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HIGH OXYGEN PRESSURES AND RECENT DEVELOPMENTS IN THE FIELD OF HIGH OXIDATION STATES

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Résumé - Les hautes pressions d'oxygène sont très importantes dans la stabilisation de hauts degrés d'oxydation des éléments de transition. En utilisant des facteurs structuraux et de liaison chimique caractérisant l'environnement anionique des configurations électroniques inusuelles peuvent être obtenues. Le fer (V) en site OH d'une part et le fer (IV) à spin fort ou le cobalt (III) de spin intermédiaire en site D4h ont été choisis pour illustrer ces diverses possibilités.

Abstract - High oxygen pressures are very suitable for the preparation of high oxidation states of transition elements. Using, in addition, appropriate structural and chemical bonding factors characterizing the anionic surrounding unusual electronic configurations can be obtained. The stabilization of Fe (V) in an OH site and high spin Fe (IV) or intermediate spin Co (III) in a D4h symmetry have been selected to illustrate these possibilities.

During the last thirty years great progress has been obtained in the stabilization of unusual oxidation states of transition elements using high oxygen pressures. Three main methods can be developed to generate high oxygen pressures:

- compressed oxygen gas (1),
- oxidizing solutions such as diluted solutions of NH_4ClO_4 in an hydrothermal device (1),
- the thermal decomposition in solid state of unstable oxides such as CrO_3 (2) or KClO_3 (3) in a "belt" apparatus.

The oxidation state of an ion of a transition metal element is a formal number reflecting the average number of d electrons involved in chemical bonding. Its stabilization closely depends on that of the corresponding electronic configuration, in particular on (i) structural factors (size and symmetry of the cationic site), (ii) nature of the cationic neighbours (covalence and influence of the competing bonds).

Using a simple model based both on the Tanabe-

Sugano's diagrams (1) and on the Krishnamurthy and Schaap's calculation of the energy of d orbitals in a D_{4h} symmetry (5), we have underlined the influence of the structural elongation of the MO_6 octahedron on the stabilization of electronic configurations (6).

I - STABILIZATION OF A VERY HIGH OXIDATION STATE: SIX-COORDINATED Fe+V IN AN OXYGEN-LATTICE

Fe+V was unknown in octahedral coordination. Its isotropic electronic configuration (t_{2g}^3) fits very well with a pure octahedral site (O_h symmetry). To stabilize Fe+V it is necessary, in addition of the use of high oxygen pressures, to select structural and chemical bonding factors able to favorize : (i) an O_h site, (ii) the covalency of the Fe-O bonds.

With this selected stoichiometry, La_2LiFeO_6 , has been prepared under high oxygen pressure (70 kbar). Chemical and physical characterizations confirm the stabilization - for the first time - of pure six coordinated Fe+V in an oxide (Table I) (7).

2 - STABILIZATION OF AN UNUSUAL ELECTRONIC CONFIGURATION: HIGH SPIN Fe+IV IN AN OCTAHEDRAL SITE

Owing to the evaluated Dq/B value for six-coordinated Fe+IV in an oxygen lattice ($Dq/B \approx 4$), in the Fe+IV oxides so far prepared - mostly with the perovskite structure - Fe+IV seems to have a low spin configuration ($SrFeO_3$) (8-11) related to some electronic delocalization ($CaFeO_3$) (1-12-15).

Using the previous model, a strong elongation of the FeO_6 octahedron seems to be appropriate to stabilize the high spin state ($t_{2g}^3 e_g^1$) (Fig. 1).

Choosing a K_2NiF_4 layer structure stacking of rocksalt and perovskite layer (Fig.2) and four weak Li-O bonds as competing bonds in the perovskite layer, such a distortion can be induced. The corresponding oxides

$A_{0.5}La_{1.5}Li_{0.5}Fe(IV)_{0.5}O_4$ ($A = Ca, Sr, Ba$) have been selected and prepared under oxygen pressure.

Chemical and physical characterizations are in agreement with Fe+IV with four unpaired electrons (high spin state)

	oxidation state	molar Curie Constant	isomer shift 300 K (Mössbauer) $mm.s^{-1}$	quadrupole splitting $mm.s^{-1}$	g value (RPE)
observed values	5,02	1,93	- 0,41	0	2,0135
theoretical values	5	1,875	unknown, but probably very negative value	0	2,0131

Table I

	oxidation state	Curie Constant	isomer shift 300 K (Mössbauer) $mm.s^{-1}$	quadrupole splitting $mm.s^{-1}$
observed values	3.97	3.06	- 0.19	1,2
low spin Fe (IV)	4	1	0.0 (in $SrFeO_3$)	small
high spin Fe (IV)	4	3	unknown	unknown but probably im- portant owing to the Jahn Teller distor- tion

Table II

Fig.1 - Ground state regions for a d^4 configuration

Fig.2 - The K_2NiF_4 structure

3 - STABILIZATION OF AN INTERMEDIATE ELECTRONIC CONFIGURATION DURING A SPIN TRANSITION: "MEDIUM SPIN" CO+III

In an oxygen lattice and in an octahedral site a low spin ($^1A_{1g}$) - high spin ($^5T_{2g}$) transition occurs with increasing temperature for Co+III (Dq/B value being close to the critical Dq/B value). Such a phenomenon has been observed in the $LnCoO_3$ perovskites (Ln = rare-earth) prepared under oxygen pressure (15) (Fig.3).

Fig.3 - Variation with temperature of the reciprocal molar magnetic susceptibility for $YCoO_3$ and $LuCoO_3$ phases

Using the simple model described earlier (Fig.4), an intermediate electronic configuration ($d_{yz}^2 d_{zx}^2 d_{xy}^1 d_{z^2}^1 d_{x^2-y^2}^0$, $S=1$) can be predicted for Co^{+III} in an elongated octahedron ($\theta > 1,15$).

Such an unusual configuration has been detected as intermediate state during the ${}^1A_{1g} \rightarrow {}^5E_g({}^5T_{2g})$ transition in the two oxides prepared under oxygen pressure:

$\text{La}_2\text{Li}_{0.5}\text{Co(III)}_{0.5}\text{O}_4$ and $\text{La}_2\text{Li}_{0.5}\text{Cu(III)}_{0.45}\text{Co(III)}_{0.05}\text{O}_4$ (16) (Fig.5) (the increasing elongation of the CoO_6 octahedron favorizing the stability of this configuration with the ${}^3B_{2g}$ term).

Fig.4 - Ground state regions for a d^6 configuration

Fig.5 - Comparison of the populations for the different terms in $\text{La}_2\text{Li}_{0.5}\text{Co}_{0.5}\text{O}_4$ and $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.4}\text{Co}_{0.1}\text{O}_4$

CONCLUSIONS

High oxygen pressures can help the synthesis of oxides containing unusual oxidation states or electronic configurations of transition elements. Such materials lead to a better understanding of the chemical bond.

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