JOURNAL OF SOLID STATE CHEMISTRY **21**, 375–385 (1977)

Infrared Investigation of Aluminum- and Chromium-Substituted Magnetites and of the Lacunar Spinels Resulting from their Oxidation*

B. GILLOT, F. BOUTON, AND J. F. FERRIOT

Laboratoire de Recherches sur la Réactivité des Solides associé au C.N.R.S., Faculté des Sciences Mirande, 21000 Dijon, France

AND F. CHASSAGNEUX AND A. ROUSSET

Laboratoire de Chimie Minérale, Université Claude Bernard, Lyon 1-43, Boulevard du 11 Novembre 1918, 69621, Villeurbanne, France

Received January 31, 1977

When Fe^{3+} ions are substituted by aluminum or chromium on magnetite octahedral sites, the ir spectrum shows the conversion of an inverse spinel to a normal spinel. Both broad bands of magnetite are gradually replaced by the four characteristic bands of normal spinels II–III. They are also observed for solid solutions, $FeCr_2O_4$–$FeAl_2O_4$, with, however, a further band at 780 cm^{-1} which may be assigned to Al^{3+} ions on tetrahedral sites. Low-temperature (<400°C) oxidation of these compounds whose sizes are less than 2000 Å results in lacunar spinels III–III. The ir spectrum of these solids is characterized by two absorption bands (as for inverse spinels II–III) except for compounds close to pure γFe_2O_3 in which an order of vacancies could be put in evidence.

Introduction

The present paper is part of a more general work on finely divided substituted magnetites and on the lacunar spinels III–III resulting from their oxidation. Interesting results on structure were obtained by ir spectrometry, as shown by Tarte and Preudhomme's (*1–3*) study of mixed oxides crystallizing in the spinel system, which supplement those obtained by other techniques such as X-ray diffraction.

In fact, magnetites substituted by trivalent Al^{3+} or Cr^{3+} ions are solids whose inversion ratio varies progressively with substituent content. In addition, with lacunar spinels, we deal with lattices where vacancies are likely to be distributed on both types of crystallographic sites and even, in some cases, to be ordered.

Therefore, the ir spectrometry investigation of substituted magnetites to make Tarte's work complete and of the new series of lacunar spinels III–III derived from the sesquioxide, γFe_2O_3, was worth undertaking.

Samples

1. Substituted magnetites. The process used to obtain substituted magnetites, $(Fe^{2+}Fe^{3+}_{2-x}M^{3+}_x)O^{2-}_4$, $0 < x < 2$, $M^{3+} = Al^{3+}$, Cr^{3+} is reported elsewhere (*4–6*). These phases were obtained with crystallites ranging from a few hundred to several thousand angstroms. On the whole, the samples investigated were of average size, i.e., less than 1000 Å (300–800 Å).

2. Solid solutions between iron(II) aluminate and chromite. A process similar to that used to synthesize substituted magnetites (*7*) allowed these compounds, $(Fe^{2+}Al^{3+}_{2-x}Cr^{3+}_x)O^{2-}_4$, 0 <

---

* Correspondence: B. Gillot, Laboratoire de Recherches sur la Réactivité des Solides associé au C.N.R.S., Faculté des Sciences Mirande, 21000 Dijon, France.

Printed in Great Britain

ISSN 0022-4596

$x < 2$, to be obtained. A structural study showed them to be normal spinels (*8*). Crystallite size was about 800 Å.

3. Solid solutions with lacunar spinel structure. Lacunar spinel-type, cubic sesquioxides were obtained by low-temperature oxidation (200–500°C) of substituted magnetites according to:

$$2(Fe^{2+}Fe^{3+}_{2-x}M^{3+}_{x})O_4^{2-} + \tfrac{1}{2}O_2 \rightarrow 3\gamma(Fe^{3+}_{1-y}M^{3+}_{y})_2O_3^{2-}$$

with $0 < x < 2$, $x = 3y$, and $0 < y < \frac{2}{3}$; $M^{3+} = Al^{3+}$, Cr^{3+}. They are derived from γFe_2O_3 through substitution of Fe^{3+} ions by Al^{3+} or Cr^{3+} ions. From the structural standpoint they may be formulated as follows: $(Fe^{3+}_{8-8y}$-$M^{3+}_{8y}\square)O^{2-}_{12}$, $0 < y < \frac{2}{3}$. A vacancy distribution on octahedral sites resulting in a structure, $Fe^{3+}_3(Fe^{3+}_{5-8y}Cr^{3+}_{8y}\square)O^{2-}_{12}$, $0 < y \leqslant \frac{5}{3}$, is to be expected from earlier crystallographic and magnetic studies (*9*), although no superstructure ray corresponding to a vacancy ordering on those sites could be detected. For higher chromium contents, $\frac{5}{3} < y \leqslant \frac{2}{3}$, some vacancies must be assumed to be on tetrahedral sites, as the Cr^{3+} ions cannot move onto these sites. For Al^{3+} ions, substitution also seems to occur on octahedral sites and, at least for iron-rich compounds, the vacancies, like the Al^{3+} ions, seem to be on octahedral sites.

In the same way, oxidation of solid solutions between iron(II) aluminate and chromite yields cubic sesquioxides of the lacunar spinel type (7):

$$2(Fe^{2+}Al^{3+}_{2-x}Cr^{3+}_{x})O_4^{2-} + \tfrac{1}{2}O_2 \rightarrow 3\gamma(Fe^{3+}_{1/3}Al^{3+}_{2/3-y}Cr^{3+}_{y})_2O_3^{2-},$$
$$0 < x < 2, \qquad x = 3y, \qquad 0 < y < \tfrac{2}{3}.$$

From the structural standpoint these phases may be written as:

$$(Fe^{3+}_{8/3}Al^{3+}_{16/3-8y}Cr^{3+}_{8y}\square)O^{2-}_{12}, 0 < y < \tfrac{2}{3}.$$

An initial, structural investigation of these compounds (7) shows that at least one-third of the vacancies are on tetrahedral sites, their formula approaching:

$$Fe^{3+}_{8/3}\square_{1/3}(Al^{3+}_{16/3-8y}Cr^{3+}_{8y}\square_{2/3})O^{2-}_{12}, \quad 0 < y < \tfrac{2}{3}.$$

The morphology of these lacunar spinels is similar to that of the initial phases (substituted magnetites, solid solutions between iron(II) aluminate and chromite); crystallite sizes, especially, are almost the same.

The reaction kinetics (*10*, *11*) were followed in a thermobalance by oxidizing very low amounts of specimens (17 mg).

Experimental

The ir spectra were recorded on an ir 4250 over the range 200–4000 cm^{-1}, but as the frequency region above 1100 cm^{-1} contains no information, only the spectra in the 200–1100-cm^{-1} region are given. A sample of about 1 mg (about 0.5 mg for inverse spinels) was ground and mixed with 200 mg of CsI before being pelleted under 160 bars. Routine conditions involve an error of about ± 1 cm^{-1} for low frequencies, whereas it may be greater for higher-frequency bands owing to their broadening.

Study of Spinels Containing Fe^{2+} Ions

1. Results

(*a*) *Solid solutions between iron*(*II*) *aluminate and chromite* $(Fe^{2+}Al^{3+}_{2-x}Cr^{3+}_{x})O_4^{2-}$. The interest of such a series of compounds lies in the fact that, theoretically, we have normal spinels with substitution occurring solely on octahedral sites. Figure 1 shows the shape of the spectrum versus the substitution ratio. When aluminum is substituted by chromium all bands shift toward low frequencies (Fig. 2). ν_3, however, is the frequency band showing the largest shift as it declines from 512 to 370 cm^{-1}, i.e., a decrease of 142 cm^{-1}, a value which agrees with that observed for other systems (Table I) differing from ours solely by a different divalent cation on tetrahedral sites (*2*, *12*).

In addition, ν_3 has a rather complex behavior, at least for low aluminum substitution ratios, since for the compound $(FeCr_{1.5}Al_{0.5})$-O_4, a multiplet is observed. The broadening and intensity of both high-frequency bands are also seen to depend basically on the nature of the trivalent cation. These bands broaden as aluminum substitution proceeds. For the solid, aluminum-rich solution a shouldering is observed around 780 cm^{-1}.

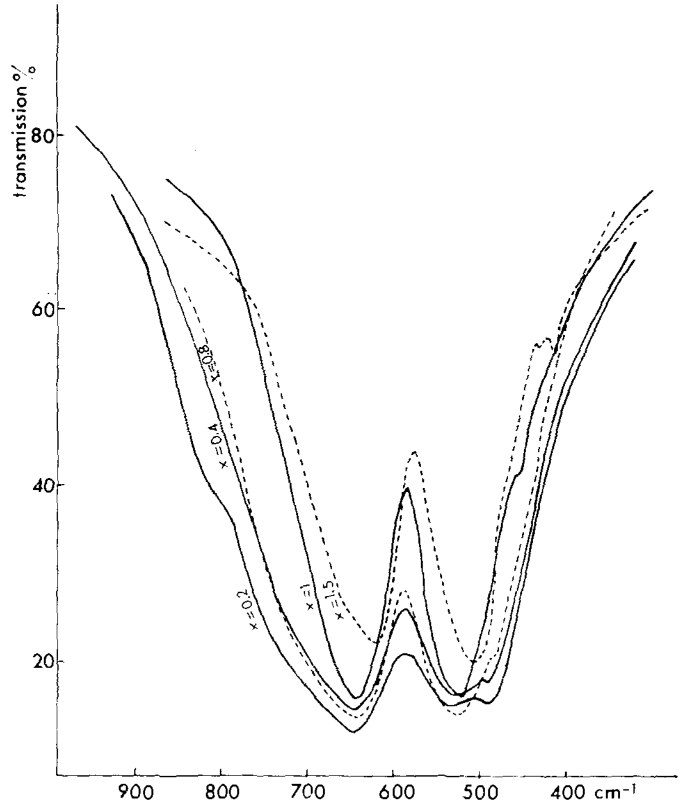

FIG. 1. Infrared spectra of solid solutions $(Fe^{2+}Al^{3+}_{2-x}Cr^{3+}_{x})O_4^{2-}$.

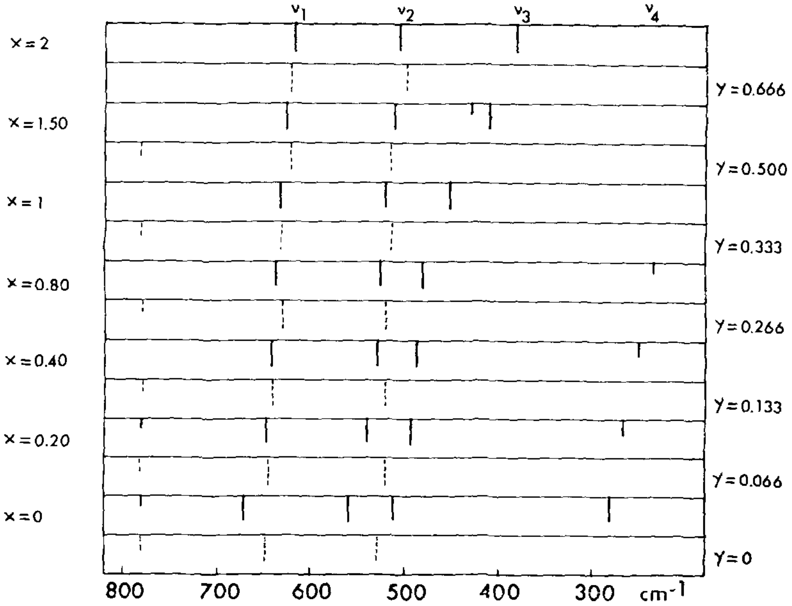

FIG. 2. Vibrational behavior: solid lines, solid solutions $(Fe^{2+}Al^{3+}_{2-x}Cr^{3+}_{x})O_4^{2-}$; dashed lines, lacunar spinels $\gamma(Fe^{3+}_{1/3}Al^{3+}_{2-y}Cr^{3+}_{y})_2O_3^{2-}$.

TABLE I

Sample	ν_3 (cm^{-1})	Shift (cm^{-1})
$FeAl_2O_4$	512	142
$FeCr_2O_4$	370	
$ZnAl_2O_4$	518	143
$ZnCr_2O_4$	375	
$CoAl_2O_4$	533	153
$CoCr_2O_4$	380	
$MgAl_2O_4$	580	150
$MgCr_2O_4$	430	

(*b*) *Iron*(*II*) *ferrichromites and iron*(*II*) *chromite* ($Fe^{2+}Fe^{3+}_{2-x}Cr^{2+}_{x})O^{2-}_{4}$. Conversion of the inverse spinel into the normal spinel over substitution is shown on the ir spectrum by a gradual sharpening of both high-frequency absorption bands, which are always observed and may be ascribed to ν_1 and ν_2, as formulated by Tarte (*2*) (Fig. 3). As soon as a substitution ratio, $x > 0.80$, is reached, a lower-frequency band ν_3 is seen to appear; its intensity rises more and more as iron chromite is approached. For intermediate compositions ($x = 1.20$ and 1.60), ν_3 is divided into two components. ν_4 could not be observed with our assembly; however, comparing with other chromites (*2*), this band should occur around 190 cm^{-1}. Finally, at a fixed frequency of 450 cm^{-1} a shouldering is observed.

Following the insertion of Cr^{3+} ions on magnetite octahedral sites a shift of all vibrational frequencies toward high frequencies is noticed (Fig. 4).

(*c*) *Iron*(*II*) *ferrialuminates and iron*(*II*) *aluminate* ($Fe^{2+}Fe^{3+}_{2-x}Al^{3+}_{x})O^{2-}_{4}$. The order of

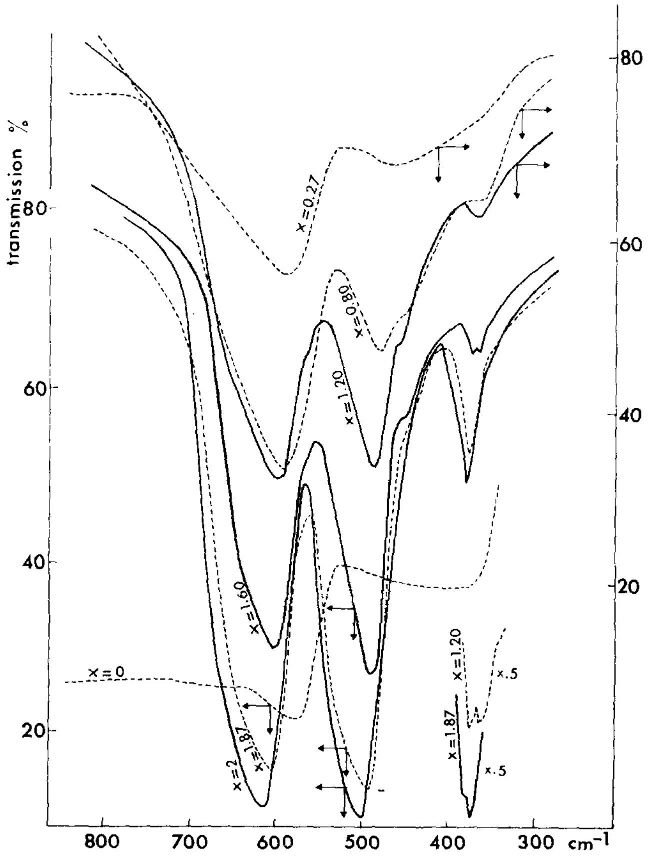

FIG. 3. Infrared spectra of chromium-substituted magnetites, ($Fe^{2+}Fe^{3+}_{2-x}Cr^{3+}_{x})O^{2-}_{4}$.

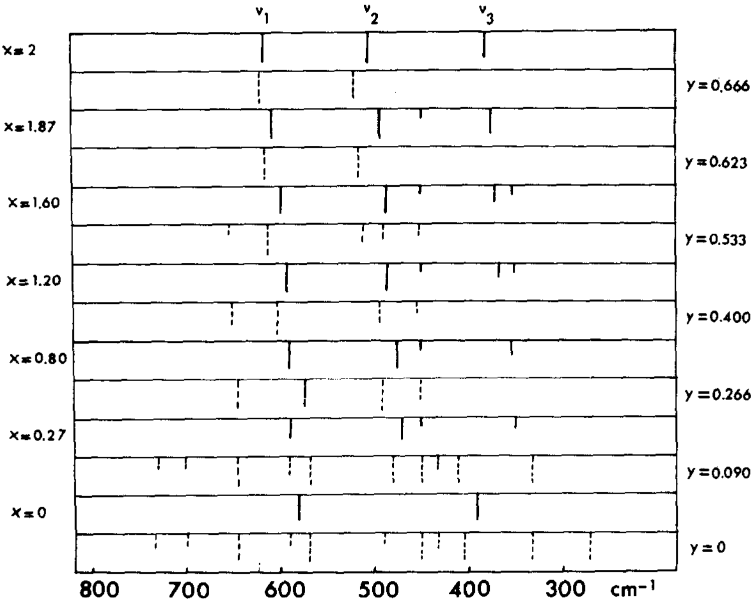

FIG. 4. Vibrational behavior: solid lines, chromium-substituted magnetites $(Fe^{2+}Fe^{3+}_{2-x}Cr^{3+}_{x})O_4^{2-}$; dashed lines lacunar spinels $\gamma(Fe^{3+}_{1-y}Cr^{3+}_{y})_2O_3^{2-}$.

band occurrence for this series of compounds is similar to that in the previous case. For magnetite, intermediate compositions, and iron aluminate, we pass from two to three and four bands, respectively (Fig. 5). They, however, remain broad whatever the substitution ratio and as in the case of ferrichromite Al^{3+} ions, insertion on the octahedral sites of magnetite causes all bands to shift toward high frequencies (Fig. 6).

Note that for iron aluminate and as observed for other aluminates (*2*) three strong bands are found in the high-frequency region. The 512-cm^{-1} band whose intensity is even higher than ν_2 (Fig. 5) is to be assigned to ν_3 since, as already seen for solid solutions $(Fe^{2+}Al^{3+}_{2-x}Cr^{3+}_{x})O_4^{2-}$, this band shifts steadily toward low frequencies, when aluminum is gradually substituted by chromium on octahedral sites, and eventually reaches 370 cm^{-1} in the pure $FeCr_2O_4$ compound.

A shouldering around 780 cm^{-1} is also noted for aluminate.

2. *Discussion*

(*a*) *Solid solutions between iron(II) aluminate and chromite.* Normal spinels II–III show the four bands corresponding to the ir active modes (*13*). Two strong, high-frequency, more or less broad bands and one or two lower-frequency, weak, and narrow bands are obtained.

Our results—which agree with those of Preudhomme and Tarte (*2*), who thoroughly investigated normal spinels II–III by varying either the tetrahedral cation (same octahedral cation), or the octahedral cation (same tetrahedral cation)—substantiate clearly that ν_1 and ν_2 depend on the nature of the trivalent cation, with maximum values of 620 to 670 cm^{-1} for ν_1 and 510 to 560 cm^{-1} for ν_2. The governing factor of these variations should be the strength of the bond between the trivalent cation and the oxygen anion; ν_1 and ν_2 are to be ascribed to the vibrations of the condensed octahedra of the lattice (*2*).

According to the same authors (*2*), the lower-frequency bands ν_3 and ν_4 are to be assigned to the complex vibrations involving both octahedral and tetrahedral cations. In our case, the complex behavior of ν_3 for $(FeCr_{1.5}Al_{0.5})O_4$ and its shift from 280 to 370 cm^{-1}, whereas the tetrahedral cation remains

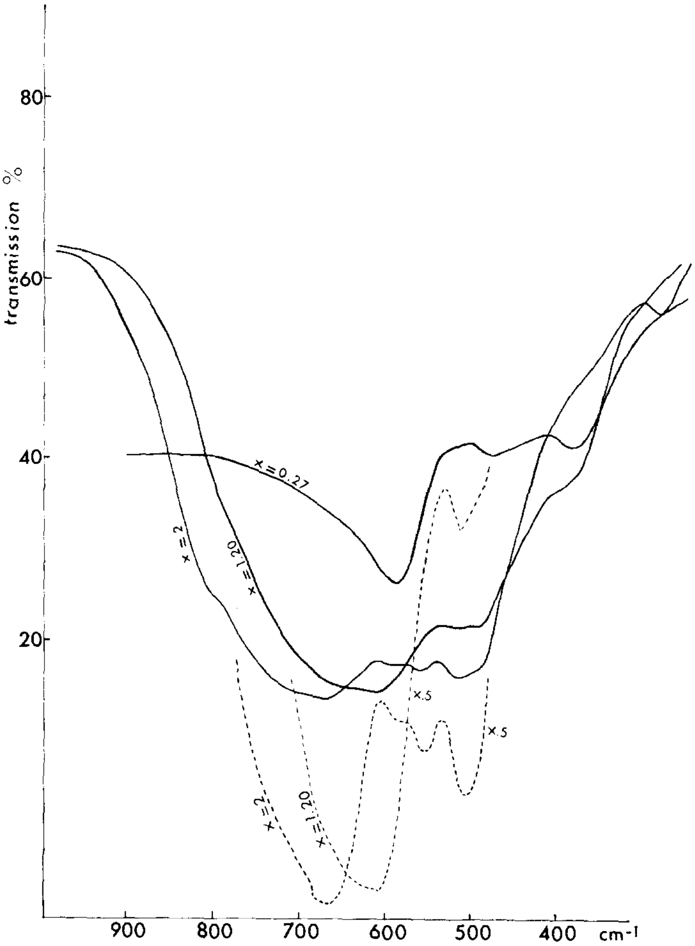

FIG. 5. Infrared spectra of aluminum substituted magnetites $(Fe^{2+}Fe^{3+}_{2-x}Al^{3+}_{x})O_4^{2-}$.

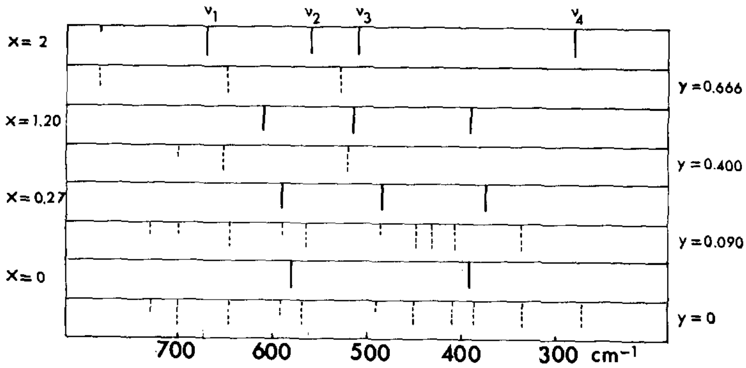

FIG. 6. Vibrational behavior: solid lines, aluminum substituted magnetites $(Fe^{2+}Fe^{3+}_{2-x}Al^{3+}_{x})O_4^{2-}$; dashed lines, lacunar spinels $\gamma(Fe^{3+}_{1-y}Al^{3+}_{y})_2O_3^{2-}$.

the same, results from a major contribution of the octahedral cation to this vibrational mode. Similar behavior was observed for solid solutions such as $ZnCr_2O_4$–$ZnAl_2O_4$ and $CdCr_2O_4$–$CdFe_2O_4$ (*2*).

As for ν_4, although it has been shown that it basically depends on the tetrahedral cation (*2*), its shift toward low frequencies as the chromium content increases suggests that the octahedral cation influence is not to be neglected.

The shouldering of iron aluminate at 780 cm^{-1} might be attributed to low amounts of Al^{3+} ions on the tetrahedral sites, despite the low temperature of preparation (<800°C). Aluminate prepared at a higher temperature (1100°C) shows a more marked shouldering, which may indicate the presence of a larger quantity of Al^{3+} ions on tetrahedral sites. Attribution of this shouldering to aluminum on tetrahedral sites is strengthened by the presence of a shouldering or a weak band in several aluminates with a spinel structure or in several ferrites when a low amount of coordinated iron is replaced by aluminum (*14*). This further band was assigned to an "isolated" AlO_4 group.

(*b*) *Aluminum- or chromium-substituted magnetites.* Interactions may always occur between the four ir active modes owing to the fact that they belong to the same representation T_{1u} (*3*). The question becomes still more complex for inverse spinels where cations with a different valence are on the same type of site and hence disturb local symmetry. Thus, that or those atoms causing a given vibration will be less readily identified.

The cation distribution versus the aluminum or chromium substitution ratio was determined from the Mössbauer effect and magnetic and crystallographic measurements (*15*, *16*). It may vary slightly depending on the nature of the substituent, whereas gradual substitution of Al^{3+} by Fe^{3+} ions on octahedral sites causes a nearly equal number of Fe^{2+} ions to move onto octahedral sites. In the case of ferrichromites this distribution is more random: For a substitution ratio such that $x < 0.20$ the spinel is totally inverse; it is totally normal for $x > 1.40$.

Both frequency bands, ν_1 and ν_2, observed whatever the substitution ratio was assigned, at least for high substitution ratios ($x > 1.40$), to the condensed octahedra vibrations in the spinel lattice. Indeed, when introducing Fe^{3+} ions on octahedral sites the shift of ν_1 and ν_2 toward lower frequencies agrees with the absorption ranges reported by Tarte (*1*) for some condensed octahedral groups, AlO_6, CrO_6, and FeO_6 in various spinels. Figure 7 shows that the lowest frequencies are related to the FeO_6 groups, those low frequencies resulting probably from a lowering of the cation–oxygen bonding force.

The shift of ν_3 toward low frequencies and its splitting for ferrichromites with $x = 1.87$ and 1.60 may be related to a significant contribution of the octahedral cation to this mode of vibration as is the case for solid solutions $FeAl_2O_4$–$FeCr_2O_4$. In addition, the weakening of ν_3 as the number of Cr^{3+} ions decreases is direct evidence of the octahedral cation influence. As the substitution ratio of Cr^{3+} or Al^{3+} ions decreases, ν_3 disappears and two broad bands, frequently observed for inverse spinels only, remain (*17*–*19*). The ir spectrum is then typical both of a disordered, inverse spinel (two diffuse bands) and of a solid compound containing mobile electrons responsible for a continuous absorption coinciding with the vibrational absorption. The abnormally high value of electric conductivity and the very low activation energy under vacuum, for $x < 0.80$ (*20*) confirm an electronic exchange made easier by the simultaneous pre-

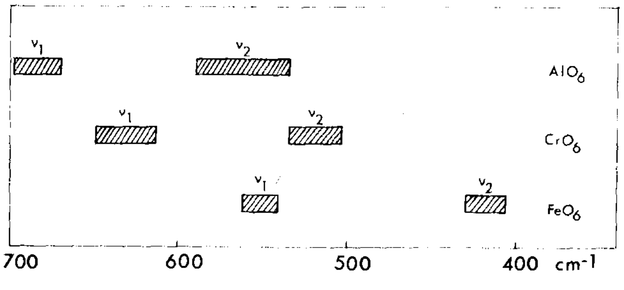

FIG. 7. Comparison of absorption ranges of condensed AlO_6, CrO_6, and FeO_6 octahedra in spinel compounds.

sence of Fe^{2+} and Fe^{3+} ions on octahedral sites.

On the whole, the ir spectrum of these compounds shows many analogies despite a slightly different distribution of cations on each site of the spinel.

Investigation of Lacunar Spinels Containing Fe^{3+} Ions

1. Results

(*a*) *Lacunar spinels*, $\gamma(Fe^{3+}_{1/3}Al^{3+}_{2/3-y}Cr^{3+}_y)_2O_3^{2-}$. The ir spectrum shows two bands (Fig. 8) which broaden and shift steadily toward high frequencies when passing from oxidized iron chromite to the aluminate (Fig. 2).

A shouldering is also observed at 780 cm^{-1} for the solid, aluminum-rich solution.

(*b*) *Lacunar spinels*, $\gamma(Fe^{3+}_{1-y}Cr^{3+}_y)_2O_3^{2-}$. Cubic sesquioxides obtained by normal spinel oxidation ($y > 0.53$) show two broad, high-frequency bands slightly shifted toward frequencies higher than those of nonoxidized materials (Fig. 4). When the chromium substitution ratio decreases new bands appear (Fig. 9); they become sharper and sharper and more and more numerous as γFe_2O_3 is approached, and eventually give the characteristic spectrum of ordered γFe_2O_3 (Fig. 9) (*3*).

(*c*) *Lacunar spinels*, $\gamma(Fe^{3+}_{1-y}Al^{3+}_y)_2O_3^{2-}$. These lacunar phases are very similar to those mentioned earlier by their ir spectrum (Fig. 10). Two differences, however, should be noted:

(i) For aluminum substitution ratios, $y > 0.40$, both high-frequency bands are far broader and shifted toward high frequencies (Fig. 6); a further band occurs at 780 cm^{-1} for oxidized iron aluminate (Fig. 10).

(ii) Lacunar spinel bands such that $y = 0.09$ are better resolved.

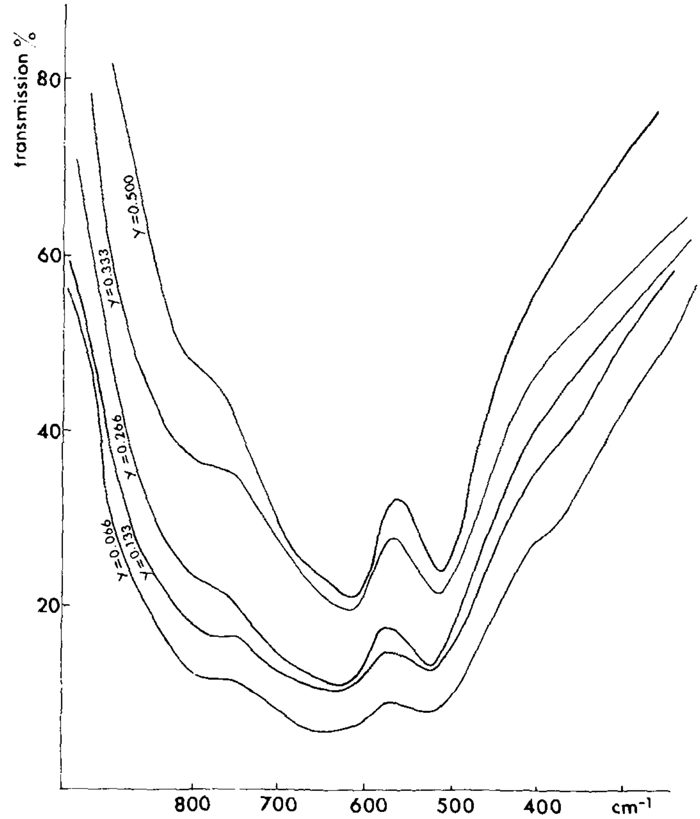

FIG. 8. Infrared spectra of lacunar spinels $\gamma(Fe^{3+}_{1/3}Al^{3+}_{2/3-y}Cr^{3+}_y)_2O_3^{2-}$.

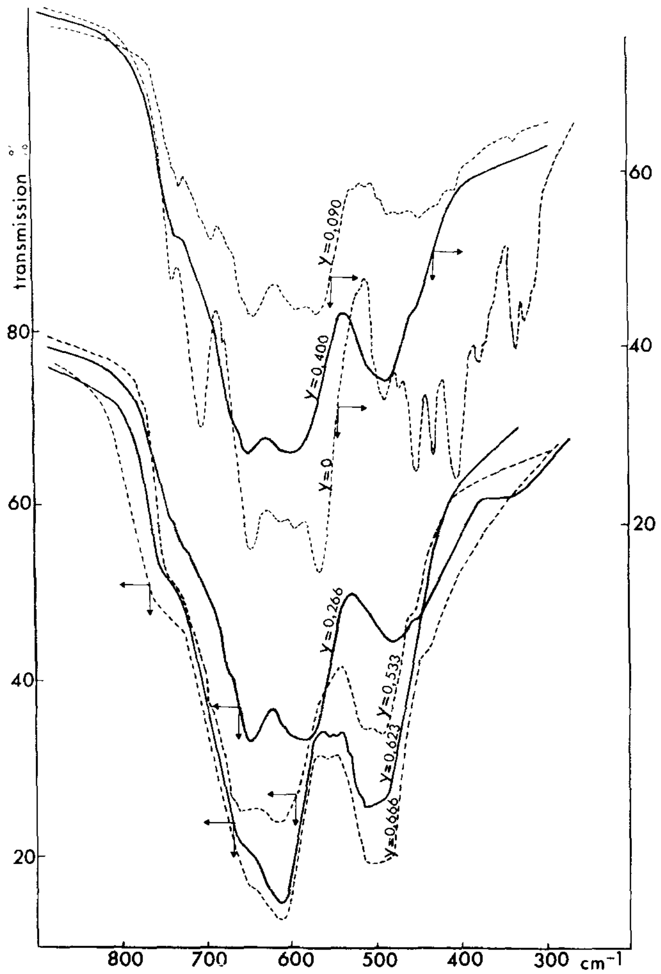

FIG. 9. Infrared spectra of lacunar spinels $\gamma(\mathrm{Fe}^{3+}_{1-y}\mathrm{Cr}^{3+}_{y})_2\mathrm{O}^{2-}_3$.

2. *Discussion*

(*a*) *Lacunar spinels*, $\gamma(\mathrm{Fe}^{3+}_{1/3}\mathrm{Al}^{3+}_{2/3-y}\mathrm{Cr}^{3+}_{y})_2\mathrm{O}^{2-}_3$. Oxidation of Fe^{2+} ions on tetrahedral sites results in the disappearance of the absorption frequency bands ν_3 and ν_4. The situation is similar to that of an inverse spinel or more precisely to that of magnetite where ions of valency three occur both on octahedral and tetrahedral sites. The ir spectrum showing two absorption bands in the regions 625–650 and 500–530 cm^{-1}, may be regarded as typical of a disordered spinel. However, continuous absorption ends due to electronic exchange cancelling, which is confirmed by a high-activation energy under vacuum (*20*). As a result, the high-frequency band cannot be assigned to the vibration of either octahedral or tetrahedral groups. It, however, depends slightly on the nature of the trivalent cation since it shifts toward high frequencies while chromium is replaced by aluminum.

The shouldering at 780 cm^{-1}, occurring as soon as we have $(\mathrm{Fe}_{1/3}\mathrm{Al}_{0.16}\mathrm{Cr}_{0.50})\mathrm{O}_3$, seems to be characteristic, as in the case of aluminate, of "isolated" AlO_4 groups, which also assumes a certain number of Al^{3+} ions on tetrahedral sites. However, as mentioned earlier, the low temperature of preparation (<800°C) does not allow us to expect a large proportion of Al^{3+} ions on tetrahedral sites. It must be added that the lattice parameters are those of a normal spinel (*21*).

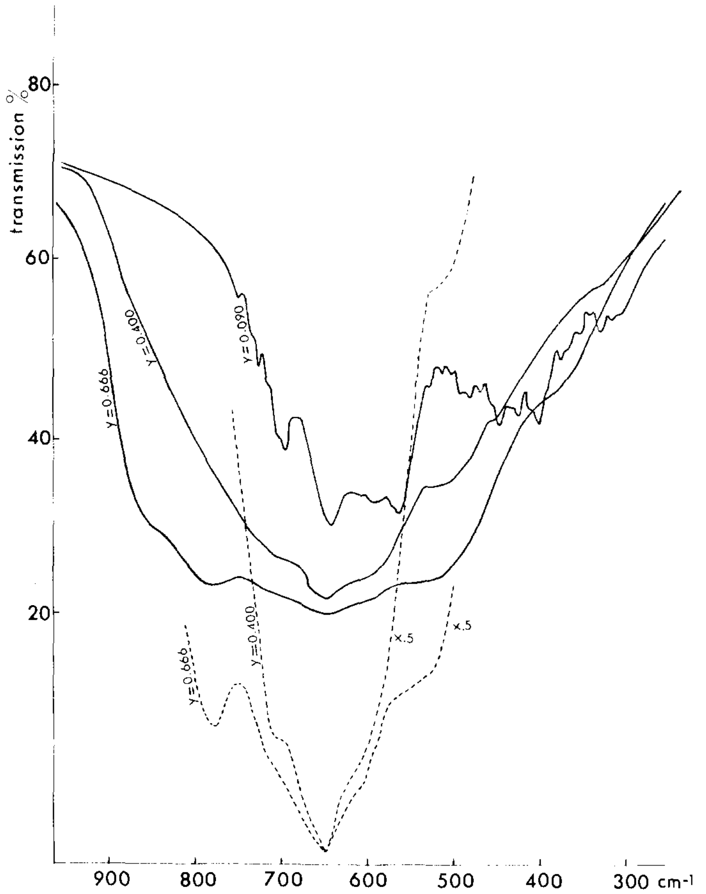

FIG. 10. Infrared spectra of lacunar spinels $\gamma(\mathrm{Fe}^{3+}_{1-y}\mathrm{Al}^{3+}_{y})_2\mathrm{O}_3^{2-}$.

(*b*) *Lacunar spinels*, $\gamma(\mathrm{Fe}^{3+}_{1-y}M^{3+}_{y})_2\mathrm{O}_3^{2-}$. For substitution ratios, $y > 0.50$, the spectrum similarity with the previous lacunar spinels involves a disordered spinel.

The occurrence of new bands, as the M^{3+} ions substitution ratio decreases (those bands become more and more numerous and they are better resolved when $\gamma\mathrm{Fe}_2\mathrm{O}_3$ is approached), indicates a transition order–disorder (*3*). From $y < 0.50$ a partially ordered spinel becoming perfectly ordered for pure $\gamma\mathrm{Fe}_2\mathrm{O}_3$ is obtained.

These results are in good agreement, at least when $0 < y < 0.10$, with magnetic and crystallographic studies (*21*) which established an order of vacancies on octahedral sites. However, for $0.10 < y < 0.40$, the fact that the ir spectrum shows a relatively large number of weak and more or less diffuse bands, which correspond to the sharper bands of the ordered type, may be explained by some kind of ordering in the distribution of vacancies and cations. In this case, X-ray analysis yields no superstructure ray.

Conclusion

Systematic investigation of the ir spectrum of chromium- and aluminum-substituted magnetites is in good agreement with results obtained for other spinels II–III. Indeed:

(a) For low substitution ratios ($x < 0.30$) there are only two, intense, broad absorption bands coinciding with a continuous absorption specific to inverse spinels II–III containing mobile electrons and hence having a high electric conductivity.

(b) The higher the substitution ratio, the narrower these bands (for ferrichromite only). A lower-frequency band ν_3 appears subjected to the prevailing influence of the cations Al^{3+} or Cr^{3+} when Fe^{3+} ions are substituted on octahedral sites.

$FeCr_2O_4$–$FeAl_2O_4$ solid solutions are characterized by a continuous shift of all vibrational frequencies toward low frequencies when aluminum is substituted by chromium. Band ν_3, depending rather largely on the trivalent cation, splits into two components, at least for solid solutions with $x = 1.50$. Finally, whatever the isomorphic substitution of each octahedral or tetrahedral cation, ν_1 and ν_2 never split in two components, which may be justified by the condensed arrangement of octahedra.

These results suggest that, on the one hand, the four bands result from the bond strength, M^{3+}–O, and on the other, that spinels containing light atoms show some anomalies. So, the Al^{3+} ions contribute more to vibration ν_3 than the heavy ion Cr^{3+}; as a result ν_3 and ν_2 have very close frequencies and ν_3 is more intense than usual (case of aluminate). These vibrational differences often cause ν_3 to be discontinuous when the Al^{3+} ion replaces a heavy cation such as chromium in an isomorphic series $(FeCr_{1.50}Al_{0.50})O_4$.

The ir spectrum varies more in the case of lacunar spinels containing trivalent ions and vacancies only. It is characterized for substitution ratios, $y > 0.50$—in the case of lacunar spinels $\gamma(Fe^{3+}_{1-y}M^{3+}_y)_2O_3^{2-}$ and whatever the isomorphic substitution ratio for solid solutions $\gamma(Fe^{3+}_{1/3}Al^{3+}_{2/3-y}Cr^{3+}_y)^2O_3^{2-}$—by two broad absorption bands. They shift toward low frequencies when either aluminum or chromium is substituted by Fe^{3+} ions or aluminum by chromium. In no case could an ordered variety of the same type as pure γFe_2O_3 be detected. Iron(II) ferrichromites and ferrialuminates having a substitution ratio $y < 0.40$, alternatively, are characterized by a relatively large number of weak bands becoming sharper and sharper and more and more numerous as pure γFe_2O_3 is approached. A partially ordered spinel is converted into a perfectly ordered spinel.

Finally, with both X-ray diffraction and ir spectrometry one may observe the order decrease on a large distance versus substitution ratio, but with ir spectrometry one may observe only a short-distance order in the inner domain.

References

1. J. Preudhomme and P. Tarte, *Spectrochim. Acta A* **27**, 961 (1971).
2. J. Preudhomme and P. Tarte, *Spectrochim. Acta A* **27**, 1817 (1971).
3. J. Preudhomme, *in* "Séminaire de Chimie de l'état solide," (J. P. Suchet, Ed.), p. 32, Masson, Paris (1974).
4. A. Rousset, Thèse Lyon (1969).
5. A. Rousset, J. Paris, and P. Germi, *Ann. Chim.* 7, 2, 57 (1972).
6. A. Rousset and J. Paris, *Bull. Soc. Chim. Fr.* 3729 (1972).
7. F. Chassagneux, Thèse Lyon (1974).
8. F. Chassagneux and A. Rousset, *J. Phys. Chem. Solids* **16**, 161 (1976).
9. A. Rousset, J. Paris, and P. Mollard, *Ann. Chim.* 7, 119 (1972).
10. B. Gillot, J. Tyranowicz, and A. Rousset, *Mater. Res. Bull.* **10**, 775 (1975).
11. B. Gillot, J. F. Ferriot, G. Dupré, and A. Rousset, *Mater. Res. Bull.* **11**, 843 (1976).
12. N. W. Grimes and A. J. Collett, *Phys. Status Solidi* (*b*) **43**, 591 (1971).
13. R. D. Waldron, *Phys. Rev.* **99**, 1727 (1955).
14. P. Tarte, *Spectrochim. Acta* **A23**, 2127 (1967).
15. M. Robbins, G. K. Wertheim, R. C. Sherwood, and D. N. E. Buchanan, *J. Phys. Chem. Solids* **32**, 717 (1971).
16. G. Dehe, B. Seidel, K. Melzer, and C. Michalk, *Phys. Status Solidi* (*a*) **31**, 439 (1975).
17. V. A. M Brabers, *Phys Status Solidi* **33**, 563 (1969).
18. M. Ishii, M. Nakahira, and T. Yamanaka, *Solid State Commun.* **11**, 209 (1972).
19. N. W. Grimes and A. J. Collett, *Nature Phys. Sci.* **230**, 158 (1971).
20. B. Gillot, J. F. Ferriot, and A. Rousset, *J. Phys. Chem. Solids* **37**, 857 (1976).
21. A. Rousset, F. Chassagneux, and P. Mollard, *C.R. Acad. Sci. Paris* **279**, 1129 (1974).