

DISCUSSION

G. W. RATHENAU: Can you explain the abnormal behaviour of the magnetostriction for $x=0.1$?

N. MIYATA: No, we can not clearly explain the characteristic temperature dependence of λ_{111} for $x=0.1$. But, it may correspond to the abnormal dependence of K_1 , the anisotropy constant, on temperature for the same composition. Both of them are thought to have the same origin as the abnormal behavior of magnetite just above the transition temperature, which may be attributable to the short range order of Fe^{2+} and Fe^{3+} on the B-site of the spinel lattice.

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Theoretical and Experimental Study of the Induced Anisotropy in Iron-Cobalt Ferrites and Disaccommodation Phenomena in Ferrites

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The mechanism of the relaxation of induced anisotropy in iron-cobalt ferrites has been studied theoretically and experimentally. It has been made clear that the relaxation time in an isothermal annealing is inversely proportional to the density of cation vacancies in a certain range of the density. The relaxation time in general has a distribution in a wide range, but it becomes single when cobalt content is very small. Quantitative expressions have been given to this relaxation time from both theory and experiment and a reasonable agreement has been obtained between the two. It is concluded that, in general, ferrites have an uniaxial anisotropy due to the presence of oriented arrangement of various cations on their regular sites, and the relaxation time of the reorientation should be also inversely proportional to the density of cation vacancies. On the basis of this conclusion, our technique of controlling cation vacancies has been applied to Mn-Zn ferrites, having shown a realization of good control of the disaccommodation phenomena.

1. Introduction

There has been a considerable progress in the last few years in the study of the induced anisotropy of iron-cobalt ferrites¹⁾⁻⁶⁾. Here we shall report a summary of our recent study of the relaxation of the induced anisotropy of this material. As a result of this study we believe now that the induced anisotropy in ferrites in general originates primarily in the oriented configuration of cation arrangements in the spinel matrix,

and so far as the density of cation vacancies is over a certain lower bound, say 10^{-8} or 10^{-9} for iron-cobalt ferrites, the process of reorientation takes place mainly through vacancy migration mechanism.

2. Theoretical Considerations

The rearrangement process of cations may be described mathematically in terms of time-dependent populations (or the probabilities) of various configurations of certain cat-

Total number of various configurations in iron-cobalt ferrites.

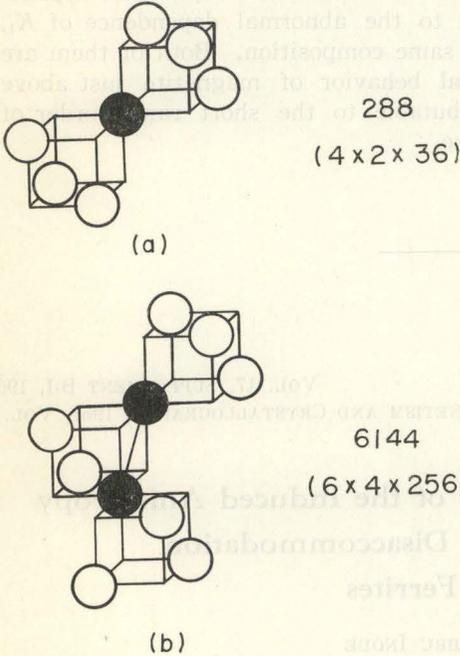


Fig. 1. Two fundamental units to the anisotropy: (a) single ion in various crystalline fields, (b) paired ions in various crystalline fields.

ion arrangements, each of which gives rise to a certain anisotropy.

As such configurations, one may choose those which are assigned to clusters such as shown in Fig. 1. For the cluster (a) the number of possible configurations amounts to 288, and for (b) to 6144 even when the difference of Fe²⁺ and Fe³⁺ is disregarded.

When a certain cluster is selected as a basis of our description, the population assigned to each configuration can be considered as a component of a vector *N*, whose dimension is equal to the number of all possible configurations. Time change of the vector *N* will then follow an equation of the type

$$\frac{d}{dt}N = \Gamma[N],$$

where $\Gamma(N)$ is the time rate of change caused by thermal migration of cations in the system. An equilibrium state defined for a fixed external condition corresponds to a vector *N_e*, which should evidently satisfy $\Gamma(N_e) = 0$. Therefore as far as the state is not far from equilibrium, the deviation of the population from the equilibrium will follow such a linear equation,

$$\frac{d}{dt}(N - N_e) = -D(N - N_e). \quad (1)$$

The relaxation process will be described by

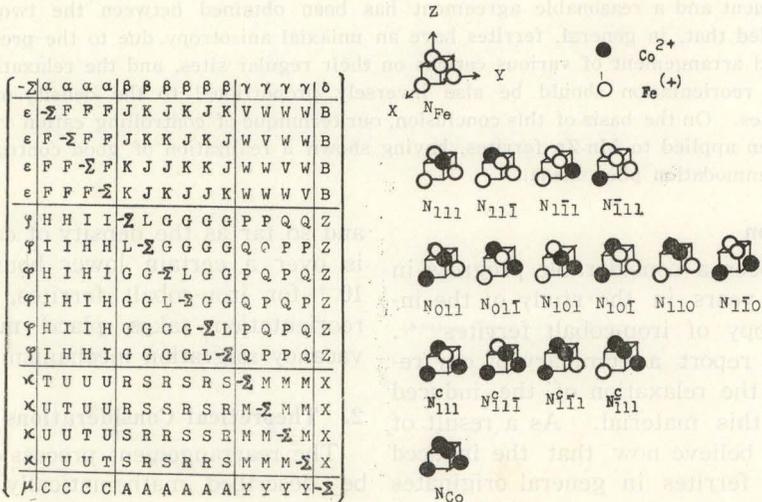


Fig. 2. All possible tetrahedral configurations on 16d sites in iron-cobalt ferrites.

this equation. In particular, the spectrum of relaxation time is given by the spectrum of the eigenvalues of the linear operator D .

As a tractable approximation, the unit tetrahedron of $16d$ site may be chosen as the basic cluster. Then 16 different configurations can be distinguished as one sees in Fig. 2. The matrix representation of D is also shown there. This general form is determined only by symmetry consideration. By virtue of a high symmetry of the matrix, there are only four relaxation times, one for the $[F]$ term in the well known expression of anisotropy

$$K_u = -[F] \sum_i \alpha_i^2 \beta_i^2 - [G] \sum_{j>k} \alpha_j \alpha_k \beta_j \beta_k,$$

and three for the $[G]$ term. This result shows that this simple model is not enough to explain a wide distribution of relaxation times for the $[F]$ term, which is in fact observed at high concentration of cobalt. Fig. 3 shows an example of $[F]$ and $[G]$ for a $\text{Co}_{0.25}\text{Fe}_{2.75}\text{O}_4$ single crystal. This also means that Néel's pair approximation is not adequate here.

However, if we confine ourselves to a rather small concentration of cobalt, then the result of the above analysis can be used by changing the definition of the basic cluster in the following way. Namely, the tetrahedral cluster with a cobalt ion in Fig. 2 is now replaced by an isolated cobalt ion with its six iron neighbors and with the same position of symmetry on $16d$ sites, and that with two cobalt ions by an isolated cobalt ion pair with its iron neighbors with the same orientation on $16d$ sites. We disregard the rest in Fig. 2. This change of

definition does not effect on the symmetry of D matrix. Now, since H and I in the D matrix become very small, the relaxation times are obtained as follows:

for $[G]$ term $1/\tau_1 = 4F$

$$1/\tau_2 = 4G + J + K + 2L, \quad (3)$$

for $[F]$ term $1/\tau_3 = 6G + J + K. \quad (4)$

J , K , and L seem to be smaller than G because of electrostatic interaction of ions. If that is so, Eqs. (3) and (4) show that

$$\tau_3/\tau_2 \sim 1.5$$

which agrees with experiment. This case was studied previously by Palmer⁷⁾. Our result is consistent with his experimental and theoretical results.

In order to analyse the physical implication of the relaxation time, one has to know more about the mechanism of atomic rearrangement. We tried to analyse τ_1 as an example assuming vacancy migration mechanism. For this we consider a cobalt ion and its six neighbors as the basic cluster (Fig. 4), the configurations of which are distinguished by the arrangement of cations or cations and a vacancy. There are 16 configurations to be considered. The transition matrix for these configurations can be set up in terms of the

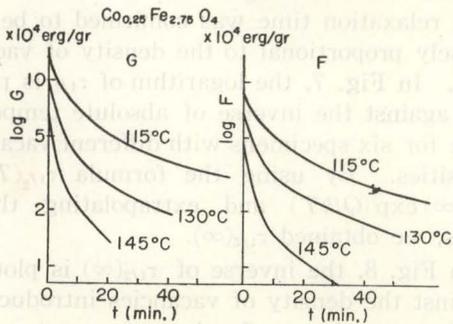


Fig. 3. Relaxation of induced anisotropy.

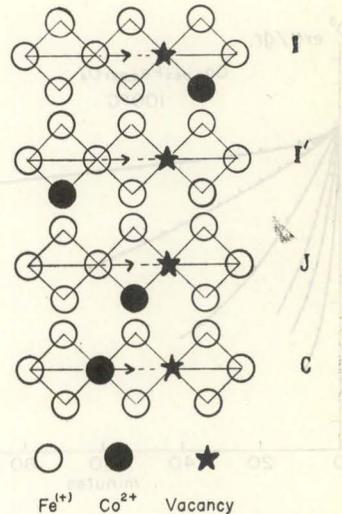


Fig. 4. Various configurations of three octahedra relevant to the vacancy migration in a cobalt diluted region.

parameters, ρ the density of vacancy, and ν_s' which characterize various jumping processes and are illustrated in Fig. 4. Furthermore a constant $p (=0.4)$ is introduced in order to take account of repeated returning process of a vacancy. An electrostatic consideration suggests that $\nu_c, \nu_J \ll \nu_I$, which makes the result of calculation considerably simpler. So we get

$$\tau \sim \frac{1}{24p\rho} \frac{1}{\nu_I} \frac{\nu_I + 2\nu_O}{\nu_O}$$

This is again simplified, if $2\nu_O \ll \nu_I$, to

$$\tau \sim \frac{1}{9.6\rho f_0} \exp(Q/kT), \quad (5)$$

where f_0 is a frequency factor approximately equal to the average frequency of lattice vibration and Q is the activation energy of vacancy migration.

3. Experiment

In order to study the mechanism of relaxation in ferrites it is very important to make specimens homogeneous and to control their oxygen contents accurately. This is not easy. But we succeeded in this by using sealed container technique.

First, a specimen with nearly stoichiometric composition was prepared by annealing

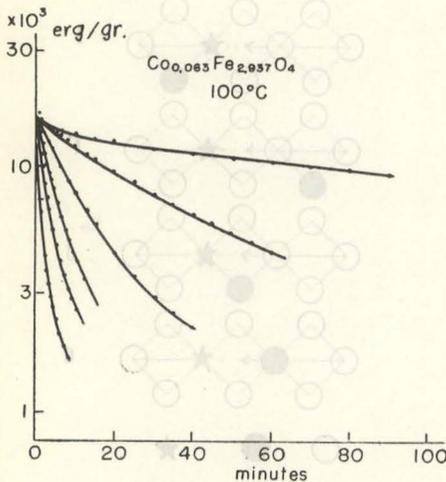


Fig. 5. Relaxation of induced anisotropy of polycrystalline $\text{Co}_{0.063}\text{Fe}_{2.937}\text{O}_4$ in isothermal annealing at 100°C . Direction of magnetic field has been rotated by 45 degrees at $t=0$.

it in an adequate vacuum. After being examined the departure from the stoichiometric composition by the observation of the relaxation time of the induced anisotropy of this specimen, it was sealed in a small quartz container with a desired amount of oxygen gas and was annealed again at about 1000°C . All measurements were made with a specimen in a sealed state.

Fig. 5 shows how the magnitude of the induced anisotropy relaxes after the direction of applied magnetic field was rotated by 45 degrees in an isothermal annealing. Each curve corresponds to a specimen with the same cobalt composition but with different oxygen content. It is noticed that the change in oxygen content introduces only the change in the scale of the time axis, and there is no change in the curve form and in the initial magnitude.

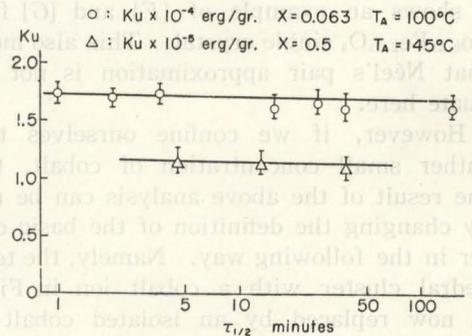


Fig. 6. Relation between final magnitude of anneal induced anisotropy K_u and relaxation time $\tau_{1/2}$.

Fig. 6 shows clearly that the final magnitude of the uniaxial anisotropy does not depend on the length of relaxation time. The relaxation time was confirmed to be inversely proportional to the density of vacancies. In Fig. 7, the logarithm of $\tau_{1/2}$ is plotted against the inverse of absolute temperature for six specimens with different vacancy densities. By using the formula $\tau_{1/2}(T) = \tau_{1/2}(\infty) \exp(Q/kT)$ and extrapolating these lines, we obtained $\tau_{1/2}(\infty)$.

In Fig. 8, the inverse of $\tau_{1/2}(\infty)$ is plotted against the density of vacancies introduced.

These results are fitted to an experimental formula

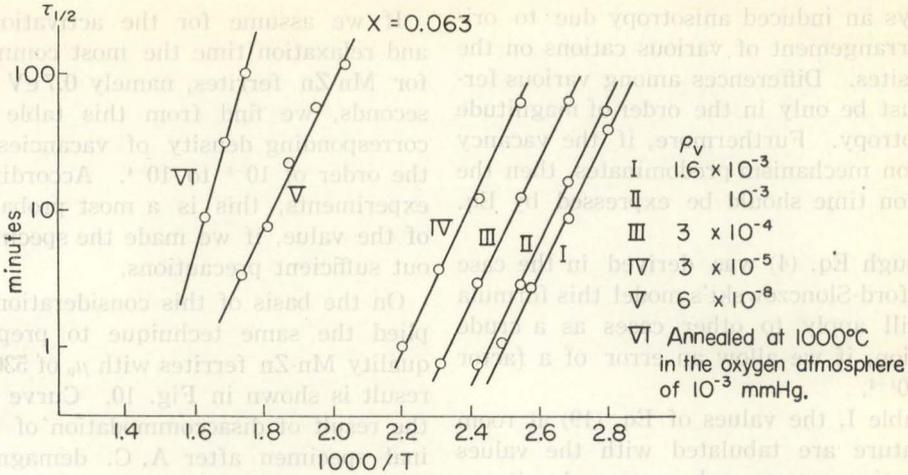


Fig. 7. Logarithm of $\tau_{1/2}$ are plotted against the reciprocal of temperature for the specimens with various concentrations of cation vacancies.

$$\tau_{1/2}(T) = \frac{\exp(Q/kT)}{\rho \cdot 5 \times 10^{13} (\text{sec}^{-1})}, \quad (6)$$

with $Q = 1.0 \text{ eV}$.

This agrees with Eq. (5) if the frequency factor f_0 is assumed to be equal to $3.6 \times 10^{12} \text{ sec}^{-1}$ which is quite a reasonable value. It should be added that precise control of oxygen content in single crystals is very difficult and also that measurements can not easily be repeated without causing serious damage.

It is noticed in Fig. 7 that when a specimen is reduced strongly the activation energy increases considerably. Fig. 9 shows the value of activation energy as a function of composition for oxidized and reduced specimens. This result suggests that some other migration mechanism such as interstitial migration takes place at reduced states.

We have made already some detailed study on this problem. It seems that interstitial migration takes place in a critical range of oxygen content; it ceases when the reduction is higher also when the reduction becomes lower. We believe now that the interstitial cations are only present when the excess of cations is of the order of 10^{-5} and they disappear when it becomes more than 10^{-4} , probably being absorbed into nucleated precipitates.

From these studies it may be concluded that in any ferrite, if cations could migrate

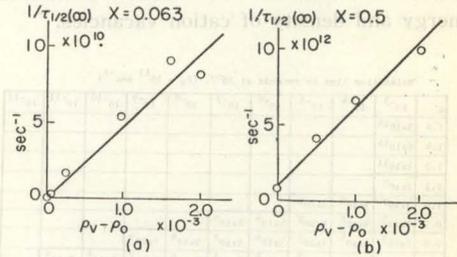


Fig. 8. Proportional relation between cation vacancy density introduced and the inverse of relaxation time $\tau_{1/2}$ for two different compositions.

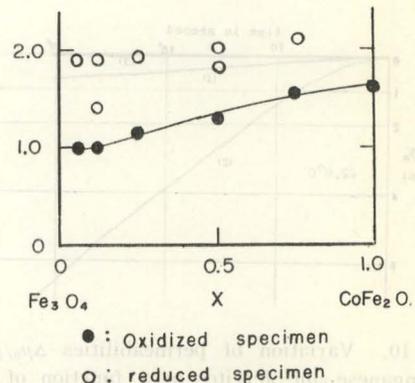


Fig. 9. Observed values of activation energy for various compositions x .

appreciably in a ferrimagnetic range, there is always an induced anisotropy due to oriented arrangement of various cations on the normal sites. Differences among various ferrites must be only in the order of magnitude of anisotropy. Furthermore, if the vacancy migration mechanism predominates, then the relaxation time should be expressed by Eq. (4).

Although Eq. (4) was derived in the case of Bickford-Slonczewski's model this formula may still apply to other cases as a crude estimation, if we allow an error of a factor up to 10^{1-2} .

In Table I, the values of Eq. (19) at room temperature are tabulated with the values of activation energy and vacancy density as

Table I. Numerical values of relaxation time of induced anisotropy in ferrites at room temperature. Parameters are values of activation energy and density of cation vacancies.

Relaxation time in seconds at 20°C. ($f_0 = 10^{13} \text{ sec}^{-1}$)											
Q	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	
1.6	3×10^{18}										
1.4	6×10^{14}										
1.2	1×10^{11}										
1.1	2×10^9										
1.0	3×10^7	3×10^6	3×10^5								
0.9	4×10^5	4×10^6	4×10^7	4×10^8	4×10^9						
0.8	5×10^3	5×10^4	5×10^5	5×10^6	5×10^7	5×10^8	5×10^9				
0.7	80	800	8×10^3	8×10^4	8×10^5	8×10^6	8×10^7	8×10^8	8×10^9		
0.6	1	10	100	1×10^3	1×10^4	1×10^5	1×10^6	1×10^7	1×10^8	1×10^9	
0.5	2×10^{-2}	0.2	2	20	200	2×10^3	2×10^4	2×10^5	2×10^6	2×10^7	
0.4	3×10^{-4}	3×10^{-3}	3×10^{-2}	0.3	3	30	300	3×10^3	3×10^4	3×10^5	

- 1 day = 0.86×10^5 ,
- 1 month = 2.6×10^6 ,
- 1 year = 3.15×10^7 ,
- 1 century = 3.15×10^9 seconds.

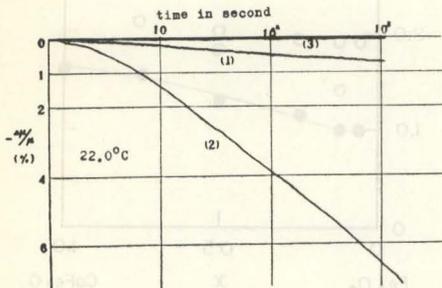


Fig. 10. Variation of permeabilities $\Delta\mu_0/\mu_0$ of manganese-zinc ferrites as a function of time after A. C. demagnetization. (1) vergin sample; (2) after homogenizing heat treatment; (3) after reduction of 0.1% of oxygen.

parameters.

If we assume for the activation energy and relaxation time the most common value for Mn-Zn ferrites, namely 0.7 eV and 10^{13} seconds, we find from this table that the corresponding density of vacancies becomes the order of 10^{-3} to 10^{-4} . According to our experiments, this is a most probable range of the value, if we made the specimen without sufficient precautions.

On the basis of this consideration, we applied the same technique to prepare high quality Mn-Zn ferrites with μ_0 of 5300*. The result is shown in Fig. 10. Curve (1) shows the result of disaccommodation of this original specimen after A. C. demagnetization. It shows an adequate industrial atmosphere controlling technique can achieve a considerable low disaccommodation of about 0.7% after 10^3 seconds. Curve (2) shows the results after applying a homogenizing heat treatment to this specimen by using our sealed container technique. The specimen was contained in a sealed quartz tube in vacuum, annealed at 1100°C for 12 hours, cooled slowly, again annealed for 12 hours at 600°C and cooled.

The large increase of the disaccommodation shows that the degree of oxidation has been homogenized and main amount of the vacancy, which was present in the surface area initially, has spread uniformly into the entire body of the specimen.

We show in curve (3) the result after applying reducing and homogenizing heat treatment. The specimen was sealed in a quartz tube with small iron metal powder, the amount of which is so adjusted to obtain 0.1% reduction of the specimen, if the entire iron powder is oxidized into $\alpha\text{Fe}_2\text{O}_3$. The heat treatment is just the same as the case of curve (2).

In this specimen the disaccommodation is well controlled to be less than 0.02% and without loss in $\tan \delta/\mu_0$.

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* These samples were kindly given by Drs. Karasawa and Hiraga of the TDK Electronics Company.

mental assistance in our disaccommodation study.

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DISCUSSION

A. A. HIRSCH: Your expression for the induced magnetic anisotropy has the same form as the magnetomechanical energy in a cubic crystal. I think that this fact can be used for a macroscopic interpretation of the induced anisotropy where a migration mechanism can lead to deformation like a stress.

S. IIDA: The fact that the expression for the induced anisotropy is just equal to the expression of magnetomechanical energy, is well known and the adequateness of this first order expression has been verified experimentally by Dr. Bickford et al, for the case of iron-cobalt ferrites. It is also well known that the magnetostrictive energy is not capable to explain so high an anisotropy energy as that in this case.

G. W. RATHENAU: In the simple cases of induced anisotropy by a redistribution of carbon and nitrogen interstitial atoms in iron it turns out that the magnetomechanical interaction is smaller than a direct electronic interaction.

worden. Es ergibt sich aus diesen Ergebnissen, dass die induzierte Anisotropie von den anwesenden Kobaltionen herrührt, und dass der zeitliche Aufbau bzw. Abbau der Anisotropie sehr vom Oxidationsgrad der Probe abhängt. So beobachten z.B. Penoyer und Bickford, dass der Aufbau der Anisotropie in leicht oxidierten Proben bei 100°C schon nach 30 min beendet ist. Demgegenüber fanden Iida und Mitarbeiter, nur eine sehr geringe Anisotropie bei reduzierten Proben, die ΔW lang bei 400°C im Vakuum im Magnetfeld gemessen wurden. Da die Oxidation von Fe^{2+} zu Fe^{3+} in den Kobalt-Eisen-Ferriten mit der Erzeugung von Kationenlücken verbunden ist, kann man dieses Verhalten durch Wanderung von Ionen erklären, die die zur Erzeugung der induzierten Anisotropie notwendige Kationenlücken erschaffen.

Untersuchungen an Einkristallen zeigen, dass die Richtungsabhängigkeit der magnetfeldinduzierten Anisotropie in folgender Weise dargestellt werden kann:

$$N_z = -F \sum_{i,j} \alpha_i \alpha_j^2 - G \sum_{i,j,k} \alpha_i \alpha_j \alpha_k \quad (1)$$

wobei die α_i und β_i die Richtungskosinus der Magnetisierung in bezug auf die Kristallachsen während der Messung und der Magnetisierung sind.

* This paper was not read at the Conference.

Eisen-Kobalt-Ferriten erschien es interessant zu untersuchen, ob bei solchen kobalthaltigen Ferriten die keine oder nur sehr wenig Kobaltionen enthalten, eine durch Magnetfeld-Temperatur induzierte Anisotropie erzeugt werden kann. Gezeigt erschien dazu der stöchiometrische Nickelkerrit, in dem ein Teil des Nickels durch Kobalt ersetzt wurde. Nach Paradoxon ist das Ni^{2+} im Nickelkerrit nicht oxidierbar; da auch Co^{2+} wesentlich stabiler als Fe^{2+} ist, dürfte bei diesen Ferriten höchstens eine sehr geringe Oxidation, und damit nur sehr wenige Kationenlücken auftreten.

Probenherstellung und Messmethoden

Untersucht wurden polykristalline Scheiben und Einkristalle aus der Zusammensetzung $Co_{0.2}Ni_{0.8}Fe_{0.2}O_4$ mit $x=0.02, 0.10, 0.20$ und 0.30 bei den polykristallinen Proben und $x=0.02$ und 0.10 bei den Einkristallen. Die polykristallinen Proben wurden nach dem üblichen keramischen Verfahren, die Einkristalle nach dem Verneuil-Verfahren hergestellt. Alle Proben wurden anschließend so getempert, dass sie ausbeugungsfrei waren. Die Magnetfeld-Temperatur wurde so durchgeführt, dass die Proben bei verschiedenen Temperaturen eine bestimmte Zeit lang in einem Feld von 2.5 kOe gelagert und anschließend