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Ferromagnetic Resonance Line Width in Ni Ferrite

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The ferromagnetic resonance absorption in Ni ferrite is observed at 9300 MC. The single crystal specimen is prepared by PbO flux method, and has the composition $(Ni_{0.96}Fe_{0.04})\ Fe_2O_4$. Experiments are made repeatedly on one and the same specimen after various heat-treatments. The width, anisotropy constants, and the g-factor change appreciably by the treatments. The results can be accounted for qualitatively to some extent, as caused by the change in the spinel phase itself, or by the effect of precipitation. The minimum width obtained, about 15 Oe, is far narrower than those reported earlier for the ferrites.

Introduction

The ferromagnetic resonance in nickel ferrite was observed previously by a number of investigators[1),2),3),4)]. In particular, Yager *et al.*[3)] made experiments on two crystals with the compositions $(Ni_{0.75}Fe_{0.25})Fe_2O_4$ and $(Ni_{0.95}Fe_{0.05})Fe_2O_4$ respectively, and found that the former shows a maximum in ΔH vs temperature curve at 160°K. They attributed it to the mechanism of electron diffusion between ferrous and ferric ions in 16*d* sites in ferrite.

The ferrite belongs to a group of compounds called Berthollide, and its oxygen content can be altered appreciably by a suitable heat-treatment. Then, the resonance line width of the ferrite might be altered by heat-treatment, because the induced change in oxygen content means the change in ferrous ion content, or the change in free electron concentration, which causes the broadening of the ferromagnetic resonance line. Here, the ferromagnetic resonance was observed on single crystal specimens, after subjecting it to various heat-treatments.

Experimentals

The single crystals of nickel ferrite were prepared by PbO flux method. Special precautions were paid to use raw materials free from cobalt. It is impossible to know the exact compositions of each crystal, for the compositions may differ slightly from one crystal to another. Accordingly, the average composition for several of them was determined with the x-ray fluorescence procedure. It was $(Ni_{0.96}Fe_{0.04})Fe_2O_4$. Crystals were ground by Bond's tumbling method to spheres about 0.3 mm in diameter. The final grit size of the grinding paper was several microns. Ferromagnetic resonance was observed by an ordinary method. The used frequency was about 9,300 Mc/sec. ΔH is defined as the width of the field between those for half the maximum absorption. The ferromagnetic anisotropy constants K_1, K_2 and the g-factor were determined from the fields for resonance along three main crystallographic directions. The line shapes approximately resemble Lorentzian. Ferromagnetic resonance was observed repeatedly on the same single crystal specimen. This procedure is indispensable to assure that the changes induced by the heat-treatments are really essential ones, and not due to the difference in surface roughness, in constituent metal ratio and so on. A number of crystals were used for the experiment. We shall here report on the results on a typical specimen without going into the slight differences in resonance character of each crystal.

(1) Fig. 1 (1) shows ΔH vs temperature curves for three main crystallographic directions, of the crystal as grown. The width is several tens of oersteds, and increases monotonically on lowering the temperature. It is maximum along ⟨100⟩, and minimum along ⟨111⟩.

(2) This specimen was heat-treated at 950°

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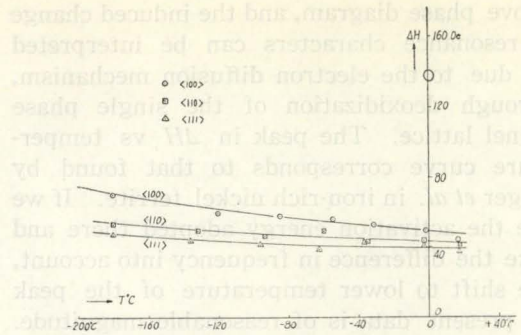

Fig. 1. The change of the width with the temperature for each main direction.
(1) As grown, without any heat-treatment.

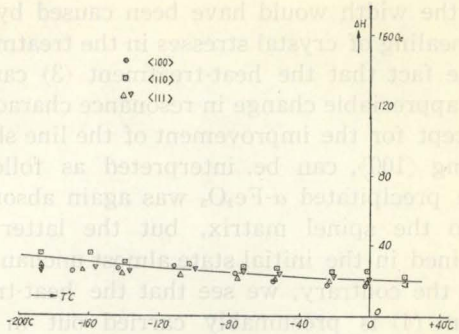

Fig. 1. (3) After heat-treated in CO_2 at 950°C for 24 hours.

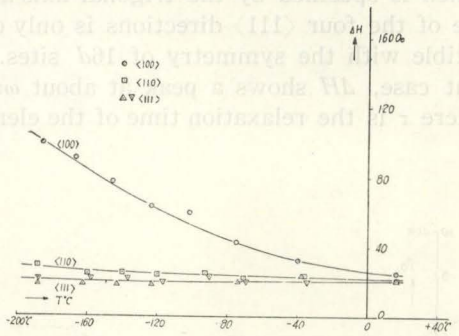

Fig. 1. (2) After heat-treated in air at 950°C for 24 hours.

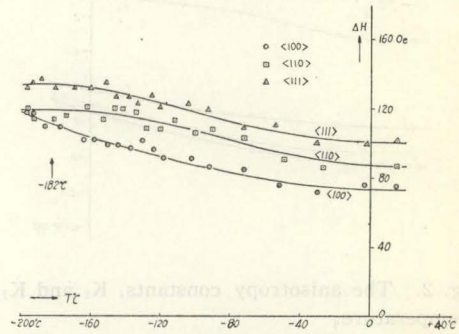

Fig. 1. (4) After heat-treated in CO_2 at 1100°C for 24 hours.

C in air for 24 hours. The width decreased appreciably, as can be seen in Fig. 1 (2), to the order of 20 Oe. This is far narrower than those reported earlier for the ferrites. The line-shape became somewhat bad and a small subsidiary peak appeared beside the main peak along ⟨100⟩. K_1 seems to have decreased a little, but we are not so sure because of the bad shape along ⟨100⟩, and the same can be said for the g-factor, too.

(3) The specimen was heat-treated again, at 950°C in CO_2 for 24 hours. (Fig. 1 (3)). The width hardly changed, except that the shape became a little better along ⟨100⟩. K_1 and g-factor returned almost to that of the initial state.

(4) Next, the specimen was heat-treated at 1,100°C in CO_2 for 24 hours. This treatment caused a remarkable change in the resonance characters. As seen in Fig. 1 (4), the width increased appreciably, to the order of one hundred Oe, and showed a broad maximum at about −180°C. The anisotropy of the width was reveresed, and it was maximum along ⟨111⟩, and minimum along ⟨100⟩. K_1 increased appreciably, K_2 decreased, and the g-factor increased and showed remarkable temperature dependence.

Discussion

The above experimental results can be understood fairly well on the basis of the phase diagram and the theory of the electron diffusion. The phase diagram of nickel ferrite was investigated by Paladino[5] and by Okazaki[6]. Fig. 4 is the phase diagram based on their data. Stable spinel phase region is the domain bounded by the solid line on the right, and by the broken line on the left. On the right of the region, α-Fe_2O_3 precipitates, and on the left, NiO does. The above heat-treatment (2) is critical, and there is a possibility that a small amount of α-Fe_2O_3 precipitates in the spinel matrix. Rather bad line shape in this case also seems to suggest the same. Thus, the large decrease

in the width would have been caused by the annealing of crystal stresses in the treatment. The fact that the heat-treatment (3) caused no appreciable change in resonance characters except for the improvement of the line shape along ⟨100⟩, can be interpreted as follows; the precipitated α-Fe_2O_3 was again absorbed into the spinel matrix, but the latter remained in the initial state almost unchanged. On the contrary, we see that the heat-treatment (4) is presumably carried out in the spinel region, as seen on extrapolating the above phase diagram, and the induced change in resonance characters can be interpreted as due to the electron diffusion mechanism, through deoxidization of the single phase spinel lattice. The peak in ΔH vs temperature curve corresponds to that found by Yager *et al.* in iron-rich nickel ferrite. If we use the activation energy adopted there and take the difference in frequency into account, the shift to lower temperature of the peak in present data is of reasonable magnitude. Clogston[7] made a calculation of electron diffusion, based on a model similar to that adopted by Néel[8]. His assumption (i), which distinguishes four groups of sites, each of which is specified by the trigonal axis along one of the four ⟨111⟩ directions is only compatible with the symmetry of 16*d* sites. In that case, ΔH shows a peak at about $\omega\tau=1$, where τ is the relaxation time of the elemen-

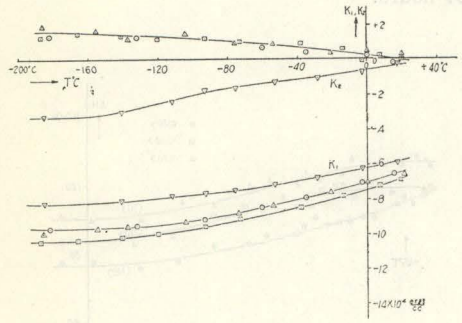

Fig. 2. The anisotropy constants, K_1 and K_2, vs temperature.
⊙ (1) As grown, without any heat-treatment.
⊡ (2) After heat-treated in air at 950°C for 24 hours.
△ (3) After hear-treated in CO_2 at 950°C for 24 hours.
▽ (4) After hear-treated in CO_2 at 1100°C for 24 hours.

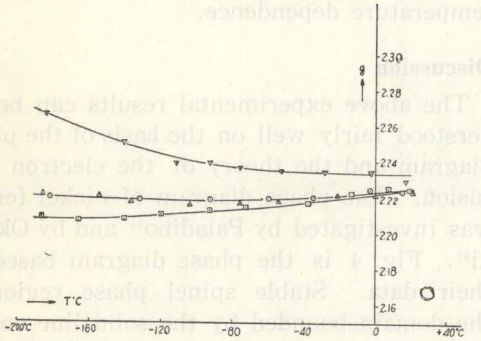

Fig. 3. *g*-factor vs temperature.
⊙ (1) As grown, without any heat-treatment.
⊡ (2) After heat-treated in air at 950°C for 24 hours.
△ (3) After heat-treated in CO_2 at 95°°C for 24 hours.
▽ (4) After heat-treated in CO_2 at 1100°C for 24 hours.

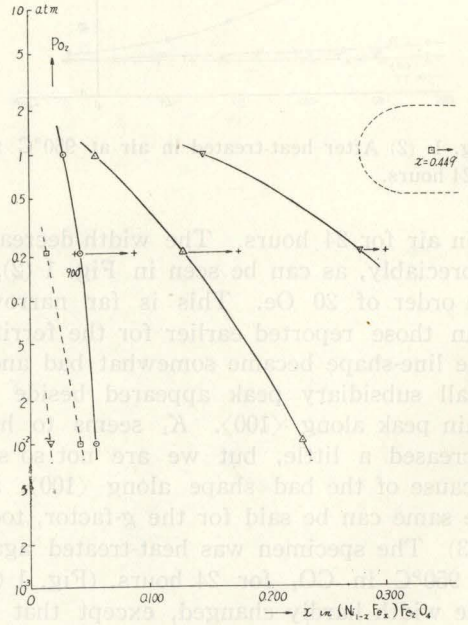

Fig. 4. The Phase diagram of $(Ni_{1-x}Fe_x)\ Fe_2O_4$ system.
⊙ 1000°C, △ 1100°C, ▽ 1200°C, ⊡ 1300°C.
The spinel region is on the left of the solid line and on the right of the broken line. α-Fe_2O_3 precipitates on the right of the solid line, and NiO on the left of the broken line. (Due to A. E. Paladino)
+ The solubility limit of α-Fe_2O_3 in Ni ferrite to each temperature. (Due to C. Okazaki)

tary jump, but it is maximum along ⟨100⟩ and minimum along ⟨111⟩. K_1 increases at about $\omega\tau=1$, and the g-factor increases too. This accords with the experimental fact in tendency, except for the anisotropy of the width. Callen and Pittelli[9] calculated the width due to the disorder in 16*d* sites, and obtained an anisotropy of the width the sign of which is opposite to that of Clogston. The anisotropy of the width can be expressed at least qualitatively combining these two, but the temperature dependence can not be accounted for A more detailed theory of electron diffusion is needed to comprehend it further well.

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DISCUSSION

J. M. Brownlow: The heat treatment (4) would produce NiO as a second phase especially if the concentration of Ni is somewhat higher than that shown by the reported chemical analysis. At least the condition of treatment (4) is very close to a phase boundary. Separation of NiO would leave a spinel of higher Fe and correspondingly higher Fe^{2+} content.

H. Sekizawa: On extrapolating the phase diagram given by Paladino, the treatment (4) is almost certainly made in the single phase spinel region. Moreover, in our experimental situation, the circulation of CO_2 in the container in heat treatment was not so good that the partial pressure of oxygen may have been somewhat higher than that for pure CO_2.

S. Iida: Concerning the symmetry of the anisotropy which may be introduced by electron diffusion, I would like to make a comment that, since there are about 50% divalent Ni ions on 16*d* sites, it is certain that F type anisotropy is also produced in a considerable amount of Fe^{2+} ions. Next I would like to know the recent information concerning the presence of electron diffusion if someone has.