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The System TiO_2–MnO_x: A Structural, Thermogravimetric, and Magnetic Study

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The unit cell parameter variations of TiO_2 on addition of up to 8% atomic ratio of manganese oxide have been investigated. Magnetic susceptibilities in the range 98–600 K have been measured, and weight loss in hydrogen atmosphere has been recorded up to 1173 K.

The results show that, at 1273 K in air, manganese is incorporated as Mn^{4+} in the TiO_2 structure up to 1.24% atomic. Manganese in excess (with respect to the solubility value) reacts with TiO_2 to form $MnTiO_3$. The Mn^{4+} ions in solid solution are reduced by hydrogen in the temperature range 723–923 K to Mn^{2+}, which precipitate as $MnTiO_3$.

Introduction

Systems based on dispersion of transition metal ions in diamagnetic oxides have revealed themselves to be very useful in the chemistry of the solid state. The incorporation in the base oxide structure stabilizes one of the possible oxidation states of the dispersed species (*1*) and in some cases the valence state of the dissolved ions can be changed depending on preparative conditions and presence of other ions (*1*–*3*). These systems therefore allow the investigation of otherwise unstable chemical species, and also permit information to be obtained on properties of ions whose bonding situation is rather different from that in the pure oxides. In addition, the detailed investigation of such systems is of great interest in the field of heterogeneous catalysis, for which a pertinent example involves manganese ions (*4*).

This paper reports data for the titanium dioxide (rutile form), with small additions of manganese ions. Amongst manganese oxides, MnO_2 has a rutile-type structure (*5*), is stable in air up to about 823 K, (*6*) and transforms to oxides of lower O/Mn ratio at higher temperature.

The purpose of this study was thus to see whether and to what extent manganese ions could be dispersed in TiO_2, and investigate in which oxidation state these ions could be stabilized in solid solution at high temperature (1273 K). The study was based on X-ray determination of the unit cell parameters, and on thermogravimetric and magnetic measurements.

Experimental Procedure

Sample Preparation

Titanium oxide was prepared by hydrolyzing $TiCl_3$ and oxidation. Equal volumes of ammonia solution (1:1) and 15% $TiCl_3$ solution (Reagent grade C. Erba R.P.) were prepared. The precipitate obtained by addition of the ammonia solution to the hot stirred $TiCl_3$ solution was filtered, thoroughly washed with distilled water until no Cl^- ions were present, and dried at 393 K. A portion of the obtained product was impregnated with a titrated solution of Erba R.P. $Mn(NO_3)_2$ of a volume comparable to that of the solid. The soaked mass was dried at 393 K, ground, heated at 623 K for 2 hr in air, carefully reground, heated at 1273 K for 5 hr in air, and finally quenched in air to room temperature. The color of the samples was found to vary from ochre to brown with increasing manganese concentration.

Another portion of the precipitate, dried at 393 K but not impregnated with manganese solution, was heated following the same procedure. After the quenching from 1273 K the product was white.

Specimens containing manganese are designated *TM*. The number after the letters gives the nominal concentrations of manganese atoms with respect to 100 Ti atoms.

In order to check the reproducibility of the data, some samples were reprepared.

Chemical Analysis

The total manganese content in the samples was determined by an atomic absorption technique. A known weight of the sample was fused with potassium bisulfate and, after cooling, dissolved in water. The standard solutions for the atomic absorption determinations were prepared from a titrated $Mn(NO_3)_2$ solution. They contained TiO_2 (fused with $KHSO_4$) in a concentration comparable to that in the sample solution. The $Mn(NO_3)_2$ solution was standardized spectrophotometrically as permanganate (at $\lambda = 526$ nm) oxidation to MnO_4^- being carried out using the periodate method (*7*). The results obtained are designated as Mn_{tot} in Table I.

X-Ray Analysis

All samples were studied by means of a Debye–Scherrer camera, 114.6 mm diam (Charles Supper Co.) using Co*K*α (Fe-filtered) radiation ($\lambda_{\alpha_1} = 1.78892$ Å, $\lambda_{\alpha_2} = 1.79278$ Å). The following seven reflexions were recorded in the back reflexion region (the second figure is the θ angle): 510 (83.0), 402 (80.3), 103 (68.0), 420 (60.5), 312 (59.6), 411 (59.0), 330 (55.7). All these reflexions gave resolved doublets. The position of the lines could be read visually to an accuracy of 0.005 cm with a measuring device. The graphical method of extrapolation against $1/2(\cos^2\vartheta/\sin\vartheta + \cos^2\vartheta/\vartheta)$ was adopted. The axial ratio $c/a = C$ was determined by minimizing the deviations of a values following a least-squares procedure. At least two determinations were made for each specimen. It was observed that the errors in both a and C are $\pm 1.10^{-4}$ Å. This means that c could be measured to $\pm 5.10^{-4}$ Å. It should be emphasized that the higher accuracy of a with respect to c is due to the occurrence of two reflexions (510, 403), at very high angle; the first one (510) is independent of the ratio C.

No thermostating was made during exposure but temperature fluctuations were less than ± 1 K. All cell parameters were

TABLE I

THERMOGRAVIMETRIC, MAGNETIC, AND ANALYTICAL DATA FOR TiO_2 CONTAINING MANGANESE OXIDE

Samples	Mn_{tot}[a]	δ[b]	Mn^{+4}[a]	$\mu_{calcd\ B}$	$\mu_{exp\ B}$	$-\theta$ K
TM 0.5	0.51	0.09	0.45	4.16	3.88	0
TM 0.7	0.70	0.13	0.66	4.02	4.03	0
TM 2	1.89	0.19	0.95	4.99	4.96	68
TM 4	4.52	0.25	1.24	5.42	5.37	130
TM 7	6.72	0.25	1.24	5.59	5.60	140
TM 8	8.30	0.25	1.24	5.65	5.65	165

[a] Manganese atoms/100 titanium atoms.

[b] Difference between the weight-loss in mg/100 mg of samples, measured at 953 K, ΔW_{TM}^{953}, and the weight-loss in mg/100 mg of TiO_2 at the same temperature, $\Delta W_{TiO_2}^{953}$.

normalized to 294 K by means of the following thermal expansion coefficients: $\Delta a/a = 6.9 \cdot 10^{-6}/K$, $\Delta c/c = 9.9 \cdot 10^{-6}/K$ (*8*). Most determinations were made within ± 4 K from 294 K. The samples have also been studied by means of a high-angle diffractometer using Cu*Kα* (Ni-filtered) radiation in order to check the crystalline phases present.

Thermogravimetric Measurements

The thermogravimetric study was carried out by means of a Cahn RG electrobalance. During each experiment the sample was kept in a constant flow of hydrogen (24 ml/min). The temperature was raised to 1173 K by a linear programmer, at a heating rate of 3 K/min. The sample was placed in a platinum bucket suspended from one arm of the microbalance while an identical empty platinum bucket was hung on the reference side of the balance beam. In order to eliminate gas effects, caused by the asymmetric geometry of the system, the position of the zero was controlled in the whole temperature range by using a platinum dummy sample the weight of which was comparable to that of the samples studied. The weight was measured to an accuracy of ± 0.01 mg. However, at each temperature the actual weight results from two determinations so the total accuracy is ± 0.02 mg.

Magnetic Measurements

These were performed by the Gouy method at 4000 and 8000 G in two temperature ranges: 78–300 K and 300–600 K. A semimicro Mettler balance reading to ± 0.01 mg was employed. The instrument was calibrated with $Hg[Co(NCS)_4]$ (*9*) in the lower temperature range. The same calibration was assumed to hold in the temperature range above room temperature since no change in the experimental set up was required except the interchange of the cooling and heating accessory.

The magnetic susceptibility of pure TiO_2 was determined experimentally with the same balance. Table II gives the values of the measured specific susceptibilities, $\chi_g^{TiO_2}$. The molar susceptibility for the samples containing manganese, χ_M, was obtained from their specific susceptibility, χ_g^{sample}, by introducing a correction for the TiO_2 contribution according to

$$\chi_M = [(\chi_g^{\text{sample}} + \%TiO_2 \times \chi_g^{TiO_2})/\%Mn] \times \text{atomic weight of Mn}$$

For the more diluted specimens (*TM* 0.5 and *TM* 0.7) the molar susceptibility was found to obey the Curie–Weiss law in both temperature ranges. For the other *TM* samples the Curie–Weiss law is obeyed only above room temperature. In the lower temperature range the χ_M^{-1} vs T curves are not linear, the deviation from linearity being larger for more concentrated samples. As an example, Fig. 1 shows the χ_M^{-1} vs T curves for *TM* 0.7 and *TM* 8 specimens. The same figure also shows the values of χ_M^{-1} for $MnTiO_3$ as measured by Syono et al. (*10*) in the temperature range 100–300 K. For each sample the Curie constant, C_M, and the Weiss temperature, θ, from the Curie–Weiss equation $\chi_M = C_M/(T - \theta)$ were evaluated using the straight part of the χ_M^{-1} vs T plots. The C_M values have been used to obtain the experimental effective magnetic moment (in Bohr magnetons), ($\mu_{\text{exp}} = 2.83 C_M^{1/2}$). These were found to be field independent.

TABLE II

SPECIFIC SUSCEPTIBILITY OF UNDOPED TiO_2, $\chi_g^{TiO_2}$, AS MEASURED AT SEVERAL TEMPERATURES

T(K)	$\chi_g^{TiO_2} \times 10^6$ (erg G^{-2} g^{-1})
113	0.44
122	0.41
130	0.41
138	0.39
157	0.39
162	0.36
184	0.36
190	0.33
196	0.33
200	0.32
211	0.31
292	0.30
293	0.32
383	0.30
415	0.29
583	0.30

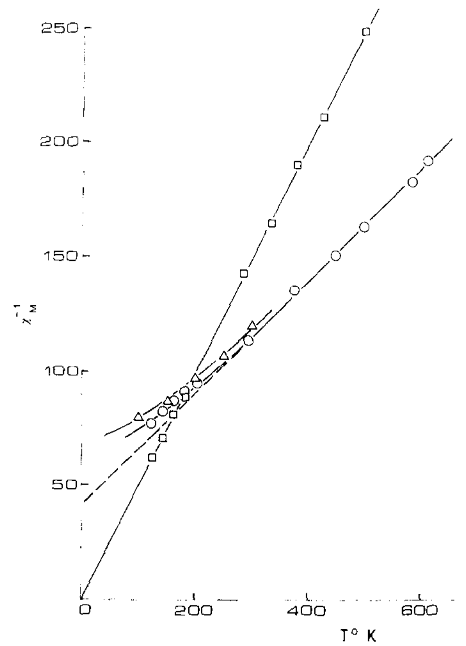

FIG. 1. χ_M^{-1} vs T plots for TiO_2 with different manganese oxide content. For clarity, only extreme concentrations are reported. Some experimental points are omitted: □ *TM* 0.5, ⊙ *TM* 8, △ $MnTiO_3$ from Ref. (*10*).

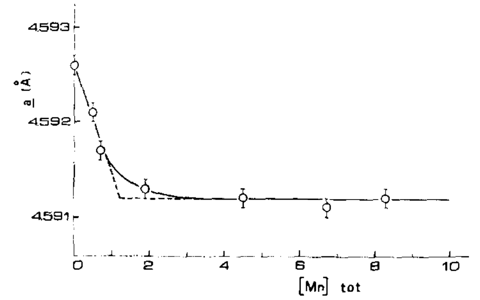

FIG. 2. Cell parameter *a* of TiO_2 containing manganese oxide vs $[Mn]_{tot}$. $[Mn]_{tot}$ = Mn atoms/100 Ti atoms.

Experimental Results

X-Ray Measurements

The results of the cell parameter measurements of specimens of different composition are listed in Table III, which also lists the results of the phase determinations.

Only the rutile phase is present in the *TM* 0.5 and *TM* 0.7 samples, whereas TiO_2 and $MnTiO_3$ reflexions are visible in the spectra of more concentrated specimens. The intensities of the manganese titanate lines increase as the Mn content increases.

The cell parameter *a* of the *TM* samples decreases for initial addition of manganese. After 1.2 Mn atoms/100 Ti atoms a constant value of *a* was observed (Fig. 2). No significant variation of axial ratio *C* was found (Table III) upon addition of manganese. Table III also gives the unit cell parameter *c* as obtained from the corresponding *a* and *C* values for all the samples studied.

TABLE III

UNIT CELL PARAMETERS *a* AND *c*, NORMALIZED TO 294 K, AND THE AXIAL RATIO *C*, FOR TETRAGONAL TiO_2 CONTAINING MANGANESE OXIDE

Samples[a]	$a_{294\,K}$ (Å)	$c_{294\,K}$ (Å)	*C*	Crystalline phases
TiO_2	4.5926	2.9591	0.6443	Rutile
TM 0.5	4.5921	2.9584	0.6442	Rutile
TM 0.7	4.5917	2.9581	0.6442	Rutile
TM 2	4.5913	2.9578	0.6442	Rutile + $MnTiO_3$
TM 4	4.5912	2.9581	0.6443	Rutile + $MnTiO_3$
TM 7	4.5911	2.9583	0.6444	Rutile + $MnTiO_3$
TM 8	4.5912	2.9578	0.6442	Rutile + $MnTiO_3$

[a] For key to designation of samples see text.

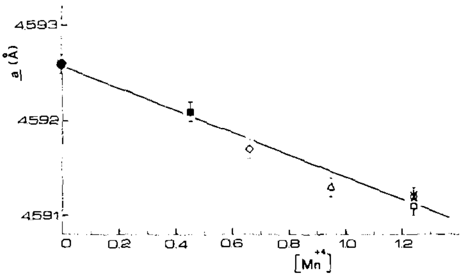

FIG. 3. Cell parameter *a* of TiO_2 containing manganese oxide vs [Mn^{4+}): ● undoped TiO_2, ■ *TM* 0.5, ◇ *TM* 0.7, △ *TM* 2, × *TM* 4, □ *TM* 7, ⊙ *TM* 8. [Mn^{4+}] = Mn^{4+}ions/100 Ti atoms.

Figure 3 reports variation of the cell parameter *a* with Mn^{4+} content.

Table IV summarizes the unit cell parameters of some samples (TiO_2, *TM* 0.7, *TM* 8) heated at 1023 K in a stream of hydrogen for 1 hr in a separate furnace. It can be seen that the cell parameters of undoped TiO_2 are not modified by the hydrogen treatment, while those of the specimens containing manganese show a marked increase. In particular, both *a* and *c* become equal to the values measured for TiO_2 without manganese. Table IV also shows that TiO_2 and $MnTiO_3$ reflexions are present in the X-ray spectra of the hydrogen-treated samples.

Thermogravimetric Measurements

The thermogravimentric curves are plotted in Fig. 4. The *TM* samples, when heated in hydrogen, show a decrease in weight with respect to TiO_2. In fact, whereas for pure TiO_2 a slight and continuous decrease in weight was observed up to 993 K for the *TM* samples a loss in weight in the temperature range 773–923 K was recorded. Outside of this temperature range the *TM* and the TiO_2 thermogravimetric curves show a similar behavior. For the *TM* 0.5, *TM* 0.7 and *TM* 2 samples the weight-loss was found to be dependent on the manganese content while the *TM* 4, *TM* 7 and *TM* 8 specimens showed the same decrease in weight. The difference δ, between the weight change ΔW^{953}_{TM} of each *TM* sample recorded at 953 K and that of undoped TiO_2 at the same temperature, $\Delta W^{953}_{TiO_2}$, is plotted against the total manganese content in the inset of Fig. 4. This inset also shows the Mn^{4+} content (right ordinate). The δ values for the different samples are also shown in Table I where they are reported besides the Mn^{4+} content. The Mn^{4+} content was evaluated assuming that the weight loss which takes place in the range 773–923 K is due to oxygen release from the *TM* samples as a result of the Mn^{4+} to Mn^{2+} reduction. In Table I and Fig. 4 the Mn^{4+} concentration is given as Mn atoms/100 Ti atoms.

Magnetic Measurements

Table II shows the experimentally measured specific magnetic susceptibility for undoped TiO_2 at several temperatures. It should be noted that the specific susceptibility of the titanium dioxide, used in this work, is slightly positive. This behavior might be accounted for in terms of small deviations from the stoichiometry (*11*) or on the basis of paramagnetic impurity contaminations (Ap-

TABLE IV

TETRAGONAL CELL PARAMETERS *a* AND *c* NORMALIZED TO 294 K, AND THE AXIAL RATIO *C*, FOR TiO_2 CONTAINING MANGANESE OXIDE HEATED AT 1023 K IN HYDROGEN

Samples[a]	$a_{294 K}$ (Å)	$c_{294 K}$ (Å)	*C*	Crystalline phases
TiO_2	4.5927	2.9588	0.6442	Rutile
TM 0.7	4.5927	2.9588	0.6442	Rutile + $MnTiO_3$
TM 8	4.5926	2.9588	0.6443	Rutile + $MnTiO_3$

[a] For key to designation of samples see text.

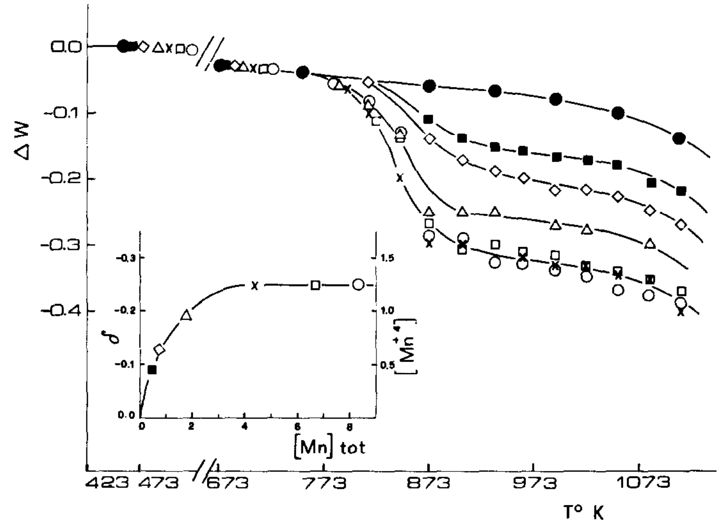

FIG. 4. Thermogravimetric curves of TiO_2 with different manganese oxide content performed in a hydrogen atmosphere. A plot of weight loss ΔW, mg/(100 of sample), vs T K: ● undoped TiO_2, ■ *TM* 0,5, ◇ *TM* 0.7, △ *TM* 2, × *TM* 4, □ *TM* 7, ⊙ *TM* 8. In the inset, $\delta = \Delta W^{953}_{TM} - \Delta W^{953}_{TiO_2}$ (see text) (left ordinate) and $[Mn^{4+}]$ (right ordinate) vs $[Mn]_{tot}$. $[Mn^{4+}] = Mn^{+4}$ ions/100 Ti atoms, $[Mn]_{tot}$ = Mn atoms/100 Ti atoms.

pendix). Since all *TM* samples have been prepared by using the starting material obtained from the same batch, the positive magnetic susceptibility contribution, ascribed to the TiO_2 matrix, was treated as a correction in evaluating the manganese molar magnetic susceptibility, χ_M. This procedure was supported by ESR measurements. Indeed ESR spectra showed a signal of Fe^{3+} both for TiO_2 without manganese and for *TM* samples. The signal in the TiO_2 spectrum was found to be comparable in intensity to that in the spectra of *TM* samples. The magnetic measurement results are reported in Table I. The Weiss temperature θ is zero for the *TM* 0.5 and *TM* 0.7 specimens. For more concentrated samples the θ values increase as the manganese content increases. The experimental magnetic moments increase with the manganese content. They range from 3.88 μ_B (*TM* 0.5) to 5.65 μ_B (*TM* 8). Calculated magnetic moments are also shown in Table I. Their calculation was carried out on the basis of the spin-only formula, the manganese in the sample being considered in the 4+ ($\mu = 3.87 \mu_B$) and 2+ ($\mu = 5.92\ \mu_B$) oxidation state. The amount of Mn^{4+} was derived from the thermogravimetric results, whereas that of Mn^{2+} was obtained from the difference between total manganese and Mn^{4+}. The spin-only formula approximation is valid since in this case the reduction of the magnetic moment due to spin-orbit coupling is absent (Mn^{2+}, d^5) or very small (Mn^{4+}, d^3) (*12*).

Discussion

The behavior of the cell parameter *a* with increasing Mn concentration shows that manganese has a limited solubility in the TiO_2 structure. The maximum amount of manganese which dissolves in solid solution is 1.2% in atomic ratio, Fig. 2. Specimens containing a total Mn concentration higher than 1.2% show a constant value of the cell parameter *a* since a saturated solution was obtained. The manganese excess, with respect to the amount dissolved in solid solution, reacts with TiO_2 to form the compound $MnTiO_3$ (Table III).

The manganese in the $MnTiO_3$ phase is present as Mn^{2+} (*10*, *13*). It will be shown below that the manganese dissolved in solid solution in TiO_2 is in the 4+ oxidation state. However, an indication as to the valence state of the incorporated manganese can be obtained from considerations of ionic radii. Since the incorporation causes a decrease of unit cell parameters (Table III) it is deduced that the valence of manganese is 4+. Indeed, ionic radii are as follows: Goldschmidt: $r_{Ti^{+}} = 0.64$ Å, $r_{Mn^{4+}} = 0.52$ Å, $r_{Mn^{3+}} = 0.70$ Å, $r_{Mn^{2+}} = 0.91$ Å; Shannon and Prewitt (*14*). $r_{Ti^{4+}} = 0.605$ Å, $r_{Mn^{4+}} = 0.51$ Å, $r_{Mn^{3+}} = 0.65$ Å, $r_{Mn^{2+}} = 0.82$ Å.

An evaluation of the unit cell contraction might be attempted following the model of an elastic matrix (*15*). Taking the Goldschmidt radii, a value of $\Delta a_{\text{calcd}} = -4.4 \cdot 10^{-4}$ Å for 1% Mn^{4+} ions is then calculated. From Fig. 2 it is seen that the experimentally observed value for the same Mn concentration is $\Delta a_{\text{exp}} = -11 \cdot 10^{-4}$ Å. The difference between the Δa_{calcd} and Δa_{exp} is even larger if the Shannon and Prewitt set of ionic radii is used. The disagreement can be explained in terms of a partial contribution of covalent bonding of Mn^{4+} dissolved in TiO_2. The bonding character of Mn^{4+} in TiO_2 has been examined by Andresen (*16*). The calculation of Mn^{4+} contribution to the cell parameter on the basis of the model of the elastic matrix would then fail because it applies only to ionic interactions. A similar behavior has been found in the case of Co^{3+} in MgO (*3*).

The conclusion drawn from the X-ray measurements receive confirmation from the thermogravimetric determinations. The thermogravimetric results show that the loss in weight, recorded in the range 773–923 K when samples are heated in hydrogen, is affected by the presence of manganese in the samples. In fact this loss varies with the manganese content and is absent for undoped TiO_2 (Fig. 4). Moreover, the decrease in weight is due to the reducing action of the hydrogen and cannot be ascribed to desorption properties of the samples. To check this point a thermogravimetric analysis was performed on the *TM* 2 sample previously submitted to another thermogravimetric determination. Both analyses were carried out in hydrogen atmosphere. Between the two measurements the sample was exposed to air overnight at room temperature. Whereas the first thermogram was similar to that shown in Fig. 4, no loss in weight was recorded during the second measure. Finally, the manganese species reducible by hydrogen is not affected by the presence of $MnTiO_3$, since the loss in weight also appears in the *TM* 0.5 and *TM* 0.7 samples, the X-ray diffraction spectra of which do not reveal this compound. The species reducible by the hydrogen is incorporated in TiO_2, as demonstrated by the following observations.

Table IV shows that the heating of the *TM* samples, (*TM* 0.7 *TM* 8), in hydrogen at 1023 K produces an expansion of the unit cell parameters, which become equal to the values for pure TiO_2. By contrast, heating TiO_2 in hydrogen at the same temperatures has no effect on *a* and *c*. Moreover, the *TM* 0.7 specimen before the reduction shows only the TiO_2 phase, while after the hydrogen treatment it contains $MnTiO_3$ in addition to TiO_2. All these results can be accounted for by assuming that the Mn species dissolved in the TiO_2 structure is reduced to Mn^{2+} during the heating in the hydrogen atmosphere and, therefore, during the thermogravimetric analysis. Due to the reduction, oxygen is released from the structure and a loss in weight is observed. The Mn^{2+} formed reacts with the matrix to give $MnTiO_3$ as a separate phase. The removal of the Mn^{4+} species from the TiO_2 structure removes the cause of the cell parameter contraction and the *a* and *c* values for the reduced *TM* samples become equal to that observed for TiO_2 without manganese. This also explains the presence of $MnTiO_3$ in the X-ray spectrum of reduced *TM* 0.7.

If the oxidation state of the dissolved species is known, the absolute amount of the incorporated manganese can be determined from the thermogravimetric measurements. Assuming that the manganese enters into solid solution as Mn^{4+} (as indicated by the contraction of the cell parameters and by Andresen's results (*16*)), from the decrease in weight the quantities of Mn^{4+} reported in Table I are obtained. As a typical example let us consider the *TM* 0.7 specimen. From Table I the δ value is 0.13 mg/100 mg of sample. This amount corresponds to a number of oxygen atoms released from the structure per 100 mg of sample, and so to the number of Mn^{4+} reduced to Mn^{2+}, given by $0.13/16 = 0.0812$ mg/100 mg of sample. Keeping in mind that the mg of MnO_2 present in 100 mg of sample results to be 0.488, a Mn^{4+} content of 0.45 Mn^{4+} ions/100 Ti atoms is obtained. The maximum amount of Mn^{4+} dissolved in solid solution in TiO_2 is 1.24 Mn^{4+} ions per 100 Ti atoms. This figure is in very good agreement with the value derived from the unit cell parameter measurements. As Fig. 3 shows, there is a linear dependence of the cell parameter a on Mn^{4+} dissolved in solid solution.

The results of the magnetic measurements confirm the above conclusions. Indeed it is found that the experimental magnetic moment is increasing with increasing manganese content. Since Mn^{4+} (a $3d^3$ ion) has a spin-only moment of 3.87 μ_B and Mn^{2+} (a $3d^5$ ion) has a moment of 5.92 μ_B, the observed increase of the magnetic moment can be accounted for by an increase of the content of Mn^{2+}. Furthermore the presence in the *TM* samples of Mn^{4+} and Mn^{2+} is demonstrated by the agreement between the value of the experimentally obtained magnetic moments μ_{exp}, and the calculated ones, μ_{calcd} (Table I). It should be recalled that the μ_{calcd} were evaluated on the basis of the thermogravimetric and analytical results so that the agreement obtained is also a proof of internal consistency of the different measurements.

From the magnetic measurements further information, regarding the dispersion state of magnetic ions, can be obtained. In the diluted samples (*TM* 0.5, *TM* 0.7) for which θ is zero, the manganese is atomically dispersed in solid solution.

Appendix

The slightly positive magnetic susceptibility of TiO_2 used in this work can be explained by the presence of paramagnetic impurities. In fact, ESR spectra showed lines characteristic of Fe^{3+}. An estimate of the amount of Fe^{3+} present can be obtained from the measured susceptibility. According to Keys and Mulay (*11*), $\chi_g^{TiO_2} = 0.065 \cdot 10^{-6}$ erg G^{-2} g^{-1}. In the present case, values from 5 to 6 times larger are measured Table II. If the major contribution to the specific magnetic susceptibility of the sample is given by the Fe^{3+} impurity, it is possible to write

$$\chi_g^{\text{sample}} = \chi_g^{Fe^{3+}} \times \%Fe^{3+}. \qquad (1)$$

From Table II at 113 K, $\chi_g^{TiO_2} = 0.44 \cdot 10^{-6}$. On the other hand Fe^{3+} (d^5) has an effective magnetic moment of 5.9 μ_B i.e., $C_M = 4.35$. At 113 K, $\chi_M^{Fe^{3+}} = C_M/T = 4.35/113 = 385 \cdot 10^{-4}$ and $\chi_g^{Fe^{3+}} = (385 \cdot 10^{-4}/55.8) = 6.9 \cdot 10^{-4}$ erg G^{-2} g^{-1}. From Eq. (1) $\%Fe^{3+} = 0.44 \cdot 10^{-6}/6.9 \cdot 10^{-4} = 0.64 \cdot 10^{-3}$, namely, in 100 mg of sample the Fe^{3+} content is 0.064 mg. This quantity is $\sim 1/5$ of the manganese content for the most diluted sample.

The loss in weight, connected with the reduction of Fe^{3+} to metal iron during the thermogravimetric determinations in hydrogen, is $(0.64 \cdot 10^{-3}/55.8) \cdot (3/2) \cdot 16 = 0.028$ mg.

This is of the same order as the experimental error (0.02 mg) and could account for the low temperature weight-loss (Fig. 4).

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