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Induced Anisotropy in Iron-Rich Nickel Ferrite with a Small Cobalt Substitution

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In order to make clear the mechanism of low loss properties of iron rich nickel ferrites with a small cobalt substitution, the induced anisotropy and its relaxation were investigated. It was found that the relaxation time was larger and the activation energy higher in the oxidized specimen than in the reduced specimen.

The role of cation vacancies and ferrous ions in relaxation are discussed.

The purpose of this investigation was to make clear the mechanism of low loss properties of iron rich nickel ferrites. There are two conditions to obtain low loss properties. The first condition is that specimens should contain no ferrous ion and the second condition is that the domain wall should be stabilized. The second condition is satisfied in ferrites with small cobalt substitution.

In spinel-ferrite with cobalt substitution magnetic annealing induces a uniaxial magnetic anisotropy[1),2),3)]. When a specimen is cooled in absence of an external field, a constricted hysteresis loop appears indicating that domain walls are stabilized by the induced anisotropy[4)]. The stabilization of domain walls is more evident for specimens with excess iron. As shown in Fig. 1, usually in iron excess ferrite the decrease of electrical resistivity is very large. It is believed that the existence of ferrous ions causes this low electrical resistivity. There is some contradiction here. If we take an iron excess ferrite, domain walls are well stabilized but there are ferrous ions. And if we take an iron deficient ferrite, there are no ferrous ions but the stabilization of domain wall is not satisfactory. The authors succeeded in producing ferrites which have high resistivity even in the iron excess range. The broken line in the figure shows the resistivity of such materials. It was found that these ferrites are oxidized to such an extent that very few ferrous ions can be detected by the chemical analysis.

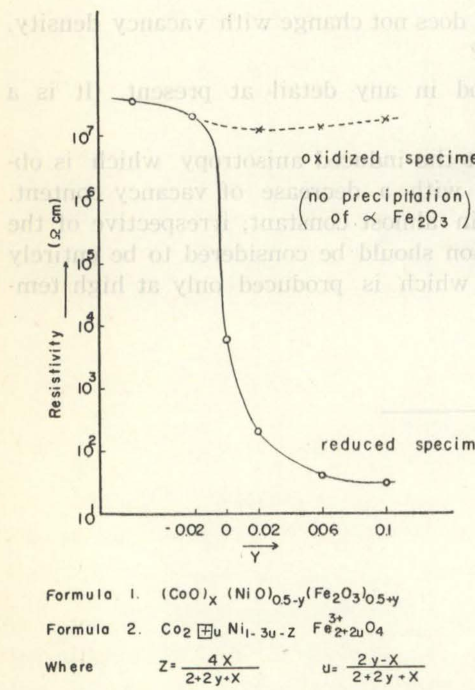

Fig. 1. Resistivity versus Fe_2O_3 composition in oxidized and reduced specimen.

The specimens which were treated are expressed by the following formula:

$$(\mathrm{CoO})_x(\mathrm{NiO})_{0.5-y}(\mathrm{Fe_2O_3})_{0.5+y}\ ,$$

where x goes from 0 to 0.04 and y goes from -0.02 to 0.1. In this case cation vacancies would appear in octahedral sites, since all excess iron ion are oxidized to the ferric state. The amount of cation vacancies in these ferrites can be expressed by the formula, $\mathrm{Co}_{z+u}\mathrm{Ni}_{1-3u-z}\mathrm{Fe}^{3+}_{2+2u}\mathrm{O}_4$ and the cobalt ion content, z, and cation vacancy content, *u*, are expressed as a function of x and y, in the following equations.

$$z=\frac{4x}{2+2y+x},$$

$$u=\frac{2y-x}{2+2y+x}.$$

The samples were prepared by firing at 1250 °C followed by an oxidizing treatment.

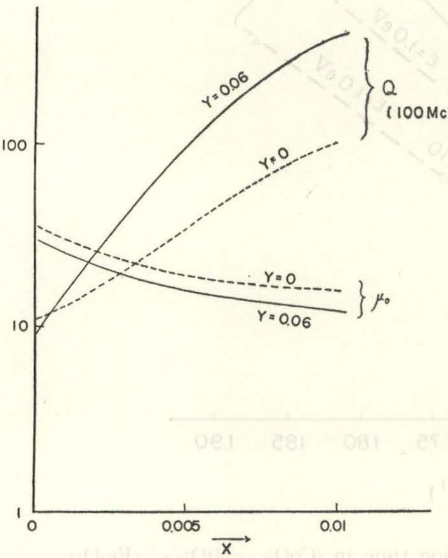

Fig. 2. Improvement of V.H.F. Q factor by Co substitution.

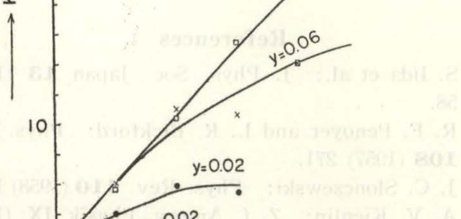

Fig. 3. The relation between the cobalt content and the value of induced anisotropy.

In these ferrites the improvement of the Very High Frequency Q-factor by Co substitution was remarkable[5]. Fig. 2 shows the effect of cobalt substitution on initial permeability and Q-value at 100 Mc. μ_i decreases and Q increases with increasing amount of Co. The contribution of domain wall motion to initial permeability is diminished and magnetic losses at high frequency are reduced[6].

The values of induced anisotropy at room temperature were measured with a torque magnetometer. The samples were cooled in a magnetic field at a difinite cooling rate. Fig. 3 shows the relation between the cobalt content and the value of induced anisotropy in ferrites containing different amounts of iron oxide. The induced anisotropy also depends on the y value, and thus on the amount of cation vacancies. Even when the cobalt content was the same, the value of induced anisotropy in iron excess ferrite was larger than in iron deficient ferrite. This agrees with the observed fact that the stabilization of the domain wall was most evident in iron excess ferrites. Even at $x=0$, we can detect a value of induced anisotropy. This is due to Co ions, since the NiO which was used as a raw material contained a small amount of CoO.

To clarify the role of cation vacancies in the induced anisotropy of these ferrites, the measurements of relaxation time of the induced anisotropy were carried out. The time when the torque becomes one half of the initial value was defined as the relaxation time, $\tau_{1/2}$. In Fig. 4 the relaxation time in various specimens is plotted against the reciprocal of absolute temperature. The relaxation time can be expressed by an activation type equation. The solid lines show the relaxation time in specimens which contained some Co ions, namely $x=0.01$, but differing cation vacancies. It is seen from these data that the cation vacancies cause a more rapid relaxation of the induced anisotropy. This is one of the reasons why iron excess ferrite has a larger value of induced anisotropy than iron deficient ferrite when these ferrites are cooled at the same rate in a magnetic field. But it was not determined whether the cation vacancies have any effect on the saturation value of induced anisotropy. The dotted line in the figure shows the relaxation time

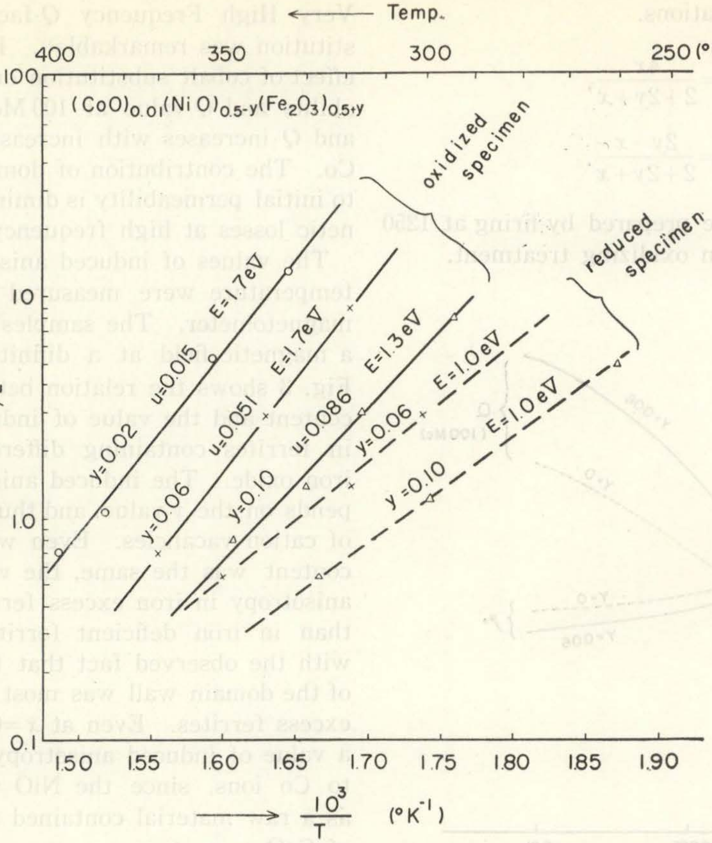

Fig. 4. The temprature dependence of the relaxation time in $(CoO)_{0.01}(NiO)_{0.5-y}(Fe_2O_3)_{0.5+y}$.

in the specimens, which were not oxidized and contained many ferrous ions and few vacancies. This specimen has low resistivity, namely about 5 ohm-cm. It was expected that the relaxation time in this reduced specimen would be larger than the oxidized specimen since the amount of cation vacancy in the reduced specimen is smaller than in the oxidized specimen. But actually, as shown in the figure, the inverse result was obtained. The activation energy is much higher in the samples which contain no ferrous ions than in those which contain some ferrous ion. Existence of ferrous ions seems to facilitate the diffusion of Co ions, because hopping of electrons between Fe^{2+} and Fe^{3+} ions which may occur simultaneously during diffusion of Co ions should smooth out the potential barrier for migration of Co ions.

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DISCUSSION

A. A. Hirsch: I want to remark that constricted hysteresis loops are also possible in single domain particles where no domain walls are present. This problem we have discussed at the Grenoble conference in 1958.

S. Iida: The constricted hysteresis loops can appear if there is an considerably stable spin arrangement which has no magnetization along the field direction. This is usually realized by the closure arrangement of domains stabilized by the presence of some kind of induced anisotropy. It seems to me improbable that in strictly single domain particles, when the orientations of the particles are random, the loops are realized.

S. Iida: I think the enhancement of the cation migration by the presence of electron diffusion is quite probable. Since cation vacancy repels electron and attracts ferric ion, and ferric ion attracts electrons, it is fairly probable that iron ion migrate always in a form of trivalent state and associates the electron migration in a reverse direction. There are two equivalent shortest linkages of cations on 16*d* sites for this eletron path. Some time ago, I considered the case of iron-cobalt ferrites and assumed that the activation energy as a function of composition may decrease with a finite decrement from $CoFe_2O_4$ to Fe_3O_4. However, actually the activation energy does not decrease so rapidly. Therefore I think it may be quite probable that in this case also the cobalt ion at a direct neighborhood of a vacancy is in trivalent state and electron diffusion still contributes to accommodate the cation migration in this case.