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# The Incorporation and the Reducibility of $Ni^{2+}$ in $MgTiO_3$

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$Ni_xMg_{1-x}TiO_3$ samples with $x$ up to 0.20 have been examined by X-ray diffraction, reflectance, and ESR spectroscopy, magnetic susceptibility, and thermogravimetric determinations, to investigate the incorporation and the reducibility of $Ni^{2+}$ in the $MgTiO_3$ ilmenite-type structure. The formation of the $Ni_xMg_{1-x}TiO_3$ solid solution is demonstrated by X-ray diffraction and ESR determinations. Reflectance spectra, magnetic susceptibility, and thermogravimetric measurements, which were also performed, cannot distinguish between a true solid solution and a mechanical mixture. The incorporation of $Ni^{2+}$ causes a slight decrease of the volume of the $MgTiO_3$ unit cell. The reduction by hydrogen of $Ni^{2+}$ in the $Ni_xMg_{1-x}TiO_3$ solid solutions takes place at approximately 700°C with segregation of metallic nickel and $TiO_2$. At higher temperatures $TiO_2$ reacts with $MgTiO_3$ giving $MgTi_2O_5$.

## Introduction

In the course of research dealing with solid solution formation and stability of mixed oxides involving MgO (*1*) and $TiO_2$ (*2–4*) with transition metal oxides, a research program was started concerning $MgTiO_3$ as a matrix. This double oxide is diamagnetic and has the ilmenite-type structure with 2/3 of the cation positions occupied by $Mg^{2+}$ and $Ti^{4+}$ while 1/3 are vacant sites. Both divalent and tetravalent ions may in principle be substituted. However, not many studies concerning solid solutions of these more complex oxides have been reported. Indeed, as previously noted (*5*), in several cases the preparation procedure of pure compounds is not easy and therefore these systems are poorly characterized.

In the present paper, the incorporation of $Ni^{2+}$ in $MgTiO_3$ was investigated in order to confirm the solid solution formation, and to test its stability against reduction in hydrogen. The system $MgTiO_3$–$NiTiO_3$ was previously studied mainly by reflectance spectroscopy (*6*). This technique yields information on the symmetry and on the bond features of the coordination polyhedron. However, it cannot provide direct evidence of the solid solution formation in cases where the coordination polyhedron and the bonding situation of the ion is very

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similar in that of the pure compound, and in the host matrix, as is the case for $Ni^{2+}$ in $NiTiO_3$, and in $NiTiO_3$–$MgTiO_3$ solid solution.

The study has been carried out mainly by X-ray diffraction techniques, thermogravimetry and ESR. Reflectance spectroscopy, and magnetic susceptibility measurements were also performed.

## Experimental

*Samples.* Undoped $MgTiO_3$ was prepared by mixing a 15% $TiCl_3$ solution (Reagent grade C. Erba R.P.), oxidized by $H_2O_2$, with a known volume of $MgCl_2$ solution. A slight excess of the magnesium salt was used in order to avoid the presence of $TiO_2$ in the final product. The $MgCl_2$ solution was prepared by dissolving MgO (Erba R.P.) in HCl solution (1 : 1). The solution containing both magnesium and titanium was neutralized, under stirring, by addition of ammonia; a white precipitate was obtained. To evaporate most of the water, and to allow complete precipitation, the solid in the presence of the supernatant liquid was heated, under stirring, at 80°C. The product was then dried at 110°C and subsequently calcined in air in several steps. In the first place, the powder was heated at 400°C, 2 hr, then at 600°C, 4 hr, and finally at 850°C for 2 days. At the end of each step the sample was ground in a agate mortar. The grinding was also carried out during the last heating step. After the thermal treatment, the powder was washed with a hot solution of HCl (1 : 1) to eliminate the excess of MgO. The solid product was then filtered, washed with water, dried at 110°C, and reheated in air at 600°C.

Samples containing nickel were prepared by following the same procedure, the only variation being the addition of known volumes of $NiCl_2$ solution to the initial $MgCl_2$ solution, in order to attain a specific Ni/Mg ratio. $MgTiO_3$ is white, while the samples containing nickel are pale yellow, with the color intensity increasing with the nickel content. In what follows, they are designated as MT N. The number after the letters gives the nominal concentration of nickel ions with respect to 100 divalent ($Ni^{2+}$ + $Mg^{2+}$) ions.

Pure $NiTiO_3$ was prepared by heating in air at 1000°C for 100 hr, a pellet of a $TiO_2$ and NiO mixture (in the stoichiometric ratio). A mechanical mixture was prepared by mixing pure $NiTiO_3$ and $MgTiO_3$ in the molar ratio 0.2. An agate mortar was used in mixing the titanates being suspended in acetone. Pure $TiO_2$ was prepared by hydrolysis and oxidation of $TiCl_3$ (*4*), while $MgTi_2O_5$ was obtained from MgO (by decomposition of the ex-carbonate at 600°C) and $TiO_2$ in stoichiometric ratio. The mixture was heated at 1100°C, 48 hr, in air.

*Chemical analysis.* The nickel content in the MT N samples was determined by atomic absorption (Varian). The samples were fused with $KHSO_4$ in a platinum crucible. After cooling, the solid was dissolved in water (slightly acidified with HCl). The standard solutions prepared by a standard $Ni(NO_3)_2$ (Fluka) solution contained $MgTiO_3$ (fused with $KHSO_4$) in a concentration comparable to that of the solid solution of the samples. The results are listed in Table I.

*X rays.* The unit cell parameter *a* and the axial ratio $C = c/a$ of the hexagonal ilmenite structure were measured by taking Debye–Scherrer powder photographs, using iron-filtered Co $K\alpha$ radiation and a Philips camera (i.d. 114.6 mm) with the asymmetric Straumanis film mounting method. For all the specimens, X-ray diffraction patterns showed no lines other than those belonging to the hexagonal ilmenite structure (*7*). The following eight $\alpha_1$ reflections in the region of Bragg angle $\theta$ = 60–90°, were read by means of a Philips measuring device with an accuracy of ±0.005 cm and used in constructing Nelson–Riley plots for extrap-

TABLE I

ANALYTICAL, THERMOGRAVIMETRIC, MAGNETIC, AND X-RAY DIFFRACTION DATA FOR THE MT N SAMPLES

| Samples | %$Ni^{anal}$ [a] | %$Ni^{TG}$ [a] | $\Delta\%_{400-700}$ | $\Delta\%_{700-1000}$ | $\mu$ (B.M.) | $a$ (Å) | $C$ | Phases |
|---|---|---|---|---|---|---|---|---|
| $MgTiO_3$ | — | — | — | — | — | 5.0565 | 2.7472 | I[b] |
| MT N 3 | 1.26 | 1.25 | 0.34 | 0.16 | 3.21 | 5.0564 | 2.7472 | I |
| MT N 5 | 2.10 | 2.09 | 0.57 | 0.27 | — | 5.0550 | 2.7472 | I |
| MT N 8 | 3.42 | 3.41 | 0.93 | 0.39 | 3.25 | 5.0548 | 2.7472 | I |
| MT N 10 | 4.36 | 4.40 | 1.20 | 0.57 | 3.24 | 5.0533 | 2.7472 | I |
| MT N 20 | 9.16 | 9.69 | 2.64 | 1.19 | — | 5.0515 | 2.7472 | I |

[a] %Nickel by weight.

[b] I = Ilmenite.

olation to $\theta = 90°$: (2 0 14) 81.6°, (1 3 10) 78.0°, (0 4 8) 75.0°, (4 1 3) 73.0°, (1 4 0) 69.5°, (3 2 4) 68.0°, (0 1 14) 67.5°, (3 1 8) 64.0°, where the numbers in parentheses are the Miller indexes and those outside parentheses the $\theta$ angles of each given reflection.

The axial ratio $C = c/a$ was determined by minimizing the deviations of $a$ values for the different reflections following a least-squares procedure. At least two determinations were made for each specimen. The error in $a$ and $C$ are $\pm 5 \times 10^{-4}$ Å, and $\pm 7 \times 10^{-4}$, respectively. Since the unit cell volume of hexagonal $MgTiO_3$ is given by $V = a^3C \sin 60$, the error in $V$ is $\Delta V = \pm 0.15$ Å$^3$. No temperature regulation was attempted during exposure, but temperature fluctuations were less than ±2°C. No thermal expansion coefficient for the $MgTiO_3$ unit cell parameters has been reported in the literature, and therefore no correction was applied. However, the majority of determinations were made ±4°C from 24°C, and it was noted that for undoped $MgTiO_3$ the X-ray patterns, taken at different temperatures in this range, gave values of $a$ and $C$ within the error limit. This indicates that the $MgTiO_3$ thermal expansion coefficient is low as expected for high melting compounds.

The phase analysis was performed by a diffractometer (Ni-filtered Cu $K\alpha$ radiation) in the region of low $\theta$ angles (up to $\theta = 30°$) and by using the Debye–Scherrer method with a camera i.d. 114.6 mm (Ni-filtered Cu $K\alpha$ radiation) in the back reflection region, with range of $\theta$ 71–75°. In the latter case both $\alpha_1$ and $\alpha_2$ lines of the doublet were considered.

*Magnetic measurements.* Magnetic measurements were performed by the Gouy method at 4000 and 8000 G in the temperature range 100–300 K. A semimicrobalance reading to ±0.01 mg was employed. The instrument was calibrated with $Hg[Co(CNS)_4]$. The magnetic susceptibility of undoped $MgTiO_3$ was determined with the same apparatus.

*Diffuse reflectance spectra.* Diffuse reflectance spectra were obtained with a Beckman DK 1 spectrophotometer in the range 2500–400 nm, at room temperature. The specimens were analized against MgO as reference.

*Thermogravimetric measurements.* The thermogravimetric study was carried out by using a Cahn RG electrobalance. During the experiment, the sample was kept at a constant flow of hydrogen (24 ml/min). The temperature was raised to 1000°C by a linear programmer (heating rate 3°C/min). The change in mass was measured to an accuracy of ±0.02 mg.

*ESR measurements.* The ESR measurements were carried out at X-band and Q-band on a Varian E-9 spectrometer at room and liquid nitrogen temperature. Relative intensities were determined from electronically integrated spectra, by using the Varian "Strong Pitch" as reference standard.

## Results

*X rays*. Table I shows the results of the X-ray measurements. The values of the $MgTiO_3$ unit cell parameter $a$ and the axial ratio $C = c/a$ for the undoped sample agree, within the limit of the errors, with those previously reported (*6*, *7*). The addition of nickel affects the unit cell parameter $a$ but not the axial ratio $C$. As the nickel content increases, the value of $a$ decreases. Figure 1 shows the variation of the unit cell volume, $V$. A small, linear contraction with the nickel content is observed.

Table I also lists the results of the phase analysis which was performed in the high $\theta$-angle region of the X-ray spectrum. $MgTiO_3$ and $NiTiO_3$ have very similar values of lattice constants, so that in the low $\theta$-angle region the majority of the reflections belonging to the two pure compounds overlap and are indistinguishable. In this region there occur some reflections which are only present in the X-ray spectrum of $MgTiO_3$ ($d = 4.18$, $I = 30$; $d = 1.809$, $I = 4$; $d = 1.471$, $I = 5$) and some others which are only observable in the spectrum of $NiTiO_3$ ($d = 2.331$, $I = 5$; $d = 2.30$, $I = 5$; $d = 2.154$, $I = 5$). This behavior is related to the different scattering factors for $Ni^{2+}$ and $Mg^{2+}$ ions; these reflections also appear in the spectrum of a true $Ni_xMg_{1-x}TiO_3$ solid solution, as well as in the X-ray pattern of a mechanical mixture between the two titanates. Thus, they cannot be used to distinguish between the two cases.

By contrast, in the high $\theta$-angle region of the spectrum, where a much higher resolution is achieved, the reflections of $MgTiO_3$ and $NiTiO_3$ are well resolved, and a phase analysis can be accomplished.

Table II shows the results of the phase analysis performed on the reflections observed in the range of $\theta$ from 71 to 75°, both in the case of a mechanical mixture between $NiTiO_3$ and $MgTiO_3$ (Ni/Mg = 0.2 molar ratio), and in that of the more concentrated samples MT N 20. It may be seen that in sample MT N 20, only the lines ascribed to $MgTiO_3$ are present, whereas in the case of a mechanical mixture, the reflections of both $NiTiO_3$ and $MgTiO_3$ are detected.

Table III shows, as an example, the X-ray diffraction spectra of the sample MT N 10, heated at several temperatures in a hydrogen stream for 3 hr. No change is observed for thermal treatments in hydrogen up to 600°C. After heating at 700°C the re-

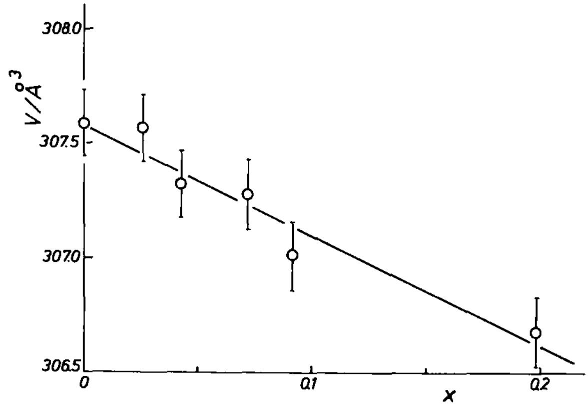

FIG. 1. Variation of the $MgTiO_3$ unit cell volume, $V$ vs $x$ for the $Ni_xMg_{1-x}TiO_3$ solid solutions.

TABLE II

HIGH ANGLE REGION OF THE X-RAY DIFFRACTION PATTERN OF SAMPLE MT N 20 AND OF A MECHANICAL MIXTURE BETWEEN $MgTiO_3$ AND $NiTiO_3$ Ni/Mg = 0.2 ATOMIC

| | | Mechanical mixture | | MT N 20 | | $d_{calc}$[a] (Å) | |
|---|---|---|---|---|---|---|---|
| *h k l* | $\lambda_{Cu}$ | $\theta_{exp}$ (°) | $d_{exp}$ (Å) | $\theta_{exp}$ (°) | $d_{exp}$ (Å) | $MgTiO_3$ | $NiTiO_3$ |
| 2 4 4 | $K\alpha_2$ | 74.66 | 0.8007 | — | — | | 0.8008 |
| | $K\alpha_1$ | 74.21 | 0.8005 | — | — | | |
| | $K\alpha_2$ | 73.78 | 0.8041 | 73.80 | 0.8041 | 0.8050 | |
| | $K\alpha_1$ | 73.30 | 0.8042 | 73.40 | 0.8038 | | |
| 3 2 10 | $K\alpha_2$ | 72.75 | 0.8098 | — | — | | 0.8092 |
| | $K\alpha_1$ | 72.22 | 0.8089 | — | — | | |
| | $K\alpha_2$ | 71.68 | 0.8134 | 71.67 | 0.8135 | 0.8141 | |
| | $K\alpha_1$ | 71.31 | 0.8132 | 71.30 | 0.8132 | | |

*Note.* Spectra taken with Cu $K\alpha$ (Ni-filtered) radiation: $K\alpha_1$ = 1.54051, $K\alpha_2$ = 1.54433.

[a] Calculated on the basis of the following values of the unit cell parameters: $MgTiO_3$ $a$ = 5.0565 Å, $c$ = 13.890 Å (present work); $NiTiO_3$ $a$ = 5.031 Å, $c$ = 13.785 Å (*6*, *7*).

flections of $TiO_2$, rutile modification, and of metallic nickel appear, in addition to those of $MgTiO_3$. After the thermal treatment at 950°C, the lines of $MgTiO_3$ and Ni are still present, while those of $TiO_2$ disappeared, and the spectrum of $MgTi_2O_5$ is revealed.

*Reflectance spectra.* The reflectance spectra of the MT N samples, $MgTiO_3$, $NiTiO_3$, and NiO were recorded. No absorption was observed for $MgTiO_3$. For the MT N samples observed absorption bands were found to be in agreement with literature data (*6*, *8*), coinciding with those of $NiTiO_3$, but shifted with respect to those of NiO. As the nickel content increases, the intensity of the MT N absorption bands increases, whereas their energy is not affected. Therefore, while the spectra rule out the presence of NiO, they are not able to distinguish whether the samples MT N contain $Ni^{2+}$ incorporated in $MgTiO_3$ or whether they consist of a mechanical mixture of $MgTiO_3$ and $NiTiO_3$.

*Magnetic measurements.* A slightly positive, field independent, specific magnetic susceptibility was measured for pure $MgTiO_3$, due to iron impurities, as also confirmed by ESR (*9*). This contribution was corrected for in evaluating the nickel magnetic susceptibility. Correction for the temperature-independent paramagnetism contribution was also made. The Curie law, $\chi = C/T$, was obeyed, and the effective magnetic moment, $\mu_{eff}$, was obtained from $\mu_{eff} = 2.83\ (C)^{1/2}$ (Table I). It may be seen that $\mu_{eff}$ is practically constant and agrees with the values reported for pure $NiTiO_3$, ranging from 3.16 (*10*) to 3.24 B.M. (*11*). Due to the very similar magnetic behavior of samples MT N and $NiTiO_3$, the magnetic data are not able to discriminate between a mechanical mixture of $NiTiO_3$ and $MgTiO_3$ or a solid solution $Ni_xTi_{1-x}O_3$ type. Pure $NiTiO_3$ complies with the Curie–Weiss law $\chi = C/(T + \theta)$ rather than $\chi = C/T$, but the $\theta$ value is low (from −55 to −11 K) (*10*, *12*, *13*). Our observation of $\theta = 0$ in our specimens, cannot therefore be taken as a firm evidence for formation of solid solutions.

*Thermogravimetric measurements.* Figure 2 shows the thermogravimetric curves for some of the samples. Two mass losses are observed in the temperature ranges 400–700°C and 700–1000°C. After the first

TABLE III

X-RAY DIFFRACTION DATA FOR THE SAMPLE MT N 10 HEATED IN HYDROGEN AT 700°C 3 hr AND AT 950°C 3 hr

| MT N 10 | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 700°C | | 950°C | | MgTiO$_3$[a] | | TiO$_2$[b] | | Ni[c] | | MgTi$_2$O$_5$[d] | |
| $d$ (Å) | $I^e$ | $d$ (Å) | $I^e$ | $d$ (Å) | $I/I_0$ | $d$ (Å) | $I/I_0$ | $d$ (Å) | $I/I_0$ | $d$ (Å) | $I/I_0$ |
| | | 5.01 | vw | | | | | | | 5.01 | 80 |
| | | 4.87 | vw | | | | | | | 4.87 | 80 |
| 4.64 | w | 4.64 | w | 4.64 | 30 | | | | | | |
| 4.18 | w | 4.18 | w | 4.18 | 30 | | | | | | |
| 3.70 | w | 3.70 | w | 3.703 | 45 | | | | | | |
| | | 3.50 | w | | | | | | | 3.50 | 100 |
| 3.25 | w | | | | | 3.245 | 100 | | | | |
| | | 2.75 | vw | | | | | | | 2.75 | 100 |
| 2.72 | vs | 2.72 | vs | 2.722 | 100 | | | | | | |
| 2.53 | m | 2.53 | m | 2.527 | 55 | | | | | | |
| 2.48 | vvw | | | | | 2.489 | 41 | | | | |
| | | 2.45 | vvw | | | | | | | 2.45 | 50 |
| | | 2.41 | vvw | | | | | | | 2.41 | 50 |
| 2.22 | s | 2.22 | s | 2.218 | 70 | | | | | 2.22 | 60 |
| | | 2.19 | vvw | | | | | | | 2.19 | 60 |
| 2.18 | vvw | | | | | 2.188 | 22 | | | | |
| 2.03 | w | 2.03 | w | | | | | 2.034 | 100 | | |
| | | 1.96 | vvw | | | | | | | 1.96 | 70 |
| | | 1.87 | vvw | | | | | | | 1.87 | 80 |
| 1.85 | m | 1.85 | m | 1.852 | 40 | | | | | 1.85 | 50 |
| 1.76 | vvw | 1.75 | vvw | | | | | 1.762 | 42 | 1.75 | 50 |
| 1.71 | vvw | 1.71 | vvw | 1.708 | 55 | | | | | | |

[a] ASTM Card 6-0494. Only reflections with intensity higher than 10.

[b] ASTM Card 4-0551. Only reflections with intensity higher than 10.

[c] ASTM Card 4-0850. Only reflections with intensity higher than 10.

[d] ASTM Card 20-694. Only reflections with intensity higher than 30.

[e] Visually estimated intensities: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, vvw = very very weak.

mass loss a plateau is observed whereas, in the case of the second the mass continues to decrease even at 1000°C, which was the maximum temperature in our studies.

In Fig. 2 the thermogravimetric curves in hydrogen atmosphere for undoped NiTiO$_3$, MgTiO$_3$, MgTi$_2$O$_5$, and TiO$_2$ are also recorded. It may be seen that while no change in mass is observed for MgTiO$_3$, in the case of MgTi$_2$O$_5$ and TiO$_2$ a loss in mass is found at temperatures higher than 800°C.

The thermogravimetric behavior of NiTiO$_3$ is very similar to that of the MT N samples.

*ESR measurements.* The ESR spectra show a single broad line at $g = 2.27$ which can be assigned to Ni$^{2+}$. In the most dilute nickel samples, this line is rather asymmetric and becomes more symmetric and nearly Lorentzian in shape as the nickel concentration increases (MT N 10, MT N 20, and NiTiO$_3$). Moreover, the signal undergoes a small broadening, passing from

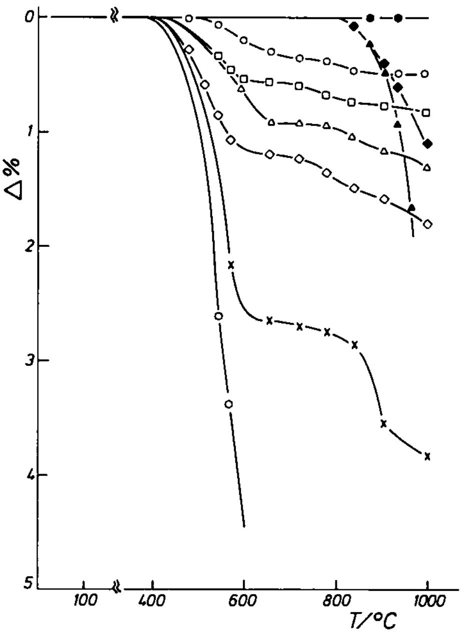

FIG. 2. Thermogravimetric curves in hydrogen. ●, $MgTiO_3$; ◆, $MgTi_2O_5$; ▲, $TiO_2$; ○, $NiTiO_3$; O, MT N 3; □, MT N 5; △, MT N 8; ◇, MT N 10; ×, MT N 20.

room temperature to 77 K, and its linewidth narrows slightly with the increase of nickel content, as shown in Fig. 3. The intensity of the line shows small deviation from the Curie law, the product $I \cdot T$ changing from 1.00 to about 0.7–0.8 at 77 K.

## Discussion

(*i*) *The formation of the solid solution.* The formation of the solid solution is demonstrated mainly by X-ray analysis and by ESR measurements. As noted earlier the reflectance, magnetic and thermogravimetric results cannot discriminate between solid solution and mechanical mixture.

The phase analysis, show that no extra lines other than those of $MgTiO_3$ are present in the high $\theta$-angle region of the powder diffraction spectrum, even in the case of the more concentrated specimen MT N 20, Table II. Furthermore, the unit cell volume of undoped $MgTiO_3$, 307.6 Å$^3$, is larger than that of pure $NiTiO_3$, 302.2 Å$^3$ (*6*); therefore, the decrease in $MgTiO_3$ unit cell volume, $V$, caused by the addition of nickel, Fig. 1, clearly indicates that the $Ni^{2+}$ enters into the $MgTiO_3$ structure. The effect caused by the incorporation of 1 $Ni^{2+}$ ion/100 bivalent ions, is calculated to be 0.047 Å$^3$. The slight variation of $V$ is indeed expected on the basis of the small difference in the ionic radii of the divalent cations, namely $Ni^{2+}$ and $Mg^{2+}$, which substitutionally interchange in the ilmenite structure ($r_{Ni^{2+}} = 0.69$ Å and $r_{Mg^{2+}} = 0.72$ Å (*14*).

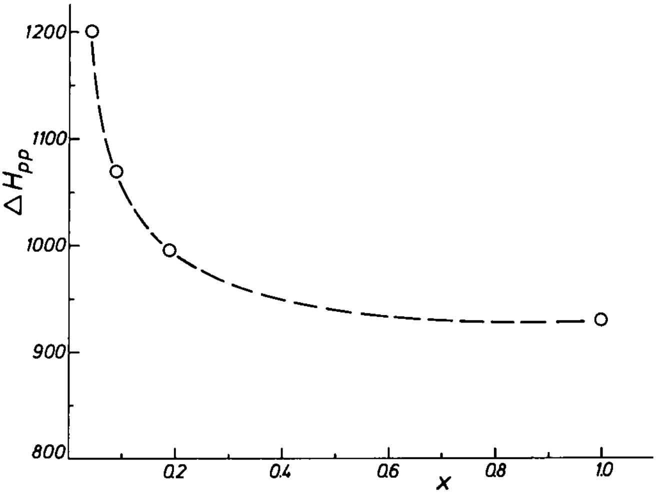

FIG. 3. Variation of the linewidth, $\Delta H_{pp}$ (Gauss) with $x$ for the $Ni_xMg_{1-x}TiO_3$.

As concerns the ESR data, the single broad band at $g = 2.27$ is a clear indication of the presence of "clustered" $Ni^{2+}$ ions with the expected behavior of weak antiferromagnetic domains, but the change in shape of the line from asymmetric (at low nickel content) to symmetrical and nearly Lorentzian at higher nickel concentration, and the variation of linewidth with nickel content (Fig. 3), seem definitely to rule out the presence in all MT N samples of individual $NiTiO_3$. The decrease in linewidth with increase of nickel content may be due to exchange narrowing.

(*ii*) *The reduction of the incorporated* $Ni^{2+}$. When the samples are heated in hydrogen the thermogravimetric results show that $Ni^{2+}$ in solid solution is reduced in the temperature range 400–700°C to metallic nickel. The metal segregates out from the ilmenite structure. The reduction taking place is

$$Ni_xMg_{1-x}TiO_3 \rightarrow (1 - x)MgTiO_3 + xNi + xTiO_2 + x/2O_2 \quad (1)$$

This conclusion is confirmed by the comparison between the nickel content as determined by chemical analysis, $\%Ni^{anal}$, and that obtained from the thermogravimetric measurements, $\%Ni^{TG}$, (Table I). The latter is obtained from the loss in mass measured in the temperature range 400–700°C, $\Delta\%_{400-700}$, due to the release of oxygen. According to reaction (1) the mass loss gives directly the nickel percentage by the formula $\%Ni^{TG} = \Delta\%_{400-700}\ 58.71/16$, where 58.71 and 16 are the atomic weights of nickel and oxygen, respectively. The formation of metallic nickel and of $TiO_2$ is directly shown by the X-ray diffraction patterns of a sample heated in hydrogen at 700°C for 3 hr (see Table III). On the other hand, the segregation from the ilmenite structure is confirmed by the expansion of the $MgTiO_3$ unit cell volume of sample MT N 10 after heating in hydrogen at 700°C. In fact, after this thermal treatment, the value of $V = 307.50$ Å$^3$, is practically coincident with that of undoped $MgTiO_3$.

For temperatures higher than 700°C, a second solid state reaction takes place. In fact, the $TiO_2$ reacts with $MgTiO_3$ according to the following reaction scheme:

$$(1 - x)MgTiO_3 + xTiO_2 \rightarrow (1 - 2x)MgTiO_3 + xMgTi_2O_5 \quad (2)$$

The formation of $MgTi_2O_5$ and the disappearance of $TiO_2$ is demonstrated by X-ray diffraction performed on samples heated in hydrogen at 950°C 3 hr (Table III). It may be noted that reaction (2) does not involve a loss in mass. Nevertheless, a decrease in weight is observed in the temperature range 700–1000°C (Fig. 2). This is due to the reduction of $TiO_2$ and of $MgTi_2O_5$, leading to oxygen-deficient nonstoichiometric compounds. The latter conclusion is in agreement with the observation that pure $TiO_2$ and $MgTi_2O_5$ undergo a loss in mass in the same temperature range (Fig. 2). On the other hand, Fig. 4 shows that $\Delta\%_{700-1000}$ is a linear function of the nickel content. This point may be accounted for by noting that in the thermogravimetric experiment the final temperature and oxygen pressure conditions are the same for the MT N samples as well as for $TiO_2$ and $MgTi_2O_5$. Therefore, the latter compounds may be considered to reach the same degree of nonstoichiometry irrespective of whether nickel is present or absent. As a result, the loss in mass in the range 700–1000, $\Delta\%_{700-1000}$, measured for the samples MT N, is proportional to the amount of $TiO_2$ and $MgTi_2O_5$ present, and hence by recalling reactions (1) and (2), to the nickel content.

*Concluding remarks.* The incorporation of $Ni^{2+}$ in $MgTiO_3$ is confirmed on the basis of X-ray diffraction and ESR measurements and is in agreement with the reflectance and magnetic data. It may be noted that due to the close structural similarity

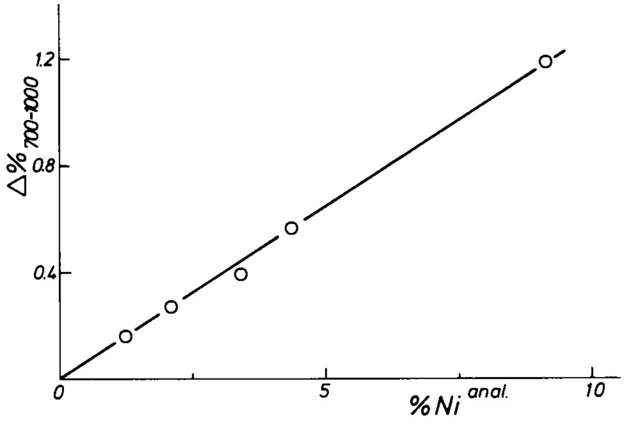

FIG. 4. Mass loss in the temperature range 700–1000°C, $\Delta\%_{700-1000}$, for the MT N samples heated in hydrogen vs the analytically determined nickel content, $\%Ni^{anal}$.

between $MgTiO_3$ and $NiTiO_3$, reflectance spectroscopy is not able to distinguish between a mechanical mixture and a solid solution. The reduction of $Ni^{2+}$ incorporated in $MgTiO_3$ takes place in the same temperature range in which the reduction of $NiTiO_3$ occurs. Therefore, this technique also fails to indicate whether solid solution formation occurs. The reduction is accompanied by the segregation of metallic nickel and $TiO_2$. At higher temperatures, the latter reacts with $MgTiO_3$ giving $MgTi_2O_5$.

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