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Interpretation of complex x-ray photoelectron peak shapes. I. Case study of Fe 2p_{3/2} spectra

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ABSTRACT

Analyzing transition metal XPS peaks is widely used to determine surface composition and chemistry. However, these peaks have a complex structure, which is still the subject of investigation. Fe 2p analysis is a case in point where the multiplet structure and many-electron-effects lead to peak shapes that cannot be analyzed using standard approaches. Examination of the literature reveals that one of the most widely used approaches to data reduction when processing Fe 2p_{3/2} spectra involves using symmetric two- or three-component peak fitting with each peak effectively acting to capture a single chemical species (chemistry fit) in the complex spectra. Herein, this approach is compared to an envelope fit approach using Biesinger multiplet components of known iron oxides to determine how effective these methods are in reproducing iron oxide composition. Mixed oxide and metal XPS Fe 2p spectra were synthesized using reference spectra collected experimentally. For the first time, the accuracy and differences between the two approaches are reported. It is demonstrated that no meaningful conclusions can be drawn using single symmetric peaks to analyze complex Fe 2p_{3/2} spectra, implying that a large portion of the literature is flawed. The envelope fit approach, however, is shown to provide useful information regarding oxide ratios in mixed iron oxide materials, though limitations do exist. A methodology for evaluating the quality of XPS analysis of Fe 2p_{3/2} spectra is proposed for benchmarking new submissions so that reviewers, authors, and editors can assess these submissions.

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I. INTRODUCTION

X-ray photoelectron spectroscopy (XPS) is the most widely used technique to determine the elemental and chemical composition of surfaces.¹ Considering that XPS has been around for 50–60 years, one would expect it to be a mature technology, and, in terms of hardware, this is indeed the case. It may then come as a surprise to those outside the field that this is certainly not the case with respect to some aspects of processing and interpretation of XPS data. Over the past two decades, hardware has continued to

become more accessible due to advances made by manufacturers. Uptake of the technique in different applications of materials science continues to grow but adequate training of users has not kept pace. The literature is dominated by examples of poor processing and interpretation regardless of the impact factor of the journal.² Many researchers appear not to have a sufficiently strong foundation in either the underlying theory or experimental methods of XPS to distinguish between correct, careful acquisition, and analysis of data, and incorrect, poor-quality approaches. As a

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result, a very significant proportion of published papers present methodologies that ignore fundamental chemical and physical processes affecting both the surface chemistry and the physics of x-ray photoemission. Over time, these incorrect and poor-quality approaches to data acquisition and analysis are being propagated through the literature. Recently, work has been undertaken by concerned experts in the XPS community to address this problem and by raising awareness and facilitating good practice through conference talks, publication of letters,³ as well as guides and tutorials.⁴

One case in point is the processing and interpretation of high-resolution spectra from transition metals. This can be exceedingly difficult depending on the core line in question and the number of phases or oxidation states present in the sample. This complexity arises not only because of the potentially complex chemistry of metal surfaces that have been exposed to the atmosphere but also due to various quantum physics processes that occur during photoemission including spin-orbit splitting, multiplet splitting, Auger signals, and satellite peaks from shake-up, shake-off, plasmon loss peaks, as well as overlap with other peaks. In addition, the background beneath the peak of interest, arising from nondescript electron interactions, is still an area of debate. This means that scientists generally resort to using Shirley or linear backgrounds.

Extraction of different species in the case of high spectral resolution XPS of first row transition metal 2p spectra is done using peak fitting (not to be confused with deconvolution).⁵ Approaches developed from fitting less complicated core lines, such as C 1s and S 2p where the chemical shift of a singlet or doublet is, among other physical and chemical mechanisms,⁶ dependent on the electronegativity of the heteroatom bonded to the element in question. This approach can be considered a “chemistry fit” as each component should be related to a known and specific chemical bond state, with the final result providing insight into how all the atoms of the element in question are bonded to other atoms. However, this method currently does not translate to these more complex peaks. Moreover, in the case of a complex peak shape, the position of the most intense maximum may not coincide with the center of gravity of the peak; however, the latter is often used for peak assignment. This approach partly originates from the use of historical databases such as the NIST database where researchers are only provided with single peak energy positions for a complex peak envelope. These positions are sourced from old papers published prior to modern day understanding of the complexity of these peaks. This suggests to the novice that a complex spectrum may be fitted with single peak representing either an oxidation state [e.g., Fe(II)] or a specific metal oxide (e.g., FeO), thus leading to incorrect assignment since multiplet structures for different compounds can be spread over tens of electron volts on the high binding energy side of the metal peak.

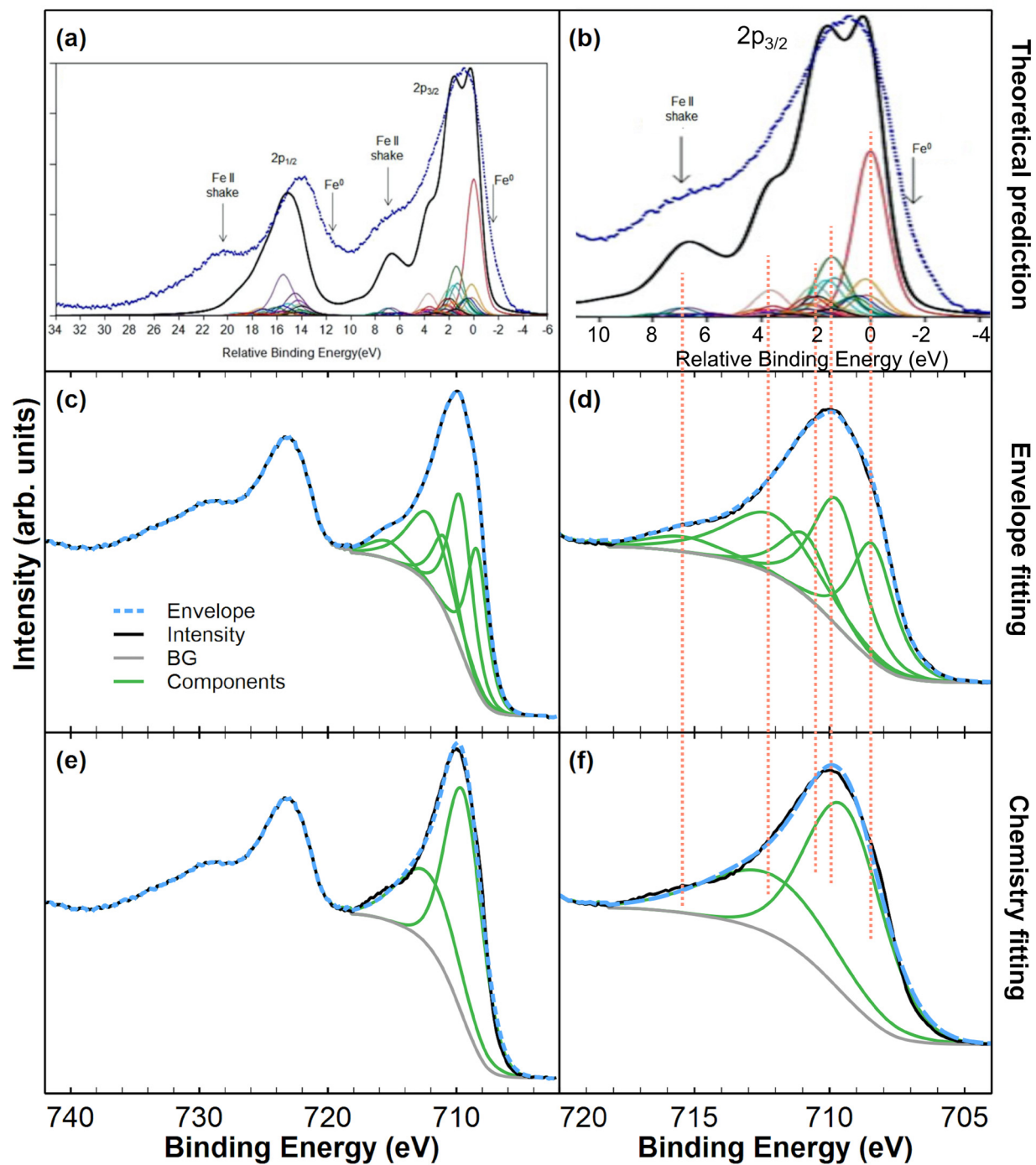
It is important here to describe the source of the complexity, which lies in the quantum physics of photoemission itself. Photoionization generates electron emission (usually considering only one electron/atom). The photoemission causes reorganization of the remaining electrons in the atom as well as adjacent ligand orbitals which the escaping electron experiences. Early interpretation of photoemission was that the photoelectron does not experience the potential of the electron rearrangement (single electron process) but current quantum mechanical (QM) modeling uses a

multielectron approach where the kinetic energy of the photoelectron reflects the final state arrangement of electrons. Specifically, unpaired electrons in the core levels and these electrons interact both with other unpaired electrons within the atom as well as electrons in ligand orbitals. This can be seen when comparing an isolated Fe(III) ion to one under the influence of the surrounding ligands.⁷ Recently, the multiplet structure has been thoroughly investigated in papers by Bagus and co-workers for FeO and Fe₂O₃ (Refs. 8 and 9) and Fujii *et al.*¹⁰ for α -Fe₂O₃, γ -Fe₂O₃, Fe_{3- δ} O₄, and Fe₃O₄. Bagus *et al.*⁸ used an *ab initio* approach to account “for ligand field and spin-orbit splittings, the covalent mixing of ligand and Fe 3d orbitals, and the angular momentum coupling of the open shell electrons.” They also extended this *ab initio* development to include “shake excitations from the closed shell orbitals associated with the O ligands into the valence open shell orbitals associated with the Fe 3d shell.”⁹ They revealed that there were over 12 000 ways that electrons could be reorganized in the final state. While many of these states were nearly degenerate (having the same energy) and of low probability of being occupied (small intensity), there were hundreds of states that did not fall into this category. All these states are multiplets since the photoemission process is a multielectron process and the escaping photoelectron carries this information in its absolute kinetic energy. Their analysis for some of the most intense multiplets in FeO in the Fe 2p_{3/2} region is presented in Figs. 1(a) and 1(d). For experimental spectra, it is important to note that these structures will change when different ligands are present. Also from a QM calculation perspective, the type of model and the effects it is attempting to account for will also change the number, intensity, and energy of the multiplet positions (Table I).

These studies are a significant step forward for understanding the complex multiplet and shake structures observed in Fe 2p spectra since the earliest work of Gupta and Sen,^{11,12} but they also demonstrate the complicated nature of these spectra. For example, in Table I, the binding energy (BE) positions of some of the more intense theoretical multiplets determined by Bagus *et al.*⁸ are compared to those of Biesinger *et al.*¹³ and Grosvenor *et al.*¹⁴ The theoretical multiplets are collected into “groups,” which refers to multiplets that are close together in the calculations of Bagus *et al.* and are listed according to their median energy (this is not the center of mass of the intensity). There is clearly some alignment as would be expected because the multiplets contribute to the overall peak intensity, so an empirical fit of the Fe 2p_{3/2} peak would be expected to reflect, to some extent, the underlying multiplet structure, particularly when the multiplets are grouped. There are also clear differences. For example, intensity around +6 eV is clearly not due to multiplets but is a satellite peak. The paper of Bagus *et al.* also demonstrated that there was significant intensity well outside this region, thus complicating both the spectroscopy of the Fe 2p_{3/2} peak (due to overlap with the 2p_{1/2} peak) as well as its quantification. These studies demonstrate why there is still no consensus in regard to a “correct” approach to performing a chemistry fit for the full Fe 2p region.

In this paper, the authors compare the approach of Biesinger *et al.*¹³ that captures the envelope of the individual oxide peak shapes using experimental multiplet structures to simple single component peak fitting for mixed metal/metal oxide systems for

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FIG. 1. FeO Fe 2p (a) and (b) theoretical prediction for the multiplet structure as reported by Bagus *et al.* (Ref. 8). Reprinted with permission from Bagus *et al.*, J. Chem. Phys. **154**, 094709 (2021). Copyright 2021, AIP Publishing LLC. (c) "Multiplets components" or envelope approach described by Biesinger *et al.* used for envelope fitting and (e) simple two-component fit erroneously based on chemical fitting. These same results are enlarged in panels (b), (d), and (f), respectively. Dotted lines are added to guide the reader and are centered on the most intense contributions from the theoretical predictions. These lines demonstrate the greater alignment of intensity between these contributions for envelope fitting, compared with the chemistry fitting approach. Table I provides the number of the highest intensity multiplets by energy region beneath the Fe 2p_{3/2} peak.

TABLE I. Comparison of multiplet structures in the Fe 2p_{3/2} region calculated by Bagus *et al.* (Ref. 8), empirical positions determined by Grosvenor *et al.* (Ref. 14), and those of Biesinger *et al.* (Ref. 13) based on work of Gupta and Sen (Refs. 11 and 12). Listed values are shifts in BE relative to the group/component at the lowest BE (eV). In the case of the data by Grosvenor and Biesinger, the BE value for the reference peak is also given (in brackets). For Bagus, the numbers in brackets indicate the number of multiplets in that group as taken from Tables I and II (Ref. 8).

Group/component No.	FeO BE shift (eV)			α -Fe ₂ O ₃ BE shift (eV)		
	Bagus	Grosvenor (708.4 eV)	Biesinger (708.4 eV)	Bagus	Grosvenor (709.8 eV)	Biesinger (709.8 eV)
1	0.0 (12)	0.0	0.0	0.0 (9)	0.0	0.0
2	1.39 (12)	1.3	1.3	1.34 (7)	0.9	1.2
3	1.65 (6)	—	—	2.27 (5)	1.6	2.4
4	2.09 (14)	2.5	2.5	2.79 (6)	2.5	3.8
5	3.70 (11)	—	3.7	—	—	—
6	—	—	6.7	—	—	6.0
7	13.14 (12)	—	—	13.88 (6)	—	12.0

iron. It can be seen in Figs. 1(c) and 1(d) that the Biesinger approach reflects, to a large extent, the QM calculations with good alignment between four and five components in (d). On the other hand, fitting two or three components has poor alignment with the QM calculations. These methods will be referred to in the paper as an envelope fit and a chemistry fit, respectively. It is shown for the first time, through synthesizing model mixed oxide and metal XPS Fe 2p spectra, that no meaningful data can be extracted from fitting mixed oxides [e.g., FeO, Fe₂O₃, etc., see Fig. 1(c)] or oxidation states [e.g., Fe(II) and Fe(III)] using single symmetric peaks to represent either category [i.e., a chemistry fit, see Fig. 1(d)]. This calls into question a significant portion of the literature where XPS is used to determine the composition of oxides for iron and steel surfaces. We outline where the Biesinger approach, an envelope fit approach, can be used to accurately extract the amount of a particular oxide in a passive layer and where this process begins to break down. In Paper II,¹⁵ specific examples of incorrect analyses of Fe 2p_{3/2} found in the austenitic stainless steel literature are provided by examining the published work for one material type, specifically austenitic stainless steels.

II. EXPERIMENT

A. Materials—Oxide and its treatment

Experimental data for all spectra have been published previously,¹³ with the exception of the FeO data, which was prepared using the approach described by Bagus *et al.*⁸ FeO powder was purchased from Sigma Aldrich (ten meshes, $\geq 99.6\%$ trace metals basis). In this approach, the FeO sample was etched for 15s using a gas cluster ion source (GCIS) to remove surface species oxidized to Fe(III) while attempting to minimize the contribution from Fe(0) induced by the ion source.

B. Instrumentation

XPS analysis was performed using an AXIS Nova spectrometer (Kratos Analytical Inc., Manchester, UK) with a monochromated Al K α source at a power of 180 W (15 kV, 12 mA), a hemispherical analyzer operating in the fixed analyzer transmission

mode and the standard aperture (analysis area: 0.3×0.7 mm²). The total pressure in the main vacuum chamber during analysis was typically between 10^{-9} and 10^{-8} mbar. Survey spectra were acquired at a pass energy of 160 eV and a step size of 0.5 eV. To obtain more detailed information about the chemical structure, oxidation states, etc., high-resolution spectra were recorded from individual peaks at 40 eV pass energy and step size of 0.1 eV (full width at half maximum of Ag 3d_{5/2} peak < 0.8 eV).

The sample was pressed onto double sided carbon tape, making sure to fill any gaps and to create a homogenous layer, and any loose material was removed by inverting the sample plate and gently taping the backside. A custom-made stainless-steel mask was placed around the powder to assist with charge neutralization. It was analyzed at a nominal photoelectron emission angle of 0° w.r.t. the surface normal. Since the actual emission angle is ill-defined in the case of particles and powders (ranging from 0° to 90°), the sampling depth may range from 0 to approximately 10 nm.

Etching was performed using an Ar GCIS (Kratos Analytical Inc. Minibeam 6) operated at a cluster size of Ar1000+ with an impact energy of 10 keV, equating to a partition energy of 10 eV per atom. For the ion beam, a raster size of 2.5×2.5 mm² was employed. A stable beam current was confirmed prior to performing the depth profile experiment by measuring the sample current on the earthed sample platen (between 10 and 20 nA).

C. Synthesized spectra

These spectra were generated from experimental Fe 2p spectra of pure oxides and oxyhydroxides, which were subsequently combined in a mix of ratios of intensities from 0% to 100% for binary mixtures. It is important to note when the two oxide components are added together, the combined background will be different from the individual background when performing a Shirley background subtraction in the mixed spectrum. This means that the background in the mixed spectrum will be different from the two individual spectra. Additionally, noise is also added to each spectrum. Thus, the fitting of the mixed oxide spectra is a realistic challenge for testing multiplet structures.

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Synthetic spectra were created using the “Replace By Envelope” option under “Spectrum Processing” → “Test data” within CASAXPS.

D. Software used and fitting parameters

CASAXPS version 2.3.25 (Casa Software Ltd., Teignmouth, UK) was used for all spectral processing which included background determination, peak shapes, relative peak positions, and optimization using the Levenberg–Marquardt optimization.

The only background used in this study was the Shirley background. Much has been written on background subtraction particularly in the context of accurate quantitative analysis. In general, the most commonly used backgrounds are linear, Shirley,^{16–18} and universal cross-sectional Tougaard.¹⁹ A fourth background approach is that of Pauly *et al.*²⁰ based on the dielectric response function of the material. In the context of this paper, only the Shirley background is employed since the paper is addressing the range of validity of current approaches that undertake fitting of Fe 2p_{3/2}. While this approach has no theoretical basis, we demonstrate that accurate ratios of oxides can be extracted from the Fe 2p_{3/2} spectra alone mainly because the process is self-consistent as discussed below. It does not require determination of Fe/O ratios using both Fe 2p_{3/2} and O 1 s but relies on the uniqueness of the fitted multiplet structure, or envelope, to obtain intensities/ratios for individual oxides that make up the Fe 2p_{3/2} spectrum obtained from a mixture of oxides.

Photoelectron peaks are, generally speaking, intrinsically Lorentzian (L) (lifetime broadening) in shape but broadened by the Gaussian (G) response function of the spectrometer. The peak shape is, therefore, a convolution of the two which is a Voigt function.²¹ However, for historical reasons, as suggested by Proctor and Sherwood,²² Gauss/Lorentz product functions were used in the original work by Biesinger *et al.*, and this approach was maintained herein. Access to modern computers has made Voigt line functions accessible and is generally recommended. In this paper, for the metal component, we use an asymmetric²³ Voigt function from CASAXPS of the form LA(α , β , m), where $\alpha = 1$ and $\beta = 3.5$ modify the wings of the Lorentzian (different Lorentzian on either side of the peak) and $m = 5$ defines the width of the Gaussian contribution. It is not sufficient to use only Gaussians for peak fitting metal peaks since they do not capture the “wing” structure of the Lorentzian line shape.

For the oxide peaks, Gauss/Lorentz product line shapes were used since these are reported almost exclusively in the literature for fitting Fe 2p_{3/2}. Free fitting of the GL(30) peaks (30% Lorentzian) was used for the 2C and 3C fits. GL(30) is very common in the literature for fitting single components. GL(70) peak shapes were used for the components making up the Biesinger oxide envelopes. Their half-widths, positions, and relative intensities were either those reported by Biesinger *et al.* or modified parameters as described below. These parameters were fixed relative to the lowest multiplet component so that only the intensity of the envelope changed when optimized. This is an important step of setting up an envelope fit as otherwise too many parameters are participating in the fit and the resultant sum of the components will likely no longer reflect the reference spectra they are based upon, making the fit meaningless. Two groups of component parameters were used.

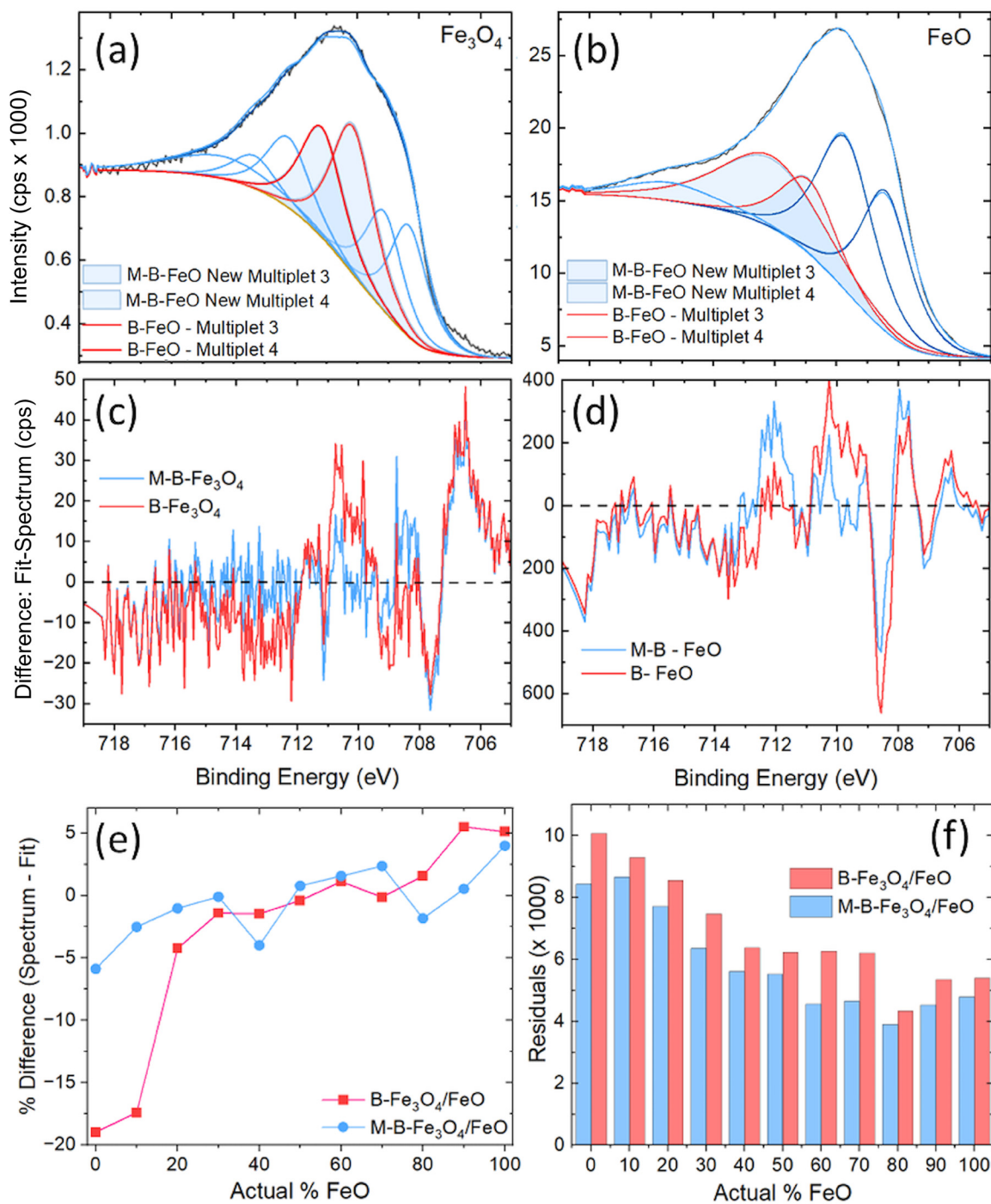
First, the original parameters were used, and in this study, all oxides were from Biesinger *et al.*¹³ apart from newly generated FeO. To achieve a higher level of agreement between fit and reference oxides, some minor modifications to the details of the original multiplets reported by Biesinger for FeO, Fe₂O₃, FeOOH, and Fe₃O₄ were required. Modifications for FeO and Fe₃O₄ are depicted in Fig. 2 with the multiplets that were changed are highlighted in red. For Fe₃O₄, the third and fourth components [first and second of Fe(III) components in Fe₃O₄ in the Biesinger paper] were allowed to vary their intensity and half width to better match the peak in the Fe₃O₄ envelope, before fixing their values for use in later envelope fitting. These modified values are reported in the supplementary material. A small underestimation of the peak using the reported Biesinger components can be seen in the residual intensities in Figs. 2(c) and 2(d), which was rectified by some minor changes to the intensities and FWHM of the third and fourth multiplet components. A similar treatment was used for third and fourth components of FeO. The rationale in this case was to better fit the higher BE side of the FeO peak. Similarly, the difference between the measured spectrum and fit is slightly improved [Fig. 2(d)]. When these modified multiplets are applied to a series of FeO/Fe₃O₄ mixed oxide spectra, there was clearly an improvement in the extraction of the actual %FeO, particularly at the low and high end of the amount of FeO in the binary mixture. Indeed, the determination of percentage of FeO below 20% FeO was improved by as much as 15% compared to using the original Biesinger values [Fig. 2(e)]. This improvement was also reflected in lower RMS values across the whole series of mixtures when comparing the new multiplet components to the original [Fig. 2(f)]. It should be noted that the process of optimizing the fitting for FeO, Fe₂O₃, and Fe₃O₄ was entirely independent from fitting the mixtures, i.e., there was no feedback to “optimize” the best fit to the oxide mixtures. It was found that as the multiplets in the envelope better approximated the real reference spectra, then the convergence to the correct solution in the mixed oxides became more robust. This indicates that optimizing the parameters of the multiplet components that combine to form the model envelope prior to application is important for obtaining reliable results.

What is often overlooked by neglecting these slight differences in the Fe 2p_{3/2} spectrum is that the fitting procedure can only converge on solutions based on the accuracy of the envelope generated by the multiplet components. If that envelope does not accurately reflect the real oxide spectrum, then the real oxide would not be available as a solution to the curvefitting. It was found that as the multiplets better approximated the real reference spectra, then the convergence to the correct solution in the mixed oxides became more robust.

III. RESULTS

Model spectra were generated comprising binary mixtures of experimental spectra from pure oxides. These spectra were then fitted based on the commonly reported chemistry fit procedures in the literature employing either two- (2C) or three-component (3C) GL(30) symmetric peaks. These were then compared to an envelope fit approach using the original and modified multiplet data of Biesinger *et al.*¹³ In the literature, the rationale for using single symmetric fits is to represent different oxidation states, so each of

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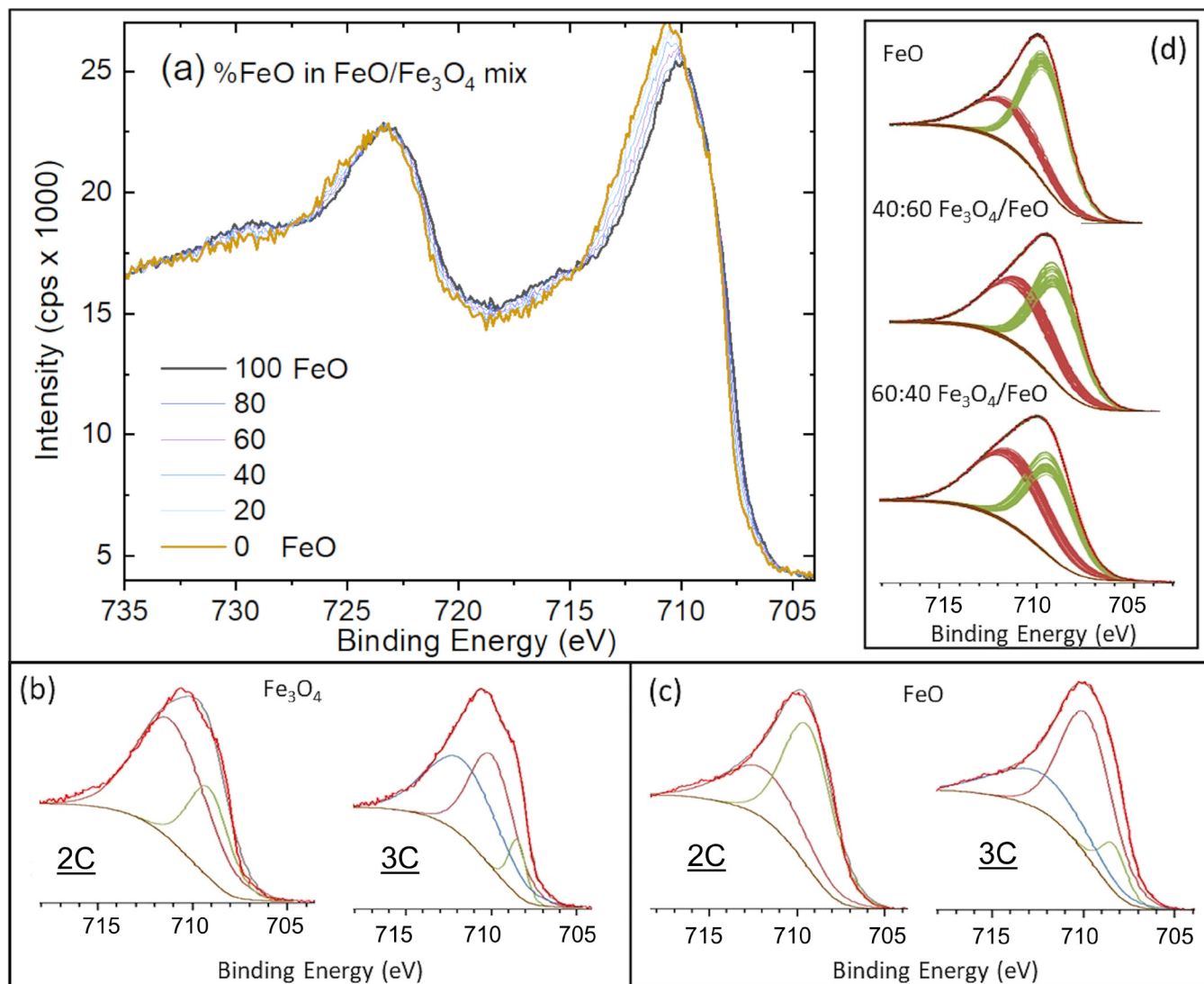
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FIG. 2. Details of modifications to the Biesinger multiplet components [GL(70)] in (a) Fe₃O₄ and (b) FeO. Here, the original components designated as "Multiplet 3 or 4" and the modified ones are designated "New" or "New Multiplet 3 or 4." Only the red highlighted components were modified. (c) Fitting residuals for Old (red) and New (blue) multiplets for Fe₃O₄. (d) Fitting residual between Old (red) and New multiplet (blue) components for FeO. (e) Composition determination for the amount of FeO comparing the Old (B-Fe₃O₄/FeO) (red) vs New (M-B-Fe₃O₄/FeO) multiplets (blue). The "% difference" is determined by subtracting the percent composition determined using fitting from the actual composition of the model spectra. (f) Root mean square values for the Old (B-Fe₃O₄/FeO) (red, right bars) and New (M-B-Fe₃O₄/FeO) (blue, left bars) multiplet components.

the peaks is assigned to either Fe(II) or Fe(III) or, alternatively, they represent different compounds such as FeO, Fe₃O₄, Fe₂O₃, or FeOOH, i.e., fitting the chemistry. As can be concluded from the multiplet structure presented in Fig. 1, a single peak will only provide a very poor reproduction of the complex envelope arising from multiplets and other effects. Two dual-mixed oxide systems were examined. The FeO/Fe₃O₄ mixture was chosen because of the overlap of the Fe(II) multiplets from both of these compounds and FeOOH/Fe₃O₄ was chosen because of the overlap of the Fe(III) components from the two compounds.

A. Comparing chemistry and envelope fitting of FeO/Fe₃O₄ oxide mixtures

The series of spectra containing the mixture of FeO and Fe₃O₄ is depicted in Fig. 3(a). The changes in the spectral envelope going from 100% FeO to 100% Fe₃O₄ are quite subtle involving a movement of maximum peak position from around 710 eV toward 712 eV. The shift is accompanied by a slight increase of intensity in the satellite regions above the main peaks, e.g., ~717 eV for Fe 2p_{3/2}.



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FIG. 3. (a) Series of model spectra constructed using mixtures of reference spectra from pure Fe₃O₄ and FeO (see legend). (b) Pure Fe₃O₄, fitted with two and three components. (c) Pure FeO fitted with two and three components. (d) Results of analyzing 2C selected fits using Monte Carlo error estimation (see the text for details).

1. Fitting spectra for pure FeO and Fe₃O₄ oxides

2C and 3C (chemistry) fits for the endpoints (either pure Fe₃O₄ or pure FeO) are presented in Figs. 3(b) and 3(c), respectively. For both FeO and Fe₃O₄, the 2C fit fails to reproduce the spectral envelope whereas the 3C fits succeeds in reproducing the envelope. Monte Carlo error analysis (available in CASAXPS) was performed for three different mixes of FeO to Fe₃O₄. This analysis looks at the convergence of the fits from 30 different starting points and is presented for FeO. Clearly, the 2C fit converges to the same fitting solution for all 30 fits for pure FeO with only minor variation of the intensity and 1/2 width for the lower BE (LBE) component [Fig. 3(d)].

2. Comparing the series of FeO/Fe₃O₄ mixed oxides

For the 60:40 and 40:60 mixes of FeO and Fe₃O₄ [Fig. 3(d)], the convergence of the 2C fit is also relatively stable but the variation in intensity of the LBE peak is higher reflecting an interplay between the LBE intensity and the HBE 1/2 width. Similar results were obtained for the 3C fit (not shown).

Figure 4 shows the amount of Fe(II) (from both FeO and Fe₃O₄) determined by fitting the model spectra depicted in Fig. 3 against the amount of Fe(II) based on the mix in the spectrum. For the 2C fit containing a low and high binding energy component (LBE and HBE respectively), the amount of Fe(II) (i.e., the full integral intensity of the LBE component) indicated by the fit actually decreases with increasing %FeO, i.e., the 2C fit goes in the opposite direction to the trendline composition. Since there are only two components, the Fe(III) component makes up the remainder of the percentage and does not follow the trendline composition. With the 3C fit, the middle component [MBE at ~710.0 eV in Fig. 4(b)] makes up most of what could be considered Fe(II) and increases over the range from 0% to 100% FeO, but quantitatively is an extremely poor match with the actual composition. Adding the LBE component increases the absolute amount of Fe(II) determined using the 3C fit but does not change the trend. With respect to BE positions [Fig. 4(b)], both 2C and 3C remain relatively constant over most of the compositional range. For the 2C fits, the BEs show a small increase of 0.5 eV over the compositional range. For the 3C fit, the HBE component drifts to higher BE, the middle binding energy component (MBE) stays relatively constant. The LBE component remains around 708.5 eV which is close to the BE of the lowest multiplet components in both FeO and Fe₃O₄.

The Biesinger envelope fits [Fe(II) Biesinger] are also shown in Fig. 4(a) and accurately reproduce the amount of Fe(II) in the oxide mix. Also shown are results achieved using a M-Biesinger fit [Fe(II)-M-Biesinger]. At 0% FeO, there is 33.3% Fe(II) from Fe₃O₄, and at the other extreme of 100% FeO, there is 100% Fe(II). The percentage of FeO calculated below 20% FeO was improved by as much as 15% with Fe(II) M-Biesinger compared to using the original Biesinger values [Fig. 4(a)]. This improvement is likely due to more pure FeO spectrum being obtained in this work due to improved FeO sample preparation with gas cluster ion beam sputtering, which was not available at the time of the original work. This improvement was reflected in lower RMS values when using the M-Biesinger components compared to the original ones. This result indicates that optimizing multiplet components for model compounds is important for obtaining reliable results. Ideally, the

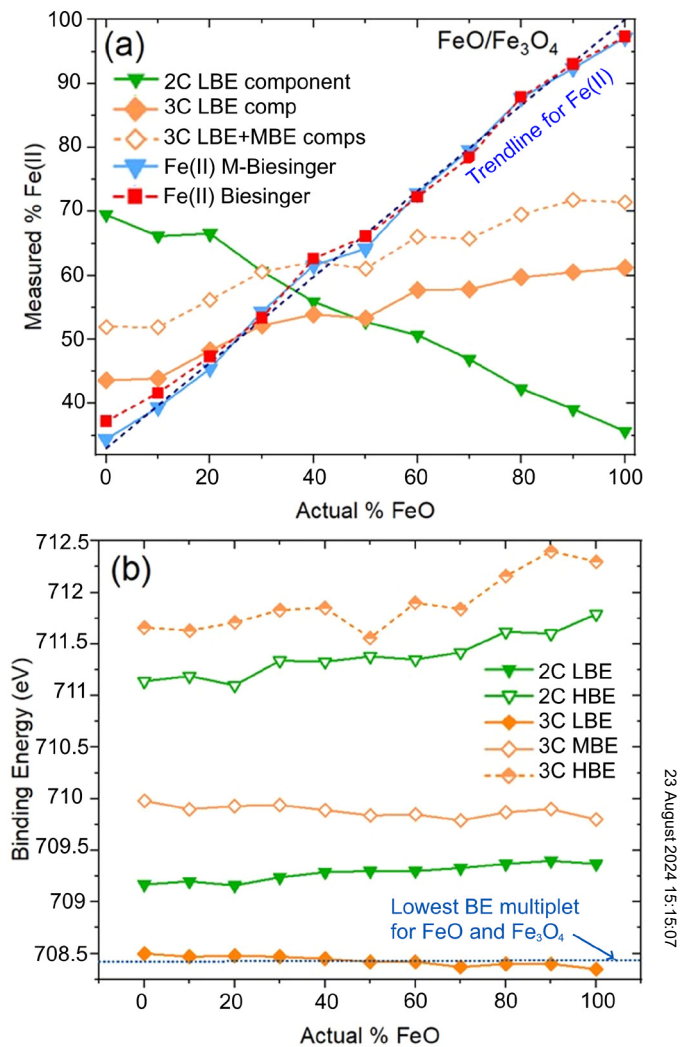


FIG. 4. Summary of (a) percent of Fe(II) for 2C, 3C, and individual components in fits to spectra with mixes of Fe₃O₄ and FeO. (b) Binding energy position of 2C and 3C peaks in fits to the mixtures in (a). Fe(II) Biesinger and Fe(II) M-Biesinger represent the original and modified Biesinger envelopes and only the sum of the two components for either FeO and Fe₃O₄. In the 2C and 3C cases, they are the lower BE component [fitted using GL(30)]. The trendline goes from 33.3% Fe(II) in Fe₃O₄ (0% FeO) to 100% Fe(II) in FeO.

model spectra should be collected on the same instrument as the sample spectra which require analysis. It also highlights the importance of reducing the fit RMS by optimizing the component parameters of the envelope fit prior to constraining these components; this can include using alternative line shapes.

B. Comparing chemistry and envelope fitting of Fe₃O₄/FeOOH oxide mixtures

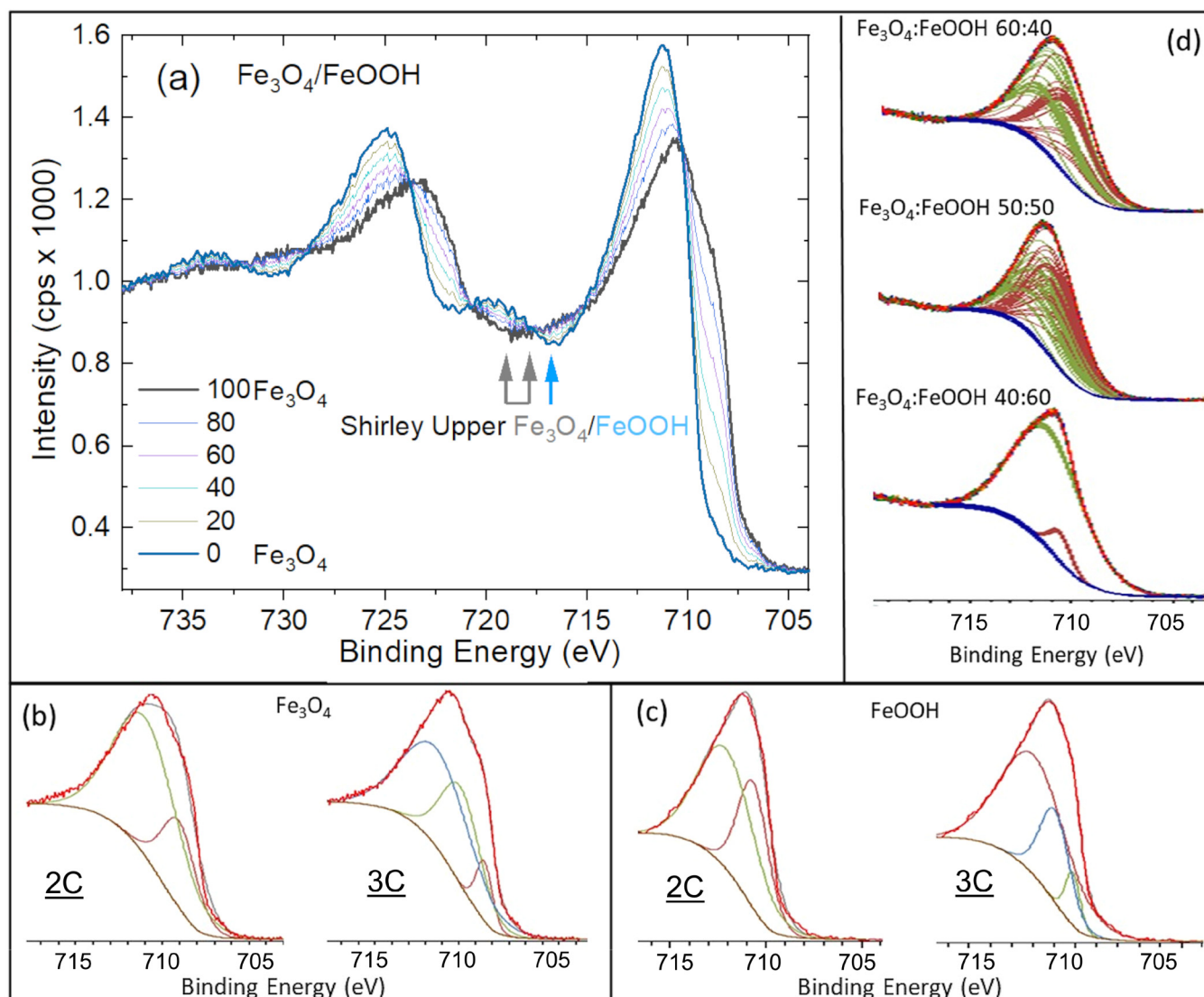
Compared to the oxide mix in Sec. III A that included a Fe(II) compound (i.e., FeO) mixed with Fe₃O₄ which is Fe(II,III), this

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combination of oxides/oxyhydroxides replaces the Fe(II) compound with Fe(III) (i.e., FeOOH), shifting the overlapping contributions to higher BE where other intensity such as satellites contribute to the spectra. The series of spectra containing the mixture of FeOOH and Fe₃O₄ is depicted in Fig. 5.

A further observation on the problematic data processing reported in the literature concerns the strong satellite structure in Fe(III): the lowest intensity between the main Fe 2p_{3/2} and 2p_{1/2} peaks tends to be nominated as an endpoint for a Shirley background; this is, of course, is quite arbitrary. The intensity at this

position is modified when there are high levels of Fe (II) resulting in an apparent flat region between the 2p_{3/2} and 2p_{1/2} peaks and the endpoint for a Shirley background is more likely to be placed at higher BE. In analyzing a series of spectra, such a shift of background will lead to inconsistencies in data processing because moving the endpoint of the Shirley background will lead to incorporation of additional intensity due to the larger processing region as noted in the literature.²⁴ The positioning of the high end of the Shirley background is not such an issue with mixes of Fe₃O₄ and FeO due to less satellite structures.



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FIG. 5. (a) Series of model spectra constructed with mixtures of spectra from pure Fe₃O₄ and FeOOH (see the legend). (b) Pure Fe₃O₄, fitted with two and three components. (c) Pure FeOOH fitted with two and three components. (d) Results of analyzing selected fits using Monte Carlo error estimation (see the text for details).

1. Fitting spectra for pure Fe_3O_4 and FeOOH

Figures 5(a) and 5(c) depict 2C and 3C (chemistry) fits to two endpoint spectra for pure Fe_3O_4 and FeOOH . For a novice using the chemistry approach to fitting these spectra, these components could represent either a mixture of Fe(II)/Fe(III) states or a mixture of the individual oxides/hydroxides. For the spectrum of pure Fe_3O_4 , the 2C fit is poor and similar to that in Fig. 3. The 3C fit has little physical meaning because there is no third oxidation state in Fe_3O_4 [only Fe(II) and Fe(III)], but it looks better because the envelope is a closer match to the model data with a lower residual RMS value. The third peak ends up filling in the mismatch between the fitting envelope and the actual spectrum and can move around considerably in an unconstrained fit. Note: it has converged to a different result from that in Fig. 3, highlighting the instability of the 3C fit. Based on this result, the following conclusions could erroneously be drawn: in the 2C fit there is a mixture of Fe_3O_4 and FeOOH due to excess Fe(III) or in the 3C fit there is a mixture of Fe_3O_4 , Fe_2O_3 , and FeOOH , both of which are clearly wrong. Similar misinterpretations can be made in the case for pure FeOOH . For the 2C fit, there is a Fe(II) component accounting for 35% of the total peak area, suggesting 100% Fe_3O_4 which is completely wrong. In the 3C fit, one might conclude that FeO was present in addition to Fe_3O_4 but only if a very narrow FWHM of the LBE peak was accepted. Thus, in this latter case, a novice might miss the identification of FeOOH altogether.

2. Comparing the series of mixed Fe_3O_4 and FeOOH oxide/oxyhydroxides

Based on conclusions of using 2C and 3C for fitting the endpoint (pure) spectra, it can be expected that fitting mixed spectra will also have problems. The data across the range of oxide mixes is presented as % FeOOH in Fig. 6(a). The trend should be linearly increasing in going from zero FeOOH to 100% FeOOH ; however, the 2C fits do not show a linear behavior. The reason for this is similar to the explanation of the endpoint spectra (under/over estimation of states due to poor matching of the fit to the data) and instability of the fit as discussed in the next paragraph.

The instability of the fit is shown in three examples of spectra with different oxide ratios [Fig. 5(d)]. Here, 30 unconstrained 3C fits to each combination are displayed for the 60:40 and 50:50 mixes of Fe_3O_4 : FeOOH . The fits converge to a range of different outcomes indicating that the fitting is unstable, i.e., *there is no unique solution*. It can help to visualize the fitting in the following way: the optimization tries to find the minimum of the residuals on an optimization surface. For two variables (e.g., only the peak positions of two components), the surface has two dimensions, and the Z axis represents the residuals. In the case of the 60:40 and 50:50 mixes of Fe_3O_4 : FeOOH , there are many different solutions (i.e., *the optimization surface is undulating with many different minima*) and using different starting points results in convergence to different minima. This means there is no unique solution for fitting three single symmetric components to the data. On the other hand, the 40:60 mix of Fe_3O_4 : FeOOH seems to be stable (has a deep minimum on the optimization surface) since all starting positions converge to the one solution. However, it is clearly the wrong solution. The optimization ends up finding a solution where the intensity of one component approaches

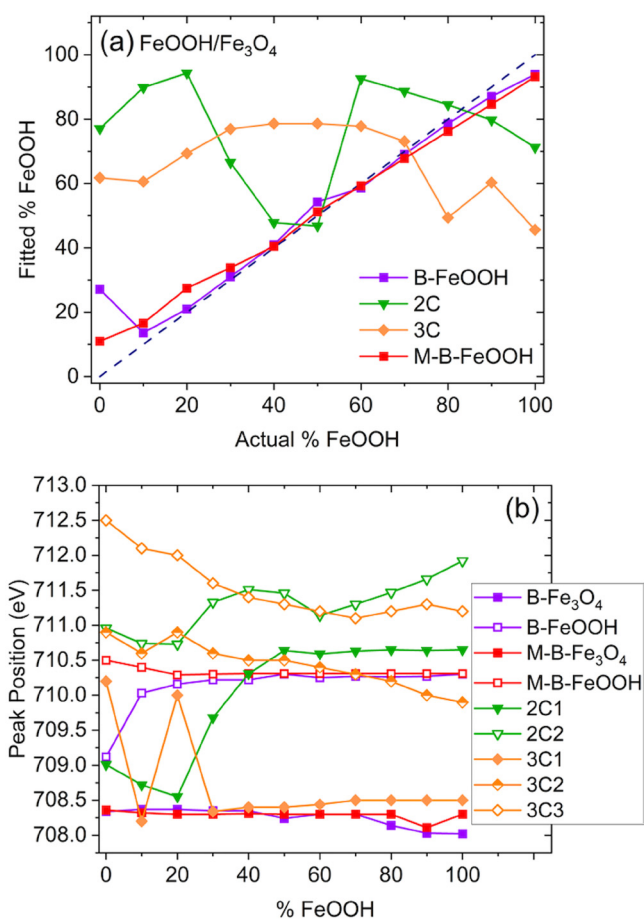


FIG. 6. Summary of (a) % FeOOH and (b) binding energy position of individual components in a two-component fit to synthetic spectra made of mixtures of Fe_3O_4 and FeOOH . In the Biesinger case, both the original (B- FeOOH) and modified (M-B- FeOOH) multiplet components are presented and were used for both FeOOH and Fe_3O_4 . In the 2C and 3C cases, GL(30) components were used.

zero, a second, excessively wide, component covers most of the peak area, and a third component fills in the gap that the second component does not cover (i.e., effectively reverts to a 2C fit). Thus, Fig. 5 clearly demonstrates the flaws in using a small number of symmetric peaks as a chemistry fit to a $\text{Fe } 2p_{3/2}$ envelope comprising two oxide/oxyhydroxide components.

Figure 6 reinforces the conclusion stated above regarding the use of a small number of components when attempting a chemistry fit for $\text{Fe } 2p_{3/2}$. The data are presented in terms of the % FeOOH , and % Fe_3O_4 makes up the rest of the composition. It can be seen that the estimated % FeOOH from the 2C and 3C fits has no correspondence to the actual amount of FeOOH used to construct the model spectra, i.e., simplistic fits should not be used for analyzing these mixtures of oxide and oxyhydroxide. Conversely, the Biesinger envelope fit approach (B- FeOOH) accurately reproduces the linear trend in Fig. 6 except for some deviation at low % FeOOH . It is in this region that

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the importance of the Modified Biesinger components (M-B-FeOOH and M-B-Fe₃O₄) is demonstrated, with an improved fit at low % FeOOH. Elsewhere, there is little difference between the two different Biesinger fits.

The positions of the components are an important consideration since it has the potential to influence the final assignment. For example, Fig. 6(b) depicts the BE positions of the 2C fit covering the range of zero to 100% FeOOH. The lower BE component [labeled Fe(II)] starts at 709.0 eV and stays at this value up to 20% FeOOH. It then shifts higher to 710.6 eV at 50% FeOOH and above. The value at 709.0 eV is slightly low for Fe(II) and the value of 710.6 eV is closer to Fe(III). In the case of the HBE component [labeled Fe(III)], it varies by as much as 1.3 eV from 710.7 to 712.0 eV. This suggests that above about 30% FeOOH, it becomes very difficult to extract any intensity associated with Fe(II), indicating that information about Fe₃O₄ is effectively lost, i.e., only two Fe(III) compounds would be identified using this approach. In this case, perhaps a correct assignment of FeOOH might be made, but the percentage would clearly be wrong because between 10% and 30% of the intensity of the Fe 2p_{3/2} peak should be Fe(II) according to the mixture of Fe₃O₄ and FeOOH.

In contrast to the above, using the Biesinger envelope fit results in a stable optimization process. The binding energies are well behaved across most of the mix ratio except at the 10% level for each component. There are obvious problems fitting spectra that have a low fraction of either FeOOH or Fe₃O₄ because finding the BE position of components with very low intensity is a difficult challenge for the optimization algorithm; this results in significant deviation of the BEs determined in these cases.

C. Fitting spectra with a mixture of metal plus oxides and oxyhydroxides

Thus far, we have examined only mixtures of oxides and/or oxyhydroxides. However, in the case, when intensity from an iron metal contributes to the spectrum, for example, passive layers on a metal surface, an Fe(0) peak will be present in the Fe 2p_{3/2} spectrum as depicted in Fig. 7 for 10% Fe(0) plus a mixture of FeO and Fe₃O₄. The spectra show most changes in the depth of the valley at ~708 eV which decreases as the amount of FeO increases, and the increase in the height of the broad peak between 710 and 714 eV as the amount of FeO increases. These very subtle changes occur because *both* FeO and Fe₃O₄ have multiplet components for Fe(II) which are close to the metal component.

1. Fitting pure FeO and Fe₃O₄ with metal present

Figures 7(b) and 7(c) show metal +2C and metal +3C fits to the 10.1% metal plus either pure Fe₃O₄ and FeO endpoints. Note that in these, cases 2C and 3C denote the number of fit components used for the oxyhydroxide portion of the spectrum, in addition to one asymmetric [LA(1,3,5,5)] component for the Fe(0) peak. For metal with pure FeO, the 2C fit converges to a component between 709 and 710 eV and the other above 712 eV as well as the metal. The Monte Carlo error analysis for this fit [Fig. 7(d)] shows that the position and intensity of the HBE peak is relatively stable, but that of the LBE peak has variation in both BE position and intensity. In the case of the 3C fit to metal plus pure FeO, the third component tends to “accommodate” the broadness of the LBE peak by converging to

position between these peaks, thus creating two peaks where only one was present in the 2C fit. For the metal plus pure Fe₃O₄, the loss of the FeO satellite peak at approximately 715 eV and the sharpening of the envelope at 711 eV leads to a broad HBE peak at BEs slightly below the 711 peak and a small LBE peak just above the metal peak. The addition of a third component in the 3C fit simply results in a peak that sits at a position between the two peaks observed for the 2C fit and effectively reduces the FWHM of the HBE peak. Oddly, both 3C fits converge to a similar result despite the fact that quite different oxides are present indicating its insensitivity to composition. Overall, it can be seen that these fitting results are clearly incorrect. This is largely due to significant Fe(II) intensity at higher BE in the FeO case and the presence of Fe(II) multiplets in the Fe₃O₄ case.

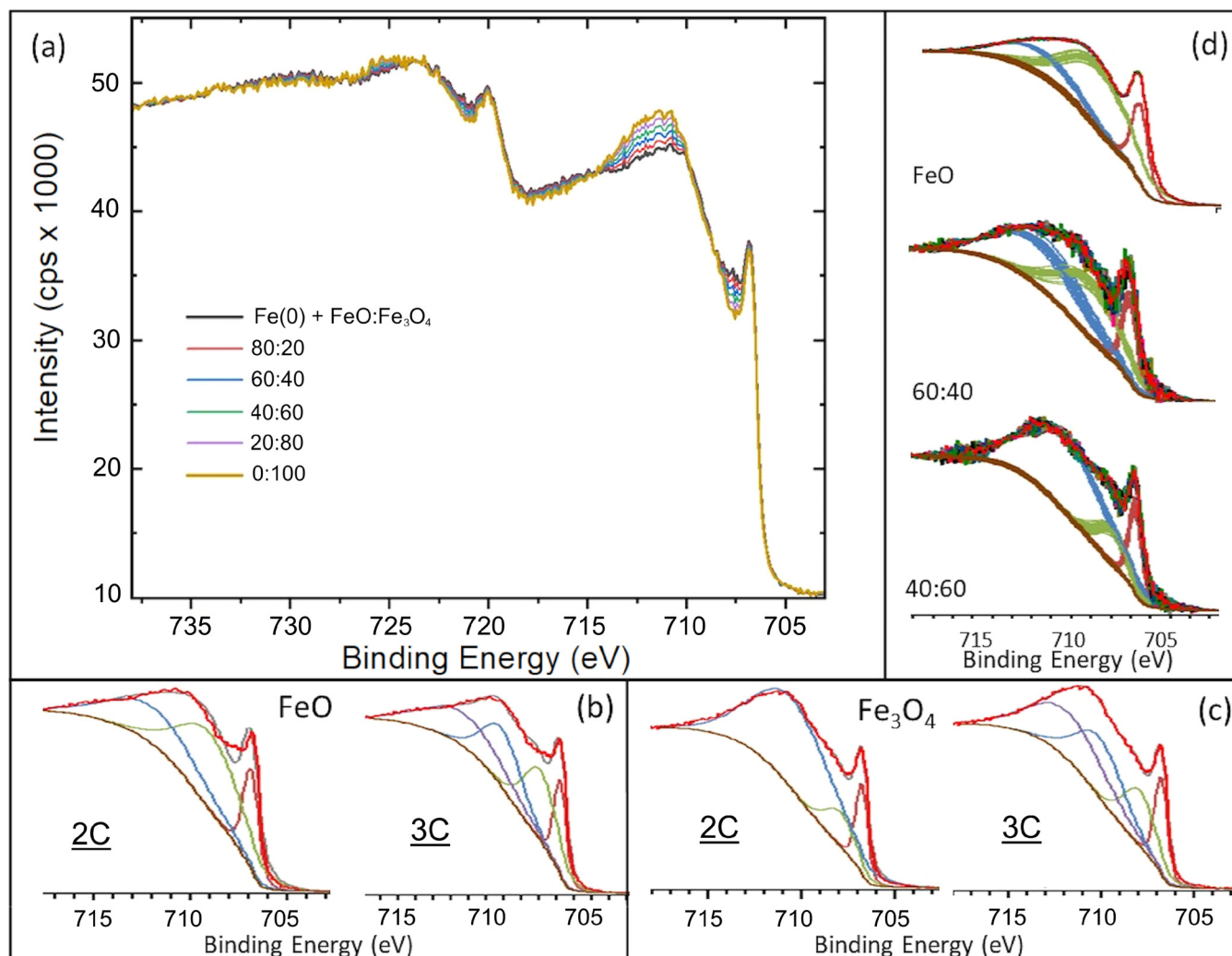
2. Comparing the series of mixed FeO and Fe₃O₄ with metal present

Figure 7(d) also shows the Monte Carlo analysis of spectra for 60:40 or 40:60 mixes for FeO:Fe₃O₄ when using 2C plus the metal. Fitting with 2C (shown) and 3C (not shown) symmetric peak shapes shows moderately stable outcomes, but with some variation in BE position and intensity particularly with the LBE oxide component. Continuing with the theme observed above, these chemistry fits converge to the wrong solution.

The imprecision of these fits is shown in Fig. 8 where the amount of FeO and Fe(II) is seriously underestimated across the whole compositional range. In the case of both the metal +2C and 3C fits, no consistent variation in composition is detected at all except at 100% FeOOH. This means fitting of each different composition produces an outcome with significant relative error. This is clearly shown in Figs. 8(a) and 8(b) where there is little sensitivity to the amount of FeO in the oxide mix from 0% to 100% FeO.

On the other hand, the modified Biesinger envelope fit (M-B-FeO) accurately reproduces the increase in the amount of FeO and also Fe(II) [combined Fe(II) components from FeO and Fe₃O₄]. However, using the original Biesinger components (B-FeO) resulted in considerable underestimation of the amount of FeO. Specifically, for Fig. 8(a), starting at 0% FeO (100% Fe₃O₄), the amount of FeO diverges immediately from the expected trend, and at 100% FeO, the fit suggests only roughly 65% FeO. This result is interesting, because there was little difference between the M-Biesinger and Biesinger fits for the mixed FeO/Fe₃O₄ mix without any metal, but there is considerable difference when metal is present. This is because the metal component contributes intensity in the region around 708.5 eV (lowest multiplet component for both FeO and Fe₃O₄), which prevents the fit converging to the correct result when the components that form the envelope are not optimized prior to utilization (i.e., for the instrument and data collected on reference oxides). This result indicates that even the Biesinger approach must be used with caution when there is Fe(0) and a sizeable amount of Fe(II) present in the sample. As new FeO data were used here, these results suggest that high accuracy from peak fitting can only be obtained by ensuring that the Biesinger envelope accurately reproduces the reference oxide. This will likely be influenced by differences between reference samples obtained from different sources and subjected to different preparation methods, instrumentation including collection parameters, and differences in the approach to fitting employed by each user.

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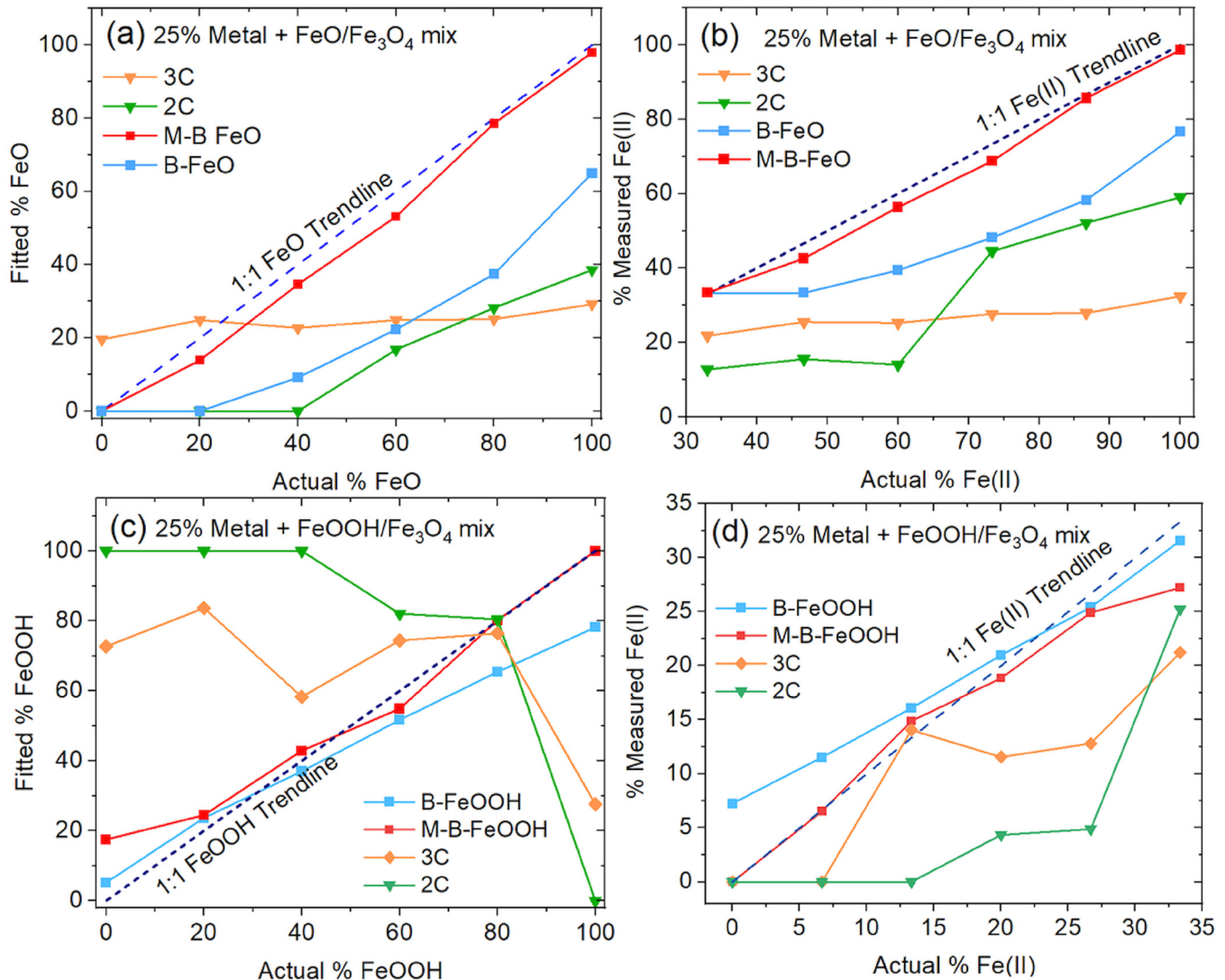
FIG. 7. Fe metal plus mixtures of FeO and Fe₃O₄. (a) shows a series of spectra with 10.1% Fe metal and mixes of FeO and Fe₃O₄. (b) Two- and three-component fits [GL(30)] to 100% FeO plus an additional peak for the Fe metal [LA(1,3,5,5)—an asymmetric Voigt line shape from CASA XPS]. (c) Two- and three-component fits to 100% Fe₃O₄ spectrum plus an additional peak for the Fe metal. (d) Monte Carlo error analysis for selected mixtures FeO and Fe₃O₄.

Another example of mixtures of metal plus oxides and oxyhydroxides is presented in the [supplementary material](#) for Fe₃O₄ and FeOOH, with the outcome for the percentages of the oxides being presented in Fig. 8(c) and the amount of Fe(II) shown in Fig. 8(d). Only the data for FeOOH are presented, but, as before, the %Fe₃O₄ is 100%FeOOH. For both metal +2C and metal +3C fits, the estimated percent of FeOOH is grossly overestimated from 0% to 80%. The percent measured Fe(II) is also poorly estimated [Fig. 8(d)]. For pure Fe₃O₄ [33% Fe(II)], both metal +2C and metal +3C fits yield between 20% and 25% for Fe(II) which is close to the value of 33% for pure Fe₃O₄. However, for the mixtures, the 2C fit grossly underestimates the amount of Fe(II) and the 3C is slightly better, but clearly unreliable. In the scenario, where the researcher is uncertain how much FeOOH is present and adds a third peak to

represent FeOOH, the fitting will clearly converge to a stable but incorrect result. On the other hand, the B-FeOOH and M-B-FeOOH reproduce the correlation with the trendline and, by inference, the Fe₃O₄ fit is also good. Using the modified Biesinger envelopes shows an overall improvement across the whole range with a slightly worse match when there was no Fe₃O₄ present.

3. Using an envelope fit for mixtures of FeO and Fe₃O₄ with different amounts of metal

A range of metal contributions to FeO/Fe₃O₄ mixtures was examined to further explore an earlier observation in Sec. III C 2 that even the envelope approach must be used with caution when there is Fe(0) and a sizeable amount of Fe(II) present in the sample.



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FIG. 8. (a) Percentage of FeO determined for 2C and 3C fits using GL(30) product functions as well as Biesinger fits for Fe metal (25%) plus mixed FeO/Fe₃O₄ mixes (75%). (b) Percentage of Fe(II) for 2C and 3C using GL(30) product functions as well as Biesinger fits to Fe metal (25%) plus mixed FeOOH/Fe₃O₄ mixes (75%). (c) Percentage of FeOOH determined using 2C, 3C, and Biesinger fits to FeO/Fe₃O₄ mixes plus 25% Fe metal. (d) Percentage of Fe(II) determined using 2C, 3C, and Biesinger fits to FeO/Fe₃O₄ mixes plus 25% Fe metal. Dashed lines in (c) and (d) are trendlines for the percentage FeOOH and amount of Fe(II), respectively. Note the bias for percentage of Fe(II) in the FeOOH/Fe₃O₄ case is only for Fe(II) in Fe₃O₄. Metal peaks were fitted with asymmetric peak shapes in (a) and (b) [LA(1,3,5,5)] and oxide envelopes were constructed using GL(70) peak shapes for their component.

Figure 9 shows the %FeO determined from fitting versus the actual %FeO for a range of different metal contents, in the case of FeO and Fe₃O₄ mixtures with metal including 0%, 3%, 10.1%, and 25% metal. The general trend is that envelope fits tend to underestimate the amount of FeO. This is minimal for 3% and 10% metal with the estimated composition being within 5% of the actual composition, but increases to as much as 15% over most of the compositional range for FeO with 25% metal, indicating that the higher the metal peak intensity in the spectrum,

the poorer the estimation of FeO is likely to be (and, consequently, that of Fe₃O₄).

IV. DISCUSSION AND RECOMMENDATIONS

The variable quality of the treatment of XPS data in published papers means the reported compositions of the outer layer Fe-oxides, based on these analyses, should be treated with skepticism. Moreover, since poor methodology is frequently being

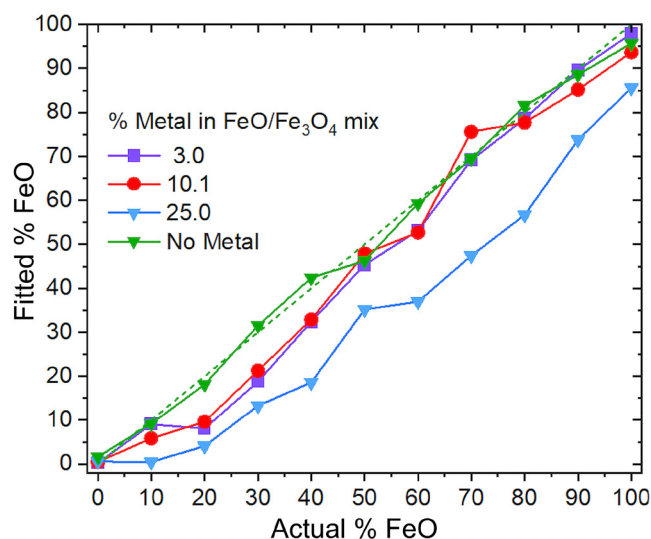


FIG. 9. Fitted percentage of FeO vs the actual percentage using M-Biesinger envelopes for FeO and Fe₃O₄ including four different amounts of Fe metal. Green dashed line indicates a 1:1 correspondence.

reported in papers that have been published in peer-reviewed, high-impact journals, those erroneous approaches are being used by other researchers, thus propagating these approaches in the literature. Fortunately, this is beginning to be understood more generally by individual researchers and scientific bodies and action is being taken,^{4,25} though the impact this is having on the intended audience is yet to be seen.

With respect to surface oxide composition of iron reported in the literature, it can generally be concluded that compositions based on single component chemistry fits for speciation [e.g., Fe(II) and Fe(III)] or used to specifically define individual compounds should not be relied upon because peak assignment and particularly peak areas (used to calculate composition) are likely incorrect. This conclusion extends to Fe(II) and Fe(III) extracted from depth profiles. A further problem is that reduction of oxides may occur through preferential etching of O atoms or hydroxyl groups since some oxides are known to be reducible under a high energy ion beam.²⁶ This effect for those reducible oxides is only partly solved with developments such as low energy Ar⁺ gas cluster ion sources.

If we acknowledge that there is a desire of those publishing these works to correctly fit Fe 2p_{3/2} spectra, then clearly a practical strategy is needed. Let us begin by reviewing the main approaches to analysis of Fe 2p which is summarized in Table II. Within the first column are the approaches where all theoretically known contributions to the Fe 2p intensity at any point in a spectrum are determined. As the work by Bagus *et al.* and others have shown, a full theoretical treatment of iron oxides would require the use and optimization of hundreds to thousands of components and a strategy has not yet been developed to deal with this issue, although grouping components is an obvious way to proceed. These would need to be combined with a known background and other

contributions to signal intensity such satellites, plasmon losses, and instrument contributions to the spectrum such as the instrument response function. Full *ab initio* calculations are machine time expensive and not currently feasible for routine analysis.

In the absence of such a protocol, a well-defined approach to deal with the numbers of multiplet components present in Fe 2p is the next best option. A semiempirical treatment of the multiplets using an envelope fit, such as that developed by Biesinger *et al.*,¹³ is the next best option available and a flow chart for its implementation is depicted in Fig. 10. In such a treatment, a limited number of components are used to reproduce the spectral envelope. We have shown this approach can reproduce iron oxide compositions within 5% of their actual composition. In light of the abysmal performance of the popular 2C and 3C protocols, the Biesinger approach is a practical semiempirical method that can be utilized until such time a full theoretical treatment is available.

This approach has evolved from using the theoretical calculations for some oxides and was subsequently extended to other compounds for which there are no calculations.^{13,14} The primary objective is to achieve a practical outcome, e.g., determination of composition using only envelopes fitted to the Fe 2p_{3/2} peak. This can be achieved in two ways. The work presented here is based on the relative fraction of oxides (or other compounds) using envelope fitting, originally based multiplet structure, as applied only to the Fe 2p_{3/2} peak. This works because each compound has a different and unique envelope. A second approach is to determine composition based on integral intensities from Fe 2p_{3/2} and O 1s; this approach requires the use of relative sensitivity factors (RSFs). In the broadest case, the envelopes need to be determined for individual compounds and the RSFs may also be different for different compounds because the ratio of area above the background to below may not be the same for all compounds. Finally, there is the simple empirical approach, such as the 2C and 3C methods, which are attempts at a chemistry fit using simple symmetric (or asymmetric) peak profiles. The pitfalls of this last approach have been demonstrated above.

The schema first addresses details of instrument calibration and sample reference energies. Next are the considerations of background subtraction. The choice of nonlinear backgrounds and where to set the limits for background calculation represent a more complex situation. The endpoints of the background should be set at a position that represents the average of the noise on either side of the peak. Generally, a Shirley background, used with the appropriate peak models and RSFs, is a viable methodology for fitting Fe 2p_{3/2} peaks, but other nonlinear backgrounds can be used with different RSF factors. Next is the choice of peak fit components, their shape and position. The ideal approach would use a wide binding energy range for analysis to capture all the multiplet and satellite structures from the 2p_{3/2} peak. This would probably mean that analysis of the Fe 2p_{1/2} peak would need to be included as well.

The current approach of fitting “empirical” multiplets as developed by Biesinger and others is the best method available and only focuses on the Fe2p_{3/2} part of the Fe 2p spectrum. The objective is to reproduce the envelope of reference compounds using multiple peaks and then use these series of components to fit unknown spectra. If the multiplet data for a particular compound is not available from a reliable source in published form, then reference spectra will need to be fitted to generate a set of multiplets. As

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TABLE II. Summary and comparison of three different approaches to analyzing Fe 2p/Fe2p_{3/2} spectra.

Attribute	Theoretical	Semiempirical (e.g., Biesinger approach)	Empirical (e.g., two- and three-component approaches)
Basis	Gupta/Sen: Hartree–Fock free-ion method Fujii: Hartree–Fock–Slater including ligands Bagus: Full <i>ab initio</i> wavefunctions. Includes ligand field and spin–orbit splittings, the covalent mixing of ligand and Fe 3d orbitals, and the angular momentum coupling of the open shell electrons	Originally based on Gupta and Sen multiplet structures calculated for free ions Fe ³⁺ and Fe ²⁺ , but includes satellite components. Has evolved to fitting multiple peaks to other compounds to emulate multiplet structure	No theoretical basis. In its most primitive form may include single symmetric peaks for individual compounds or oxidation states
Effects	Identify many contributions to the structure of Fe 2p	Largely confined to multiplets	No real relation to spectroscopic contributions
Application	Gupta/Sen: Ions Fujii: α -Fe ₂ O ₃ , γ -Fe ₂ O ₃ , Fe _{3–x} O ₄ , and Fe ₃ O ₄ Bagus: FeO and Fe ₂ O ₃	Grosvenor: α -Fe ₂ O ₃ , γ -Fe ₂ O ₃ , α -FeOOH, γ -FeOOH, FeBr ₃ , FeCl ₃ , FeF ₃ , Fe ₃ O ₄ , FeBr ₂ , FeCl ₂ , FeF ₂ , FeSO ₄ , Fe _{1–x} O, and K ₄ Fe(CN) ₆ Biesinger: FeO, α -Fe ₂ O ₃ , γ -Fe ₂ O ₃ , α -FeOOH, γ -FeOOH, Fe ₃ O ₄ , FeCO ₃ , and NiFe ₂ O ₄	Any compound or mix of compounds or states. Single symmetric peaks a poor representation
Peak shapes	Gupta/Sen: no fitting Fujii: no fitting Bagus: Voigt	Grosvenor: not defined Biesinger: GL(x)	Predominantly some form of GL usually a product function. Voigt also used
Background	Fujii: Shirley Bagus: Shirley various including full Fe 2p as well as Fe 2p _{3/2} Tougaard	Shirley for Grosvenor and Biesinger only Fe 2p _{3/2}	Usually Shirley and confined to Fe 2p _{3/2}
Fitting convergence	Should be a unique solution	Not clear that optimization produces a unique solution, may only converge on a local minimum on the optimization surface	Optimization may converge but produces a solution that has no relation to the underlying chemistry and physics
Outcomes	Potentially reproduce full spectra but only for compounds where calculations have been performed	Can potentially reproduce compounds mentioned above	Generally poor reproduction of underlying chemistry or even oxidation states
Drawbacks	Limited application. Compounds examined probably need to be as close as possible to the QM modeled compounds described above Probably not good where substitution causes changes in the crystal/ligand field	Difficult to transfer “experimental” components of multiplets to other compounds All other compounds will have unique multiplets and satellite structures and position, e.g., peak shape of Fe(III) oxide (Fe ₂ O ₃) will be very different from Fe(III) sulfate, or nitrate or phosphate (i.e., each species has a unique peak shape and position)	Complete lack of any relationship of fitted components to physical and chemical processes

always, quality control on the purity of the compound will be necessary. Ideally, obtaining other evidence for a particular species from other techniques will facilitate the choice of envelope to fit (see the [supplementary material](#)). The data presented here indicates that it is important for the envelope of the “multiplet” structure to accurately reproduce the experimental profile for the reference compound. The recent work of Bagus *et al.*⁸ suggests that asymmetric peak shapes are necessary since the individual “multiplet” components used in the work of Grosvenor *et al.*¹⁴ and Biesinger *et al.*¹³ are themselves probably made of a high number of theoretical multiplet peaks. Semiempirical approaches like the Biesinger approach which does have its limitations and, as we have shown

herein, will not work in every scenario. It can produce poor results in instances where multiple iron oxides and iron metal are all present simultaneously. It is particularly sensitive in cases where there are compounds with a significant contribution from Fe(II) close to a pronounced metal peak. In the case of the passive layer, these are Fe₃O₄ and FeO. The maximum proportion of metal studied here was 25% and the modified Biesinger “multiplet” components coped reasonably well with this amount of metal in the spectrum. Reviewers and editors should recommend authors produce results from Monte Carlo simulations to determine if the fit is unique as shown, for example, in [Figs. 3](#) and [7](#). A straightforward implementation of this has been developed in

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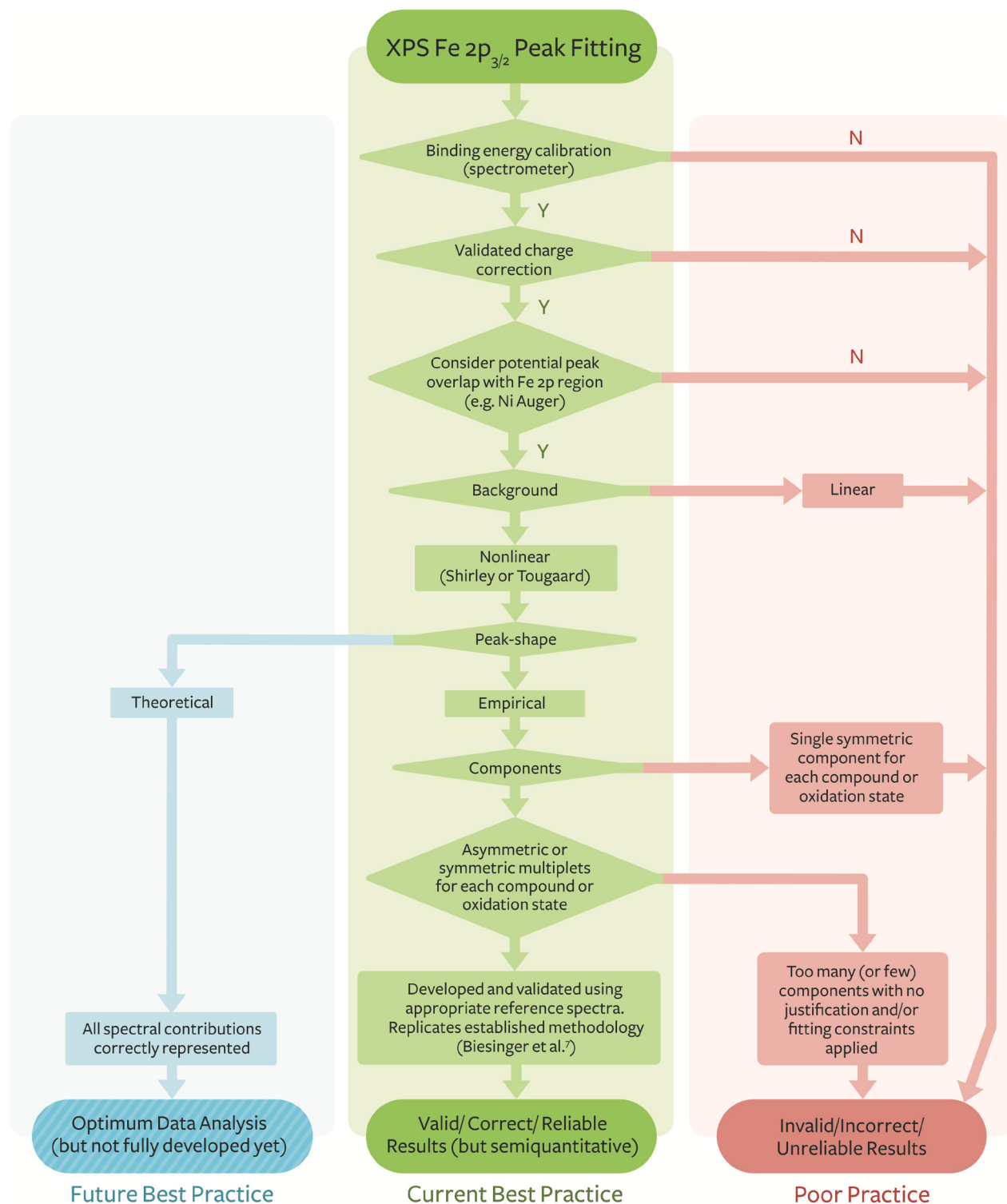


FIG. 10. Schema for generating reproducible fits to the Fe 2p_{3/2} region.

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CASA XPS, specifically the “Test Peak Model” button on the “Components” tab of the “Quantification Parameters” window.

Finally, attempting chemistry fitting using simplistic protocols such as individual symmetric components for either Fe(II) or Fe(III) species or using single components to fit individual compounds leads to erroneous outcomes. This is primarily because the multiplets for oxides and oxyhydroxides are spread out over a binding energy range covering the whole Fe 2p_{3/2} binding energy region (and beyond) and cannot be represented by a single symmetric peak. In the literature, there seems to be an attitude that presenting some fitting data are better than nothing. However, it is misleading and should be considered worse than presenting only the experimental data; in the latter case, no incorrect analysis is presented.

Summary of results and recommendations:

- Chemistry fits employing single components to represent iron oxidation states [i.e., Fe(II)] or iron oxides (i.e., FeO) should not be used as the results will likely be incorrect.
- The current best practice for fitting Fe 2p_{3/2} data follows semiempirical methodologies such as an envelope fit by Biesinger *et al.*¹³ and should be followed.
- Reviewers and editors should follow the schema in Fig. 10 to evaluate papers containing Fe 2p_{3/2} data.
- Authors attempting to judge the quality of data handling of Fe 2p_{3/2} in papers, or wanting to confirm their approach is satisfactory, can use the schema in Fig. 10 to facilitate this process.
- For complex Fe 2p_{3/2} fitting, it is recommended that Monte Carlo simulations be performed and presented to confirm that optimized fits are unique.
- Envelope fitting also breaks down in complex systems where even the current best practice does not yield reliable results.
- It is clear that researchers should not rely on analysis performed in general science or materials specific journals to guide their learning on peak fitting complex XP spectra. The authors recommend greater collaboration with experts in the field of XPS to ensure that analysts are adequately trained and supervised.

V. CONCLUSIONS

In this paper, we demonstrate that commonly used chemistry fit approaches for the analysis of the Fe 2p_{3/2} peak as published in the literature are too simplistic. The use of two or three symmetric components to fit Fe 2p_{3/2} spectra is likely to lead to incorrect interpretation of the species present in the spectrum. This is because the real structure of the Fe 2p lines is a complex mixture of many multiplet and satellite components. Unfortunately, this approach is utilized in the vast majority of publications reporting fitted Fe 2p_{3/2} data.

The extensive use of 2C or 3C fitting of Fe 2p_{3/2} data in the literature indicates a lack of awareness of the level of misinterpretation introduced by this approach to curve fitting. Accordingly, the authors report a protocol that can be used by authors, reviewers, and journal editors to assess the correctness of XPS in submitted papers. The protocol clearly describes what steps need to be taken

to correctly fit Fe 2p_{3/2} data using an envelope fit approach. The paper also clearly outlines in which cases fitting of the Fe 2p_{3/2} peak does not yield reliable results; in those cases, authors should avoid using peak fitting at all.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for A—an additional example of peak fitting iron oxyhydroxide mixtures, specifically Fe₃O₄/FeOOH mixtures in the presence of a metal peak; B—details regarding the modified Biesinger components used in the main text; and C—details regarding supporting techniques for iron oxide and oxyhydroxide phase identification.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

A. E. Hughes: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **C. D. Easton:** Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Resources (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **T. R. Gengenbach:** Data curation (supporting); Formal analysis (supporting); Writing – original draft (supporting); Writing – review & editing (supporting). **M. C. Biesinger:** Resources (lead); Visualization (supporting); Writing – original draft (supporting); Writing – review & editing (supporting). **M. Laleh:** Conceptualization (supporting); Data curation (supporting); Writing – original draft (supporting); Writing – review & editing (supporting).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#).

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