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Redox Behavior of Mn^{2+}, Fe^{2+}, and Cr^{2+} in Solid Solution in Magnesium Oxide by ESR and X-Ray Diffraction Techniques

D. CORDISCHI, D. GAZZOLI, AND M. VALIGI*

Istituto di Chimica Generale ed Inorganica, University of Rome, Rome, Italy and Centro di Studio su "Struttura ed attività catalitica di sistemi di ossidi," Istituto di Chimica Generale ed Inorganica University of Rome, Rome, Italy.

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MgO samples containing a few percent of Mn^{2+} or Fe^{2+} or Cr^{2+}, heated in air at a set temperature, have been investigated in order to study the effect of the electronic structure on the redox behavior of the guest species and on the resulting solid state processes. The data obtained by ESR and X-ray diffraction techniques show that Mn^{2+}, Fe^{2+}, Cr^{2+} are oxidized to Mn^{4+} Fe^{3+}, and Cr^{3+}, respectively in the temperature range 500–700°C. However, while for manganese and iron the formation of Mg_6MnO_8 and $MgFe_2O_4$ is observed, for chromium the Cr^{3+} species remains largely in solid solution even after a firing treatment at 1100°C. The different behavior is accounted for on the basis of the low diffusion coefficient observed for Cr^{3+} in MgO as consequence of the high stabilization energy of the d^3 configuration in an octahedral site.

Introduction

The study of the redox behavior of species dispersed in solid solution is very important in the field of solid-state chemistry. Indeed, the valence state greatly affects the solubility and the reactivity between solid reactants. The effect of the host oxide matrix and of the firing atmosphere on the stability of some oxidation states of manganese ions has been recently discussed (*1*).

The present paper describes the redox properties of Mn^{2+}, Fe^{2+}, and Cr^{2+} dispersed in MgO. Experiments have been carried out to obtain deeper insight on the influence of the electronic structure on the redox behavior of the guest species and on the subsequent solid-state processes.

A further interest in magnesium oxide systems containing transition metal ions comes from the importance of magnesium oxide as a refractory material. It is known that sintering is markedly affected by the presence of foreign ions and by their valence state. The study of the influence of the atmosphere is therefore relevant to the field.

The investigation has been carried out mainly by X-ray diffraction techniques (precise measurements of the unit cell parameter, phase identifications) and by ESR measurements.

Experimental

Materials. Manganese-doped specimens were prepared by impregnation of magnesium oxide (ex carbonate, 600°C air) with a solution of $Mn(NO_3)_2$. After drying at 110°C the specimens were mixed, ground, fired at 600°C (1 hr) in air, and ground again. The samples were finally heated for 5 hr at 1000°C in a stream of hydrogen (purified through a De-Oxo cartridge and liquid nitrogen trap).

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* To whom correspondence should be addressed.

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For the preparation of iron-containing samples a similar procedure was adopted but spec-pure MgO (Johnson and Matthey) was used in order to have a low level of impurity. In addition, the final heating at 1000°C for 5 hr was performed in a stream of CO and CO_2 mixture with the ratio $CO/CO_2 = 1:12.8$ ($p_{O_2} = 10^{-12}$ atm). At the end of the calcination, the samples were cooled rapidly to room temperature (always in CO/CO_2 atmosphere). Details of the calcination procedure have been reported previously (*2*).

Chromium-doped specimens were prepared starting from magnesium oxide (ex carbonate, 600°C, in air) by impregnation with chromium nitrate solution. After drying, the specimens were mixed, ground, and heated in air at 600°C for 1 hr then reground, pelleted, and heated at 1600°C in a hydrogen stream (from cylinder purified through a De-Oxo cartridge dried through a drierite column). Details of the preparation are reported elsewhere (*3*).

The samples are designated as MM, MF, MC when containing manganese, iron, and chromium, respectively. The atmosphere of preparation is specified by the letter h (hydrogen) or R (reducing atmosphere by CO and CO_2), while the number after the letters indicates the nominal concentration of the transition metal ion, expressed as atomic percent.

The characterization by chemical analyses, X-ray, and magnetic techniques of the samples has been described elsewhere (*1–4*). Here a summary is given.

Two samples containing manganese were prepared; MM–h 0.3 and MM–h 1. Both resulted to be solid solutions of Mn^{2+} in MgO (*1*). One specimen containing iron was studied, MF–R 1. The sample was found to be a solid solution of Fe^{2+} in MgO (*5*). Two specimens containing chromium have been investigated, MC–h 0.5 and MC–h 4. The total chromium content, determined by analysis, is 0.53 and 4.52 at.%, respectively. Both samples contain Cr^{3+} and Cr^{2+}. Cr^{2+} is in solid solution and by chemical analysis its concentration was found to be 0.15 for MC–h 0.5 and 1.44 at.% for MC–h 4. In the case of MC–h 0.5 the Cr^{3+} is essentially all in solid solution, whereas for MC–h 4 the Cr^{3+} is partially in solid solution and partially as $MgCr_2O_4$. For the latter sample, the concentration of Cr^{3+} in solid solution has been estimated to be 0.3 at.% (*4*).

Thermal treatments. Portions of the samples were submitted to a thermal treatment in air for 5 hr at temperatures ranging from 200 to 1100°C.

X-ray and ESR spectra. All the specimens, both as prepared and after the thermal treatment in air, were studied by X-ray and ESR techniques.

Precise measurements of the unit cell parameter of MgO have been described previously (*4*). A Debye–Scherrer camera (i.d. = 114.6 mm) was used, employing Cu$K\alpha$ (Ni-filtered) radiation, to detect the crystalline phases.

ESR spectra were recorded at room temperature and liquid nitrogen temperature on a Varian E—9 spectrometer operating at X-band frequencies with a 100-kHz field modulation. Absolute concentrations were estimated from electronically integrated spectra, using a single crystal of $CuSO_4 \cdot 5H_2O$ as standard.

Results and Discussion

Samples Containing Manganese, Prepared in Hydrogen (MM–h)

The MM–h samples initially consist of a solid solution of Mn^{2+} ions dispersed in MgO. This conclusion comes from earlier studies (*6*) as well as from the present results, namely, X-ray (the unit cell parameter *a* of MgO is increased, Fig. 1, on addition of manganese) and ESR spectra (Fig. 2). The Mn^{2+} concentration evaluated from the unit cell parameter expansion and from integrated ESR spectra, compares well with the nominal manganese content. In addition, the ESR spectra of unoxidized samples show that the Mn^{2+} distribution in the MgO structure is not

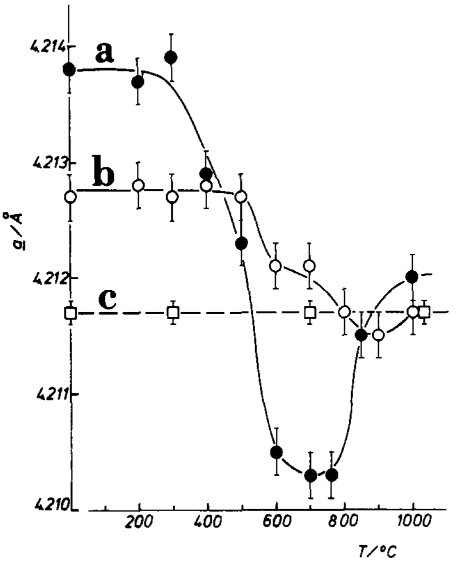

FIG. 1. Variation of the unit cell parameter *a* for MM–h 1 (curve a), MM–h 0.3 (curve b), and MgO–h (curve c) vs the temperature of the treatment in air for 5 hr. Starting from 600°C the reflections of the phase Mg_6MnO_8 are observed in the X-ray spectra of the MM–h 1 sample.

completely uniform. In fact, in the spectrum of the untreated MM–h 1 sample (Fig. 2A) a narrow sextet with the same splitting is superimposed on the broad sextet. The broad sextet is assigned to the Mn^{2+} ions in the more concentrated regions which are probably in the external layers of the MgO crystallites, the narrow one to Mn^{2+} present in the diluted regions of MgO. The same effect, though less evident, is observable in the more diluted sample (MM–h 0.3).

Heating of the MM–h samples in air at 400°C (Fig. 1) produces a negligible change both in the unit cell parameter and in the ESR spectra. Above 400°C a sharp decrease in *a* is observed: for MM–h 1 (curve a) a minimum is reached at around 700°C and at higher temperatures *a* increases and reaches the value of undoped MgO. For MM–h 0.3 (curve b) at 700°C only an inflection is observed. In contrast the *a* value of undoped MgO is unaffected by treatments in air (curve c). Starting from 600°C the reflections of the phase Mg_6MnO_8 are observable in the X-ray spectra of the MM–h 1 sample. The ESR spectrum of the samples treated in air at temperatures above 400°C also shows that a deep modification takes place, since a progressive line sharpening of the sextet of the Mn^{2+} ions, and the appearance of another signal at $g = 1.997$ is observed (Fig. 2). In the

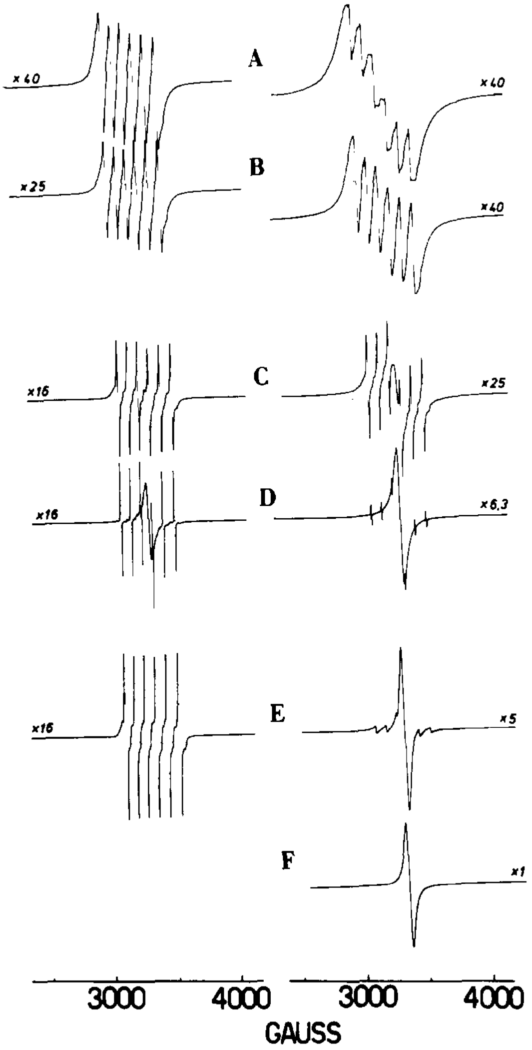

FIG. 2. ESR spectra of MM–h 0.3 (left) and MM–h 1 (right) recorded at room temperature after heating in air at different temperatures for 5 hr. A: untreated samples, B: 500°C, C: 600°C, D: 700°C, E: 1000°C, F: Mg_6MnO_8. For each spectrum the number indicates the relative gain.

sample MM–h 1, treated at the highest temperatures (800–1000°C), this new signal has a strictly Lorentzian lineshape ($\Delta H_{pp} = 30$ G) and is identical to that of Mn^{4+} ions in the pure Mg_6MnO_8 phase (Fig. 2F). In the treatments at intermediate temperatures (600–700°C) it is somewhat broader ($\Delta H_{pp} = 40$ G) and shows a marked deviation from the Lorentzian lineshape. This signal is assigned to associated Mn^{4+} ions, both in the phase Mg_6MnO_8 or still in solid solution in MgO.

The absolute concentration of Mn^{2+} ions was evaluated by ESR from integrated spectrum when Mn^{2+} is the only species present. When the signal of Mn^{4+} ions is also present, this gives the main contribution to the area of the integrated spectrum and then its concentration can be evaluated. An approximate estimate of the Mn^{2+} ions present in this case is arrived at from the intensity of the Mn^{2+} sextet of the derivative spectrum. The concentrations of Mn^{2+} and Mn^{4+} ions, so evaluated, are reported in Figs. 3 and 4.

The progressive oxidation of Mn^{2+} to Mn^{4+} in the MgO matrix is inferred from the strong decrease of the unit cell parameter of MgO observed up to 700°C, where a minimum is reached (Fig. 1a). In fact, the Mn^{2+}, causing the unit cell expansion, is substituted by a species (Mn^{3+} and/or Mn^{4+}) having an ionic radius smaller than that of Mg^{2+}. In the case of MM–h 1 heated at 700°C, a decrease in *a* of 14×10^{-4} Å with respect to the value of undoped MgO ($a = 4.2117$ Å) is observed. Since for the specimen MM–h 1 the concentration of total manganese is close to the nominal one, the magnitude of the contraction in *a* may be accounted for only if most of the manganese is present in MgO as Mn^{4+}. In fact, the following Δa have been measured for the incorporation in MgO of 1 at.% of Mn^{3+} and Mn^{4+} together with an equivalent amount of Li^+: $\Delta a_{Mn^{3+}} = -6 \times 10^{-4}$ Å, $\Delta a_{Mn^{4+}} = -16 \times 10^{-4}$ Å (*6*), the last value being close to the observed one. However, as the temperature increases, progressively more Mg_6MnO_8 is formed and the unit cell parameter of MgO increases reaching the value characteristic of undoped MgO.

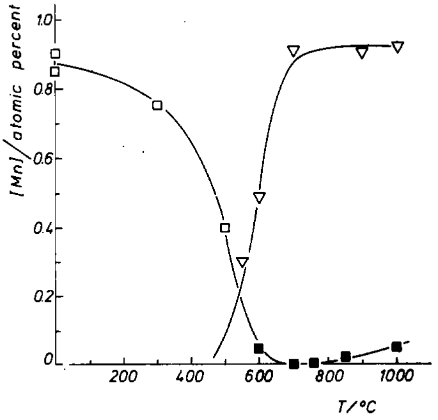

FIG. 3. Variation of manganese concentration, evaluated by ESR, with the temperature of the treatment in air, 5 hr, for the MM–h 1 sample. □, Mn^{2+} from integrated spectra; ■, Mn^{2+} (isolated ions) from derivative spectra; ▽, Mn^{4+} from integrated spectra.

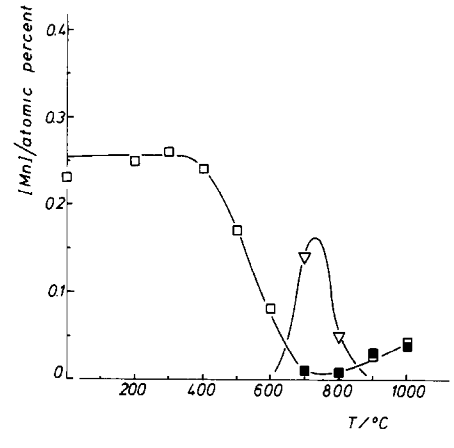

FIG. 4. Variation of manganese concentration, evaluated by ESR, with the temperature of the treatment in air, 5 hr, for MM–h 0.3 sample. □, Mn^{2+} from integrated spectra; ■, Mn^{2+} (isolated ions) from derivative spectra; ▽, Mn^{4+} from integrated spectra.

The oxidation $Mn^{2+} \rightarrow Mn^{4+}$ is also confirmed by the decrease in the intensity of the Mn^{2+} ESR signal and by the concomitant increase of the intensity of the Mn^{4+} signal (Figs. 3 and 4). The line sharpening of the spectrum of Mn^{2+} ions indicates that the oxidation of Mn^{2+} ions is easier for the ions which are in the external and more concentrated regions of the MgO crystallites. Isolated ions in bulk MgO in perfect cubic symmetry are not oxidized even after heating in air at the highest temperature (1000°C). The difference in the oxidation behavior of isolated and clustered Mn^{2+} ions explains why the *a* value for the diluted specimen (MM–h 0.3) heated at 700°C is higher than that for undoped MgO. After the treatment at 700°C practically all clustered Mn^{2+} ions are oxidized to Mn^{4+}, whereas isolated Mn^{2+} remain unchanged and, because of the low manganese content, the contraction effect on *a* (due to Mn^{4+} ions) does not cancel the expansion produced by isolated $Mn^{2}+$ ions.

The $Mn^{2+} \rightarrow Mn^{4+}$ oxidation in solid solution in MgO takes place with the formation of cationic vacancies on the surface. However, as soon as enough thermal energy is provided, the Mn^{4+}, Mg^{2+} and cationic vacancies order themselves and Mg_6MnO_8 (*7*) forms. Note that the Mn^{2+} oxidation to Mn^{4+} may involve Mn^{3+}. However, for temperatures higher than 600°C the manganese is present chiefly as Mn^{4+}. This result is in agreement with the conclusions based on oxygen and hydrogen adsorption (*8*).

Samples Containing Iron, Prepared in Reducing Atmosphere (MF–R)

In the sample MF–R 1, prepared in CO/CO_2 atmosphere, practically all the iron exists as Fe^{2+} in solid solution in MgO (*5*). The ESR spectrum (Fig. 5) indeed shows the presence of a very weak signal of Fe^{3+} ions in solid solution together with the signal of other ions (Mn^{2+}, Cr^{3+}) present at impurity level in the starting MgO. The asymmetric shape of the Fe^{3+} signal and the presence of satellite lines on both sides of it arise from the "cubic zero field term" (*5*) (Fig. 5A). From the integrated intensity a concentration of a few percent of the total iron present is estimated. From the unit cell parameter expansion with respect to the value of undoped MgO (Fig. 6, curve a) a concentration of about 1 Fe^{2+} ions/100 Mg atoms is estimated, knowing that the Δa for 1% of Fe^{2+} in MgO is 13×10^{-4} Å (*2*).

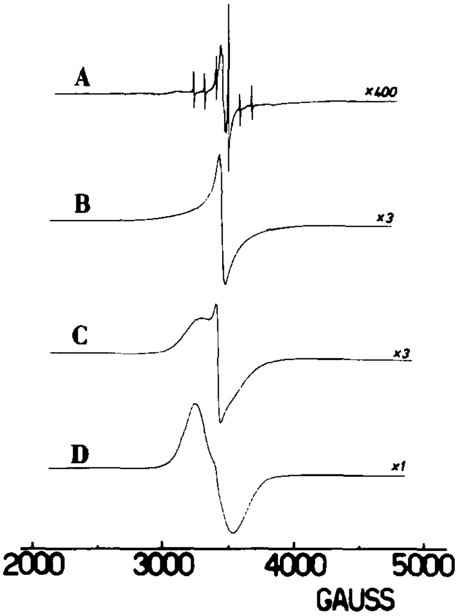

FIG. 5. ESR spectra of MF–R 1 recorded at room temperature after heating in air at different temperatures, 5 hr. A: untreated sample, B: 600°C, C: 630°C, D: 700°C. For each spectrum the number indicates the relative gain.

Both the X-ray and ESR measurements indicate that the main variations in the system occur between 500 and 700°C. At 500°C negligible change in the unit cell parameter (Fig. 6, curve a), and in the ESR intensity of the Fe^{3+} signal is noted. The sharp shrinkage of the unit cell parameter (Fig. 6, curve a) occurring for treatments at temperatures higher than 500°C, indicates that extensive oxidation of the Fe^{2+} dissolved in MgO takes place. In fact, whether the Fe^{3+} species produced remain in solid solution or segregate out of the MgO structure, a contraction of the unit cell is to be expected since, in both cases, the cause of its expansion is removed ($r_{Fe^{2+}} = 0.78$ Å, $r_{Fe^{3+}} = 0.645$ Å, $r_{Mg^{2+}} = 0.72$ Å (*9*)). Starting from 700°C the segregation of Fe^{3+} is certain since the lines of $MgFe_2O_4$ appear in the X-ray patterns.

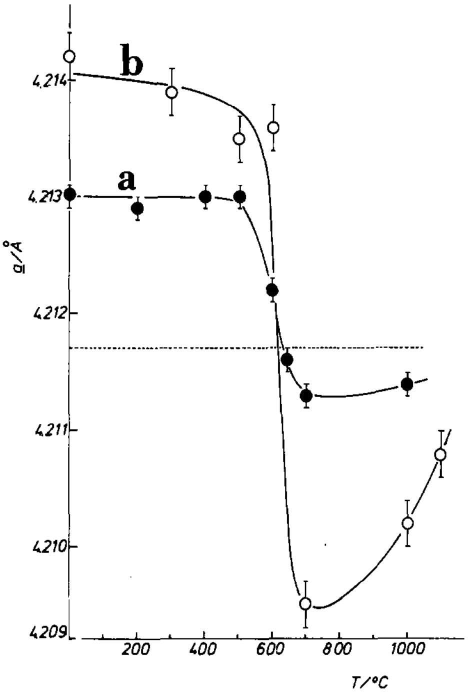

FIG. 6. Variation of the unit cell parameter *a* for MF–R 1 (curve a) and MC–h 4 (curve b) vs the temperature of the treatment in air, 5 hr. The dotted line represents the *a* values for undoped MgO. Starting from 700°C the reflections of $MgFe_2O_4$ are observed in the X-ray spectra of MF–R 1 specimen.

The variations observed in the ESR spectra may be explained along the same lines. The treatment at 600°C produces a very strong increase (100 times) in the intensity of the ESR signal. The signal becomes somewhat broader (ΔH_{pp} = 55 G) and symmetric, and the characteristic shape of the signal of isolated Fe^{3+} ions in solid solution disappears (Fig. 5B) (*5*). Nevertheless, the presence of these ions are revealed by the satellite lines, which are still detectable. The treatment in air at higher temperatures causes the appearance of a strong signal of the Fe^{3+} ions in the ferrite phase (Fig. 5C). At 700°C the intensity from integrated spectra is further increased by a factor of about eight and corresponds to an apparent Fe^{3+} concentration much higher than the nominal one. The ESR spectra of these samples are very similar to that of pure $MgFe_2O_4$, described previously (*5*). As was pointed out in Ref. (*5*), when the ferrimagnetic $MgFe_2O_4$ is present a reliable quantitative evaluation of the Fe^{3+} concentration is no longer possible. The increase in the signal intensity does not indicate only the progressive oxidation of the Fe^{2+} ions, but mainly the ordering of the Fe^{3+} ions into the ferrite phase. The variation of the intensity of the integrated spectra with the temperature of treatment in air is reported in Fig. 7. In summary the X-ray and ESR spectra show that at 500°C, the iron is still in solid solution in MgO mainly in the 2+ oxidation state; at 600°C extensive oxidation to 3+ occurs, with some incipient segregation, and finally at 700°C the segregation process in the ferrite phase is almost complete.

Samples Containing Chromium, Prepared in Hydrogen, (MC–h)

Figure 6 (curve b), shows the variation of the unit cell parameter *a* for the more concentrated sample (MC–h 4) after treatment in air. The *a* value decreases sharply for treatments in air at temperatures higher than 500°C, becoming lower than the value for undoped MgO. After a minimum, observed at

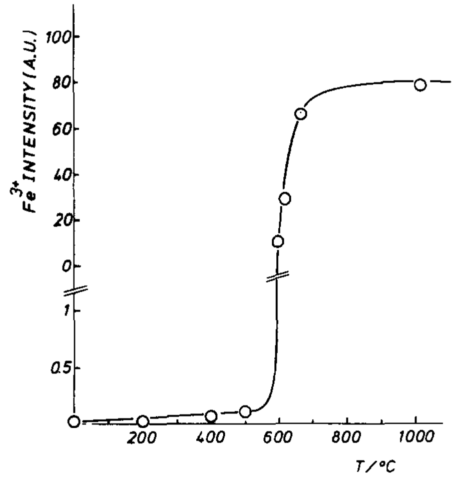

FIG. 7. Variation of the intensity (arbitrary units) of Fe^{3+} ESR signal with the treatment temperature in air, 5 hr, for MF–R 1 sample.

about 700°C, the unit cell parameter increases for treatments at higher temperatures. However, it remains substantially lower than that in pure MgO, even after treatment at 1100°C. This behavior indicates that in the range 600–700°C the main process is the oxidation $Cr^{2+} \rightarrow Cr^{3+}$ in solid solution. In fact, at 700°C a $\Delta a = (a_{MC-h4} - a_{MgO}) = -22 \times 10^{-4}$ Å is measured and, since the incorporation of 1 at.% of Cr^{3+} in MgO causes a variation in a of -14×10^{-4} Å (*11*), a value of $(-22 \times 10^{-4}/-14 \times 10^{-4}) = 1.57$ is derived for the Cr^{3+} concentration in solid solution. Recalling that in the untreated specimen the Cr^{2+} content was determined to be 1.44 at.% and that the Cr^{3+} in solid solution is estimated to be about 0.3 at.% (*4*), it appears clear that at 700°C the Cr^{3+} formed from the oxidation of Cr^{2+} remains largely in solid solution, only a very small fraction being segregated as $MgCr_2O_4$. The formation of magnesium chromite takes place with difficulty even at higher temperature. At 1100°C, a considerable fraction of Cr^{3+} is still in solid solution, as demonstrated by the low value of a (Fig. 6, curve b).

The ESR spectra confirm this picture and give some additional information on the symmetry of the Cr^{3+} ions. The ESR spectra of untreated samples, recorded at room temperature and at liquid nitrogen temperature, show the presence of three distinct signals assigned to Cr^{3+} ions in different environments: (i) A single symmetrical line at $g = 1.800$ (α-peak) with ΔH_{pp} 5–20 G, due to isolated Cr^{3+} ions in sites of cubic symmetry in solid solution in MgO; (ii) A broad symmetric line at $g = 1.980$ (β-peak) present only in the more concentrated sample and assigned to associated Cr^{3+} ions in $MgCr_2O_4$ phase (detected by X-ray) or in solid solution in MgO. The room temperature width of this line is 200–220 G, slightly different from that of similar samples fired at 1000°C (*10*). (iii) Several asymmetric peaks (γ-peaks) assigned to isolated Cr^{3+} ions in site of axial symmetry in solid solution in MgO. The axial field ($D = 0.080$ cm^{-1}) is believed to arise from the presence of a cation vacancy or a monovalent ion impurity as the nearest neighbor of the site occupied by the Cr^{3+} ion (*10*).

Figure 8 shows the variation of total Cr^{3+} content evaluated from integrated spectra for the sample MC–h 4 treated in air at different temperatures. The marked increase of the signal intensity in the range 600–700°C parallels the sharp variation of the unit cell parameter and provides further evidence for the oxidation of Cr^{2+}.

The ESR spectra indicate that only a small fraction of Cr^{3+} in solid solution exists as isolated ions in site of cubic symmetry (α-peak). A rough estimate of the concentration of Cr^{3+} in cubic symmetry (which is assumed to be proportional to $h(\Delta H)^2$, where h is the amplitude of the α-peak and ΔH its linewidth in the normal derivative presentation) shows that, starting from 600°C, it continuously increases. At 1100°C it reaches the value of about 0.1%, i.e., always much lower than the total Cr^{3+} present in solid solution. In addition, the concentration of Cr^{3+} in cubic symmetry is also independent of the total chromium content, since the same value is found for the diluted (MC–h 0.5) and concentrated sample

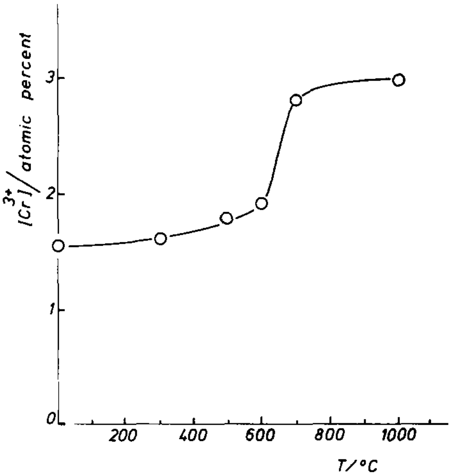

FIG. 8. Variation of Cr^{3+} concentration, evaluated by ESR, with the treatment temperature, air 5 hr, for MC–h 4 sample.

(MC–h 4). However at temperatures between 500 and 700°C, a sharpening of the linewidth of the α-peak and the attenuation of the γ-peaks is observed; this is more evident in the spectra of the diluted sample in which β-peak is absent.

Comparison between the Different Systems

The negative values of ΔG for the process $MeO + \frac{1}{2}O_2 \rightarrow \frac{1}{2}Me_2O_3$ both for Me = Mn and Fe (*12*) point out the tendency of these species to be oxidized when pure oxides are considered. For chromium this tendency is expected to be stronger since CrO is reported to be metastable at all temperatures (*13*). In spite of this the results show that for all the systems studied the transition metal ions in solid solution in MgO are oxidized only in the range 500–700°C. This behavior is explained by recalling the stabilization effect of the MgO matrix on the 2+ oxidation state (*3*). This stabilization is more effective for isolated ions which are, indeed, oxidized at higher temperature.

For the MM–h system the Mn^{2+} is converted to Mn^{4+}, the oxidation taking place by incorporation of cationic vacancies. Vacancies, Mn^{4+}, and Mg^{2+} ions order themselves and the Mg_6MnO_8 structure forms (*7*). The Mn^{2+} oxidation depends on the dispersion of the ions. Isolated Mn^{2+} ions in perfect cubic symmetry are not oxidized even at 1000°C in air.

In the case of MF–R and MC–h systems the oxidation of Fe^{2+} and Cr^{2+} to Fe^{3+} and Cr^{3+}, respectively, also takes place with formation of cationic vacancies. However, in the case of iron-doped MgO, the spinel $MgFe_2O_4$ is readily formed whereas, for the system containing chromium the Cr^{3+} does not exsolve easily to form $MgCr_2O_4$. This different behavior may be accounted for by considering that the diffusion coefficients in MgO for the trivalent cations involved are very different. At 1300°C the diffusion coefficient for Fe^{3+} has been measured to be $\sim 10^{-9}$ cm^2 sec^{-1} (*14*) whereas for Cr^{3+} at 1350°C a value of the order of 10^{-13} cm^{2}sec^{-1} has been reported (*15*). The formation of the spinel structure requires clustering of the trivalent cations which are dispersed in solid solution. As shown by Stone and Tilley (*16*) the path for the movement of the trivalent ion involves tetrahedral holes. For Cr^{3+} this process is unlikely at low temperatures (say, 700°C) because of its high crystal field stabilization energy for an octahedral site (*17*), whereas it is easier for Fe^{3+} (high spin configuration (*2*)) which has no stabilization energy for the octahedral or tetrahedral position.

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