JOURNAL OF SOLID STATE CHEMISTRY 27, 329–341 (1979)

Mössbauer Study of Co and Fe Spinels Acting as Sources and Absorbents

J. TEJADA*

Departamento de Optica, Universidad de Barcelona, Avda. Generalisimo, 647, Barcelona 28

J. FONTCUBERTA AND R. RODRIGUEZ

Departamento de Cristalografía, Universidad de Barcelona, Avda. José Antonio, 585, Barcelona 7

Received March 9, 1978; in revised form June 23, 1978

Mössbauer spectra and X-ray powder diagrams of synthetic ^{57}Co and ^{57}Fe oxides having the two lattice-site spinel structure have been obtained. The distribution of iron and cobalt atoms between the octahedral and tetrahedral lattice sites has been determined by means of isomer shift and quadrupole splitting measurements. A new mechanism is proposed in order to explain the distribution of ^{57}Fe as well as its charge state when it enters the lattice as an impurity. At high temperature a mixed valence structure of Co_3O_4 was found. It is argued that the charge state of the daughter iron depends on the vacancy concentration in the environment of those sites where the corresponding decay takes place. Single line sources are obtained under well determined conditions.

Introduction

The spinels are double oxides which can be considered as a cubic close-packed structure (space group F $d3m$) of oxygen atoms with cations in 8 tetrahedral (to be denoted T) and 16 octahedral (O) sites. They fit to the general formula $(A_\delta B_{1-\delta})[A_{1-\delta}B_{1+\delta}]O_4$ where A represents divalent cations and B represents trivalent cations; the parenthesis ( ) encloses the cations in tetrahedral positions while the bracket [ ] encloses those in octahedral positions. The so-called normal-spinels correspond to the case $\delta = 1$ while those with $\delta = 0$ are termed inverse-spinels.

The distance between the cations and the oxygen atoms is a function of a parameter u which depends on ionic radii and cation distribution among the two sublattices (*1*).

The equilibrium cation distribution at temperature T(°K) is given (*2*) by:

$$-NKT \ln \frac{\delta(1+\delta)}{(1-\delta)^2} = P(A) - P(B) \quad (1)$$

where $P(A)$ and $P(B)$ are respectively the preferential energies (*3*) of A and B cations for the octahedral coordination, N is the number of A cations and K is the Boltzman constant. When $|\Delta P| = |P(A) - P(B)| \ll NKT$ the entropy term (*2*) dominates against the cation's natural tendency, based on crystal field stabilization effects. Therefore cations distribute randomly.

Most studies on spinels (*4–9*) refer to compounds containing Fe as a constituent

---

* All correspondence should be sent to J. Tejada.

0022-4596/79/030329-13$02.00/0

Printed in Great Britain

element or ^{57}Fe and ^{57}Co as substitutive impurities. We report here Mössbauer spectroscopy results for this kind of spinel prepared under different experimental conditions. We establish in this work several correlations between our preparative method, lattice sites and cationic distribution. Experiments made on ^{57}CoO, MgO: ^{57}Co and other oxides (*4*) show the appearance of higher charge states for the daughter iron than those of ^{57}Co. In order to give an answer to these problems, we investigate, for the case of sources, the influence of after effects on the anomalous states of electric charge together with their relation to the defects present in the lattice.

Under the same experimental conditions as those used by previous workers (*5–9*) we obtain similar Mössbauer spectra. By changing the experimental conditions we obtain a new set of Mössbauer spectra. In this paper, we present a new mechanism to explain the difference in Mössbauer spectra caused by the change of experimental conditions. Our theory explains in a consistent way both: our new data and the previous results (*4–9*).

Experimental

Our samples were prepared by mixing stoichiometric amounts of the desired metals in the form of chlorides or nitrates, depending on the kind of spinels under preparation. The salts were dissolved in distilled and deionized water in order to assure a perfect mixing of the compounds. After stirring they were dried in a dessicator. The solid residue was finely crushed. Sources were prepared by adding 0.5 to 1 mCi of ^{57}Co dissolved in HCl to the mixed solution. Absorbents not containing Fe were enriched with ^{57}Fe dissolved in HCl.

The spinels were obtained by oxidation of nitrate mixtures at different temperatures: 1000°C ($FeCr_2O_4$, $CoCr_2O_4$, $CoRh_2O_4$), 900°C (Co_3O_4) and 750°C ($ZnCo_2O_4$) and different oxygen pressures (to be denoted PO_2) in a quartz tube. Later quenching was achieved by first introducing the tube in water and then in liquid nitrogen; slow cooling condition was obtained by removing the quartz tube from the heater and leaving it at room temperature. X-ray powder diagrams were obtained in order to verify the presence of the desired spinel structure.

The Mössbauer spectra were determined using a conventional multichannel analyzer, working in multiscale mode. The source employed in the case of absorbents was ^{57}Co in Rh while in the case of sources the single line absorbent was stainless steel. An iron sheet enriched in ^{57}Fe was used in the calibration. The reported measurements concerning sources and absorbents were performed at room temperature. The spectra were fit to Lorentzian curves by the least squares method; statistical test for the fit accuracy is given by

$$\chi^2 = \sum_i \frac{(y(i) - z(i))^2}{2\sigma^2(i)}$$

being $y(i)$ and $z(i)$ the true and measured values. The minimal value of x^2 is roughly $x^2_{\text{min}} \approx i - m$ where i is the number of data points and m is the number of free parameters. It was assumed that the intensities of lines corresponding to O and T-sites are solely determined by the cation distribution.

Results

$FeCr_2O_4$

According to magnetic susceptibility studies (*10*), $FeCr_2O_4$ is a paramagnetic substance at room temperature.

Tanaka *et al.* (*11*) prepared this spinel by firing the mixture Fe_2O_3–Cr_2O_3 in a H_2–CO atmosphere; they obtained a Mössbauer spectrum consisting of a single line corresponding to $Fe^{2+}(T)$. This result has been also obtained by other authors (*7, 12*).

When we prepared the $FeCr_2O_4$ spinel at 1000°C in air (Fig. 1a), the Mössbauer spectrum consisted of a quadrupole pair with isomer shift characteristic of Fe^{3+}. At 10^{-5} torr. pressure of oxygen the spectrum presented a Fe^{2+} single line and a Fe^{3+} doublet (Fig. 1b). Quenching of samples produces no modification of the spectra in agreement with the known values for the preferential energies (*3*). We therefore assume that all the above lines correspond to iron cations on *T* sites (see Table I).

$CoCr_2O_4$

When $CoCr_2O_4$ (a normal spinel (*3*, *10*)) is used as a source a three line spectrum was found which was interpreted in terms of tetrahedrally coordinated $^{57}Fe^{m2+}$, $^{57}Fe^{m3+}$ and $^{57}Fe^{m4+}$, the two last being stabilized by cation vacancies (*13*). Spencer and Schroeer (5) found a two line spectrum which they interpreted as $^{57}Fe^{m2+}$ (*T*) and $^{57}Fe^{m3+}$ (*T*).

For $CoCr_2O_4$: ^{57}Fe absorbents prepared in air, Spencer and Schroeer (*5*) found a spectrum consisting of Fe^{3+} quadrupole; they interpreted it as Fe^{3+} (*O*).

Our absorbents were prepared at different oxidation pressures; later they were subjected to a quenching process (slow cooling conditions gave similar results). As can be seen in Fig. 2, we obtain one Fe^{3+} quadrupole when the absorbent is prepared in air.

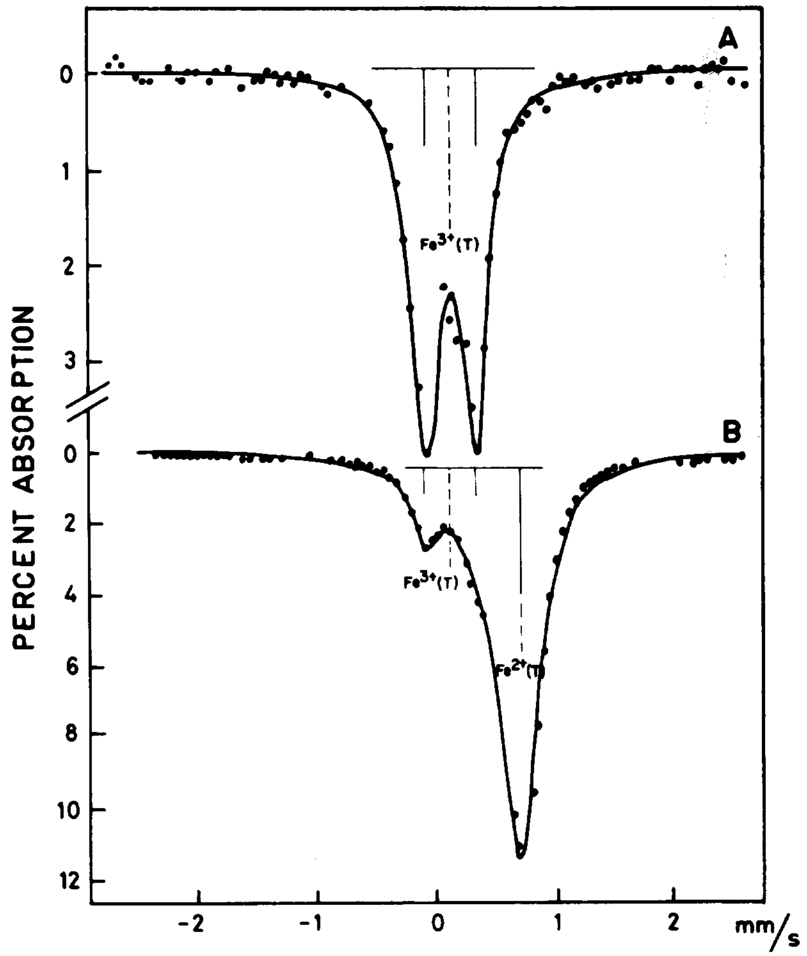

FIG. 1. Mössbauer spectra of $FeCr_2O_4$ synthesized: (A) in air, (B) At $PO_2 = 10^{-5}$ torr.

TABLE I

	PO_2	Rate of cooling	I.S. (Fe^{3+}–A) mm/s	ΔQ (Fe^{3+}–A) mm/s	% (Fe^{3+}–A)	I.S. (Fe^{2+}–A) mm/s	ΔQ (Fe^{2+}–A) mm/s	% (Fe^{2+}–A)	I.S. (Fe^{3+}–B) mm/s	ΔQ (Fe^{3+}–B) mm/s	% (Fe^{3+}–B)	χ^2
$FeCr_2O_4$:^{57}Fe	air	slow quench	0.19	0.41	100							115
	10^{-5} torr.	slow quench	0.20	0.41	22	0.76	0	78				130
$CoCr_2O_4$: ^{57}Co	air	slow quench	−0.441	0	49	−1.112	0	51				160
	10^{-2} torr.	slow quench	−0.431	0	15	−1.11	0	85				200
	10^{-5} torr,	slow quench				−1.115	0	100				120
$CoCr_2O_4$: ^{57}Fe	air	slow quench	0.17	0.40	100							100
	10^{-5} torr.	slow quench	0.16	0.41	80	0.77	0	20				150
$CoRh_2O_4$: ^{57}Co	air	slow quench	−0.53	0	100							92
	10^{-2} torr.	slow quench	−0.40	0	58	−1.38	0	42				93
	10^{-5} torr.	slow quench	−0.293	0	47	−1.27	0	53				165
[a] Co_3O_4: ^{57}Co	air	slow	−0.301	0	32				−0.388	0.52	68	210
	air	quench	−0.311	0.27	32				−0.378	0	68	230
[a] Co_3O_4: ^{57}Fe	air	slow	0.14	0.54	100							140
	air	quench	0.22	0.44	70				0.35	0	30	220
[b] $ZnCo_2O_4$: ^{57}Fe	air	slow quench	0.127	0.559	100							85
[b] $ZnCo_2O_4$: ^{57}Co	air	slow quench							−0.386	0.551	100	100

[a] Co_3O_4 can only be synthesized at 900°C and air atmosphere.

[b] $ZnCo_2O_4$ structure doesn't depend on PO_2.

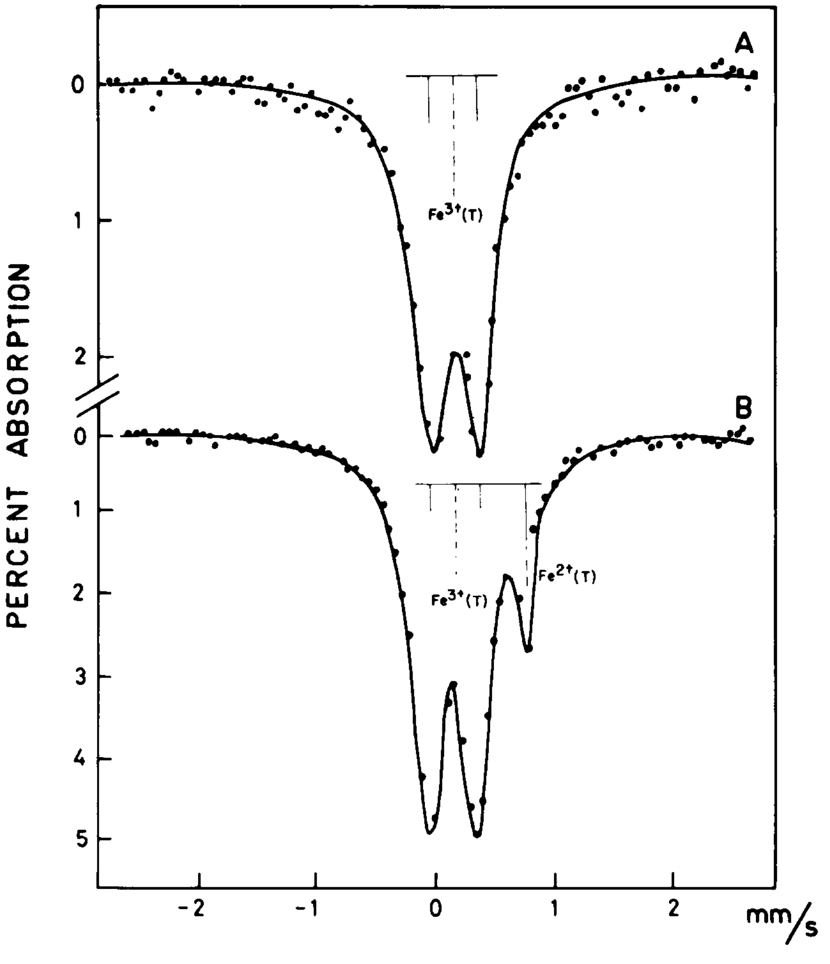

FIG. 2. Mössbauer spectra of $CoCr_2O_4$: ^{57}Fe synthesized: (A) in air, (B) at $PO_2 = 10^{-5}$ torr.

At low oxidation pressures we obtain this doublet plus one Fe^{2+} singlet. According to McClure's predictions (*3*) we interpret our results as corresponding to iron atoms located on *T*-sites.

We prepared the $^{57}CoCr_2O_4$ sources under slow and quenching process and found that the ratio of the Fe^{3+} and Fe^{2+} lines depends on the oxidation pressure. The $CoCr_2O_4$ spinel, prepared in air presents 50% Fe^{3+}; while prepared at 10^{-6} torr. only shows a single line spectrum corresponding to Fe^{2+} (Fig. 3). Quench and slow cooling conditions gave similar results.

Co_3O_4

Under slow cooling condition Co_3O_4 is a normal spinel (*3, 11*); and it has been extensively studied (*5, 14*) as a source. These studies fit the spectra with two lines of equal percent absorption and equal widths and with a third line, corresponding to a Fe^{3+} (*O*) doublet and a Fe^{3+} (*T*) singlet.

The published results (*5*) from dopping 0.5 at % impurity iron into Co_3O_4 were interpreted as a Fe^{3+} (*O*) doublet. However when the absorber is cooled below the magnetic transition temperature, the new

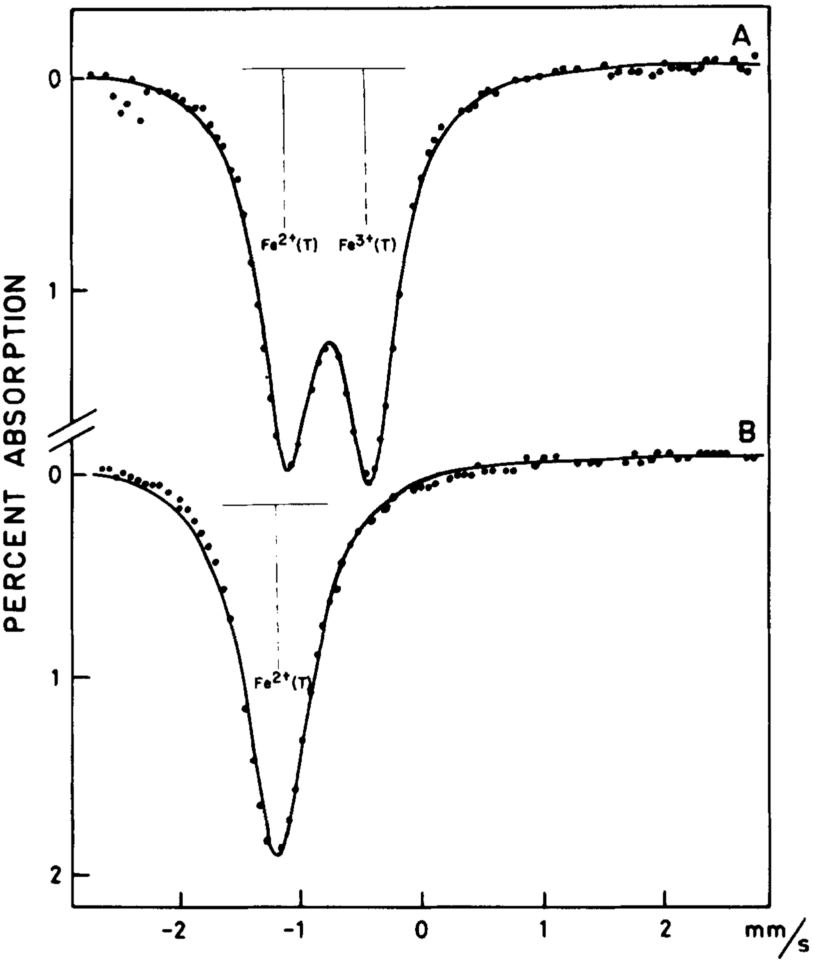

FIG. 3. Mössbauer spectra of $CoCr_2O_4$: ^{57}Co synthesized: (A) in air, (B) at $PO_2 = 10^{-5}$ torr.

spectra exhibit six lines; this would not be expected if the iron atoms were on *O* sites.

Our results in sources with slow cooling conditions are in full agreement with those previously published (*5*, *14*). In the case of quenched sources, however, the spectrum has to be fitted (Table 1) by a Fe^{3+} (*O*) singlet and Fe^{3+} doublet (*T*) (see Fig. 4).

In the case of slow cooled absorbents we obtain a Fe^{3+} doublet. Taking into account the corresponding I.S. and Co^{3+} and Fe^{3+} preferential energies (*3*) we interpret that they are located on *T*-sites.

Finally, the quenched Co_3O_4: ^{57}Fe absorbents (Fig. 5) give the same spectrum as the sources prepared in the above conditions, hence we conclude that iron atoms are randomly distributed over *T* and *O*-sites.

$ZnCo_2O_4$

$ZnCo_2O_4$ is a normal spinel (*3*). We prepared these spinel with different cooling rates, the spectra obtained were always similar according with published values of preferential energies (*3*). Acting as source we obtain a Fe^{3+} (*O*) doublet in the Mössbauer spectrum in agreement with Spencer and Schroeer (*5*).

As can be seen in Fig. 6, the Mössbauer absorber spectrum of $ZnCo_2O_4$: ^{57}Fe

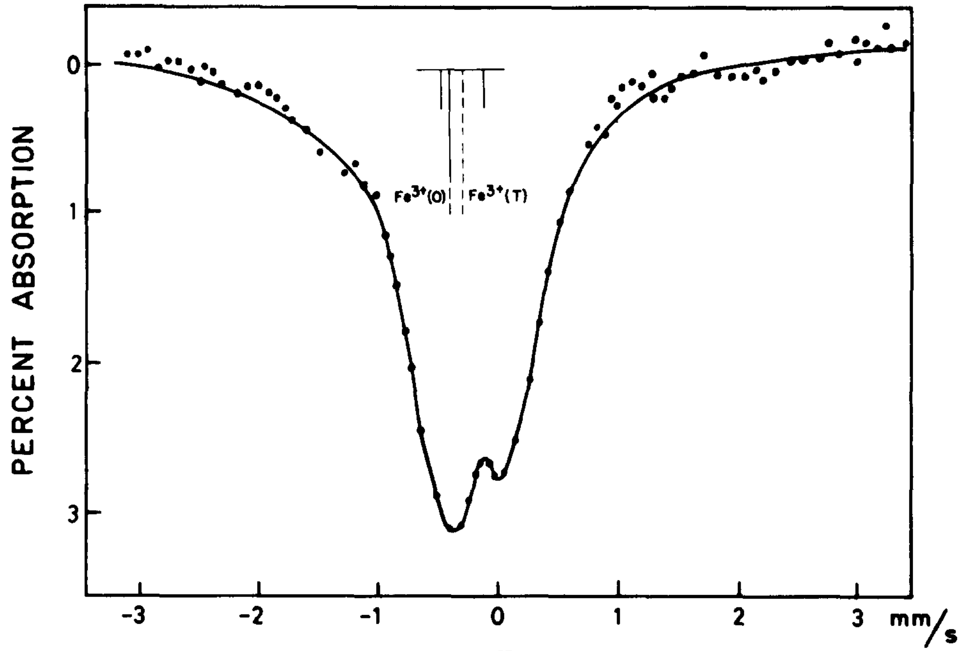

FIG. 4. Mössbauer spectrum of Co_3O_4: ^{57}Co synthesized in air and quenched.

consists of a quadrupole doublet of Fe^{3+}. Based on I.S. values and Zn^{2+} and Co^{3+} preferential energies values (*3*) we assigned the line to Fe^{3+} (*T*). Spencer and Schroeer (*5*) obtained the same experimental result but they assigned the Fe^{3+} cations to the *O*-sites.

$CoRh_2O_4$

The (normal, inverse or partially inverse) character of this spinel has never been predicted due to the lack of information about the Rh preferential energy for *T* and *O*-sites. In order to answer this question, we have made different synthesis at different rates of cooling; they always lead to similar spectra. Thus we conclude that ΔP in equation (*1*) must be very different (greater or smaller) from *NKT*.

For $^{57}CoRh_2O_4$ sources, (see Fig. 7) from I.S. values, we conclude that Fe occupies *T*-sites and will be Fe^{2+} (*T*) or Fe^{3+} (*T*) depending only on the PO_2. As shown in Fig. 7a, at high value of PO_2, a Fe^{3+} single line appears; at lower PO_2 (Figs. 7b and 7c), single lines corresponding to Fe^{2+} and Fe^{3+} appear. Therefore we conclude that $CoRhO_4$ is a normal spinel and the cubic symmetry around the *T*-sites is perfectly cubic.

These results are in agreement with those published (*5*), however in an earlier work (*9*) the cubic symmetry around the *T*-sites has been found broken.

Summary of Results

a. Absorbents

If iron enters into the lattice as an impurity, it substitutes for the cation which has a lower preferential energy for the *O* sites.

The iron oxidation state is a function of the PO_2 during the synthesis, the Fe^{2+} fraction increases when the PO_2 decreases.

Substitution of divalent cation by a trivalent cation on a *T* site produces the rupture of the *T*-sites cubic symmetry. When the replaced cation is divalent, the symmetry remains perfectly cubic.

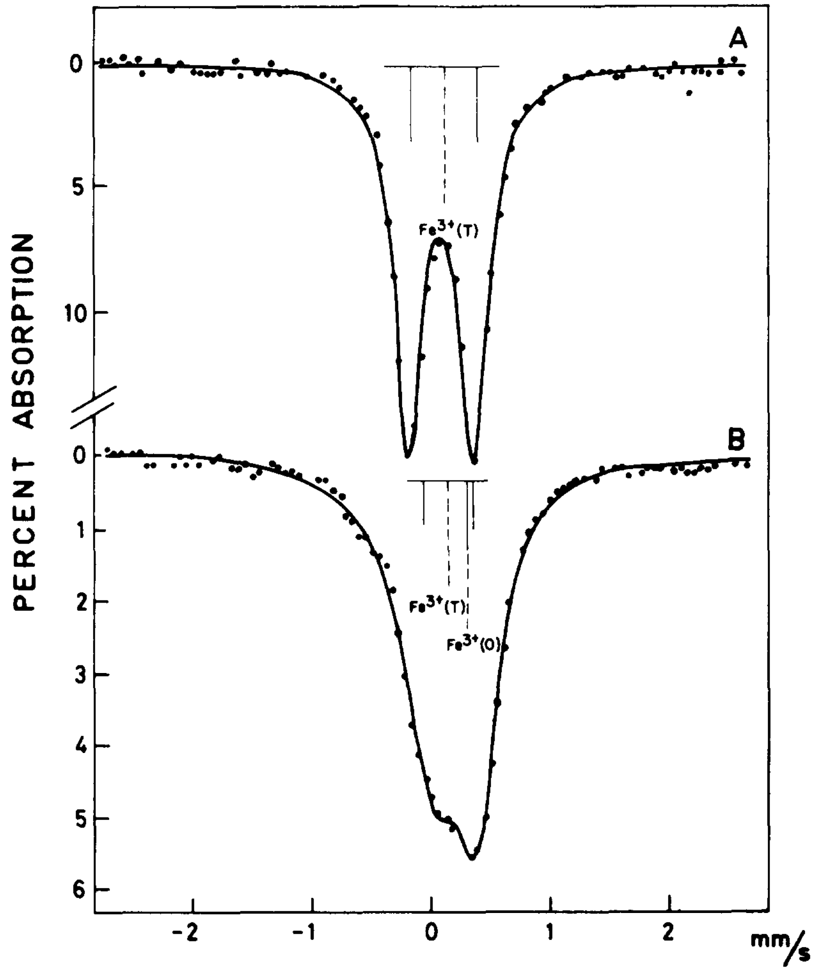

FIG. 5. Mössbauer spectra of Co_3O_4: ^{57}Fe synthesized in air and: (A) slow cooling, (B) quenched.

The quadrupole splitting is independent of the PO_2.

b. Sources

Cation distribution is in agreement with McClure's predictions (*3*).

$^{57}Fe^{2+}$ and $^{57}Fe^{3+}$ are obtained from $^{57}Co^{2+}$ in a ratio depending on the PO_2 during the synthesis.

Single line divalent iron Mössbauer sources can be obtained by synthesizing at a PO_2 lower than 10^{-6} torr.

Discussion

a. Absorbents.

The equilibrium configuration of cations and vacancies distribution in the lattice, depends on preferential energies, on PO_2 and on temperature. As a rule *O*-sites are occupied by those cations with higher preferential energy for that position. Iron, in a divalent or trivalent state, has very small preferential energy (*3*) for the *O*-sites (3.9 and 0.0 Kcal mol respectively). As a

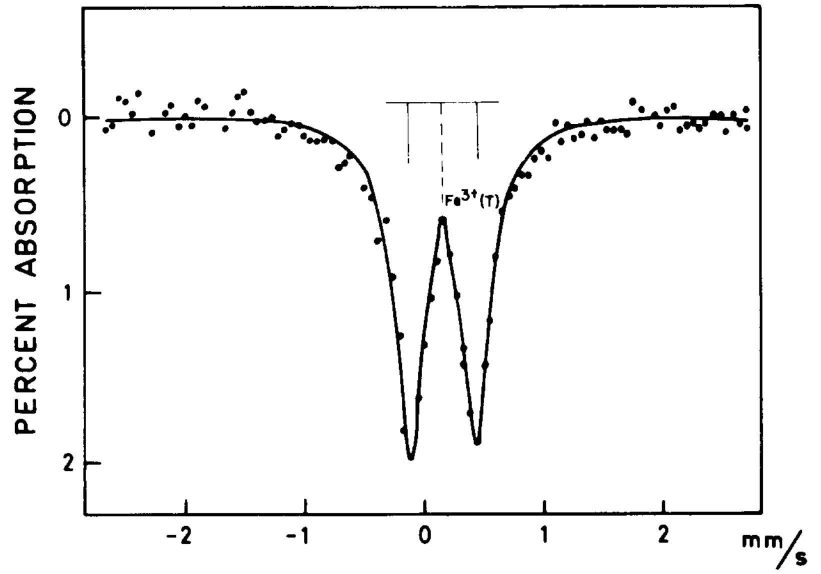

FIG. 6. Mössbauer spectrum of $ZnCo_2O_4$: ^{57}Fe synthesized at air and slow cooling conditions.

consequence, the iron as an impurity in a spinel lattice will not remove the cations which occupy *O*-sites but the ones occupying *T*-sites.

$CoCr_2O_4$: ^{57}Fe, $FeCr_2O_4$, Co_3O_4: ^{57}Fe are normal spinels at room temperature and the Fe will substitute divalent cations on *T* sites. At high PO_2 synthesis conditions, Fe enters as Fe^{3+}, in agreement with the shift of the equilibrium $Fe^{2+} \rightleftarrows Fe^{3+}$ to the right side.

We propose two different mechanisms to explain what happens when a Fe^{3+} cation substitutes an A^{2+} cation.

(i) When during the process of synthesis a Fe^{3+} ion introduces in a *T*-site, it generates a greater polarization of the surrounding oxygens ions than the usual when an A^{2+} cation occupies this site. The surrounding *O*-sites of this position will have a lower tendency to be occupied by B^{3+} cations and they will tend to become vacancies which distort the surroundings of the *T*-sites occupied by Fe^{3+}. The excess charge created by the substitution of A^{2+} by Fe^{3+} will be compensated by the excess oxygen and by the octahedral vacancies generated when Fe^{3+} enters into the lattice. If we assume the preferential energies to be the dominant factor in the cation distribution the presence of Fe ions in the *T* sites will remove *A* cations. The following formula holds:

$$(Fe_x^{2+}Fe_y^{3+}A_{1-y-x}^{2+})[B_{2-y/3}^{3+}\square_{y/3}]O_{4+z}$$

where $\square$ is a vacancy located on *O*-sites, y is the fraction of A^{2+} which was substituted by Fe^{3+}, and z is the anionic excess produced during the synthesis which depends on PO_2, temperature and cation constituents.

(ii) When a full occupation of the 8*T*-sites and 16 *O*-sites is assumed, the condition necessary for electric neutrality is:

$$(Fe_x^{2+}Fe_y^{3+}A_{1-y-x}^{2+})[B_{2-y}^{3+}A_y^{2+}]O_{4+z}$$

The cubic symmetry around Fe^{3+} (*T*) is always broken probably due to the surrounding concentration of B^{3+} and A^{2+}, both in *O*-sites: Each Fe^{3+} (*T*) cation creates the same distortion in its surrounding; therefore the quadrupole splitting will be independent of the PO_2 in accordance with our results. The presence of vacancies, i.e. possibility (i), might be a better explanation of the large measured values of the quadrupole splitting.

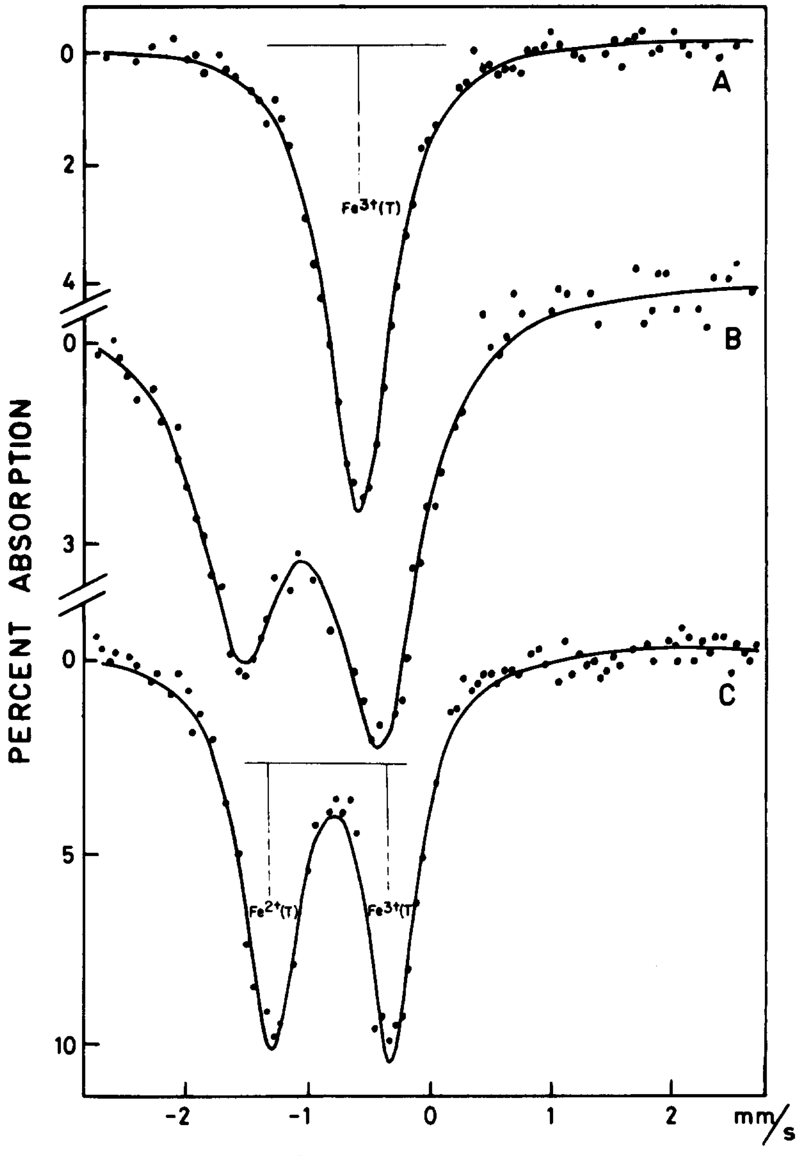

FIG. 7. Mössbauer spectra of $CoRh_2O_4$: ^{57}Co synthesized: (A) in air, (B) at $PO_2 = 10^{-2}$ torr. (C) at $PO_2 = 10^{-5}$ torr.

In the case of the spinel prepared at low PO_2, Fe^{2+} enters into the structure on T-sites; no vacancies or cations A^{2+} on O-sites are produced, the cubic symmetry around the T sites will be retained and we find a single line for the Fe^{2+} (T).

Quenched Co_3O_4; ^{57}Fe has a Mössbauer spectrum consisting of lines corresponding to Fe^{3+} (T) and Fe^{3+} (O). This is only possible if the difference between the preferential energies for the O-sites of Co^{3+} (or Co^{2+}) and Fe^{3+} is close to 3 Kcal/Mol (2). The Fe^{3+} cations will be shared by the two sublattices. In this case the entropy term controls the cation distribution. The Fe^{3+} distribution the two sublattices will depend on the difference $P[Co^{3+}(O)] - P[Fe^{3+}(O)] = \Delta P$.

When Boltzman statistics (*15*) are applied to the Fe^{3+} distribution (see formula [1]), taking the δ factor as the Fe^{3+} (*O*) proportion, we obtain $\Delta P = 6.03$ Kcal/mol allowing the possibility of the existence of a mixed valence structure. This value corresponds to the energy necessary to interchange Co^{3+} (*O*) for Fe^{3+} (*T*) or Co^{2+} (*T*).

When comparing quenched and slow-cooled Co_3O_4 samples we observe also completely different X-ray powder diagrams. Our X-ray diagrams from slow-cooled samples exactly fit the data in the ASTM card (*16*). In the case of quenched samples we observe an important reduction in the number of lines and a slight shift of the peak positions. This result also suggest the existence of the mixed valence structure, which can be interpreted as a new high temperature phase. The X-ray data can be explained with the same assumptions we used to interpret the Mössbauer data. This subject will be further analysed in a future communication (*17*).

b. Sources

The $^{57}Fe^{m}$ daughter in the prepared source spinels ($^{57}CoCr_2O_4$, $^{57}CoRh_2O_4$, $^{57}Co_3O_4$ and Zn $^{57}Co_2O_4$) occupies the same site as the radiactive ^{57}Co.

It has been observed for simple transition metal oxides (*18*) that the cationic vacancy concentration increases with increasing PO_2. Similar behaviour can be assumed in the case of our double oxides.

We find that the $^{57}Fe^{m3+}/^{57}Fe^{m2+}$ ratio in the Mössbauer spectra depends on PO_2 (see Fig. 8). According to Tejada (*9*) we assume that the Fe^{3+} fraction will depend on the vacancies concentration which in turn depends on PO_2. This result has also been found in ^{57}CoO (*19*).

After the electronic capture by the ^{57}Co, due to Auger process the $^{57}Fe^{m}$ remains for a very short time interval (less than 10^{-10} seconds) in a very high oxidation state. When a vacancy exists near the ^{57}Fe, there is a high probability for one of the

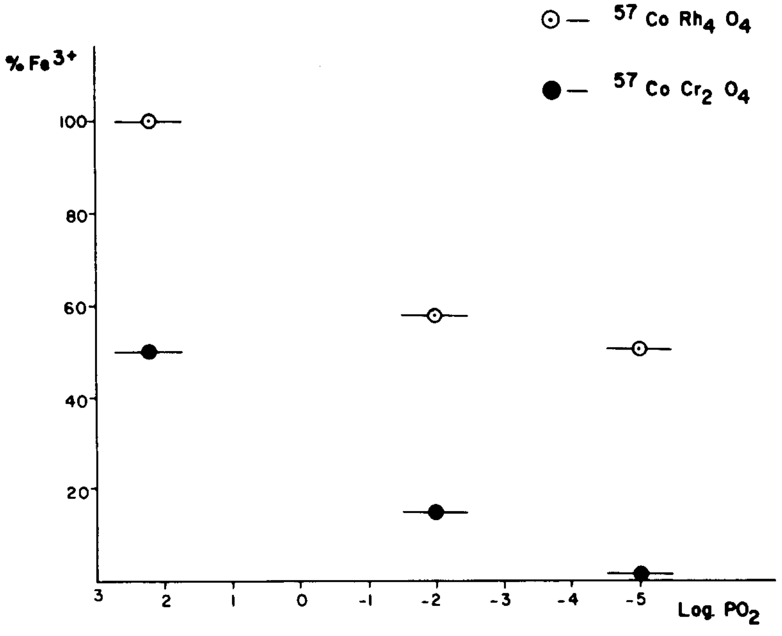

FIG. 8. Dependence of the Fe^{3+} fraction on the PO_2 during the oxidation process.

emitted Auger electrons to be trapped by the vacancy.

In the cases of $^{57}Co_3O_4$ and $^{57}CoRh_2O_4$ (the last one prepared in air) we always find that Co^{2+} goes to Fe^{3+}. The Auger mechanism cannot solely account for the $Co^{2+} \rightarrow Fe^{3+}$ decay since it does not occur in practice in a 100% of the electron capture decays. In order to explain the appearance in this case of a unique ferric line we assume, by analogy with the simple oxides, the existence of cation vacancies. Because of charge neutrality there will be a small Co^{3+} (T) fraction, which after electronic capture, goes to Fe^{3+} hiding in so doing the non existence of 100% Auger cascade processes (*20*). In order to take into account the structure stability we have to admit that each vacancy affects several cations.

The source $^{57}CoCr_2O_4$ synthesized at 10^{-5} torr. gives a single Fe^{2+} line spectrum, this seems to indicate that the lattice is practically free of vacancies.

The $^{57}Co_3O_4$ spectrum obtained by slow cooling has been fitted with a Fe^{3+} (T) singlet and a Fe^{3+} (O) doublet; the last one is due to a displacement of the oxygen atoms during the cooling process. In view of our results after a quenching process, it seems, however, that the symmetry around Fe^{3+} (T) is broken. As in the case of absorbents, the quenched sources give different results as compared with slow-cooled sources. The best fitting is obtained by means of a Fe^{3+} (T) doublet and a Fe^{3+} (O) singlet, meaning that the cubic symmetry around the O-sites is preserved.

Conclusions

1. The decay of $^{57}Co^{2+}$ to $^{57}Fe^{3+}$ is made possible by the presence of vacancies in the lattice. Only those spinels synthesized at low PO_2 (10^{-6} torr. for $^{57}CoCr_2O_4$) can be considered vacancy free. At low PO_2 synthesis conditions one single line spinel is obtained. The purity of the starting material is very important in order to minimize the Fe^{3+} fraction.

2. Iron as constituent or impurity, in the air synthesized spinels, is always trivalent regardless of its position. When a cation Fe^{3+} is present in T-sites, its cubic symmetry is broken. The only plausible interpretation for the high value of ΔQ for Fe^{3+} (T) and Fe^{3+} (O) seems to be the presence of B vacancies in the case of Fe^{3+} (T) and the movement of oxygens along [111] in the case of Fe^{3+} (O).

3. At high temperature a mixed valence structure of Co_3O_4 has been found. New X-ray powder measurements are necessary in order to further explain this point.

Acknowledgments

One of us (J.T.) is very grateful to Professor G. M. Kalvius and Dr. F. Parak for their hospitality at the Physik-Department E-15 of the Technische Universität München, where part of this work was performed.

References

1. A. Hudson and H. J. Whitfield, *Mol. Phys.* **12**, 165 (1967).
2. N. N. Greenwood "Cristales iónicos, defectos reticulares y no estequiometría." Chapter 5 (S. A. Alhambra, Ed.), Madrid, México (1969).
3. D. S. McClure, *J. Phys. Chem. Solids* **3**, 311 (1957).
4. C. H. Song and J. G. Mullen, *Nucl. Instrum. Methods* **140**, 81 (1977).
5. C. D. Spencer and D. Schroeer, *Phys. Rev. B* **9**, 3658 (1974).
6. P. J. Murray and J. W. Linnett, *J. Phys. Chem. Solids* **37**, 1041 (1976).
7. M. Robbins, G. K. Wertheim, R. C. Sherwood, and D. N. E. Buchanan, *J. Phys. Chem. Solid* **32**, 717 (1971).
8. M. P. Gupta and H. B. Mathur, *J. Phys. C Solid State Phys.* **8**, 370 (1975).
9. J. Tejada, *An. Fis.* **73**, 39 (1977).
10. P. Cosee, *J. Inorg. Nucl. Chem.* **8**, 484 (1958).
11. N. Tanaka, T. Tokoro, and Y. Aiyama, *J. Phys. Soc. Japan* **21**, 262 (1966).
12. M. J. Rossiter, *J. Phys. Chem. Solids* **26**, 775 (1965).
13. R. Jagannathan and H. B. Mathur, *Inorg. Nucl. Chem. Lett*, **5**, 89 (1969).

14. W. KUNDIG, W. KOBELT, H. APPEL, G. CONSTABARIS, AND P. H. LINDQUIST, *J. Phys. Chem. Solids*, **30**, 819 (1969).
15. G. A. SAWATSKY, F. VAN DER WOULDE, AND A. H. MORRISH, *Phys. Rev.* **187**, 747 (1969).
16. ASTM Standard card No 9-418.
17. J. FONTCUBERTA, R. RODRIGUEZ, J. TEJADA, AND A. TRAVERIA, to be published.
18. Z. M. JARZEBSKI, Oxide semiconductors, "International series of Monographs in the Science of the Solid State." Vol. 4, (B. R. Pamplin Ed.) Pergamon Press, Wydawnictwa Naukowo-Techniczne, Warszawa, 1973.
19. J. TEJADA, Tesis Universidad Barcelona, 1975.
20. H. POLLAK, *Phys. Status Solidi* **2**, 720 (1962).