JOURNAL OF SOLID STATE CHEMISTRY **45**, 88–92 (1982)

Unusual Oxidation States and Electronic Configurations of Iron*

G. DEMAZEAU, B. BUFFAT, M. POUCHARD,
AND P. HAGENMULLER

*Laboratoire de Chimie du Solide du CNRS, 351, cours de la Libération,
33405 Talence Cedex, France*

Received March 31, 1982

A good correlation between electronic configuration and structural and chemical bonding factors makes possible the stabilization of unusual oxidation states of transition elements. Such a predictive approach is illustrated by the synthesis and characterization of the first six-coordinated high-spin iron(IV) and iron(V) oxides.

The oxidation state of an ion is a formal number reflecting the average number of *d* electrons involved in chemical bonding. Its stability is not an intrinsic atomic property: it depends both on structural factors (size and symmetry of the site, etc.) and on the nature of the chemical bonding (covalency, influence of competing bonds, etc.). Moreover, it is related to the adopted electronic configuration when several are possible. The purpose of this paper is to point out how a good agreement between the abovementioned factors and a given electronic configuration may help the stabilization of an unusual oxidation state. This argument will be applied to the synthesis of high-spin iron(IV) and iron(V) oxides.

I. Stabilization of Six-Coordinated High-Spin Iron(IV): $Sr_{0.5}La_{1.5}Li_{0.5}Fe_{0.5}O_4$

Few oxides containing six-coordinated iron(IV) are so far known. Most of them derive from the perovskite structure and have oxygen vacancies. The first stoichiometric oxides prepared under oxygen pressure have been $SrFeO_3$ and $CaFeO_3$ (*1*–*4*). In the former, due to the O_h symmetry of the FeO_6 octahedra and the strong covalency of the Fe–O bonds, metallic behavior is observed. In the latter, higher electron localization leads at low temperature to disproportionation: 2 Fe(IV) $\rightarrow$ Fe(III) + Fe(V). Such a disproportionation has also been observed in the related ternary phases $La_{1-x}Sr_xFeO_3$ and $Ca_{1-x}Sr_xFeO_3$ (*5*–*8*). Its mechanism would assume a high-spin configuration of iron(IV). As no physical characterization had ever been carried out on this configuration, it was worthwhile to try to stabilize high-spin iron(IV) at room temperature in an oxide lattice.

With O_h symmetry, the relative energy of the cubic-field terms of a d^4 configuration vs Dq/B may be given roughly by a Tanabe–Sugano diagram (*9*). The high-spin configuration (^5E_g ground term) appears to be stable for $Dq/B < 2.7$, the low-spin configuration ($^3T_{1g}$ ground term) for $Dq/B > 2.7$.

---

[*] Presented at the Symposium on the Electronic Structure and Bonding in Solids, 183rd National Meeting, American Chemical Society, held in Las Vegas, Nevada, March 30–31, 1982.

0022-4596/82/130088-05$02.00/0

However, we tried to take into account, in a more general approach, the influence of an elongation along the c axis of the FeO_6 octahedra on the term stability. Such a distortion leads to lower symmetry (D_{4h}) and to splitting of the previous ground terms (Table I). If we neglect the mixing of the various terms, we may assume a linear variation of the relative energies with Dq/B,

$$E/B = a/B + bDq_{xy}/B + cDq_z/B,$$

where Dq_{xy} and Dq_z are the crystal-field parameters in the $x0y$ plane and along the c axis and B is the Racah parameter. As Dq is roughly in inverse ratio to the fifth power of the cation–anion distance (*10*), the crystal-field anisotropy parameter δ may be written as

$$\delta = \frac{Dq_z}{Dq_{xy}} = \frac{d^5_{c-a(xy)}}{d^5_{c-a(z)}}.$$

Along the separation curve between the stability domains of two different terms of E/B and E'/B energies, $E/B = E'/B$ and therefore

$$a/B + (Dq_{xy}/B)(b + c\delta)$$
$$= a'/B + (Dq_{xy}/B)(b' + c'\delta),$$

or, if $k = (a - a')/B$, $p = b' - b$, and $q = c' - c$.

$$\frac{Dq_{xy}}{B} = \frac{k}{p + q\delta}.$$

If we define the average crystal-field parameter $\overline{Dq}$ as

$$3\overline{Dq} = Dq_z + 2\ Dq_{xy} = Dq_{xy}(2 + \delta)$$

and the distortion parameter as

$$\theta = \frac{d_{c-a(z)}}{d_{c-a(xy)}},$$

$\delta = \theta^{-5}$ and the equation of the cross-over line $\overline{Dq}/B = f(\theta)$ is

$$\frac{\overline{Dq}}{B} = \frac{k(2\theta^5 + 1)}{3(p\theta^5 + q)}.$$

TABLE I

Electronic Configurations Corresponding to the Various Terms in D_{4h} Symmetry

O_h	D_{4h}	Electronic configuration
5_{E_g}	$\rightarrow 5_{B_{1g}}$	$d^1_{zx}d^1_{yz}d^1_{xy}d^0_{z^2}d^1_{x^2-y^2}$
	$\rightarrow 5_{A_{1g}}$	$d^1_{zx}d^1_{yz}d^1_{xy}d^1_{z^2}d^0_{x^2-y^2}$
$3_{T_{1g}}$	$\rightarrow 3_{A_{2g}}$	$d^1_{zx}d^1_{yz}d^2_{xy}d^0_{z^2}d^0_{x^2-y^2}$
	$\rightarrow 3_{E_g}$	$(d_{zx}d_{yz})^3d^1_{xy}d^0_{z^2}d^0_{x^2-y^2}$

Taking the energies of the d orbitals in Dq_{xy} and Dq_z units proposed by Krishnamurthy and Schaap (*11*), we can express the relative energies of the $^5A_{1g}$ and ^3E_g ground terms corresponding to the high- and low-spin configurations in D_{4h} symmetry as

$$^5A_{1g}: E/B = \quad -(Dq_{xy}/B)(12.28 - 6.28\ \delta),$$
$$^3E_g: E'/B = 27 - (Dq_{xy}/B)(13.14 + 2.86\ \delta).$$

Therefore, the equation of the cross-over line is

$$\overline{Dq}/B = \frac{27(2\theta^5 + 1)}{3(0.96\,\theta^5 + 9.14)}.$$

Such a curve, represented in Fig. 1, shows clearly that the high-spin configuration $^5A_{1g}$ can be stabilized by a large elongation of the FeO_6 octahedron, in spite of a strong crystal field or covalency.

The bidimensional K_2NiF_4 structure is known to be particularly suitable for favoring an elongation of the BO_6 octahedra. To increase this distortion and to isolate the Fe atoms from each other, the presence of relatively ionic Li–O bonds competing with the Fe–O bonds inside the perovskite layers also appeared to be appropriate (Fig. 2).

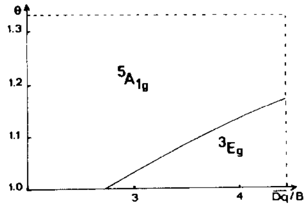

FIG. 1. Stability domains of the ground terms $5_{A_{1g}}$ and 3_{E_g} vs $\overline{Dq}/B$ and θ.

TABLE II

COMPARISON BETWEEN OBSERVED AND EXPECTED PARAMETERS OF IRON(IV)

	Average oxidation state (redox titration)	Molar Curie constant	Isomer shift at room temperature (from Mössbauer spectrosc. data) ($mm \cdot sec^{-1}$)	Quadrupole splitting ($mm \cdot sec^{-1}$)
Observed values	3.97	3.06	−0.19	1.2
Low-spin Fe(IV)	4	1[a]	~0.0 (measured in $SrFeO_3$ (*20*))	Weak
High-spin Fe(IV)	4	3[a]	Unknown	Unknown, but expected large (Jahn–Teller distortion)

[a] Calculated assuming a spin-only contribution.

These conditions led to the composition $Sr_{0.5}La_{1.5}Li_{0.5}Fe_{0.5}O_4$.

Such a phase has been actually prepared in oxidizing conditions. The X-ray powder diffractogram characterizes a tetragonal K_2NiF_4 structure, but the presence of weak superstructure lines leads to an indexation with a supercell ($a = a_0 2^{1/2}$, $c = c_0$), suggesting Li–Fe ordering in the perovskite layers (*12*). A neutron diffraction study is in progress to determine this point.

Different physical characterization methods (structural, magnetic, and Mössbauer parameters) confirm the high-spin configuration of Fe(IV) in the material (Table II).

II. Stabilization of Six-Coordinated Iron(V): La_2LiFeO_6

Only a few compounds containing Fe(V) with highly basic character—K_3FeO_4, Na_3FeO_4, and Rb_3FeO_4—in which iron occupies a tetragonal site have been reported in the past (*13–16*), but no physical characterization has been performed on these oxides. As mentioned above, Mössbauer investigations have pointed out the occurrence of the disproportionation 2 Fe(IV) → Fe(III) + Fe(V) at low temperature in some perovskite oxides (*5–8*).

It was worthwhile therefore to attempt to

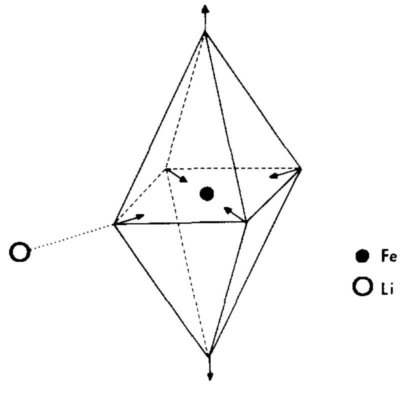

FIG. 2. Elongation of the FeO_6 octahedron in $Sr_{0.5}La_{1.5}Fe_{0.5}Li_{0.5}O_4$.

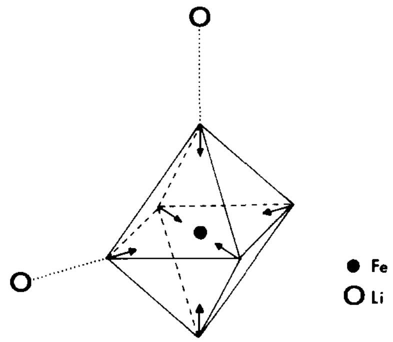

FIG. 3. Contraction of the FeO_6 octahedron in La_2LiFeO_6.

TABLE III

COMPARISON BETWEEN OBSERVED AND EXPECTED PARAMETERS OF IRON(V)

	Average oxidation state (redox titration)	Molar Curie constant	Isomer shift at room temp. (from Mössbauer spectrosc. data) ($mm \cdot sec^{-1}$)	Quadrupole splitting ($mm \cdot sec^{-1}$)	g value (EPR)
Observed value	5.02	1.93	−0.41	0	2.0135
Theor. or already obs. value	5	1.875[a]	Unknown, but probably strongly negative (δ_{Fe_α} Fe(VI) ≃ −0.9 in T_d site (*22*))	0	2.0131 (*21*)

[a] Calculated assuming a spin-only contribution.

stabilize Fe(V) in order to determine some characteristic features of this unusual oxidation state.

With a $t_{2g}^3 e_g^0$ configuration, six-coordinated iron(V) has a highly isotropic electronic distribution ($^4A_{2g}$ ground term) which fits with a site of O_h symmetry (undistorted octahedron). The synthesis of such a high oxidation state requiring high oxygen pressure, the perovskite structure, which may be stabilized in such conditions and contains almost undistorted octahedral sites, appeared to be well adapted. Moreover, an environment of six weak competing Li–O bonds seemed useful for enhancing the covalency of the Fe–O bonds (which has a highly stabilizing effect in the absence of e_g^* electrons) (Fig. 3).

With respect to these structural and chemical bonding considerations the La_2LiFeO_6 stoichiometry appeared to be especially adapted for stabilizing iron(V).

This phase, which has been prepared under high oxygen pressure (60 kbar), has a perovskite-type structure with a small rhombohedral distortion. Some physical characterization measurements confirm the existence, for the first time, of six-coordinated iron(V) in an oxide lattice (*17*) (Table III).

The use of similar arguments led recently to stabilization of other unusual electronic configurations in oxides. For the first time, the low-spin → high-spin transition of nickel(III) at rising temperature has been studied by introducing Ni(III) in an octahedral site which is large enough in $Sr_2NbIn_{0.9}Ni_{0.1}O_6$ and $BaLaNiO_4$ (*18*). On the other hand, a new electronic medium-spin configuration of cobalt(III) ($d_{yz}^2 d_{zx}^2 d_{xy}^1 d_{z^2}^1 d_{x^2-y^2}^0$, $S = 1$), which is intermediate between low-spin ($S = 9$) And high-spin ($S = 2$) states, has been detected in the strongly elongated octahedra of the $La_2Li_{0.5}Co_{0.5}O_4$ oxide (*19*).

The predictive character of such investigations must be emphasized. Such an approach, which leads to the synthesis of new materials with specific physical properties, can be quite useful for obtaining more knowledge of chemical bonding.

Acknowledgments

The authors are indebted to Drs. F. Menil, L. Fournes, P. B. Fabritchnyi, J. M. Dance and to N. Chevreau for their contribution to this work.

References

1. F. KANAMARU, H. MIYAMOTO, Y. MIMURA, M. KOIZUMI, M. SHIMADA, AND S. KUME, *Mater. Res. Bull.* **5**, 257 (1970).

2. Y. Takeda, S. Naka, M. Takano, T. Shinjo, T. Takada, and M. Shimada, *Mater. Res. Bull.* **13,** 61 (1978).
3. M. Takano, N. Nakanishi, Y. Takeda, S. Naka, and T. Takada, *Mater. Res. Bull.* **12,** 923 (1977).
4. J. B. McChesney, R. C. Sherwood, and J. F. Potter, *J. Chem. Phys.* **43,** 1907 (1965).
5. S. Komornicki, L. Fournes, J. C. Grenier, F. Menil, M. Pouchard, and P. Hagenmuller, *Mater. Res. Bull.* **16,** 967 (1981).
6. M. Takano, J. Kawachi, N. Nakanishi, and Y. Takeda, *J. Solid State Chem.* **39,** 75 (1981).
7. M. Takano, N. Nakanishi, Y. Takeda, and S. Naka, *J. Phys.* **40,** C2-313 (1979).
8. Y. Takeda, S. Naka, M. Takano, and N. Nakanishi, *J. Phys.* **40,** C2-331 (1979).
9. B. N. Figgis, "Introduction to Ligand Fields," p. 162, Interscience, New York (1966).
10. H. G. Drickamer, *Solid State Phys.* **17,** 1 (1965).
11. R. Krishnamurthy and W. B. Schaap, *J. Chem. Educ.* **46,** (12), 799 (1969).
12. G. Demazeau, M. Pouchard, N. Chevreau, M. Thomas, F. Menil, and P. Hagenmuller, *Mater. Res. Bull.* **16,** 689 (1981).
13. K. Wahl, W. Klemm, and G. Wehrmeyer, *Z. Anorg. Allg. Chem.* **285,** 322 (1956).
14. R. Scholder, H. V. Bunsen, F. Kindervater, and W. Zeiss, *Z. Anorg. Allg. Chem.* **282,** 268 (1955).
15. R. Scholder, *Angew. Chem. Int. Ed. Engl.* **1,** 220 (1962).
16. R. Scholder, *Bull. Soc. Chim. Fr.,* 1112 (1965).
17. G. Demazeau, B. Buffat, F. Menil, L. Fournes, M. Pouchard, J. M. Dance, P. Fabritchnyi, and P. Hagenmuller, *Mater. Res. Bull.* **16,** 1465 (1981).
18. G. Demazeau, J. L. Marty, B. Buffat, J. M. Dance, M. Pouchard, P. Dordor, and B. Chevalier, *Mater. Res. Bull.* **17,** 37 (1982).
19. G. Demazeau, M. Pouchard, M. Thomas, J. F. Colombet, J. C. Grenier, L. Fournes, J. L. Soubeyroux, and P. Hagenmuller, *Mater. Res. Bull.* **16,** 353 (1981).
20. P. K. Gallagher, J. B. McChesney, and D. N. E. Buchanan, *J. Chem. Phys.* **41**(8), 2429 (1964).
21. K. A. Müller, Th. von Waldkirch, and W. Berlinger, *Solid State Commun.* **9,** 1097 (1971).
22. R. H. Herber and D. Johnson, *Inorg. Chem.* **18,** 2786 (1979).