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Mössbauer study of several cobalt spinels using Co^{57} and Fe^{57}†

Charles D. Spencer* and Dietrich Schroeer
Department of Physics, University of North Carolina, Chapel Hill, North Carolina 27514

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The Mössbauer spectra produced by 10^{-4}-at.% Co^{57} and 0.5-at.% Fe^{57} doped in the normal spinels Co_3O_4, $CoRh_2O_4$, $CoCr_2O_4$, $CoMn_2O_4$, and $ZnCo_2O_4$ have been obtained. Based on properties of the spinel structure and on correlations with Mössbauer data from the natural-iron spinels, these spectra are interpreted in terms of the daughter and impurity iron being located on the tetrahedral and octahedral lattice sites. The charge state of the daughter iron is not always the same as that of the parent cobalt; instead, it is generally that of natural iron in the parallel spinel compounds Fe_3O_4, $CoFe_2O_4$, $FeCo_2O_4$, $FeCr_2O_4$, $FeMn_2O_4$, and $ZnFe_2O_4$. From this and other evidence, we propose that the daughter-iron's valence is determined primarily by the chemical bonding properties of iron (as distinct from cobalt) in the environment where it is created. Of the several models of spinel crystal chemistry, that of Goodenough and Loeb roughly accounts for our conclusions.

I. INTRODUCTION

The state of iron in compounds having the two-lattice-site spinel structure has been extensively studied by the Mössbauer effect.[1] Well-established correlations between the measured isomer shift and the number of d electrons in the valence band allow a determination of the valence state of iron.[2,3] Further, several of the Mössbauer parameters of iron on octahedral spinel sites have been found to be distinguishable in most cases from those of iron on tetrahedral spinel sites.[4] This allows a determination of the distribution of iron over the two sites. The results of both the valence and site distribution studies are generally in accord with what is known from other techniques.

The above determinations utilize the resonant absorption by iron (in the spinel compound) of γ rays emitted during the decay of Co^{57} in some standard single-line-source compound. We were interested in the possibility of studying the valence and distribution of *cobalt* over the two spinel lattice sites by having a small fraction of the cobalt radioactive and using the Mössbauer effect to determine the state of the iron created by the decay of the cobalt. In this case, the iron of interest is the source of γ rays which are reasonantly absorbed by stable iron in some standard single-line-absorber compound.

Kündig *et al.*[5] and Cruset and Friedt[6] have studied the spinels Co_3O_4 and $CoFe_2O_4$ with parts-per-million radioactive cobalt and have found that the correlations between site symmetry and Mössbauer parameters derived from stable iron hold. Since the effects of the decay are not sufficient to remove the iron from the initial cobalt's lattice position, the Mössbauer results can be used to determine (or verify) the distribution of the cobalt over the two lattice sites. On the other hand, Kündig *et al.*[5] found the valence of the iron at the tetrahedral site of Co_3O_4 to always be 3+ even though the parent cobalt is divalent. Similarly, Cruset and Friedt[6] found that Co^{2+} at the octahedral spinel sites of $CoFe_2O_4$ always decays to Fe^{3+}.

It has been known for some time that the valence of iron produced by the decay of cobalt cannot be relied on to be the same as that of the cobalt. What usually happens is typified by the case of CoO where initially divalent cobalt decays to both divalent and trivalent iron, with the ratio of valences dependent on preparation and sample temperature.[3,7–9] Extensive studies of CoO and other compounds have not produced an understanding of what mechanisms are responsible for the observed valence changes. The spinel results reported by Kündig *et al.* and by Cruset and Friedt differ from those generally found in that the valence changes are 100%, whereas, in all other cases, some fraction of the iron has the same valence as the initial cobalt.

With the goal of further evaluating the usefulness of Mössbauer source studies of cobalt spinels, and with an interest in the unique valence changes cited above, we repeated the earlier work on Co_3O_4 and then studied the additional spinels $CoRh_2O_4$, $CoCr_2O_4$, $CoMn_2O_4$, and $ZnCo_2O_4$. All five compounds are paramagnetic at room temperature, thus freeing the Mössbauer results from the added complexity of magnetic hyperfine splitting.[10] Further, they are all normal spinels with the lattice site distribution and valences well known.[10] Finally, in addition to source studies using Co^{57}, we also doped these compounds with iron as a dilute impurity and did absorber studies.

Sample preparation and the experimental procedure will be discussed in Sec. II. In Sec. III, the source and absorber Mössbauer spectra will be presented and analyzed. In Sec. IV, we will show that the observed valences of the daughter iron are consistent with those of stable iron in the parallel spinel compounds $CoFe_2O_4$, $FeCo_2O_4$, Fe_3O_4, $FeCr_2O_4$, $FeMn_2O_4$, and $ZnFe_2O_4$. From this and other evidence, we will propose that the final charge state of the iron is determined by the chemical bonding characteristics of iron (not cobalt) at the lattice sites occupied initially by Co^{57}. At the end of Sec. IV, we will relate our results to the various spinel site-preference theories.

II. EXPERIMENTAL PROCEDURE

The samples were prepared by dissolving in water appropriate proportions of the chlordies or nitrates of the transition metals needed for the various cases. For the sources, 2 to 3 mCi of Co^{57} in 0.1 ml of HCl was added to the solution. For the absorbers, Fe_2O_3 enriched in Fe^{57} was dissolved into the solution, typically to 0.5 mole%, using hydrochloric or nitric acid. In both cases, the final mixtures were dried and then annealed under an oxygen atmosphere for 10 h at (i) 850 °C for Co_3O_4; (ii) 1000 °C for $CoRh_2O_4$, $CoCr_2O_4$, and $CoMn_2O_4$; and (iii) 450 °C for $ZnCo_2O_4$. A nonradioactive standard sample was prepared simultaneously with all the sources. This standard and the absorber sample were analyzed by Mo x rays in a goniometer. Using the Powder Diffraction File as a reference, all source standards and all absorbers were determined to have only the desired spinel structure.[11]

The Mössbauer spectra were collected using a constant-acceleration spectrometer coupled to a multiscaling multichannel analyzer (as described in Ref. 12). Calibration was via a Co^{57}-in-copper source and a metallic-iron absorber. For source studies, the absorber was single-line sodium ferrocyanide. The cobalt-in-copper source was used for the absorber studies. The temperature was varied using typical cryostats. A standard least-squares curve-fitting program was employed to analyze the data.

III. EXPERIMENTAL RESULTS AND ANALYSIS

The spinel structure consists of two metal-ion sublattices held together by a face-centered-cubic arrangement of oxygen (or some other) anions. One sublattice has the metal ions tetrahedrally surrounded by oxygens and the other has the metal ions octahedrally surrounded. There are twice as many octahedral (*B*) sites as tetrahedral (*A*) sites. Each oxygen atom has as nearest neighbors three metal ions at *B* sites and one metal ion at an *A* site. A small trigonal distortion of the anion sublattice leads to a crystal-field gradient at the octahedral sites but not at the tetrahedral sites.[13]

Many different metal ions combine in a variety of valences and site distributions with oxygen to form the spinel structure. The chemical mechanisms that determine the valence and lattice site preferred by a given cation have been discussed in the literature and will appear later in this paper. The simplest spinel configuration, and the one relevant to the present work, involves cations only in 2+ and 3+ charge states. Such spinels come in what are known as normal, inverse, and mixed configurations. Adopting the convention of denoting the *B*-site ion or ions with brackets, the normal structure is (for the case of 2 metal ions) $(M_a)^{2+}[(M_b)_2^3]O_4$. The inverse structure is $(M_b)^{3+}[(M_a)^{2+}(M_b)^{3+}]O_4$ or $(M_b)^{2+}[(M_a)^{3+}(M_b)^{3+}]O_4$ and the mixed structure is part normal and part inverse, with the degree of inversion dependent on preparation.

A. Co_3O_4

Co_3O_4 has the normal spinel structure—$Co^{2+}[Co_2^{3+}]O_4$.[10,14–16] Its magnetic properties have been studied by Blass[17] and by Roth.[14] They concluded that Co^{2+} on the *A* site becomes antiferromagnetically ordered at 40 °K, and that Co^{3+} ($3d^6$) on the *B* site (in a low-spin state) is diamagnetic.

As previously indicated, Kündig *et al.* doped radioactive Co^{57} into Co_3O_4 and determined the Mössbauer spectrum using a single-line absorber. We repeated this experiment and obtained the same results. As shown in Fig. 1(a), the spectrum has been fitted by two lines of equal percent absorption and equal widths and by a third line. The claim is that the doublet originates from the decay of Co^{3+} to Fe^{3+} at the *B* sites and the singlet originates from the decay of Co^{2+} to Fe^{3+} at the *A* sites. The evidence for this is listed below:

(i) The isomer shift of the singlet is typical of Fe^{3+} at *A* spinel sites and that of the centroid of the doublet is typical of Fe^{3+} at *B* spinel sites. The values of these shifts and those of stable iron at the *A* and *B* sites of several other spinel compounds are listed in Table I.[18–24] Also, the shifts characteristic of Fe^{3+} at the two sites are discussed in detail in Ref. 4.

(ii) The *B*-site line is a doublet and the *A*-site

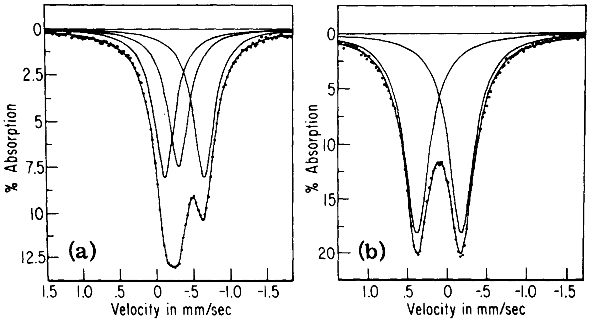

FIG. 1. (a) Mössbauer spectrum of a $Co_3O_4:Co^{57}$ source against a sodium ferrocyanide absorber. (+ velocity is for source approaching absorber in all spectra.) (b) Spectrum of a $Co^{57}:Cu$ source against $Co_3O_4:Fe^{57}$ absorber.

line is a singlet. This is consistent with the fact that the *A* site is cubic and the *B* site is not. Further, the value of the quadrupole splitting is consistent both with that found in similar iron spinel compounds (see Table I) and with that found from calculations of the electric field gradient.[18]

(iii) The area ratio of the singlet to doublet of $\frac{1}{2}$ is consistent with the known one-to-two *A*-to-*B* site occupation. (The Mössbauer recoilless fraction has been shown to be roughly the same for iron at *A* and *B* spinel lattice sites.[25])

(iv) Finally, when Co_3O_4 is cooled below the magnetic transition temperature, the doublet does not change while the single line goes to the standard six-line magnetic hyperfine pattern. This is consistent with the fact that only the *A* sublattice becomes magnetically ordered.

The one feature of the Co_3O_4 source results not entirely straightforward is the isomer shift of the single line, which indicates that only Fe^{3+} is at the *A* site, where the initial cobalt is 2+.

The results from doping $\frac{1}{2}$-at.% impurity iron (enriched in Fe^{57}) into Co_3O_4 is shown in Fig. 1(b). Two lines of equal percent absorption and width. have been fitted to the data. They have an isomer shift and separation the same as that of the doublet in the source spectrum. The numbers are listed in Table I. A straightforward interpretation is that parts-per-hundred iron substitutes in a trivalent charge state for cobalt on the *B* sites of Co_3O_4. However, when cooled below the magnetic transition, the absorber goes to six lines, indicating the iron atoms are magnetically ordered. This is not expected if the iron has indeed substituted on the diamagnetic *B* sublattice. (The doublet in the source spectrum does not show such a splitting.) A possible explanation for the observed splitting is that the impurity iron forms clusters.

B. $CoRh_2O_4$

In order to look further at the *A* site, we studied the cobalt-rhodium spinel $Co^{2+}[Rh_2^{3+}]O_4$.[10,26] Because Rh^{3+} ($4d^6$) is chemically similar to Co^{3+} ($3d^6$), $CoRh_2O_4$ should have many of the properties of Co_3O_4. Indeed, Blass[26] found the magnetic states of the two compounds to be the same: a diamagnetic *B* sublattice and an *A* sublattice which becomes antiferromagnetically ordered at 27 °K (compared to 40 °K for Co_3O_4).

The Mössbauer spectrum obtained from $CoRh_2O_4$ doped with radioactive cobalt [Fig. 2(a)] shows a single line with an isomer-shift characteristic of Fe^{3+}. At 4.2 °K, the spectrum shows a six-line magnetic pattern identical to that found for Co_3O_4. Both these spectra support the straightforward interpretation that the single line (or six lines) results from the decay of cobalt to iron at the *A* spinel site. Again, the only inconsistency is that the iron is 3+ instead of the 2+ of the parent cobalt, just as in the case of Co_3O_4. (As can be seen in Table I, the isomer shift differs somewhat from those of Fe^{3+} on the *A* sites in the other cases. Reasons for this might involve the ionic charge radius of Rh^{3+} being larger than Co^{3+} and/or the lattice spacing in $CoRh_2O_4$ being larger than Co_3O_4. This difference does not affect the charge-state assignment.)

We also doped $\frac{1}{2}$-at.% impurity iron into $CoRh_2O_4$ and obtained the spectrum shown in Fig. 2(b). It consists of a single line with the same isomer shift as the single line in the source spectrum. (The numbers are in Table I). At 4.2 °K, a six-line spectrum identical to the one in the source is found. Both these results support the straightforward interpretation that Fe^{3+} substitutes on the *A* site for Co^{2+}.

Over the years, as the multiple valences produced by the decay of cobalt to iron in various compounds were being studied, a standard procedure was to dope stable iron into the same compounds and compare its state with that of the daughter iron.[8,9,27] Only occasionally were worthwhile results obtained. Usually the absorber spectra do not duplicate any part of the source spectra, making it unlikely that the iron had substituted for the cobalt. However, in the case of $CoRh_2O_4$, we can say where the impurity iron substitutes and we can further say that its valence is not that of the cobalt, which it replaces on the *A* sites, but instead that of the daughter iron.

C. $CoCr_2O_4$

Cobalt-chromium oxide is a normal spinel with Co^{2+} again on the *A* site and Cr^{3+} on the *B* site.[10] Radioactive cobalt doped into this compound produced the Mössbauer source spectrum shown in Fig. 3(a). Two lines have been fitted to the data: one with an isomer-shift characteristic of Fe^{3+} at *A* spinel sites and the other with a shift char-

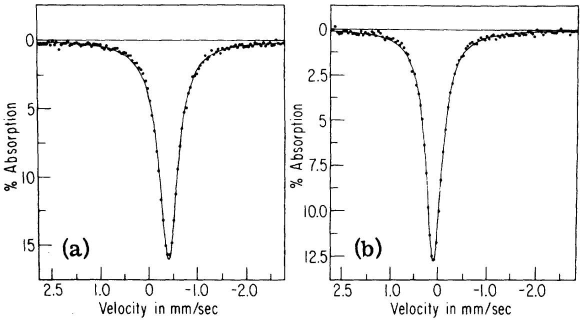

FIG. 2. (a) Mössbauer spectrum of a $CoRh_2O_4:Co^{57}$ source against a sodium ferrocyanide absorber. (b) Spectrum of a $Co^{57}:Cu$ source against a $CoRh_2O_4:Fe^{57}$ absorber.

TABLE I. Summary of Mössbauer isomer shifts and quadrupole splittings for several iron and cobalt spinels. All results are for room temperature and are in mm/sec. The source shifts are relative to a metallic-iron absorber and the absorber shifts are relative to a metallic-iron source.

Compound	Lattice constant (Å)	Isomer shift (Fe^{3+}–*B*)	Quadrupole splitting (Fe^{3+}–*B*)	Isomer shift (Fe^{3+}–*A*)	Isomer shift (Fe^{2+}–*A*)	Reference
Fe_3O_4	8.39	a	a	0.25	···	19
$FeCr_2O_4$	8.38	···	···	···	0.936	20–22
FeV_2O_4	8.41	···	···	···	0.94	21, 22
$CdFe_2O_4$	8.71	0.368	0.748	···	···	18
$ZnFe_2O_4$	8.43	0.354	0.335	···	···	20, 23
$CuFe_2O_4$	8.22	0.37	a	0.27	···	24
$CoFe_2O_4$	8.38	0.35	a	0.28	···	6
$CoFe_2O_4 : Co^{57}$	8.38	-0.36^b	a	···	···	6
$Co_3O_4 : Co^{57}$	8.07	-0.330	0.535	-0.250^b	···	present
$Co_3O_4 : Fe^{57}$	8.07	0.325	0.540	···	···	present
$CoCr_2O_4 : Co^{57}$	8.33	···	···	-0.262^b	-0.942	present
$CoCr_2O_4 : Fe^{57}$	8.33	0.345	0.395	···	···	present
$CoMn_2O_4 : Co^{57}$	8.10	···	···	-0.275^b	-0.928	present
$ZnCo_2O_4 : Co^{57}$	8.05	-0.315	0.540	···	···	present
$ZnFe_2O_4 : Fe^{57}$	8.05	0.320	0.535	···	···	present
$CoRh_2O_4 : Co^{57}$	8.50	···	···	-0.335^b	···	present
$CoRh_2O_4 : Co^{57}$	8.50	···	···	0.345^b	···	present

[a] Not measurable due to effects of magnetic ordering.

[b] Daughter-iron valence not the same as parent cobalt.

acteristic of Fe^{2+} at *A* spinel sites. The numbers are given in Table I. In addition to the values of the shifts, the absence of quadrupole splitting also shows that the daughter iron is on *A* spinel sites. From the area under the lines, one can conclude that Co^{2+} decays to Fe^{2+} 80% of the time and to Fe^{3+} the remaining 20%.

The results here are similar to those in other types of compounds, such as CoO, where Co^{2+} decays to Fe^{2+} and Fe^{3+}. However, we have found that unlike these other cases, the ratio of valences observed in $CoCr_2O_4$ is not sensitive to sample preparation or to sample history.

The spectrum produced by doping $\frac{1}{2}$-at.% impurity iron in $CoCr_2O_4$ is shown in Fig. 3(b). There are two lines of equal width and percent absorption. The isomer shift and quadrupole splitting are consistent with those which characterize Fe^{3+} on *B* spinel sites (see Table I). This indicates that Fe^{3+} substitutes for Cr^{3+} on the *B* spinel sites of $CoCr_2O_4$. However, the conclusion is not as clear cut as in the case of $CoRh_2O_4$, where the absorber and source results agree completely.

D. $CoMn_2O_4$

In the cobalt-manganese spinel, Co^{2+} occupies the *A* sites, and Mn^{3+} the *B* sites. Mn^{3+} ($3d^4$) is electronically degenerate in octahedral crystal fields and this degeneracy is removed by a Jahn-Teller distortion of the lattice.[10,28,29] The Mössbauer spectrum produced by the decay of Co^{57} doped in this compound is shown in Fig. 4(a). Two doublets have been fitted to the data—two pairs of lines of equal width and percent absorption. One doublet has an isomer-shift characteristic of Fe^{3+} at *A* spinel sites and the other doublet has a shift characteristic of Fe^{2+} at *A* spinel sites (see Table I). The quadrupole splitting is due to the Jahn-Teller distortion, which produces an electric field gradient at the *A* site. From the areas under the lines, one can conclude that Co^{2+} at the *A* sites of $CoMn_2O_4$ decays to Fe^{2+} 20% of the time and to Fe^{3+} 80% of the time.

We also doped $\frac{1}{2}$-at.% impurity iron into $CoMn_2O_4$ and produced the Mössbauer spectrum shown in

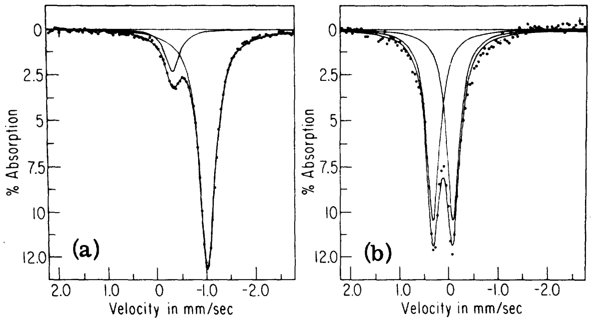

FIG. 3. (a) Mössbauer spectrum of a $CoCr_2O_4 : Co^{57}$ source against a sodium ferrocyanide absorber. (b) Spectrum of a $Co^{57} : Cu$ source against a $CoCr_2O_4 : Fe^{57}$ absorber.

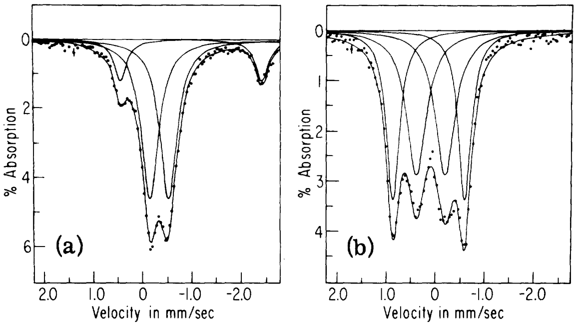

FIG. 4. (a) Mössbauer spectrum of a $CoMn_2O_4 : Co^{57}$ source against a sodium ferrocyanide absorber. (b) Spectrum of a $Co^{57} : Cu$ source against a $CoMn_2O_4 : Fe^{57}$ absorber.

Fig. 4(b). Two doublets have been fitted to the data, both with isomer-shifts characteristic of Fe^{3+}. Neither duplicates either of the source doublets, the iron apparently does not substitute on the *A* sites. The isomer shifts of 0.318 and 0.354 mm/sec relative to a metallic-iron source are in the range of those characteristic of Fe^{3+} on *B* spinel sites, but more-detailed information would be needed to be sure the iron substitutes there rather than at some interstitial position. Filoti *et al.*[30] have studied 10-at.% impurity iron in $CoMN_2O_4$ and obtained results similar to ours. They claimed that the iron occupied inequivalent *B* sites.

E. $ZnCo_2O_4$

The final compound studied was the zinc cobalt spinel where Zn^{2+} occupies the *A* site and Co^{3+} the *B* site.[10] Figure 5(a) shows the Mössbauer source spectrum, which consists of a quadrupole doublet with an isomer-shift characteristic of Fe^{3+}. The presence of quadrupole splitting and the value of the isomer shift are consistent with what is expected for iron on *B* spinel sites (see Table I). Thus, Co^{3+} on the *B* site decays to Fe^{3+}.

As can be seen in Fig. 5(b), the Mössbauer absorber spectrum of $\frac{1}{2}$-at.% iron doped into $ZnCo_2O_4$ is identical to the source spectrum [Fig. 5(a)]. The numbers are given in Table I. This means that Fe^{3+} substitutes for Co^{3+} on the *B* sites.

IV. DISCUSSION

One of our goals was to determine the usefulness of Mössbauer studies of cobalt in spinels. The results of the five cases treated show that the correlations between several of the Mössbauer parameters and the lattice site symmetry, established for stable iron in spinels, hold for iron created by the radioactive decay of cobalt. Hence, it is possible to determine the distribution of cobalt over the two lattice sites, something that is especially worthwhile in the several cases where such information is not definitely available from other techniques.

A. Chemical stabilization of higher valences

As stated previously, the valence of iron created by the electron-capture decay of Co^{57} cannot be relied on to be the same as that of the initial cobalt. This was the case in four of the five compounds discussed above. The mechanism that determines the final valence of the iron has been sought for a decade. It was first believed that only a fraction of the iron, initially ionized by the Auger process which follows electron capture, had returned to the valence required by lattice charge conservation when the Mössbauer γ rays were emitted (an average of 148 nsec after the decay of the cobalt).[7,31,32] Later it was shown that the fraction of the iron in an anomalous valence did not depend on the time after electron-capture decay, at least on the scale of 0 to 200 nsec.[9] It was then proposed that preexisting lattice defects couple with the Auger ionization to stabilize the higher valences for long times.[3,9] Recently, chemical mechanisms have been proposed to explain the observed charge-state changes. These include ionic size correlations in a sequence of rutile florides[27] and electrostatic energy differences in the simple ligand compounds CoF, CoCl, CoBr, and CoOH.[33]

We would like to propose a chemical mechanism to explain the observed valences in the five spinels studied by us, and in $CoFe_2O_4$ studied by Cruset and Friedt.[6] The idea is simply that iron, created at a lattice site initially occupied by cobalt, assumes a valence determined primarily by the bonding preferences of iron, not cobalt, at that lattice site. This can be shown by comparing our experimental results with cases where iron naturally

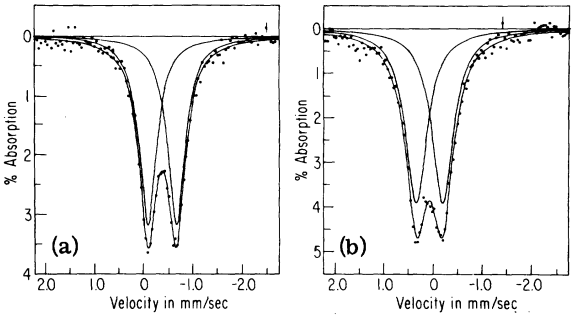

FIG. 5. (a) Mössbauer spectrum of a $ZnCo_2O_4 : Co^{57}$ source against a sodium ferrocyanide absorber. (b) Spectrum of a $Co^{57} : Cu$ source against a $ZnCo_2O_4 : Fe^{57}$ absorber.

TABLE II. Comparison of the observed valence changes with the state of iron in parallel compounds.

Compound	At *A* site	At *B* site	Compares with
CO_3O_4	$Co^{2+} \rightarrow Fe^{3+}: 100\%$	$Co^{3+} \rightarrow Fe^{3+}: 100\%$	$Fe_3O_4 : Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$
$CoRh_2O_4$	$Co^{2+} \rightarrow Fe^{3+}: 100\%$	...	$FeCo_2O_4 : \simeq Co^{2+}[Fe^{3+}Co^{3+}]O_4$ $CoFe_2O_4 : \simeq Fe^{3+}[Co^{2+}Fe^{3+}]O_4$
$CoCr_2O_4$	$Co^{2+} \rightarrow Fe^{2+}: 80\%$ $\rightarrow Fe^{3+}: 20\%$	...	$FeCr_2O_4 : Fe^{2+}[Cr_2^{3+}]O_4$
$CoMn_2O_4$	$Co^{2+} \rightarrow Fe^{2+}: 20\%$ $\rightarrow Fe^{3+}: 80\%$	...	$FeMn_2O_4 : Fe_{0.3}^{2+}Mn_{0.7}^{3+}[Fe_{0.7}^{2+}Mn_{1.3}^{3+}]O_4$
$ZnCo_2O_4$	...	$Co^{3+} \rightarrow Fe^{3+}: 100\%$	$ZnFe_2O_4 : Zn^{2+}[Fe_2^{3+}]O_4$
$CoFe_2O_4$	...	$Co^{2+} \rightarrow Fe^{3+}: 100\%$	$CoFe_2O_4 : \simeq Fe^{3+}[Co^{2+}Fe^{3+}]O_4$

occurs in the same or similar environments. Such comparisons are outlined below and summarized in Table II.

(i) At the *A* site of Co_3O_4 and $CoRh_2O_4$, Co^{2+} decays only to Fe^{3+}. This compares with $FeCo_2O_4$, $CoFe_2O_4$, and Fe_3O_4 (all inverse or nearly inverse spinels),[10,34,35] where Fe^{2+} never occurs on the *A* site but does occur on the *B* site. In other words, an ion with six 3*d* electrons does not bond on the *A* site when the *B* site contains ions with six 3*d* electrons. At the *B* site of Co_3O_4, Co^{3+} decays to Fe^{3+}, which is consistent with $FeCo_2O_4$,[10] where Co^2 is on the *A* site and Co^{3+} and Fe^{3+} are on the *B* site.

(ii) In contrast with Co_3O_4 and $CoRh_2O_4$, most (80%) of the Co^{2+} decays to Fe^{2+} on the *A* site of $CoCr_2O_4$. This compares with the normal spinel $FeCr_2O_4$,[20–22] where Fe^{2+} also occurs on the *A* site. So, a six-3*d*-electron ion can exist on the *A* site when the *B* site is occupied by a three-3*d*-electron ion.

(iii) $FeMn_2O_4$ is a 70–90% inverse spinel in which iron is mostly 3+ and occurs on both the *A* and *B* sites.[36] (The exact composition is not well established.) While the site and valence preferences are apparently not as strong as $FeCr_2O_4$ and $FeCo_2O_4$, the tendency for the fraction of iron on the *A* site to be 3+ is roughly consistent with our results in $CoMn_2O_4$, where 80% of the Co^{2+} decays to Fe^{3+}.

(iv) There is no valence change in $ZnCo_2O_4$, where Co^{3+} decays to Fe^{3+}. This compares with normal $ZnFe_2O_4$, which shows Fe^{3+} does exist on the *B* site when the *A* site contains Zn^{2+} ($3d^{10}$).[20,23]

(v) Cruset and Friedt found in $CoFe_2O_4$ that Co^{2+} on the *B* site decays to Fe^{3+} rather than to Fe^{2+}.[6] This is consistent with the behavior of iron in the same compound, since Fe^{3+} shares the *B* sublattice with Co^{2+}.

So in the spinels studied by radioactive cobalt and the Mössbauer effect, the charge state of the daughter iron is at least 80% and generally 100% consistent with that of stable iron in parallel compounds. (The only exception is $CoMn_2O_4$-$FeMn_2O_4$, where there is only a qualitative agreement between the state of daughter and stable iron, and this is a consequence of $FeMn_2O_4$ being partially inverse.)

Two additional arguments can be made to support our contention that chemical site-selection mechanisms are primarily responsible for the observed valence of the iron.

(i) In $CoRh_2O_4$, impurity iron in a trivalent charge state substitutes for divalent cobalt on the *A* site. Certainly the dominant factor leading to this result is the chemical preference for iron to be in *A*-site symmetry and to be 3+ as opposed to 2+ or some other valence. When iron is created on the same site by the decay of divalent cobalt, it is also 3+ (instead of 2+) and we argue that the reason for this is the chemical bonding preference demonstrated in the case of impurity iron. (In Co_3O_4, $CoCr_2O_4$, $ZnCo_2O_4$, and probably $CoMn_2O_4$ no such valence differences between Fe and Co are observed.)

(ii) The Auger ionization process has always been assumed to play a dominant role in producing a fraction of the daughter iron with a valence different from that of the parent cobalt. However, the Auger process does not occur after 100% of the electron-capture decays. Current data on *K*/*L* ratios and fluorescence yields show that in 6–8% of the decays the inner vacancy is filled by outer electrons, with energy conserved only by the emission of x rays (not Auger electrons).[31,37] Using $CoRh_2O_4$ as an example, Fig. 2(a) shows no trace of a 2+ line (which would be several linewidths to the right of the 3+ line). Since a 2–3% peak would be detected, we conclude that Co^{2+} goes to Fe^{3+} even in cases when Auger ionization does not occur. Thus, whatever mechanism produces the higher valence can occur, independent of the Auger process. The chemical stabilization we are suggesting could be initiated either by the effects of x-ray or Auger-electron emission.

Finally, when a higher daughter charge state is observed, an electron has been removed from the valence band of the newly formed iron to some other place in the lattice. Because the radioactive cobalt is extremely dilute (parts-per-million) and because the Mössbauer parameters are only sensitive to the immediate environment (first or second neighbors), it is possible that the extra electron could be trapped in some distant defect or added to the conduction band without observable consequences. Further, the fact that a lattice site with a 2+ ion ends up with a 3+ ion does not necessarily require a charge-compensating lattice defect or a physical distortion of the neighboring atoms. Indeed, in many inverse and partially inverse spinels, 2+ and 3+ valences statistically share the same sublattice with charge conservation maintained only over many lattice spacings.

B. Site preference theories

We would like to conclude by relating our results to the various spinel site-preference theories that have been developed. In early work on the subject, Verwey and Heilmann[38] and Gorter[13] concluded that the observed site distributions of metal ions found to have the spinel structure could not be explained on the basis of electrostatic considerations alone. Later, McClure[39] and Dunitz and Orgel[40] proposed a crystal-field model which explained many of the observed spinel configurations, and also provided a basis for understanding the measured magnetic moments and the occurrence of Jahn-Teller distortions. In this model the five d-electron orbitals are split by the crystal field into a doublet and a triplet. In octahedral symmetry the triplet (the d_{xy}, d_{yz}, and d_{xz} orbitals) is lower in energy, and in tetrahedral symmetry the doublet (the d_{z^2} and $d_{x^2+y^2}$ orbitals) is lower. Electrons in the lower orbitals increase the stabilization energy while those in the upper orbitals decrease the stabilization, with the degree of stabilization and destabilization dependent on the magnitude of the crystal field. From values of the field obtained from optical measurements, the site stabilization energies can be determined as a function of the number of d electrons. By comparing the octahedral and tetrahedral stabilizations of a given ion, its site preference can be deduced.

Blass[10] employed a pure molecular-orbital model to arrive at similar information about the octahedral and tetrahedral stabilizations and hence the site preferences.

Both the molecular-orbital and crystal-field approaches predict many of the observed spinel configurations, including the five cobalt compounds studied by us. But they do not show sufficient tetrahedral stabilization differences between Fe^{2+} and Fe^{3+} or between Co^{2+} and Fe^{3+} to explain the inversion of $CoFe_2O_4$ and $FeCo_2O_4$ or to explain the valence changes we observe.

The problem with these approaches may be that they consider the octahedral and tetrahedral stabilizations separately. Our results indicate that the ion occupying the B site influences what happens on the A site. Goodenough and Loeb[41] (GL) have proposed a qualitative model of spinel crystal chemistry which couples the A- and B-site atoms. They pointed out that each oxygen anion is bonded to three B-site ions (located in the x, the y, and the z directions) and to one A-site ion (located in the $-x$, $-y$, $-z$ direction). Because of this, if the oxygen orbitals form covalent or partial covalent bonds with the B-site cations, their spatial configurations would make covalent bonds with the A-site ion unlikely (and vice versa). Hence, the A- and B-site stabilizations cannot be treated separately, since the bonding on one sublattice influences the bonding on the other. Goodenough and Loeb also noted that Cr^{3+} ($3d^3$) has an affinity for partial covalent bonding in octahedral symmetry via d^2sp^3 hybrid orbitals. Similarly, Fe^{3+} ($3d^5$) and Zn^{2+} ($3d^{10}$) have an affinity for partial covalent bonding in tetrahedral symmetry via sp^3 hybrids.

We believe these ideas provide a basis for understanding why iron is 3+ when created on the A sites of Co_3O_4 and $CoRh_2O_4$, while it is mostly 2+ when created on the A sites of $CoCr_2O_4$. In the latter case, Cr^{3+} forms partial covalent bonds on the B site, thus making the preferred covalent Fe^{3+} unlikely on the A sites; in the former case, Co^{3+} and Rh^{3+} are not covalently bound on the B site, thus allowing covalent Fe^{3+} to bond on the A site when it is created by the decay of Co^{2+}. (Low-spin Co^{3+} and Rh^{3+} have empty d_{z^2} and $d_{x^2+y^2}$ orbitals, which could allow covalent bond formation, the same as in the case of Cr^{3+}. This, however, is confirmed not to be the case by magnetic studies, which show pure ionic states at the B sites of Co_3O_4 and $CoRh_2O_4$.)

The case may be crudely made, but we believe the ideas of Goodenough and Loeb (in terms of a competition for partial covalency between the A- and B-site cations) qualitatively explains spinel site preferences, particularly when iron and chromium are involved.

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[*] Present address: Dept. of Physics, Ithaca College, Ithaca, N. Y. 14850.

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