Synthetic 10-Å and 7-Å phyllomanganates: Their structures as determined by EXAFS—Discussion

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INTRODUCTION

Stouff and Boulégue (1988) have recently studied synthetic 10-Å and 7-Å phyllomanganates by EXAFS, paying particular attention to the location of some 3d elements: Co, Ni, Cu, and Zn. The results presented cannot be substantiated for two reasons: (1) the EXAFS data reduction is particularly crude, sometimes physically meaningless, leading in some cases to unjustified interpretations; and (2) the structural model of adsorption sites violates the most elementary rules of crystal chemistry.

PHYSICAL BASIS OF THE EXAFS DATA REDUCTION

For a good understanding of the discussion, it is necessary to recall here the basic formula of EXAFS and its conditions of validity (see, e.g., Teo, 1986). In the classical plane-wave approximation, the photoelectron ejected by the central atom is assumed only to be backscattered at \( \pi \) by neighboring atoms. This condition is fulfilled only at high kinetic energy of the free electron \( (E_e > 40-50 \text{ eV}) \), that is, for wavevector values greater than \(-3 \text{ Å}^{-1}\). At lower energy, multiple-scattering events have a high probability, thus rendering the general formulation of EXAFS invalid. In the classical plane-wave approximation, EXAFS is defined as the function \( \chi(k) \):

\[
\chi(k) = \sum_j \frac{N_j}{kR_j^2} \exp\left(-2\sigma_j k^2\right) \exp\left(-\frac{2R_j}{\lambda_j}ight) \cdot \left| f(k, \pi) \right| \sin(2kR_j + \phi_j(k)).
\]

The summation is made over the \( j \) atomic shells surrounding the central absorber. \( N_j \) is the number of backscatterers in the \( j \) shell at the distance \( R_j \), \( \sigma_j \) is a Debye-Waller factor used to simulate disorder effect. \( \lambda_j \) is the mean free path of the electron, accounting for inelastic losses in the scattering process. \( |f(k, \pi)| \) is the backscattering amplitude and depends on the type of atom in the \( j \) shell and the electron-wave phase shift \( \phi_j \) induced by the potential of both the central atom and the backscatterer.

Interatomic distance

Interatomic distances can be derived from the experimental spectrum if \( \phi_j(k) \) is known. In the first place, Stouff and Boulégue used phase shifts calculated by Teo and Lee (1980) for \( 3.8 < k < 15 \text{ Å}^{-1} \) for a wide number of elements. The low \( k \) limit is dictated by the physical approximation aforementioned. Spectral fits of the first coordination shell reported by Stouff and Boulégue extend down to \( k = 1 \text{ Å}^{-1} \) and thus cover a \( k \) region where EXAFS theory is not valid in the plane-wave approximation. In the second place, the precision of metal-metal distances as derived by EXAFS is of concern. A precise determination requires the knowledge of the backscatterer and the use of good atomic potentials. As the phase-shift variation with \( Z \) is small and monotonous, the error in distance \( (R) \) induced by a wrong choice of the backscatterer is not large, but it becomes significant between Mn and Zn (0.05 Å). When using calculated potentials, one has first to test their validity on a model compound by evaluating the discrepancy with structural information determined by X-ray diffraction. This difference can be measured on chalcophanite, the only studied manganese oxide whose structure has been refined (Wadsley, 1955; Post and Appleman, 1988): Stouff and Boulégue reported a Mn-Mn distance equal to 2.81 Å, whereas XRD gives 2.85 Å. Finally, given the uncertainty on \( Z \) and the use of uncorrected theoretical phase shifts, the precision of interatomic distances may be as low as \(-0.09 \text{ Å} \) and prevents any precise structural determination. Contrary to Stouff and Boulégue’s statements, the mathematical treatment they used is not “obsolete,” and the sensitivity of EXAFS to distance determination has not been improved with time, as the physical process responsible for EXAFS has remained unchanged! Instead, their large uncertainty mainly arises in the incorrect data reduction and interpretation.

EXAFS amplitude and coordination number

Throughout the article, Stouff and Boulégue avoided discussion of the precise significance of the \( N \) parameter: “\( N \) refers to the apparent number of neighbors, indicating the degree of order” (Stouff and Boulégue, 1988, Table 1). “The amplitude indicates a level of ordering at a distance from the central atom; it can be related to the number of surrounding neighbors in the shell” (Stouff and Boulégue, 1988, p. 1163). “One should note that the number of neighbors is obtained as a parameter that is a function of the average distance of the free electron [italics added]” (Stouff and Boulégue, 1988, p. 1163). This last sentence has no physical meaning; the authors probably meant to make reference to the mean free path \( (\lambda) \) of the electron. Because of the inexact nature of these statements, it is appropriate to discuss briefly the way in which the coordination number can be derived from EXAFS analysis and the precise significance of the “\( N \)” parameter. For additional general information, the reader is referred...
The exafs amplitude includes four factors: \(|f(k, \pi)|\), \(\sigma\), \(\lambda\), and \(N\). The backscattering amplitude has been calculated for numerous elements by Teo and Lee (1980); choice of \(Z\) determines this amplitude factor. As for phase shifts, an error in \(Z\) does not significantly influence determination of the three other parameters owing to the relatively low \(Z\) dependence of \(|f(k, \pi)|\). Unfortunately, \(\sigma\), \(\lambda\), and \(N\) are not known a priori and are highly correlated. \(\lambda\) is always determined by using a structurally known compound and then transferred to the unknown. The expression for disorder (\(\sigma\)) used in Equation 1 assumes a Gaussian distribution of interatomic distances and harmonic motion of atoms. If these requirements are met, \(N\) is equal to the effective number of atoms in the \(j\)th shell. In the case of large static or thermal disorder, the pair-distribution function is asymmetric, and the above approximations no longer hold and may lead to a drastic reduction of derived coordination number: \(N_{\text{EXAFS}} \neq N_{\text{XRD}}\).

The analysis of the exafs amplitude by Stouff and Boulague is wrong for the following reasons:

1. \(\delta\text{MnO}_2\) has been used as a reference compound to determine \(\lambda\) relative to the Mn-Mn pair since Stouff and Boulague found six Mn neighbors (Stouff and Boulague, 1988, Table 1). This model compound is a particularly bad choice because of its high structural disorder and the presence of octahedral vacancies (Giovanoli, 1970, 1980). For these reasons the “apparent number of neighbors” reported by Stouff and Boulague is overestimated. This overestimation can be quantified by looking at the \(N\) value of chalcophanite (6.65); Wadsley (1955) and Post and Appleman (1988) showed that in chalcophanite, octahedral vacancies are ordered and each Mn is surrounded by five nearest Mn atoms (Fig. 1a).

2. In the absence of reference compounds for (Co,Ni,Cu,Zn)-Mn pairs, Stouff and Boulague have transferred \(\lambda\) from the fitting of \(\delta\text{MnO}_2\) exafs data. Such a procedure increases the inaccuracy of \(N\) because the transferability of \(\lambda\) between similar structures is only rigorously valid for a given atomic pair, with the condition that the interatomic distance be roughly preserved in the model and the unknown compound.

For these reasons, and some others not detailed here, the \(N\) parameter must be regarded as an amplitude factor without straightforward relation with the average crystallographic number of nearest atomic neighbors. Finally, given the large imprecision of interatomic distances and coordination numbers in this case, there is some futility in trying to establish the structure of phyllomanganates by exafs.

Recommendations for future EXAFS work

Because of the large number of factors that can influence an exafs data set, more information should be specified in papers to give the readers a basis for evaluating the reliability of the results. For example, authors should state the details of the data analysis, such as \(\sigma\), \(\lambda\), and the energy of glitches, the choice of energy zero, and the Fourier-filtering window functions in \(k\) and \(r\) space; they should also give realistic error bars (if present!) on fitted parameters. The section on experimental procedure must include the description of the monochromator crystal type and method of rejecting harmonics, the origin of which has—contrary to the statement of Stouff and Boulague (1988, p. 1163)—nothing physically to do with that of glitches.

Discussion of Results and General Interpretation

The local structure of \(\text{Cu(OH)}_2\), derived from exafs disagrees with results derived from xrd. Stouff and Boulague rightly concluded that waves backscattered by the two Cu subshells are nearly out of phase, lessening the exafs signal and, hence, the accuracy of data analysis. As a consequence, one must question the significance of the analysis of the cation contribution in Cu-containing birnessite and Cu-containing buserite, inasmuch as the magnitude of their second RDF peak is lower than that of \(\text{Cu(OH)}_2\) and not significantly larger than the surrounding noise. In other words, the structural reality of these second peaks is not certain, and at least for Cu-containing birnessite, they are probably caused by noise or termination effects in the Fourier transform. A thorough exafs study would have required that these spectra be recorded at low temperature to reduce the thermal smearing of the exafs peaks and with a counting time large enough to improve statistics.

Stouff and Boulague proposed a structural model for the location for 3d elements on the layer surface of birnessite and buserite. Their schematic diagram showing the position of Me ions (Fig. 9) does not possess the same scale in the horizontal and vertical directions, and the text includes two errors (p. 1168, line 12: “Bl” instead of “B1”; line 18: “1.71 Å” instead of “2.01 Å”), making it difficult to understand their model. For more clarity, in Figure 1 of the present paper, the schematic structure of chalcophanite is projected in the \(a-b\) plane and in a plane through Zn and Mn atoms. Following Stouff and Boulague’s nomenclature, the B1 site is identical to that of Zn in chalcophanite (that is, above and below Mn vacancies), and Zn (O, H, O)\(_6\) octahedra share three oxygens with three distinct Mn\(_{\text{O}}\) octahedra. According to xrd refinements (Wadsley, 1955; Post and Appleman, 1988), in this “B1” position, each Zn atom has six nearest Mn neighbors at a distance of 3.55 Å and is located at \(h = 2.1\) Å off the Mn plane. In this situation, six-fold-coordinated Zn atoms are extremely close to the oxygens of the phyllomanganate layer as the Zn-O bond length is the same as in tetrahedral coordination (1.95 Å). Each Zn octahedron is indeed sharing a face with the vacant adjacent Mn\(_{\text{O}}\) octahedron. The site location of Zn corresponds to a close-packed structure, and it is impossible to imagine a situation where a metal would be closer to the Mn plane. A similar site for the other 3d elements...
Fig. 1. Schematic structure of chalcophanite (after Wadsley, 1955). (a) Projection onto (001); (b) projection onto a plane through Mn and Zn atoms. For clarity, the Zn atom located below the Mn vacancy has not been drawn.

would result in larger Me-Mn distances, because their ionic radii are similar to, or larger than, the Zn$^{2+}$ radius. From the above-mentioned arguments, the fr value is at a minimum in chalcophanite. However, it is by far larger than the I values reported in Table 2 of Stouff and Boulègue (1988), which violates all the elementary rules of topology (Wells, 1984; Manceau and Combes, 1988). For instance, in buserite and birnessite, the Ni adsorption site would be located just below the oxygen layer! In buserite, Zn is exactly located within the oxygen sheet, that is, at the center of a face of a vacant octahedron, an unknown situation for a transition element. Such an improbable arrangement combined with internal inconsistencies (Me-O distances show an octahedral coordination) indicates that the model is untenable. To conclude, let me cite Stouff and Boulègue’s statement (p. 1168): “However, the B1 pole more closely corresponds to that of Cu-bir [that is, Cu-containing birnessite], for which we did not obtain any fit of the second atomic shell...” [italics added].

**ALTERNATIVE INTERPRETATION**

Most of the Me-Me distances reported by Stouff and Boulègue range between 2.8 and 3.3 Å. Taking the variation of ionic radii into account, these distances are typical of a 2D local order possessing either a phyllomanganate-like or a brucite-like structure. For example, the Me-Me distance in Ni(OH)$_2$, Co(OH)$_2$, and Zn(OH)$_2$ is roughly equal to 3.12, 3.17, and 3.19 Å, respectively.

**Nickel**

Such a situation is known in Ni asbolane, where MnO$_2$ layers regularly alternate with Ni(OH)$_2$ layers (Chukhrov et al., 1980a, 1980b; Manceau et al., 1987). In asbolane the Ni-Ni distance is reduced by 0.1 Å as compared to free Ni(OH)$_2$ layers because of the existence of hydrogen bonds between successive Mn-Ni sheets. There is no conclusive evidence to prove whether Ni atoms build a hydroxide layer in the synthesis conditions used in the Stouff and Boulègue study, but supports for such a hypothesis are many: (1) The Ni-Mn distance reported by Stouff and Boulègue (2.98 Å) is very close to the Ni-Ni distance in asbolane (3.02–3.03 Å). Whatever the model may be, this Ni-Me distance is typical of edge-sharing octahedra, proving beyond reasonable doubt that Ni atoms are included within a layered structure. (2) An enlargement of birnessite and buserite Ni K EXAFS spectra shows that these closely resemble the Ni(OH)$_2$ and Ni asbolane spectra. (3) The dilution of Ni atoms cannot be put forward to reject the presence of Ni clusters. Recently, several EXAFS studies have demonstrated the heterogeneous structure of low-temperature materials, and there is now growing awareness that cations are largely unmixed on a microscopic scale (Manceau and Calas, 1985, 1986; Decarreau et al., 1987; Manceau et al., 1987; Manceau and Combes, 1988). Furthermore, hydroxide precipitation at solid-solution interfaces is widely documented in the literature, the hydrated metal oxide surface being thought to act as a template for the formation of a surface coating of the hydroxide of the sorbed cation (see, e.g., Anderson and Rubin, 1981).

**Cobalt**

Stouff and Boulègue found that Co atoms are surrounded by two Me shells at 2.88–3.02 Å and 3.30 Å. The relative number of neighbors in each of these atomic shells is reversed in birnessite and buserite. It is interesting to note that this difference of apparent number of neighbors (N) fits with the predominantly trivalent state of Co in birnessite and the divalent state in buserite. The shorter Co-Me distance is typical of an edge-linkage between octahedrally coordinated Co$^{3+}$ and Co$^{3+}$-Mn$^{4+}$ ions. The larger distance is compatible with the presence of a large nearest-neighbor cation like Co$^{2+}$. It turns out that the variation of N reported by Stouff and Boulègue might be reasonably attributed to variable amounts of CoOOH$_2$ and Co(OH)$_2$-like layers. Once more, the lack of well-chosen reference compounds prevents a choice of any definite structural model.

**REFERENCES CITED**


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MANCEAU: SYNTHETIC 10-Å AND 7-Å PHYLLOMANGANATES—DISCUSSION

Manuscript received February 13, 1989
Manuscript accepted July 17, 1989

Stouff, P., and Boulègue, J. (1988) Synthetic 10-Å and 7-Å phyllomanganates: Their structures as determined by EXAFS, American Mineralogist, 73, 1162-1169.
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