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# Two New Iron(IV) Oxides with High-Spin Configuration

## $SrLaMg_{0.50}Fe_{0.50}O_4$ and $SrLaZn_{0.50}Fe_{0.50}O_4$*

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Two new iron(IV) oxides have been prepared using high oxygen pressure: $SrLaM_{0.50}Fe(IV)_{0.50}O_4$ ($M$ = Mg, Zn). In both phases with a $K_2NiF_4$-type-derived structure the elongation of the $(FeO_6)$ octahedron is sufficient to stabilize a high-spin state ($t_{2g}^3 d_{z^2}^1$). The electronic configuration has been characterized by structural, magnetic, and Mössbauer spectroscopic investigations.

## Introduction

Development of the high oxygen pressure techniques has contributed largely to the stabilization of unusually high oxidation states of the 3*d* elements (e.g., Fe(IV), Fe(V), Co(III), Co(IV), Ni(III), Cu(III)) in oxide lattices (*1–11*).

Some of these 3*d* cations can show two, or even more, electronic configurations. Recently the influence of the local distortion of the octahedral site occupied by the cation (elongation or compression) on the nature of the electronic configuration has been discussed (*12, 13*).

Tetravalent iron ($3d^4$) may exhibit two electronic configurations: one of high-spin character ($t_{2g}^3 e_g^1$) and another of low-spin type ($t_{2g}^4 e_g^0$).

Iron(IV) has been stabilized, in particular, within stoichiometric or nonstoichiometric oxides derived from the perovskite structure. If in the $A_{0.50}La_{1.50}Li_{0.50}Fe_{0.50}O_4$ ($A$ = Ca, Sr, Ba) phases with $K_2NiF_4$-type structure, iron(IV) has unambiguously a high-spin configuration ($t_{2g}^3 d_{z^2}^1$) (*2, 14*), then in the $AFeO_3$ ($A$ = Ca, Sr, Ba) perovskites (*15–31*), the nature of the electronic configuration of iron(IV) leads to somewhat different interpretations. Because the iron polyhedra are not isolated from each other by intermediate lithium atoms, and because of the strongly covalent character of the Fe(IV)–O bond, a certain electronic delocalization may result (*32–34*).

A study of $CaFeO_3$ at low temperature by Mössbauer spectroscopy gives evidence of a disproportionation: $2Fe(IV) \rightleftarrows Fe(III) + Fe(V)$ (*16*). A hopping mechanism between the $e_g$ orbitals account for such behavior and hence involves a high-spin configuration ($t_{2g}^3 e_g^1$) for iron(IV) (*18*).

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* This article is published as a token of esteem and deep friendship of John Goodenough who has played a major role in the development of modern solid state chemistry.

For $SrFeO_3$ the magnetic moment of iron(IV) at 77 K appears to be 2.7 ± 0.4 $\mu_B$ (*21*), whereas it drops to 1.6 $\mu_B$ in nonstoichiometric $SrFeO_{2.90}$ after deduction of the moment of high-spin iron(III) present (*22*). Such data indeed suggest a low-spin configuration ($t_{2g}^4e_g^0$). Nevertheless, recently Takeda *et al.* have found by extrapolation for $x = 0$ ($\mu = 3.373\ \mu_B$), in $SrFe_{1-x}Co_xO_3$ phases, a much higher moment value of iron(IV) (*35*). This result should involve rather a high-spin state ($t_{2g}^3e_g^1$). In $SrFe_{1-x}Co_xO_3$ phases, the competing Co(IV)–O bonds, more covalent than the Fe(IV)–O bonds, could decrease the crystal field at the iron(IV) site and favor a high-spin state for iron(IV). On the other hand one must notice that the values of the chemical shifts at 300 K observed by Mössbauer spectroscopy are very close in the whole range of the solid solutions ($0.00 \leq \delta \leq 0.05$ mm · $sec^{-1}$) and differ strongly from those detected for the $A_{0.50}La_{1.50}Li_{0.50}Fe_{0.50}O_4$ ($A$ = Ca, Sr, Ba) oxides ($-0.20 < \delta < -0.16$ mm · $sec^{-1}$), where isolated iron(IV) has been unambiguously characterized with a high-spin configuration (*2*).

If the electronic delocalization is not too large in the corresponding oxides, comparison of the values of the ionic radii of iron(IV) should allow detection of the nature of the configuration. A recent study by X-ray absorption on iron oxides such as SrFe(IV)$O_3$ and $Sr_{0.50}La_{1.50}Li_{0.50}Fe_{0.50}O_4$ has shown some differences in the average ionic radii: $\bar{r}_{(FeIV)}(SrFeO_3) \simeq 0.525$ Å $\bar{r}_{(FeIV)}$ ($Sr_{0.50}La_{1.50}Li_{0.50}Fe_{0.50}O_4$) $\simeq 0.55$ Å (*26*). Such values suggest a low-spin configuration in $SrFeO_3$ and a high-spin one in $Sr_{0.50}La_{1.50}Li_{0.50}Fe_{0.50}O_4$.

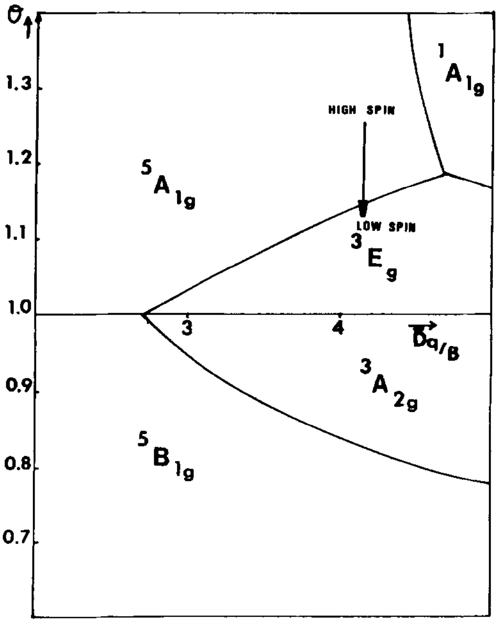

FIG. 1. Ground state domains for a $d^4$ configuration as a function of the structural distortion $\theta$ of the $MX_6$ octahedron and of the $\overline{Dq}/B$ ratio ($\overline{Dq}$, average crystal field; $B$, Raccah parameters).

TABLE 1

CRYSTALLOGRAPHIC PARAMETERS FOR SOME IRON(IV) AND IRON(III) OXIDES WITH $K_2NiF_4$-TYPE STRUCTURE

| | $a_0$ (Å) | $c_0$ (Å) | $a = a_0\sqrt{2}$ (Å) | $c_0/a_0$ |
|---|---|---|---|---|
| $SrLaMg_{0.50}Fe_{0.50}O_4$ | 3.822 | 12.87 | 5.405 | 3.37 |
| $SrLaZn_{0.50}Fe_{0.50}O_4$ | 3.847 | 12.93 | 5.440 | 3.36 |
| $Ca_{0.50}La_{1.50}Li_{0.50}Fe_{0.50}O_4$ | 3.73 | 12.84 | 5.275 | 3.44 |
| $Sr_{0.50}La_{1.50}Li_{0.50}Fe_{0.50}O_4$ | 3.76 | 13.03 | 5.317 | 3.46 |
| $Ba_{0.50}La_{1.50}Li_{0.50}Fe_{0.50}O_4$ | 3.78 | 13.14 | 5.346 | 3.47 |
| $SrLaFe^{III}O_4$ | 3.88 | 12.76 | 5.487 | 3.29 |

A general investigation of the influence of the distortion of the octahedral site of iron(IV) emphasizes that for an average $\overline{Dq}/B$ value, a decrease of the $FeX_6$ elongation is able to stabilize a low-spin configuration (see the Tanabe–Sugano-type diagram of Fig. 1). Starting from $K_2NiF_4$-type $(A,A')_2Li_{0.50}Fe(IV)_{0.50}O_4$ such a decrease of the $FeO_6$ elongation can be expected by substituting in the perovskite layers the weak Li–O bonds by more covalent Mg–O or Zn–O bonds. It sets the problem of the electronic configuration of iron(IV) in the new materials as far as they are available.

## Experimental

The $SrLaM_{0.50}Fe_{0.50}O_4$ ($M$ = Mg, Zn) compounds have been prepared in three steps:

The first one is calcination of the stoichiometric mixture of the nitrates at 600°C for 1 hr. The second step is a 72-hr oxidizing treatment in an oxygen stream at 750°C. During the last step the mixture is submitted for 48 hr to high oxygen pressures varying from 1 to 1.5 kbar at a temperature between 750 and 800°C, according to the nature of the divalent cation ($M$ = Mg or Zn).

The oxidation number of iron, determined by redox titration, is $3.92 \pm 0.05$.

## Structural Study

The classical X-ray diffractometers of $SrLaM_{0.50}Fe_{0.50}O_4$ ($M$ = Mg, Zn) phases characterize a $K_2NiF_4$-type structure with tetragonal symmetry ($a_0$, $c_0$). But the presence on the Guinier films of a very weak line leads to propose an indexation with a multiple cell ($a = a_0\sqrt{2}$, $c = c_0$). Such a result involves obviously long-range $M$–Fe ordering within the perovskite layers.

In oxides with the $K_2NiF_4$-type structure, the observed value for the $c_0/a_0$ ratio is a good indication of the local distortion of the octahedral site (*37*). The experimental $c_0/a_0$ values close to 3.36 are significantly lower than those observed for the isostructural lithium phases $A_{0.50}La_{1.50}Li_{0.50}Fe_{0.50}O_4$ ($A$ = Ca, Sr, Ba) ($c_0/a_0 = 3.44 - 3.47$) (Table I).

Such a difference suggests, as expected, less elongation of the $FeO_6$ octahedron when the competing weak Li–O bonds are replaced by more covalent Mg–O or Zn–O ones. However, those $c_0/a_0$ values are higher than the one detected for $SrLaFeO_4$ ($c_0/a_0 = 3.29$), where the hexacoordinated iron(III) cations have an isotropic electronic configuration ($t_{2g}^3e_g^2$). Such a comparison suggests indeed an anisotropic electronic configuration for iron(IV) in the $SrLaM_{0.50}Fe_{0.50}O_4$ oxides.

## Magnetic Study

The magnetic susceptibilities of the $SrLaM_{0.50}Fe_{0.50}O_4$ ($M$ = Mg, Zn) phases have been measured from 4.2 up to 300 K using a Faraday balance.

The evolution of $\chi_M'^{-1} = f(T)$ is given in Figs. 2 and 3 after elimination of the diamagnetic atomic contributions. In the paramagnetic domain the values of the Curie constants, i.e., $C_{Mg} \simeq 3.12$, $C_{Zn} \simeq 3.00$, are very close to those observed for the homologous $A_{0.50}La_{1.50}Li_{1.50}Fe_{0.50}O_4$ ($A$ = Ca, Sr, Ba) phases ($3.09 < C < 3.12$) (*2*). They give evidence that despite less elongation of the $FeO_6$ octahedra iron(IV) has a high-spin configuration ($t_{2g}^3e_g^1$) ($C_{theor.} = 3.00$ for a spin-only contribution). The small discrepancy detected for $SrLaMg_{0.50}Fe_{0.50}O_4$ probably results from the presence

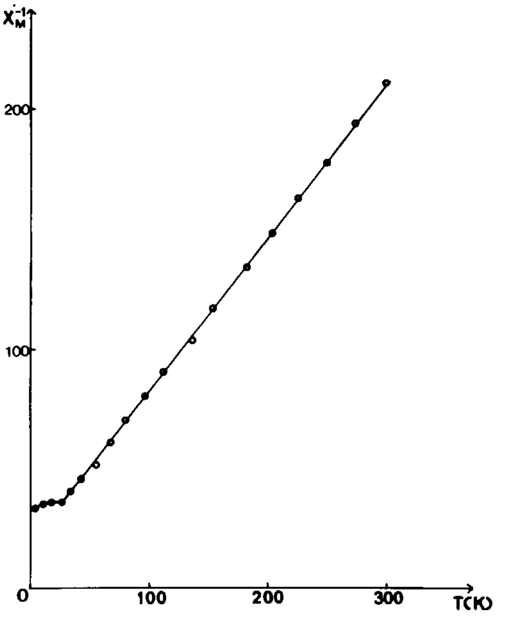

FIG. 2. Thermal evolution of the reciprocal molar susceptibility of $SrLaMg_{0.50}Fe_{0.50}O_4$.

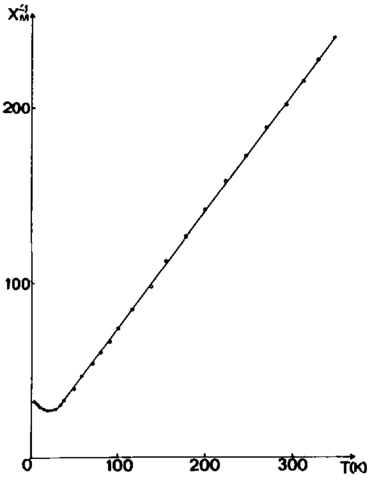

FIG. 3. Thermal evolution of the reciprocal molar susceptibility of SrLaZn$_{0.50}$Fe$_{0.50}$O$_4$.

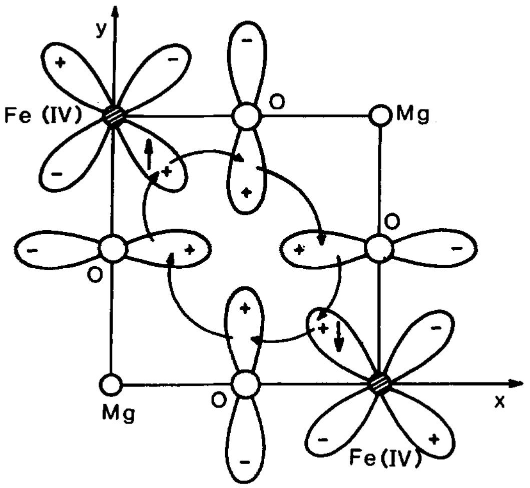

FIG. 4. Magnetic supersuperexchange couplings between iron(IV) $t_{2g}$ orbitals involving two nearest neighboring oxygen atoms.

of small amounts of iron(III) ($C_{\text{theor.}} \simeq 4.32$), which are actually confirmed by chemical analysis.

The evolution of $\chi_M'^{-1} = f(T)$ shows an antiferromagnetic behavior at low temperature ($T_N(\text{Mg}) \simeq 27 \pm 5$ K, $T_N(\text{Zn}) \simeq 20 \pm 5$ K). The couplings are of supersuperexchange type between $t_{2g}$ orbitals involving two nearest neighboring oxygen atoms (Fig. 4). Their antiferromagnetic nature should result from the fact that the $d_{xy}$, $d_{yz}$, and $d_{zx}$ orbitals of iron(IV) are only half-filled. This is consistent with the high-spin configuration of iron(IV).

To ascertain whether the low $c_0/a_0$ values result from a smaller elongation of the FeO$_6$ octahedra, rather from eventual presence of some isotropic iron(III) ($t_{2g}^3e_g^2$), a Mössbauer spectroscopic investigation was performed.

## Mössbauer Spectroscopic Study

The Mössbauer resonance spectrum of SrLaMg$_{0.50}$Fe$_{0.50}$O$_4$ at 300 K is given in Fig. 5. It can be analyzed in three relatively narrow distributions of the quadrupole splitting Δ (Table II). Two of them cor-

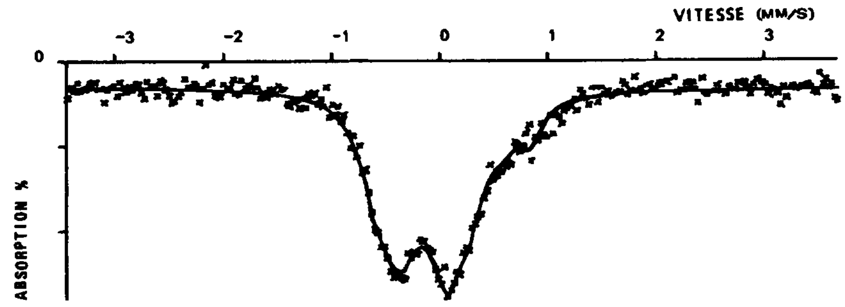

FIG. 5. Mössbauer resonance spectrum of SrLaMg$_{0.50}$Fe$_{0.50}$O$_4$ at 300 K.

TABLE II

MÖSSBAUER RESONANCE PARAMETERS OF THE VARIOUS IRON SITES AT 293 K IN $SrLaMg_{0.50}Fe_{0.50}O_4$

| | $\delta$ (mm · sec$^{-1}$) | $\bar{\Delta}$ (mm · sec$^{-1}$) | Distribution of $\Delta$ | Approx. population (%) |
|---|---|---|---|---|
| I | −0.15 | 0.39 | $0.15 \le \Delta \le 0.60$ | 40 |
| II | −0.14 | 0.84 | $0.55 \le \Delta \le 1.12$ | 40 |
| III | +0.34 | 0.80 | $0.43 \le \Delta \le 1.00$ | 20 |

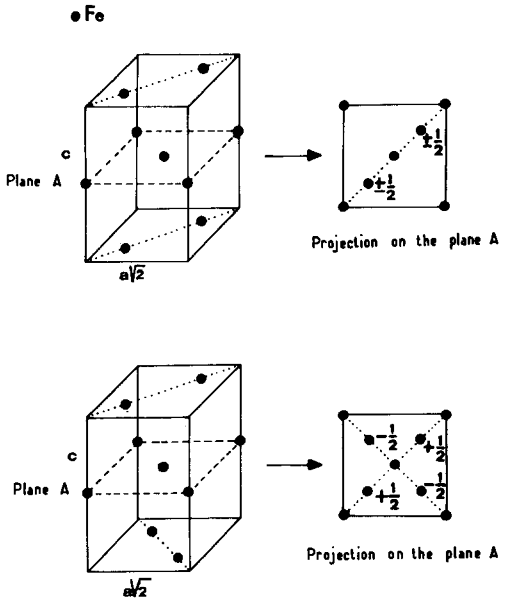

FIG. 6. Representation of two possible cationic surroundings for iron(IV) in $(A,A')_2M_{0.50}Fe_{0.50}O_4$ oxides with $M$/Fe ($M$ = Mg, Zn) ordering in the perovskite layers (the diamagnetic cations have been omitted).

respond unambiguously to high-spin iron(IV) ($\delta_{II} \simeq -0.14$ mm · sec$^{-1}$ and $\delta_I \simeq -0.15$ mm · sec$^{-1}$). They confirm the existence of two different sites for iron(IV), as previously found for the $A_{0.50}La_{1.50}Li_{0.50}Fe_{0.50}O_4$ phases ($A$ = Ca, Sr, Ba), mainly due to cationic stacking along the $z$-axis (Fig. 6). The third distribution observed corresponds to the presence of some iron(III) in the lattice ($\delta \simeq +0.34$ mm · sec$^{-1}$).

For iron(IV) the average quadrupole splitting values ($\Delta \simeq 0.39$ and 0.84 mm · sec$^{-1}$) are clearly lower than those found for $Sr_{0.50}La_{1.50}Li_{0.50}Fe_{0.50}O_4$ ($\Delta \simeq 1.00$ and 1.28 mm · sec$^{-1}$) (*2*). Such a difference obviously results from the smaller elongation of the iron(IV) site in the magnesium compound. A slight increase of the chemical shift value $\delta$ (from −0.19 to −0.15 mm · sec$^{-1}$) from the lithium oxide to the magnesium one is due to a small decrease of the covalency of the Fe–O bond. It illustrates strengthening of the competing bond (from Li–O to Mg–O) within the perovskite sheets.

The spectrum of $SrLaMg_{0.50}Fe_{0.50}O_4$ at 4.2 K is given in Fig. 7. It gives evidence of magnetic ordering consistent with the antiferromagnetic behavior observed at low temperature ($T_N < 27$ K) by susceptibility

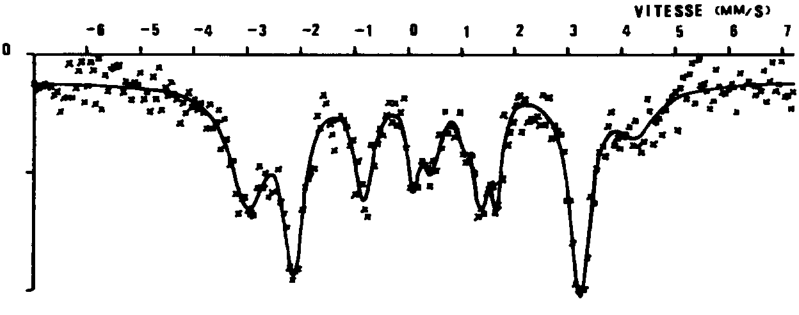

FIG. 7. Mössbauer resonance spectrum of $SrLaMg_{0.50}Fe_{0.50}O_4$ at 4.2 K.

TABLE III

MÖSSBAUER RESONANCE PARAMETERS FROM THE SPECTRUM RECORDED AT 4.2 K FOR $SrLaMg_{0.50}Fe_{0.50}O_4$

| Site | $\delta$ (mm · sec$^{-1}$) | $H(T)$ |
|---|---|---|
| I | −0.10 | 18.3 |
| II | −0.08 | 18.0 |

measurements. The Mössbauer resonance parameters established in first approximation without involving iron(III) are reported in Table III. The observed values are close to those found for $Sr_{0.50}La_{1.50}Li_{0.50}Fe_{0.50}O_4$.

A Mössbauer resonance investigation at 293 K for $SrLaZn_{0.50}Fe_{0.50}O_4$ using the same analysis of the $\Delta$ values in three distributions gives parameters close to those determined for $SrLaMg_{0.50}Fe_{0.50}O_4$ (Table IV).

## Conclusions

Iron(IV) has been stabilized as an isolated cation in two new oxides: $SrLaMg_{0.50}Fe_{0.50}O_4$ and $SrLaZn_{0.50}Fe_{0.50}O_4$. Despite less elongation of the $FeO_6$ octahedra, as compared with $Sr_{0.50}La_{1.50}Li_{0.50}Fe_{0.50}O_4$, due to stronger covalency of the Mg–O and Zn–O bonds in the perovskite phases, a high-spin configuration arises. This interpretation has been supported by structural, magnetic, and Mössbauer spectroscopic investigations.

Obtaining a smaller elongation of the $FeO_6$ octahedra, in order to stabilize the low-spin state (Fig. 1), requires probably consideration not only of the competitive $M$–O bonds in the perovskite layers but also of the $A,A'$–O bonds along the $z$-axis. Weaker $(A,A')$–O bonds could reinforce the covalency of the Fe–O bonds perpendicular to the layers and induce compression of the octahedral favoring a low-spin configuration of iron(+IV) under isolated conditions (Fig. 8).

TABLE IV

MÖSSBAUER RESONANCE PARAMETERS OF THE VARIOUS IRON SITES AT 293 K IN $SrLaZn_{0.50}Fe_{0.50}O_4$

| | $\delta$ (mm · sec$^{-1}$) | $\bar{\Delta}$ (mm · sec$^{-1}$) | Distribution of $\Delta$ (mm · sec$^{-1}$) |
|---|---|---|---|
| I | −0.15 | 0.33 | $0.27 \leq \Delta \leq 0.45$ |
| II | −0.14 | 0.80 | $0.60 \leq \Delta \leq 0.85$ |
| III | +0.35 | 0.94 | $0.70 \leq \Delta \leq 1.10$ |

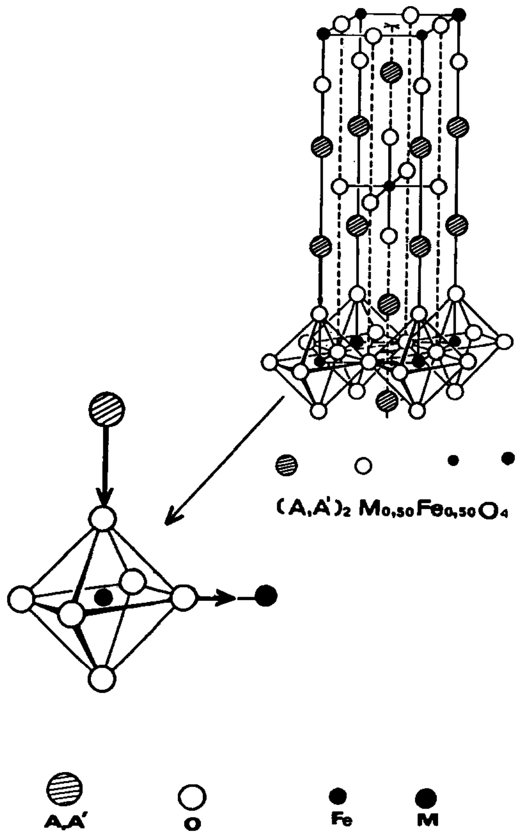

FIG. 8. Competing bonds around the $FeO_6$ octahedra in $(A,A')_2M_{0.50}Fe_{0.50}O_4$ oxides in the $K_2NiF_4$-type structure.

## References

1. G. DEMAZEAU, Doctorat ès sciences physiques, University of Bordeaux (1973).

2. G. Demazeau, N. Chevreau, L. Fournes, J. L. Soubeyroux, M. Thomas, and M. Pouchard, *Rev. Chim. Miner.* **20,** 155 (1983).
3. G. Demazeau, B. Buffat, F. Menil and L. Fournes, M. Pouchard, J. M. Dance, P. Fabritchnyi, and P. Hagenmuller, *Mater. Res. Bull.* **16,** 1465 (1981).
4. G. Demazeau, M. Pouchard, and P. Hagenmuller, *J. Solid State Chem.* **9,** 202 (1974).
5. B. Buffat, G. Demazeau, M. Pouchard, and P. Hagenmuller, *Mater. Res. Bull.* **18,** 1153 (1983).
6. B. Buffat, G. Demazeau, R. Black, Y. Takeda, M. Pouchard, and P. Hagenmuller, *C.R. Acad. Sci.* **295,** 557 (1982).
7. G. Demazeau, A. Marbeuf, M. Pouchard, P. Hagenmuller, and J. B. Goodenough, *C.R. Acad. Sci.* **272,** 2163 (1971).
8. G. Demazeau, J. L. Marty, M. Pouchard, T. Rojo, J. M. Dance, and P. Hagenmuller, *Mater. Res. Bull.* **16,** 47 (1981).
9. G. Demazeau, J. L. Marty, B. Buffat, J. M. Dance, M. Pouchard, P. Dordor, and B. Chevalier, *Mater. Res. Bull.* **17,** 37 (1982).
10. G. Demazeau, C. Parent, M. Pouchard, and P. Hagenmuller, *Mater. Res. Bull.* **7,** 913 (1972).
11. G. Demazeau, M. Pouchard, B. Buffat, and P. Hagenmuller, *J. Phys. C* (Suppl. II), **45,** 345 (1985).
12. B. Buffat, G. Demazeau, M. Pouchard, and P. Hagenmuller, *Proc. Indian Acad. Sci. (Chem. Sci.)* **93,** 313 (1984).
13. M. Pouchard, G. Demazeau, B. Buffat, and P. Hagenmuller, "Images de la Chimie, 1983–84, suppl. n° 56, p. 56. Courrier, CNRS.
14. N. Chevreau, Thèse 3ème cycle, University of Bordeaux I (1982).
15. F. Kanamaru, H. Miyamoto, Y. Mimura, M. Koizumi, M. Shimada, S. Kume, and S. Shin, *Mater. Res. Bull.* **5,** 257 (1970).
16. M. Takano, N. Nakanishi, Y. Takeda, S. Naka, and T. Takada, *Mater. Res. Bull.* **12,** 923 (1977).
17. Y. Takeda, S. Naka, M. Takano, T. Shinjo, T. Takada, and M. Shimada, *Mater. Res. Bull.* **13,** 61 (1978).
18. Y. Takeda, S. Naka, and M. Takano, *J. Phys. C2,* **40,** 331 (1979).
19. J. B. Mac Chesney, R. C. Sherwood, and J. F. Potter, *J. Chem. Phys.* **43,** 1907 (1965).
20. P. K. Gallagher, J. B. Mac Chesney, and D. N. E. Buchanan, *J. Chem. Phys.* **41,** 2429 (1964).
21. T. Takeda, Y. Yamaguchi, and H. Watanabe, *J. Phys. Soc. Japan* **33,** 967 (1972).
22. H. Oda, Y. Yamaguchi, H. Takei, and H. Watanabe, *J. Phys. Soc. Japan* **42,** 101 (1977).
23. H. J. Van Hook, *J. Phys. Chem.* **68,** 3786 (1964).
24. P. K. Gallagher, J. B. Mac Chesney, and D. N. E. Buchanan, *J. Chem. Phys.* **43,** 516 (1965).
25. T. Negas and R. S. Roth, *J. Res. NBSA,* **73,** 425 (1969).
26. S. Mori, *J. Phys. Soc. Japan* **28,** 44 (1970).
27. M. Zanne and C. Gleitzer, *Bull. Soc. Chim. Fr.* **5,** 1567 (1971).
28. M. Zanne, C. Gleitzer, and J. Aubry, *Bull. Soc. Chim. Fr.* **7,** 2451 (1971).
29. Y. Takeda, M. Shimada, F. Kanamaru, M. Koizumi, and N. Yamamoto, *Mater. Res. Bull.* **9,** 537 (1974).
30. M. Shimada, Y. Takeda, H. Taguchi, F. Kanamaru, and M. Koizumi, *J. Crystal Growth* **29,** 75 (1979).
31. T. Takeda and H. Watanabe, *J. Phys. Soc. Japan* **33,** 973 (1972).
32. M. Takano, N. Nakanishi, Y. Takeda, and T. Shinjo, Ferrites *in* "Proceedings, International Conference, Sept./Oct. 1980, p. 389.
33. M. Takano and Y. Takeda, *Bull. Inst. Chem. Res. Kyoto Univ.* **61,** 406 (1983).
34. C. Gleitzer and J. B. Goodenough, "Structure and Bonding," p. 61, Springer-Verlag, Berlin/Heidelberg (1985).
35. Y. Takeda, S. Komura, and H. Fujii, *Mag. Mag. Mater.* **31–34,** 797 (1983).
36. B. Buffat, M. H. Tuilier, H. Dexpert, G. Demazeau, and P. Hagenmuller, *J. Phys. Chem. Solids* **47,** 491 (1986).
37. J. B. Goodenough and J. M. Longo, "Crystallographic and Magnetic Properties of Perovskite and Perovskite Related-Compounds," Landolt–Bornstein Tabellen, Neue Serie, III/Vol. 4a, Springer, Berlin (1970).