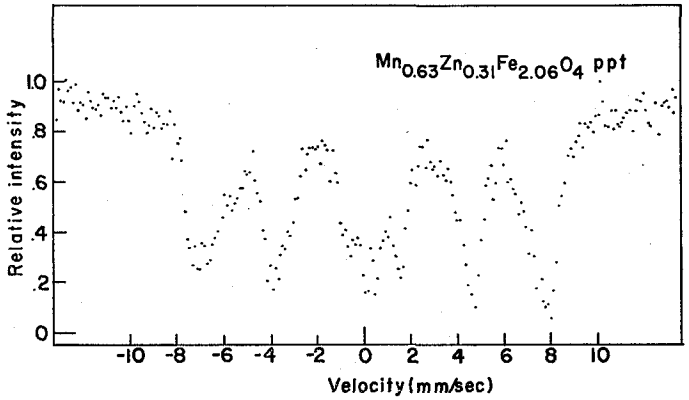

Fig. 15. Mössbauer spectrum of MZ2 at 300 K.

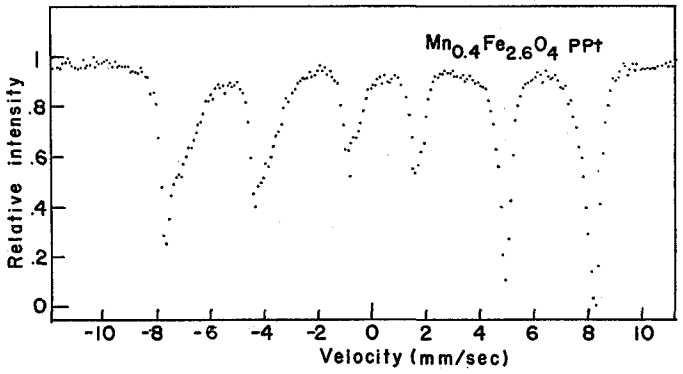

Fig. 16. Mössbauer spectrum of MZ4 at 300 K.

particles do not exist independently of ferrimagnetic particles, for the ferrimagnetic particle which shows the sextet Mössbauer spectrum will show magnetic relaxation if the ferrimagnetic part behaves independent of superparamagnetic particles. Then these paramagnetic and ferrimagnetic particles are not independent of each other. Magnetization of ferrimagnetic part is interfered with the superparamagnetic particles and the magnetic relaxation is not observed for MnZn ferrites MZ1–3 with ferrous ions though dielectric relaxation is observed.

ACKNOWLEDGEMENTS

The author is very thankful to Mr. Y. Yamamoto of Toda Kogyo Co. and Dr. M. Kiyama of this institute for preparing samples.

REFERENCES

(1) K. Iwauchi, Y. Kita, and N. Koizumi, *J. Phys. Soc. Jpn.* **49**, 1328 (1980).
(2) K. Iwauchi, N. Koizumi, M. Kiyama, and Y. Bando, *Bull. Inst. Chem. Res. Kyoto Univ.*, **54**, 255 (1976).
(3) S. Iida, K. Mizushima, N. Yamada, and T. Iizuka, *J. Appl. Phys.* **39**, 818 (1968).
(4) K. Iwauchi and N. Koizumi, Proceedings of Int. Conf. on Ferrites, Kyoto, 106 (1980).
(5) K. Iwauchi, *Jpn. J. Appl. Phys.*, **10**, 1520 (1971).
(6) M. Kiyama, *Bull. Chem. Soc. Jpn.*, **51**, 143 (1978).