Variation in Crystal Structure, Ionic Conductivity, and Magnetic Properties with the Water Uptake of a New Hydrated Sodium β″ Ferrite

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The room temperature single-crystal X-ray data of $Na_{1.5}(H_3O)_{0.5} Fe_{10}ZnO_{17} + 0.3H_2O$ (hydrated sodium β″ alumina-like ferrite) were refined. The space group is $R\bar{3}m$ and the hexagonal cell parameters are $a = 5.940$, $c = 35.731$ Å. Water molecules are localized in the conduction region and the total amount of absorbed water depends on hydration conditions, leading to different possible chemical compositions. By thermogravimetric methods the amount of the absorbed water could be measured. This compound is a poor ionic conductor ($\sigma_{25°C} = 1.27 \times 10^{-10} \Omega^{-1} cm^{-1}$) in comparison with β″ aluminas. Two distinct types of magnetic behavior were observed for crystals of the same preparation, but in all cases water uptake leads to an enhancement of a ferromagnetic component. Dilatometric measurements performed on single crystals revealed the influence of water desorption on cell parameters. © 1990 Academic Press, Inc.

1. Introduction

β and β″ aluminas are well-known superionic conductors. By substituting Fe^{3+} cations for Al^{3+}, new magnetic compounds (β and β″ ferrites) can be obtained. Several studies have been reported on the synthesis, the stoichiometry, and the magnetic and conductivity properties of the β ferrites (*1–8*). In β ferrites deviation from simple stoichiometry is responsible for the high ionic conductivity, which is comparable to that of β aluminas: both electronic and ionic conductivities depend on the Fe^{2+} content of the structure.

Little work has been done up to now con-

cerning the β″ ferrite properties in comparison with β ferrites. A rhombohedral compound of approximate chemical composition $K_2O \cdot 5Fe_2O_3$ had been obtained by different researchers (*2, 9, 10*). Recently, a crystallographic study on the β″ (Na, K) ferrite structure stabilized with Zn^{2+} was reported (*11, 12*). In this structure the chemical formula is $(Na, K)_{1+x} Fe_{11-x}Zn_xO_{17}$ ($x \approx 0.33$) and the excess Na, K cations are balanced by substituting some Fe^{3+} cations for Zn^{2+}. Microprobe analysis has shown that the β″ (Na, K) crystals stabilized with Zn^{2+} and Co^{2+} to be nonstoichiometric (*11–14*).

The β″ (Na, K) ferrite crystals are ferri-

magnetic, and the weak ferrimagnetic component seems to depend significantly on the chemical composition of the compound (*13, 15*). The β'' (Na, K) ferrite stabilized with Zn^{2+} (or Co^{2+}) is a poor ionic conductor ($\sigma_{25°C} \approx 1.5 \times 10^{-7} \Omega^{-1} cm^{-1}$) and the presence of Fe^{2+} cations is excluded (*12*). Recently, Nariki et al. (*16*) reported that β'' (K) ferrite stabilized with Cd^{2+} has higher conductivity ($\sigma_{25°C} \approx 10^{-2} \Omega^{-1} cm^{-1}$).

Hydration of β'' ferrites is also observed (*11, 13*) but until now no experimental data have been available to clarify the reactivity of these compounds with water. In isomorphous divalent β'' aluminas, hydration affects significantly the physical properties (e.g., ionic conductivity; *17, 18*). It seemed interesting to study how hydration affects the crystal structure, the ionic conductivity, and the magnetic properties of a divalent β'' ferrite compound.

2. Experimental

Single crystals of β'' Na ferrite were synthesized using the flux method. The flux had a eutectic composition $0.63Fe_2O_3$, $0.37Na_2O$ and the initial powder mixture had the composition $Na_2O.5Fe_2O_3$, to which small amounts of ZnO were added in order to stabilize the structure (Zn/Fe ratio was 1/35). The whole powder mixture was introduced into a platinum crucible and fired at 1300°C for 24 hr; then it was cooled slowly (10°C per hour) to 1000°C. The single crystals extracted from the flux were platelet shaped with faces reaching 5×5 mm. Those crystals examined by a precession camera revealed rhombohedral symmetry (space group $R\bar{3}m$). A crystal structure determination has been carried out using a four-circle Enraf–Nonius X-ray diffractometer (MoKα radiation) at room temperature, on platelet-shaped single crystal (dimensions $0.15 \times 0.22 \times 0.08$ mm). This crystal was extracted from the flux, exposed to open atmosphere, and mounted on the diffractometer. The hexagonal cell parameters (space group $R\bar{3}m$, $Z = 3$) are: $a = 5.9401(1)$ Å, $c = 35.731(12)$ Å. All collected reflections (5535) were measured from a semi-Ewald sphere using the $\bar{\omega}$ scan technique in the $\vartheta < 43°$ range with a scan width of 1.5° (in ϑ). All reflections were corrected as far as the background and the Lorentz polarization factor are concerned; then 902 reflections were averaged in the Laue class $\bar{3}m$.

Absorption corrections have been applied *in situ* with the DIFABS program (*19*). The weight attributed to each reflection during the refinement was $w = 1/\sigma^2(F_0)$, where $\sigma(F_0)$ was defined as in Ref. (*20*) with an instability factor $p = 0.02$. The list of observed and calculated structure factors may be obtained by request to the authors.

For thermal gravimetry experiments a Setaram thermobalance TG 85 was used. Experimental results are summarized in Table IV. Samples consisted of small single crystals hydrated under different conditions. Samples of Experiments 2 and 3 were exposed in the same way in a moist atmosphere, although those of Experiment 1 were exposed to the air. Some hydration experiments (Experiments 1 and 2) have been carried out under atmospheric pressure and Experiment 3 was carried out under vacuum (10^{-3} Torr).

Ionic conductivity measurements were carried out by the complex impedance method. Experiments have been performed on a sample consisting of very small monocrystals of β'' Na ferrite compacted into a cylindrical shape. Thin films of platinum were deposited on both sides of the cylindrical sample for electrical contacts. The dimetric measurements were performed on single-crystal β'' Na ferrite preliminarily exposed (10 days) to the air, then mounted to an Enraf–Nonius four-circle diffractometer. Cell parameters were obtained after a least-squares refinement of 25 reflections collected at high θ angles, using MoKα radi-
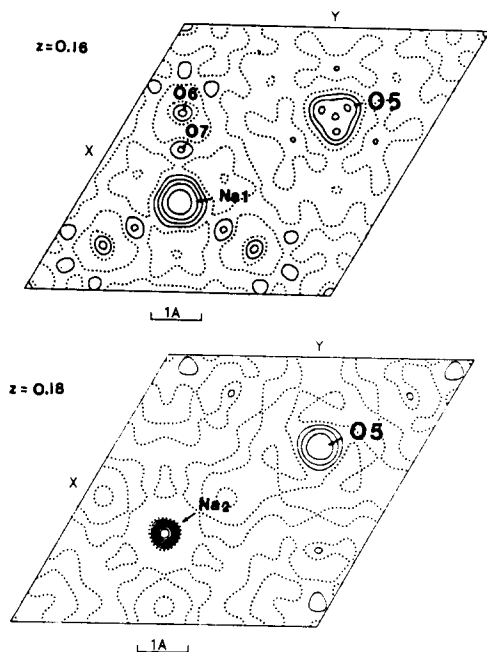
FIG. 1. Projection of the electron density distribution (for $z = 0.16$, $z = 0.18$) showing the oxygen anions and the sites of the sodium atoms in the conduction region (zero contour dotted; contour interval in arbitrary units).

ation. The temperature was obtained by blowing a stream of hot gas on the crystal; temperature and blow were regulated within $\pm 3°C$ (21).

3. Results and Discussion

In the refinement of the β'' Na structure we used as starting atomic parameters those of sodium–potassium ferrite in the $R\bar{3}m$ group (11, 12). In Fig. 1 some Fourier sections of the β'' Na structure for $z = 0.16$ and 0.18 are shown. The following aspects should be noted:

(a) the emergence of two electronic density peaks for $z = 0.16$ and $z = 0.18$ (at $18h$ and $6c$ sites) which could be interpreted as Na density in analogy with β'' (Na, K) structure (12).

(b) the presence of three equivalent peaks

in the $9d$ (mO site) at $z = 0.16$ and of a residual peak centered at $x = 0.76$, $y = -x$, and $z = 0.16$ ($18h$ site) reveal the possible existence of oxygen in these sites as a result of absorption of water into the structure. In fact, crystal refinement in the isostructural β'' (H^+, H_3O^+) alumina shows that $9d$ (mO) and some $18h$ sites in the conduction region are occupied by either (H_2O) molecules or (H_3O^+) radicals (17); such water molecules (or (H_3O^+)) could occupy vacant sites or replace some Na cations in isostructural β'' Na ferrite.

Because the single crystal we studied was exposed to the air, an exchange reaction between Na and H_3O^+ (or H_2O) presumably occurred: because of this exchange, for very long exposures to the atmosphere the surface of β'' Na ferrite crystals was covered by a thin film of NaOH (22).

We proceed further in the refinement of the β'' Na structure by considering two positions for Na atoms (Na(1), Na(2)) and two positions for oxygen atoms (O(6), O(7)) in the conduction region. The existence of several oxygen and sodium sites (totally or partially occupied) in the conduction region introduces a high correlation between temperature factors and atomic parameters. Therefore, to achieve convergence it was found necessary to refine first their atomic positions and then their isotropic thermal parameters and site occupancies.

The refined atomic parameters of the β'' Na structure are shown in Table I. Observed distances at the different coordination polyadra are shown in Table II. Because of the quality of our data collection we did not localize the position of hydrogen atoms with high precision.

At this stage of refinement two questions remain unanswered: the placement of the Zn^{2+} cations and the number of water molecules (or H_3O^+ radicals) in the structure. In isostructural β'' (Na, K) ferrite of chemical formula $(Na, K)_{1+x}Fe_{11-x}Zn_xO_{17}$ ($x \approx 0.33$) excess Na and K cations are balanced by

TABLE I

POSITIONAL, POPULATION, AND TEMPERATURE FACTOR COEFFICIENTS IN HYDRATED SODIUM β'' FERRITE[a]

Atom	Position	Occupancy	x	z	U_{11}	U_{33}	U_{12}	$U_{13(\text{Å}^2)\times 10^5}$
Fe(1)	18h	0.999(1)	0.16949(9)	−0.06972(2)	446(9)	607(19)	231(14)	31(12)
Fe(2)	6c	0.990(6)	0	0.35066(3)	386(27)	315(38)	$U_{11}/2$	0
Fe(3)	6c	0.990(6)	0	0.44981(3)	431(28)	257(35)	$U_{11}/2$	0
Fe(4)	3a	0.996(12)	0	0	399(40)	254(53)	$U_{11}/2$	0
O(1)	18h	0.984(12)	0.15482(42)	0.03398(9)	923(66)	387(105)	477(87)	−38(63)
O(2)	18h	0.984(11)	0.16413(44)	0.23612(9)	530(52)	584(98)	248(73)	124(60)
O(3)	6c	0.990(18)	0	0.29680(16)	63(131)	791(206)	$U_{11}/2$	0
O(4)	6c	0.990(18)	0	0.09631(18)	803(160)	775(233)	$U_{11}/2$	0
O(5)	18h	0.237(9)	0.02269(175)	0.49851(124)	3415(309)			
O(6)	9d	0.160(2)	0.5	0.5	3398(1367)			
O(7)	18h	0.050(6)	0.73320(140)	0.16322(50)	3250(1320)[b]			
Na(1)	18h	0.118(7)	0.75380(290)	0.16740(54)	3353(350)[b]			
Na(2)	6c	0.450(18)	0	0.17254(72)	3120(268)[b]			

[a] $R = 0.037$, $wR = 0.046$, $y = -x$.
[b] Values of U(iso) (Å × 10^5), $U_{11} = U_{22}$, $U_{13} = -U_{23}$.

substituting some Fe^{3+} cations for Zn^{2+} in the tetrahedral Fe(2) sites of the spinel block *(11, 12)*. Also in β'' aluminas, tetrahedral Al(2) sites are partially substituted by divalent cations stabilizing the β'' structure *(23)*.

Bond strengths and effective valencies of Fe cations have been calculated using the Brown relation *(24)*. For nearly all Fe sites effective valence is approximately 3 (Table III), revealing the Fe^{3+} presence: only the valence of Fe(2) ion appears to be 2.59, thus indicating the presence of Zn^{2+} at this site. If we exclude the existence of Fe^{2+}, as in the case of isostructural β'' (Na, K) ferrite *(12, 15)* the Zn^{2+} content per formula unit is $x = 1.0(1)$. We can arrive at the same result by comparing the mean Fe–O distance of tetrahedral spinel sites observed in β'' Na

TABLE II

INTERATOMIC DISTANCES FOR β'' Na (H_2O, H_3O^+) FERRITE (IN Å)

	Distance				
Fe(2) tetrahedron		**Fe(3) tetrahedron**		**Fe(4) octahedron**	
Fe(2)–O(1)	1.931(2)	Fe(3)–O(2)	1.872(2)	Fe(4)–O(1)	2.003(3)
−O(3)	1.925(1)	−O(5)	1.807(9)		
O(1)–O(1)	3.182(4)	O(2)–O(2)	3.015(6)	O(1)–O(1)	2.760(3)
O(1)–O(3)	3.119(3)	O(2)–O(5)	3.038(4)	O(1)–O(1)	2.904(7)
Fe(1) octahedron		**Na(1) polyedron**		**Na(2) polyedron**	
Fe(1)–O(1)	2.106(3)	Na(1)–O(4)	2.659(6)	Na(2)–O(4)	2.723(6)
−O(2)	1.953(2)	−O(2)	3.331(2)	−O(2)	2.833(3)
−O(3)	2.062(1)	−O(2)	2.892(3)	−O(5)	3.440(9)
		−Na(2)	2.541(4)	−Na(2)	3.455(5)
−O(4)	1.986(3)	−Na(2)	3.961(6)	−Na(1)	2.541(4)

TABLE III

BOND STRENGTHS AND EFFECTIVE VALENCIES OF Fe CATIONS

Site	Ions	O(1)	O(2)	O(3)	O(4)	O(5)	Cation valence
18h	Fe(1)	(×2) 0.392 (×2)	(×2) 0.585 (×2)	(×1) 0.439 (×3)	(×1) 0.535 (×3)		2.93
6c	Fe(2)	(×3) 0.622 (×1)	(×1) 0.632 (×1)				2.49
6c	Fe(3)		(×3) 0.732 (×1)			(×1) 0.884 (×2)	3.08
3a	Fe(4)	(×6) 0.732 (×1)					3.07

ferrite ($d = 1.928(2)$ Å) and $BaFe_{12}O_{19}$ ($d = 1.89(1)$ Å), $ZnFe_2O_4(1.97(3)$ Å) ferrites (25, 26); $BaFe_{12}O_{19}$ and $ZnFe_2O_4$ do not contain Fe^{2+} cations. According to this comparison the amount of Zn^{2+} is $x = 0.9(1)$.

On the other hand, in β'' (H^+, H_3O^+) alumina the $9d$ (mO) site is occupied by (H_3O^+) ion (17). If we suppose that (H_3O^+) also occupies the $9d$ site in the conduction region of isostructural hydrated β'' Na ferrite then the chemical formula could be written as

$$Na_{1.5(1)} (H_3O^+)_{0.4(1)}Fe_{10.1(1)}Zn_{0.9(1)}O_{17} + 0.3H_2O. \quad (1)$$
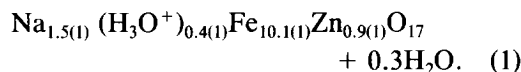
In this compound, in analogy with the hydration of β'' Na alumina, Na(1) and Na(2) ions can be replaced partially or totally by H_3O^+ cations (or water molecules). This fact leads to some ambiguity about the exact chemical formula of the compound, as we cannot distinguish between Na and oxygen atoms by means of X-ray refinement.

If Na(1) is replaced by (H_3O^+) and both the O(6) and O(7) oxygens belong to (H_2O) molecules, then there are a total of 1.48 (H_2O and H_3O^+) in the conduction region: the formula may be written

$$Na_{0.9(1)} (H_3O^+)_{0.7(1)}Fe_{10.1(1)}Zn_{0.9(1)}O_{17} + 0.78H_2O. \quad (2)$$
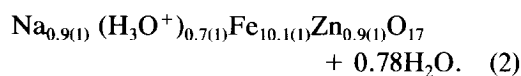
If Na(2) ion is replaced by (H_3O^+) and both O(6) and O(7) oxygens belong to water mole-

cules, then there exists a total of 1.68 (H_2O and H_3O^+) in the conduction region and the formula would be

$$Na_{0.7(1)} (H_3O^+)_{0.9(1)}Fe_{10.1(1)}Zn_{0.9(1)}O_{17} + 0.78H_2O. \quad (3)$$
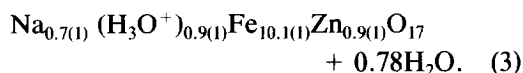
It is obvious from the above discussion that there is an ambiguity about the water content in the structure of the β'' Na ferrite. The quantity of absorbed water depends on several factors, such as the crystal grain size and the temperature. Bekka and Kalogirou (11, 13) claim that β'' (Na, K) ferrite crystals are covered by a thin film of white powder when they are exposed to the atmosphere for a long time, probably because of the exchange reaction Na $\leftrightarrow$ H_2O; in fact, there is formation of Na_2CO_3 (and also NaOH). The same behavior is also observed in β'' Na ferrite compounds (22), but up to now no experimental data were available to clarify its reactivity with water.

In Table IV is shown the amount of water entering the β'' Na ferrite as revealed by dehydration experiments. This amount varies from 1.22 (H_2O) to 1.8 (H_2O), depending upon the initial hydration conditions, in good agreement with crystallographic refinement (formulas 2 and 3).

Analysis of thermogravimetric traces allowed us to determine the kinetic parameters of pyrolysis reactions according to the

TABLE IV

DEHYDRATION DATA OF THE β'' Na (H_2O, H_3O^+) FERRITE

Percent structural water by weight		Structural water per conduction region	Dehydration temperatures[a] (°C)	Comments
Expt. 1	2.07	1.22	250, 350[b]	Two steps
Expt. 2	3.42	1.80	205, 250	Two steps
Expt. 3	3.45	1.81	164, 277[b]	Two steps

[a] Referring only to structural water desorption.
[b] Calculated reference temperatures T_s from the kinetic study of the dehydration process.

method proposed by Horowitz et al. (27). By assuming that the dehydration reaction in the β'' Na ferrite is of first order, we used the following expression to determine the value of pyrolysis energy E^*,

$$\ln \ln \left[\frac{W_o - W_{ft}}{W - W_{ft}} \right] = \frac{E^* \theta}{RT_s^2},$$

where W is the weight remaining at a given temperature and W_0 and W_{ft} are the initial and final weights, respectively, R is the gas constant, T is the absolute temperature, and θ is a temperature defined as $T = T_s + \theta$ where T_s is the temperature where

$$\left[\frac{W_0 - W_{ft}}{W - W_{ft}} \right] = \frac{1}{e}.$$

A plot of the ln ln of the reciprocal of the fraction pyrolysed against θ gives a straight line whose slope is related to the activation energy. With this method two different steps are revealed as far as the structural water desorption is concerned (see Fig. 2b); this result indicates that (H_3O^+) ions (or H_2O)) are not bound in the same conduction region sites. The value of pyrolysis energy in the case of β'' Na ferrite (0.72 eV) is very close to the value of the binding energy of water in β'' Na alumina (0.78 eV) (18).

The weight gain of the polycrystalline sample of β'' Na ferrite is shown in Fig. 3; the sample was first dried and was then exposed to a moist atmosphere.

As in the case of isostructural β'' aluminas (17), there are two steps in the water uptake process in the β'' Na ferrites: a fast process which corresponds to water absorption in the surface (or in its vicinity) of the crystallites and a much slower process corresponding to water which enters into the conduction region (structural water).

The curve of the weight gain can be described by the relationship

$$\frac{\Delta P}{P_0} = \frac{\Delta P_{max}}{P_0} - \frac{\Delta P_1}{P_0} e^{-t/\tau_1} - \frac{\Delta P_2}{P_0} e^{-t/\tau_2},$$

where t is time (in hours), P_0 is the sample weight before hydration, and ΔP_{max} is the maximum weight gain of the sample for long-time exposure in the moist air. By means of the FIT (28) program, we refined the τ_1, τ_2 values: τ_1 is a time constant corresponding to the fast process of water uptake and is found to be 0.36 hr; τ_2 relates to the slower process and is found to be 49 hr. It is worth noting that in the case of β'' aluminas the process of water uptake is much slower ($\tau_1 = 9.4(2)$ hr and $\tau_2 = 259$ hr).

In Fig. 4 we can see the variation of conductivity with temperature. The activation energy at low temperature ($E = 0.828$ eV) reveals that the hydrated β'' Na (H_2O, H_3O^+) compound is a poor ionic conductor ($\sigma_{25°C} = 1.27 \times 10^{-10}$ Ω^{-1} cm^{-1}) compared to β'' Na alumina, where $\sigma_{25°C} = 1.4 \times 10^{-1}$ Ω^{-1} cm^{-1} (29); this may be due to a complete
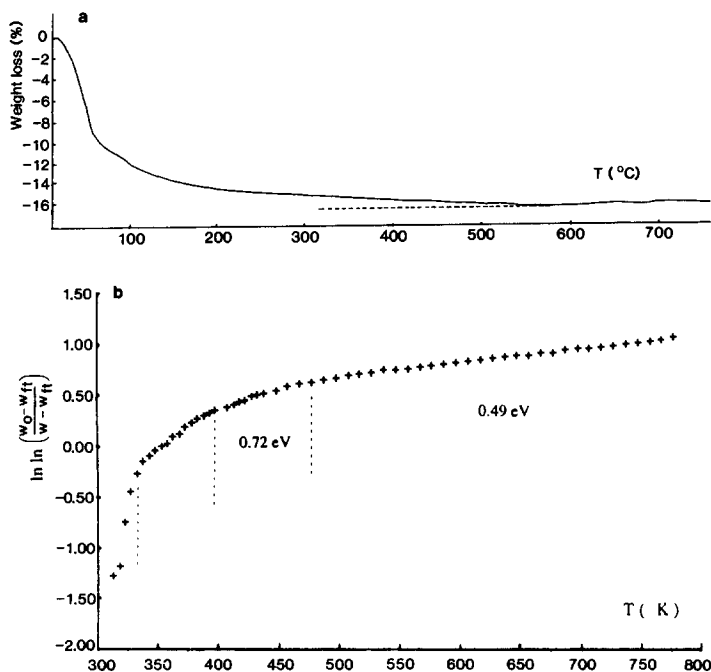
Fig. 2. (a) Dehydration thermogravimetric curve (Experiment 3) for hydrated sodium β'' ferrite. (b) Variation of ln ln $(W_0 - W_{ft})/(W - W_{ft})$ with T showing two distinct steps (linear parts of the curve corresponding to 0.72 and 0.49 eV, respectively) as far as structural water is concerned. The linear parts at the beginning of the curve correspond to superficial water desorption.

occupation of the sites in the conduction region by Na, H_2O, and H_3O^+.

Also in β'' (Na, K) ferrite, the ionic conductivity is $\sigma_{25°C} = 4 \times 10^{-10}$ Ω^{-1} cm^{-1} and refinement shows that all sites in the conduction region are occupied by Na, K

Fig. 3. Weight gain as a function of time for a sodium β'' ferrite.

ions $(11, 12)$. Recently (16), for β'' (K) ferrite stabilized by Cd^{2+} higher conductivity was reported $(\sigma_{25°C} \approx 10^{-2} \, \Omega^{-1}$ cm$^{-1})$. The conductivity value of hydrated β'' (Na) ferite is close to that of β'' (K) ferrite $(\sigma = 3 \times 10^{-9}$ Ω^{-1} cm$^{-1})$ (2) and also to that of β'' (H_3O^+) alumina $(10^{-11} \, \Omega^{-1}$ cm$^{-1})$ (30).

In β'' (H_2O, H_3O^+) alumina the conductivity mechanism involves slow diffusion of H_3O^+ into the conduction region (17). Since the conductivity values for hydrated β'' Na ferrite and hydrated alumina are comparable, probably the same conduction mechanisms are involved in both compounds.

The activation energy decreases as temperature increases: three steps with different activation energies are observed (Fig. 4). These distinct bendings of the conductivity curve are observed for $T = 210(10)°C$ and $T = 340(10)°C$, and are related to water de-
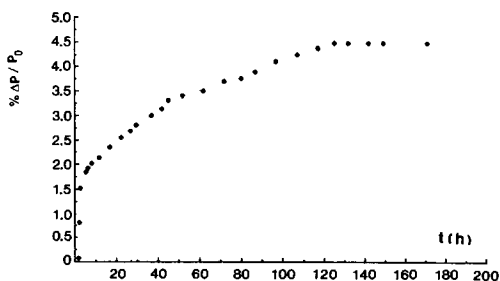
FIG. 4. The ionic conductivity of hydrated sodium β'' ferrite as a function of reciprocal temperature.

FIG. 5. Variation of spontaneous magnetization with temperature for nm sodium β'' ferrite (polycrystalline sample).

sorption at these temperatures. The decrease in activation energy can be explained by water desorption from the conduction region, allowing the more mobile Na cations to be displaced.

Two types of magnetic behavior were encountered in β'' Na ferrite crystals. After annealing at $T = 150°C$ some single crystals extracted from the same preparation of β'' Na ferrite seemed nonmagnetic (nm) while others were magnetic (m). After exposure to humid air previously nm crystals became magnetic.

The coexistence of two types of magnetic properties in single crystals from the same preparation has also been reported (11–13) in the case of β'' (Na, K) ferrite crystals stabilized by Zn^{2+} and Co^{2+}; this behavior may be related to the Zn^{2+} (or Co^{2+}) content in the structure (12), but no data have been available until now concerning the influence of water on the magnetic properties of the β'' ferrite crystals.

In our study, the coexistence of m and nm single crystals of β'' Na ferrite arose from dehydration at $T = 150°C$ of several crystals extracted from the same preparation. Figure 5 shows variation of spontaneous magnetization with temperature: the

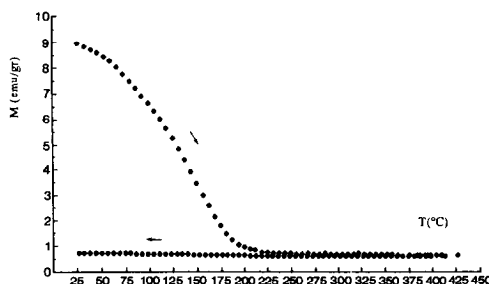sample consisted of some selected nm single crystals which were previously exposed to humid air. We could observe complete disappearance of the ferromagnetic component both above $T = 185°C$ and during the temperature reduction to room temperature. Water desorption above $T = 185°C$ can be the origin of such magnetic behavior.

The same behavior is also observed for nm single crystals of β'' Na ferrite previously exposed in humid air; in Fig. 6 we can see the variation of magnetization with field parallel to the platelet plane (easy magnetization plane (12, 22)) at room temperature.
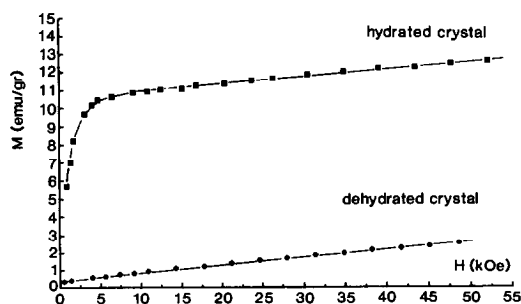
The crystal dehydrated at $T = 180°C$

FIG. 6. Comparison between magnetization curves (field $H \perp c$ axis) at room temperature for a nm single crystal of sodium β'' ferrite before and after dehydration.
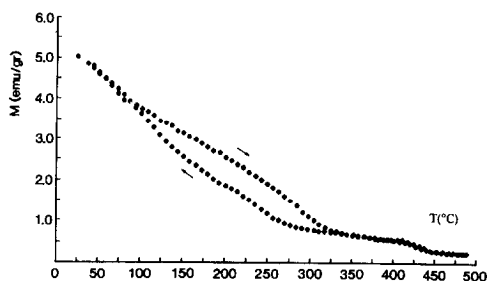
FIG. 7. Variation of the spontaneous magnetization with temperature for m sodium β'' ferrite (polycrystalline sample).

FIG. 9. Variation of the unit cell volume (v) with temperature for a single crystal of hydrated sodium β'' ferrite.

shows a complete antiferromagnetic behavior with field (Fig. 6). Water absorption results in a ferromagnetic component in the nm β'' Na ferrite crystals. The oxygen atoms of water molecules (or H_3O^+) can modify the superexchange interactions in the conduction region leading to a ferromagnetic component. Figure 7 shows the variation of magnetization with temperature for m β'' Na ferrite crystals: we noticed no significant influence of hydration on magnetic behavior. However, some influence of water uptake on magnetization is seen in a polycrystalline sample of m β'' Na ferrite when it is exposed to moist air for a long time ($t = 95$ hr; Fig. 8). Therefore, for both m and nm β'' Na crystals water absorption leads to an
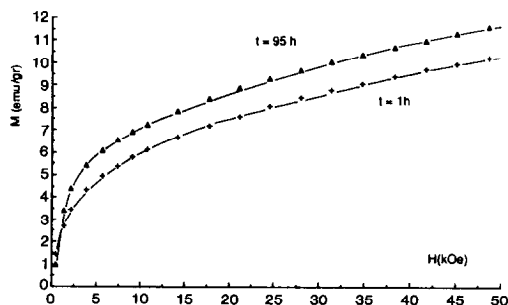
enhancement of a ferromagnetic component.

Dilatometric measurements on a single crystal of hydrated β'' Na ferrite show (Fig. 9) the decrease in the unit cell volume at $T > 260°C$, revealing water desorption at high temperatures.

4. Conclusions

Crystal structure refinement of the hydrated sodium β'' Na ferrite structure revealed a localization of water molecules (and H_3O^+ radicals) in the conduction region, in quantitative agreement with thermogravimetric measurements. This material is a poor ionic conductor compared to β'' Na alumina. Variation of ionic conductivity with temperature showed that water desorption occurred, leading to a lowering of activation energy at high temperatures. Two kinds of magnetic behavior were observed, and in all cases the absorption of water molecules in the conduction region enhanced the ferromagnetic component of this compound. Dilatometric measurements have shown that water desorption sets in at $T > 260°C$.

FIG. 8. Magnetization curves at room temperature for m sodium β'' ferrite exposed under different hydration conditions.

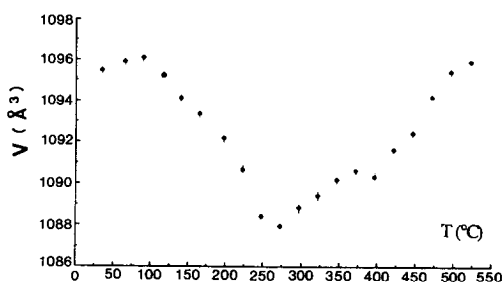## Acknowledgments

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