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Prediction of the Cu Oxidation State from EELS and XAS Spectra Using Supervised Machine Learning

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Abstract

Electron energy loss spectroscopy (EELS) and X-ray absorption spectroscopy (XAS) provide detailed information about bonding, distributions and locations of atoms, and their coordination numbers and oxidation states. However, analysis of XAS/EELS data often relies on matching an unknown experimental sample to a series of simulated or experimental standard samples. This limits analysis throughput and the ability to extract quantitative information from a sample. In this work, we have trained a random forest model capable of predicting the oxidation state of copper based on its L-edge spectrum. Our model attains an R^2 score of 0.85 and a root mean square valence error of 0.24 on simulated data. It has also successfully predicted experimental L-edge EELS spectra taken in this work and XAS spectra extracted from the literature. We further demonstrate the utility of this model by predicting simulated and experimental spectra of mixed valence samples generated by this work. This model can be integrated into a real time EELS/XAS analysis pipeline on mixtures of copper containing materials of unknown composition and oxidation state. By expanding the training data, this methodology can be extended to data-driven spectral analysis of a broad range of materials.

Keywords: Machine Learning, EELS, XAS, Cu, Spectral Analysis

Introduction

Due to their wide range of accessible oxidation states and materials applications, the ability to determine the oxidation state of third row transition metals is essential to a wide variety of applications. These include the development of catalysts [1], photovoltaic devices [2], and biotechnology [3]. Core level spectroscopy is often used to probe transition metal oxidation states, and two main types are electron energy loss spectroscopy (EELS) and X-ray absorption spectroscopy (XAS). EELS provides detailed atomic scale information, such as oxidation state, coordination number and local symmetry of a nanomaterial [4, 5]. When probing nanomaterials, EELS is often combined with scanning transmission electron microscopy (STEM). In STEM-EELS, an electron beam is scanned over an area of a sample and a full spectrum is acquired and stored at each probe position. This technique is particularly valuable in the study of nanomaterials due to its combination of high spatial and high energy resolution. [6–8]. Like EELS, XAS has also attained wide usage in determining oxidation state and local environment in nanomaterials [9–11]. XAS, however, is typically limited to a spatial resolution of a few nanometers [12], rather than the sub angstrom spatial resolution possible with STEM-EELS [13]. The main advantages of XAS compared to EELS for core-loss spectroscopy are the ability to attain higher signal to noise ratios (SNR) and higher energy resolution, particularly at higher excitation energies [14], and functionality on thicker samples for hard x-ray excitation [15]. Due to the myriad use cases for both techniques, they are commonly applied to the nanoscale study of materials containing third row transition metals. However, since EELS and XAS spectra encode the electronic properties of the sample in an abstract way, extracting physical descriptors is a non-trivial task in spectral analysis.

Therefore, quantitative spectral analysis is often the rate limiting step in materials characterization, and can typically only be conducted by trained experts. This is especially true of L-edge spectra of transition metals, where variations in oxidation state can manifest in small shifts in edge location, L_2/L_3 ratio and peak width that are not immediately obvious to a non expert, particularly for samples containing multiple oxidation states [16]. Oxidation state assignment is typically done by mapping the unknown spectrum to known experimental or simulated standards, a process which can be time intensive and requires significant domain knowledge. Particularly challenging to analyze are mixed valence materials, which are often interpreted as combinations of spectra of integer valence structures [17]. The prevailing solution to this problem is to fit integer valence spectra to the unknown spectrum using least squares. This allows a user to input known standards and determine the coefficients of a linear combination of the standard spectra that reproduce the experimental spectrum [17–20].

Least squares fitting has allowed quantitative oxidation state analysis of mixed valence samples and is widely implemented as the state-of-the-art procedure for quantitative analysis of unlabeled XAS/EELS L-edge data. However, in the case of experimental standards, it has a few serious limitations. First, this procedure requires fresh standards to be taken for each instrument, and often each day, as changes in detector setup and alignment can lead to non trivial changes in the spectra. Second, this procedure is highly sensitive to experimental variation in the acquisition of the

standard samples. Contamination with materials of other oxidation state, surface oxidation and beam damage can have a significant impact on the shape of the standard spectrum, and therefore interfere with the fitting of the unknown sample. Additionally, inconsistencies in standard spectrum processing, such as baseline subtraction or the incomplete deconvolution of multiple scattering from the standard sample, can have a similar impact. Third, the presence of any oxidation state or coordination environment unaccounted for by the standards will not only be missed by the prediction of the makeup of the material, potentially missing an important fundamental discovery, but will also lead to an inaccurate representation of the oxidation state as the standard components are forced to represent a signal not originating from any of them. In a similar vein, experimental standards must be taken for every material expected to be present in order to perform the oxidation state analysis. For example, a standard for CuO may not be suitable for an experiment involving CuS due to non trivial differences between the spectra, although they are both a Cu(II) oxidation state [21, 22]. Simulated standards suffer from fewer experimental limitations, but instead are limited by the level of approximations used in the theory and often can not perfectly reproduce experimental spectra. This can cause systematic errors leading to significant misidentifications, particularly when applied to noisy experimental spectra or experimental spectra more challenging to simulate. It is rare for simulated standards for L-edge transition metal spectra to be quantitatively accurate enough to fit an unknown experimental spectrum using least squares fitting [23]. Instead, these are used to qualitatively match components of an unknown spectrum. Therefore, there is a need for a procedure that can determine oxidation state from XAS/EELS L-edge data that is more robust than the least squares fitting of a handful of standard spectra.

An avenue for a more broadly applicable automated analysis procedure is machine learning (ML). Despite some recent advancements in automated L-edge XAS/EELS analysis of transition metals using ML approaches [24], overall, the transition metal K-edge has received more focus from the ML community [25–27]. Numerical analysis of L-edge transition metal XAS/EELS data has mainly been performed using principle component analysis (PCA) to reduce the dimensionality of the spectrum. This field has been well developed, comprising numerous applications of PCA on L-edge XAS/EELS data [28–31]. Additionally, PCA dimensionality reduction procedures have been used to successfully de-noise low SNR core loss EELS data [32–34]. PCA has also been extended into analysis of oxidation states. Applying component analysis to a mixed valence XAS/EELS spectrum can result in components that mimic the unique oxidation states present. This can be used as a qualitative estimation of the different oxidation states present in a sample, however, it is difficult to ensure each of the resulting components match the pure form of an oxidation state. Therefore, the lack of rigorous physical interpretation of the components makes any quantitative analysis challenging [35].

Supervised machine learning approaches have found success predicting oxidation states in manganese and iron samples, using neural networks and support vector machines [36–38]. However, these models were trained on a small subset of materials and, with the exception of [37] on Mn spectra, only focused on integer valence states. Therefore, the more complicated question of L-edge spectra oxidation state regression

of an arbitrary Cu material containing a wide range of oxidation states has not been thoroughly explored. The lack of focus on mixed valence structures generally is especially notable, as such a model is necessary to analyze an in-situ experiment where 1000s of spectra are generated quickly with minor variations in oxidation state.

This work has developed a supervised ML model capable of conducting a regression task on an unlabeled Cu $L_{2,3}$ -edge XAS/EELS spectrum and predicting the average oxidation state. An outline of this model is shown in Figure 1. The $L_{2,3}$ -edge was selected as the focus due to the prohibitively high energy of the transition metal K-edge for electron detectors. We utilized the simulated L-edge XAS spectra of transition metals stored in the Materials Project [39, 40] as a seed to construct our training set. Despite the differing physical origins of XAS vs EELS, with XAS caused by excitation from a photon and EELS by an electron, under the long wave-length limit and dipole approximation, both spectroscopic methods involve evaluating the same transition matrix element. Therefore, a model trained on XAS data is able to effectively predict EELS data [41, 42] for features where the quadrupole contribution is not significant.

Cu was selected as the focus of this work due to the myriad applications of Cu nano-materials. Specifically, Cu nanoparticles (CuNPs) are used in antimicrobial agents [43], catalysts [44] and renewable energy devices, particularly the electrochemical reduction of CO_2 [45]. Examining the oxidation state of Cu nanomaterials is critical to their function, as CuNP preparation procedures can lead to unintended surface oxidation that disrupts many of their applications [43]. Additionally, the major trends in Cu L-edge spectra can be captured accurately in Cu metal, Cu_2O and CuO using the multiple scattering¹ method implemented in the FEFF9 code [39, 46]. Figure S1a-c shows good agreement in the L_2 - L_3 spacing and well preserved intensity ratios between the L_2 and L_3 peaks. Fine detail such as the splitting of the L_3 peak in Figure S1a is demonstrated as well. The limitations of this method include the treatment of the partially filled $3d$ bands in Cu(II), where the many-body effects, such as multiplet effects, require higher levels of theory beyond the mean-field level [23, 46]. This can produce some spurious artifacts in the simulations, such as the L_3 shoulder in the CuO simulation (Figure S1c) which is not present in the experimental sample. Although the quadrupole contribution can play an important role in pre-edge features, distinct spectral features in the main edge regions are found to be sensitive to the oxidation state from feature importance analysis. Therefore, neglecting the quadrupole contribution will not have a significant impact in this analysis. The overall success of FEFF9 in producing Cu L-edge spectra allows Cu materials to serve as a model system for this type of automated analysis procedure. In this work we present a framework for predicting the Cu oxidation state that can be readily extended to other transition metals by acquiring a volume of corresponding simulated XAS data.

¹In this case multiple scattering refers to the interference of multiple scattering paths, not to be confused with sequential inelastic events originating from the same excitation source.

Results

Performance on Simulated Spectra

Our RF model shows a high level of accuracy on a test set of simulated data. Figure 2a shows the R^2 plot of the predictions of this test set, which contains roughly 2400 spectra. The R^2 for this model is 0.85, and shows a visible high degree of correlation across all the well represented oxidation states. The largest errors come from integer valence misprediction, most commonly when a Cu(0) or Cu(I) spectrum is predicted as mixed valence. However, as shown in Figure 2a, these mispredictions can often be differentiated from the accurate predictions by using the prediction standard deviation (described in the methods section). The feature importance plot from Figure 2c offers insights into the origin of these errors. The model takes a small amount of information from the pre-edge and then bases its prediction mostly on the location and shape of the L_3 peak. As Cu(0) and Cu(I) have L_3 peaks at almost exactly the same energy, these are harder to differentiate than Cu(II), which is red shifted by roughly 3 eV. Despite this difficulty, Cu(0) and Cu(I) are accurately identified far more often than they are mispredicted, as shown in Figure 2a. As can be seen from Figure 2b, a full integer miss, i.e. a Cu(0) spectrum incorrectly called a Cu(I) spectrum, essentially never occurs. Additionally, as shown in Figure 2a and 2b, the simulated mixture samples are frequently predicted with a high degree of accuracy, showing this model has significant potential in predicting mixed valence samples.

Model Uncertainty Metric

In this work we have developed a method for quantifying the uncertainty in our RF model’s prediction. This is done by examining the predictions of each of the 500 decision trees which comprise the random forest as well as the averaged value used as the final prediction. This uncertainty analysis is visualized by generating a prediction histogram, as shown in Figure 1 (IV) and Figure 3d-3f. Beyond the qualitative spread of predictions shown in the prediction histograms, the uncertainty can be understood quantitatively by calculating the standard deviation of these predictions. This is indicated by the horizontal green line in the prediction histogram plots shown in Figures 1 and 3, and is used here as the RF model’s internal uncertainty measurement. To leverage this quantitative uncertainty, the standard deviation can be used to filter out predictions that are highly uncertain, and therefore presumably less accurate. Figure S2 illustrates this concept, where a standard deviation threshold was imposed, and all predictions with a standard deviation higher than this value were discarded due to their high uncertainty. The standard deviation can be used as a powerful tool in determining significantly inaccurate predictions on simulated data, as can be seen when the threshold is set at 0.35 (red rectangle in Figure S2a and S2b). When this threshold is used, 15% of the predictions of our test set are higher than the threshold and discarded (Figure S2a). However, imposing this threshold causes the RMSE of the remaining 85% of our test set to decrease 8% from the full test set value of 0.24 to 0.22 (Figure

S2b). Therefore, the 15% of the test set discarded by this method is comprised of predictions less accurate than average, showcasing the utility of this uncertainty metric in informing the accuracy of the model’s predictions for unknown samples.

Validation Using Experimental Spectra

To test the RF model’s validity when applied to experiments, we used it to predict a set of metallic Cu and Cu oxide EELS standards taken with our home instrument as well as a series of XAS spectra extracted from the literature. The simulated spectra corresponding to the EELS standards were left out of both the training and test sets previously discussed, to simulate a situation where the model is being applied to previously unseen materials. These standards were smoothed using a Savitzky-Golay filter with a window size of 1.5 eV and a polynomial order of 3. From Figure S3 it can be seen that the level of smoothing does not impact prediction accuracy. The smoothing window of 1.5 eV was selected as the default method due to qualitative observations that it removed the vast majority of the noise but also preserved the overall shape of the spectrum (Figure S4). From Figure 3e and 3f it can be seen that the model has a high degree of accuracy when predicting Cu(I) and Cu(II), rendering essentially perfect predictions for each of these standards, regardless of whether the mean or the median of the decision tree ensemble is used as the prediction. However, Figure 3d shows the Cu(0) standard appears to be slightly over estimated, with the mean prediction rendering a larger overestimate than the median, as the two predict 0.3 and 0.05, respectively.

There are likely two factors responsible for the overprediction of Cu valence for metallic absorbers. First, as has been discussed above, random forest models average predictions across individual decision trees, in this case 500. Therefore, it will always be more challenging for this model to predict Cu(0) as exactly zero, as all Cu atoms in our training data have non-negative valence. Consequently, any spread in the predictions will result in an overestimate. It is also worth noting that Figure 3d shows that the mode of our prediction histogram contains Cu(0) by a factor of four over the next highest bar, and that the median is much closer to a prediction of Cu(0). A second factor may also partially explain this overestimate, which is that our Cu(0) likely experienced some surface oxidation. Therefore, it may be assumed that this material no longer had a true oxidation state of zero at the time of measurement. This is reflected in the spectrum, which can be seen to have visibly taken on some additional Cu(I) character relative to simulated Cu(0) and Cu(0) observed in XAS studies taken from the literature (Figure S5, [21]). Specifically, our Cu(0) spectrum shows a drop in intensity of the two higher energy peaks in the L_3 edge and an increase in intensity in the lowest energy peak, which are characteristic of surface oxidation leading to more visible Cu(I) character. This, combined with the logistics surrounding the attainment of our Cu(0) sample, the sample was not shipped in vacuum sealed vial, and the fact that we were unable to reduce the sample in the microscope, supports the supposition that our Cu(0) EELS sample has undergone some surface oxidation. Therefore, we believe that this prediction of a mixed valence material closer to Cu(0) than Cu(I) matches our experimental realities and a detailed examination of the experimental spectrum.

However, it is also important to note that an XAS spectrum of Cu(0) extracted from the literature (Figure 4d) is also overestimated by our model. This is unlikely to be a result of surface oxidation, both from an instrumental perspective and a qualitative examination of the spectrum, which shows a much more characteristic Cu(0) sample than our experimental EELS sample due to the relatively equal heights of the three L₃ edge peaks and the L₃ being lower in intensity than the L₂ edge (Figure S1, S5). We attribute the overestimation of the literature Cu(0) mainly to the fact that our model does not allow for non-positive predictions, which causes any uncertainty in the prediction of Cu(0) to result in an overestimate, as discussed above.

In addition to the experimental spectra predicted in Figures 3 and 4, 8 other spectra extracted from the literature were predicted using this model (Figure S6, S7)[47–49]. 7 of these 8 spectra were materials with a Cu(I) oxidation state and all are predicted to within 0.1 of Cu(I) when the edge alignment is correct, and most retain their accuracy when the edge is misaligned by 0.5 eV in either direction (Figure S7). The one Cu(II) material, CuS, is predicted as roughly 1.5. However, our model’s prediction is likely inaccurate due to this spectrum’s high intensity post the L₃ region (Figure S8). As the Cu(II) L₃ edge is roughly 2eV lower in energy than Cu(I) and Cu(0), this increased intensity is likely mimicking a mixed valent spectrum, with this extra intensity appearing to come from absorption from a Cu(I) material. XAS is impacted by multiple photon scattering in very thick samples, which produces artificially high intensity in the tail of the L_{2,3} edge spectrum. Therefore, we believe that this was simply a spectrum of a very thick sample, leading to multiple scattering induced changes to the spectrum that the model is unable to account for.

Energy Axis Misalignment

Given that we have performed a manual edge alignment correction to our training data, we also examine the impact of energy axis misalignment on our predictions of experimental spectra. To explore this, we created a set of experimental spectra where the onset energy was shifted by controlled amounts and tracked how this shift impacted the oxidation state prediction (Figure 4). From Figure 4a we see that the energy misalignment has the greatest impact on the Cu(0) sample, and an offset of -0.4 eV or greater causes an inflection point where the prediction jumps from 0.3 to nearly 0.5. Misalignment in the positive direction has a far less dramatic impact, and an energy shift of +0.5 eV produces essentially no change in the prediction. The Cu(I) sample, shown in Figure 4b, is more stable, with a shift of nearly 1 eV in either direction resulting in a change of less than 0.2 in the oxidation state prediction. In Figure 4c, we see that Cu(II)’s prediction is virtually independent of shift plus/minus 1 eV, which is likely explained by the greater than 2 eV gap between the onset energy of Cu(II) vs Cu(I) and Cu(0).

To further examine the utility of our model when applied to experimental spectra, and to further study the impact of absolute energy shift, an additional experimental validation was done using an extracted set of XAS spectra of Cu oxides [21]. This set of spectra has been measured to be shifted from the experimental spectra used to validate this model by -1.0 eV for the Cu metal spectrum and -1.2 eV for the Cu₂O and CuO spectra (Figure S1, S5), and provides a test case for how the model

will respond to spectra with their energy axes significantly misaligned. From Figure 4d-f, we can see that our ML model produces excellent results for the XAS spectra when they are correctly aligned to our training data (red line in Figure 4d-f) and the results are robust even when the raw spectra are predicted, which are severely misaligned (black line in Figure 4d-f). When such a misalignment has occurred, the Cu(I) and Cu(II) spectra are predicted with near perfect accuracy, while the Cu(0) spectrum appears to be slightly over estimated, returning a prediction of around 0.5 when the correct alignment prediction is 0.28. It is worth reflecting that this prediction is still an overestimate, although closer to zero than our experimental EELS spectrum shown in Figure 3d, reflecting this model’s propensity to overestimate Cu(0). With these observations, it is clear that the ML model trained on properly aligned spectra can achieve highly accurate results on spectra with significant energy misalignment. Additionally, a potential avenue to determine the true alignment location is to vary the energy axis and seek out regions of consistent stability and low prediction standard deviation, as these regions are often associated with more accurate predictions for our experimental data.

Prediction of Experimental Mixed Valence Samples

Post successful proof of concept for our model on standard experimental samples, we turn our attention to a more valuable, but also more challenging, experimental case, the prediction of samples of mixtures of different oxidation states. As shown in Figure 2a, our model has already demonstrated a high degree of accuracy on simulated mixed valence samples. Additionally, we show how smooth variance in simulated mixed valence materials excluded from the training data is captured by our model by showing simulated mixtures of Cu(0), Cu(I) and Cu(II) in Figure S9. The important test for the utility of this model in experimental spectra is how well this process works on experimental mixtures of oxidation states. Due to the difficulty in engineering a system with smoothly varying mixed valence states, and inherent uncertainties in quantifying such a system, we have generated mixed valence experimental spectra through linear combinations of our standard samples. The labeled value for these experimental mixtures is determined by multiplying their formal oxidation state by their contribution to the final mixture spectrum, as was done with the labeling for the simulated mixtures. For example, a mixture of 40% Cu(0) standard and 60% Cu₂O standard would be calculated as follows:

$$0.00 * 0.4 + 1.00 * 0.6 + 2.00 * 0.0 = 0.6 \quad (1)$$

The results are shown in Figure 5. From Figure 5a-b, both plots contain regions of high accuracy, particularly for mixtures of Cu(I) and Cu(II) (Figure 5b). Mixtures of Cu(I) and Cu(II) are accurately predicted to within less than 0.1 in close to half of the mixture samples. However, there are also sections of low accuracy, particularly at inflection points where the prediction changes quickly. This is particularly true for mixtures of Cu(0) and Cu(I) (Figure 5a), where the inflection region drives the prediction into a region of significant overestimation which is not recovered until the mixture becomes entirely Cu(I). However, in most cases the overall trend of the prediction is correct, as in both Figure 5a and b the higher valence sample is frequently identified

as such until a pure sample is predicted, regardless of any absolute inaccuracies in the prediction.

Both mixed valence cases tend to overestimate the oxidation state when the higher oxidation state sample comprises greater than 50% of the mixture. We believe this to be a feature of the higher maximum intensity and sharper peaks of higher oxidation state spectra. This can be seen in Figure 3a-c, where the edge intensity relative to the tail of each spectrum is shown. This is also noticeable in the cumulative spectrum, which is the actual input into the model, (inset in Figure 3a-c) where the lower intensity in the Cu(0) peak results in an almost linear cumulative spectrum, while the higher intensity of Cu(I) and Cu(II) are very noticeable as a sharply increasing region in the L_3 edge region of the cumulative spectrum. The higher intensity of the higher oxidation state may make the fine features of Cu(0) difficult to detect at low mixture fractions, as Cu_2O and Cu(0) have their onset edges and L_3 peaks at essentially the same energy. Additionally, The slight red shift in Cu(II) spectra yields an immediately noticeable feature for model identification, and a sample which is 75% Cu(II) and 25% Cu(I) may simply be predicted as a Cu(II) with a shoulder or other unusual transition, which is relatively common in the simulated data.

We have also predicted random experimental mixtures of Cu(0), Cu_2O , and CuO. This was done using mixtures of the literature XAS spectra and our experimental EELS data. The results are shown in Figure S10a and c, respectively. They contain a characteristic overestimation as seen in the smoothly varying mixed valent binary mixtures, which inspired the creation of an empirical correction to random mixed valent spectra. The literature XAS predictions were used to train a linear regression model to predict the true oxidation state based on the prediction of the unknown spectrum. This was done using the mean, median and standard deviation of the decision trees as input. The model was trained and validated using the random mixtures of the literature XAS data and tested on the predictions of the random mixtures of EELS data. Figure S10a-b shows the predictions on the training data, the literature XAS sample, and how the empirical correction improves the predictions. Upon generation of this empirical model, it was used to correct the predictions of mixtures of Cu(0), Cu_2O , and CuO experimental EELS spectra. The results of applying this correction are shown in Figure S10c-d. The generation of this empirical model shows that, despite the challenges of predicting a pure Cu(II) in the empirical model's predictions, the overall trend of the mixed valent overestimation can be captured and corrected.

Comparison of Prediction Methods

As Figure 3d clearly shows that the median/mode of the decision trees yields a prediction much closer to Cu(0) for our experimental EELS Cu(0) sample, and Figure 5 shows a characteristic overestimation in both types of experimental mixtures, it is worth exploring whether using the median or the mode as the prediction, rather than the mean, is more accurate overall. This idea is explored in detail in Figure S11, which shows the full prediction histogram for various mixtures of Cu(0) and Cu_2O (Figure S11a-f) and compares the median, mean and mode predictions directly (Figure S11g-i). From Figure S11 we see that, although the median is more accurate for pure Cu(0), it quickly begins to overestimate the oxidation state by a margin significantly greater

than the prediction using the mean of the decision trees. The mode prediction is even more extreme, returning exclusively integer oxidation state predictions, regardless of mixture composition. Therefore, for predictions of mixtures of oxidation states, the mean prediction is more likely to be accurate, and median/mode statistics can be helpful in instances where a pure oxidation state is assumed, particularly if the material is expected to be metallic.

Impact of Noise on Simulated Data

To test the impact of noise on the simulated data, random Poisson noise was added to each simulated spectrum in the test set to produce a test set augmented by noise. To ensure that this process echoed our approach on experimental spectra as much as possible, the simulated spectra, which are on a 0.1 eV resolution, were re-sampled using `scipy's 1d` interpolation function with a higher resolution of 0.03 eV, matching that of our experimental samples. Noise was then added to the interpolated spectra, and these spectra were then smoothed in the same method as the experimental spectra and integrated to produce a cumulative spectrum (Figure S4). These spectra were then predicted by the model to test its accuracy on noisy data.

As shown in Figure 6a, the simulated data are relatively sensitive to noise augmentation, and the addition of a small amount of Poisson noise resulted in an increase in RMSE from 0.24 to 0.3 as compared to results from the noiseless spectra. Further increase in noise led to an even larger RMSE, however the decline in accuracy becomes less sharp than the initial slope. A similar trend is seen in Figure 6b for R^2 , where a drop in R^2 is observed after adding a small amount of noise, however this decline is less sharp than the increase in RMSE, and adding additional noise has a more pronounced decline on R^2 than subsequent noise does on RMSE. Despite this observation, our experimental spectra, which have a higher volume of noise than the simulated low noise case, do not appear to be as affected by noise as the simulated noisy spectra (Figure 3). An examination of the quantitative noise level of the experimental spectra can be found in Figure S12, which shows that the noise STD for the experimental EELS spectra is between 0.03 and 0.05. Additionally, the selection of the random seed for the addition of noise appears to have a significant impact on the overall accuracy of the noisy test set. This is shown with the error bars in Figure 6a and 6b, which represent the standard deviation across 100 different random noise seed states. The presented RMSEs and R^2 s are the average values across these 100 random states. A detailed examination of the noise profiles for these higher error random states shows that in these spectra the region around the baseline experiences noise spikes that mimic features around the baseline region, similar to how an inaccurate power law subtraction of an EELS spectrum baseline appears. This observation further enforces that the accuracy of this model relies heavily on the accurate identification and subtraction of the baseline.

Discussion

In this work, we have built a random forest model trained on simulated L-edge XAS spectra which is capable of predicting the oxidation state of copper based on its L-edge

XAS/EELS spectrum. We have also developed a database of Cu XAS spectra containing 3500 unique materials that have been accurately aligned to experimental spectra, and augmented this database with 6000 simulated mixture spectra. Our random forest model attains an R^2 of 0.85 on simulated data with an RMSE of 0.24 and has been shown to accurately predict experimental spectra taken from our home institution and from the literature. Additionally, this model has proven successful predicting mixed valence samples, showing its applicability to track Cu oxidation state in in-situ experiments where oxidation state is changing fluidly as a reaction occurs. Beyond this model’s utility to Cu materials, we have also developed a broader methodology which can be extended to the analysis of other materials by acquiring a spectral database of accurate simulated L-edge spectra for the corresponding material.

Methods

Training Set Generation

In this work, simulated FEFF9 XAS spectra of Cu materials were extracted from the Materials Project. This initial extraction produced a dataset of site averaged spectra for 1533 materials, which contains the 59 materials shown in Figure 1I labeled as neither predicted stable nor synthesized [39]. To increase the volume of our training data, an additional 2000 structures were selected by searching the Materials Project for all Cu containing materials that had either been previously synthesized or were predicted to be stable by theory [40]. This choice screens a broad material space that is likely accessible to experiments. We computed 2000 site averaged spectra using the *Lightshow* workflow [50] and FEFF9 [46]. The combination of this augmentation step and the initial extraction of L-edge spectra already generated by the Materials Project provided 1199 materials that both have been experimentally synthesized and are predicted to be stable (Figure 1I). For each structure, unique Cu sites are determined by the space group symmetry. Then site specific spectra were calculated using FEFF9. The L_2 and L_3 spectra for each site were combined into the $L_{2,3}$ spectrum by summing the L_2 and L_3 spectra, after first interpolating onto the same energy grid (Figure S13). The site averaged spectrum is calculated from the weighted sum of site-specific spectra based on the multiplicity of the unique sites in the unit cell. The oxidation states of the site averaged spectra were determined using the Materials Project’s “average oxidation states” function [40]. Despite this averaging procedure, greater than 93% of the site averaged spectra retained integer valence. When FEFF9 failed to converge for some, but not all, of the sites in a material, converged site spectra were averaged leaving out the failed spectra.

To prepare our training set of 3500 site averaged spectra, several additional steps were performed. This workflow is summarized in Figure 1. First, spectra were interpolated to ensure they were all on a 0.1 eV energy resolution. Second, the non uniformity in the energy range of the L_3 edge, specifically at the starting point, was addressed by fitting a 6th order polynomial to connect the lowest energy point to [925, 0] (i.e., vanishing intensity at 925 eV) for every spectrum (see Figure S14). The spectra were then aligned to ensure their onset edges were in the same general energy range as

those seen in experimental EELS Cu materials, as it was observed that FEFF9 was producing a systematic misalignment in the absolute energy of the $L_{2,3}$ edge.

To accomplish this alignment, two systematic errors were corrected. First, a high degree of onset energy variability was observed across zero valence materials, which would be expected to all have similar onset energies. Second, the absolute energy of the simulated spectra were several eV off from experimental standards. Both of these issues were fixed simultaneously by our automated alignment procedure. Below is a brief summary of our edge alignment procedure following the Δ SCF method [51, 52], as shown in equation (2):

$$E_{align} = E_{raw} + (\epsilon_{core} - \epsilon_{Fermi}) + (\epsilon_{XCH} - \epsilon_{GS}) + \Delta \quad (2)$$

where E_{raw} and E_{align} are the excitation energies before and after alignment. In order to correct the inaccuracy in the calculated excitation energy, we scale the raw spectrum by the difference between the Fermi energy (ϵ_{Fermi}) and Cu 2p core level (ϵ_{Core}) and by the total energy difference between the core-hole excited state (ϵ_{XCH}) and the ground state (ϵ_{GS}). In the core-hole excited state, the core electron is placed at the bottom of the conduction band, known as the excited core-hole (XCH) method. After this alignment, there is a single empirical constant (Δ) calibrated on a reference system to account for the residual discrepancy between theory and experiment. In our study, ϵ_{Fermi} is taken from the FEFF9 output corresponding to $k=0$, where k is the photoelectron wave number. ϵ_{Core} is set to -916.8226 eV, which is determined by the VASP estimation of the energy of a 2p core hole in Cu[52, 53]. ($\epsilon_{XCH} - \epsilon_{GS}$) was computed using the VASP code base, and the values are -650.888 eV, -650.748 eV and -651.945 eV for Cu, Cu₂O and CuO, respectively [53]. In principle, one should perform VASP calculations for all the systems in the database. However, this will lead to a very high computational cost, which is impractical for the scope of this study. Therefore, we treated ($\epsilon_{XCH} - \epsilon_{GS}$) as constant for each oxidation state, using the Cu, Cu₂O and CuO values listed above for Cu(0), Cu(I) and Cu(II) spectra respectively. This resulted in a simplification of equation (2), where ($\epsilon_{XCH} - \epsilon_{GS}$) + Δ is treated as a constant, δ_{ox} , with different values for each oxidation state. These are: 1849.06 eV, 1849.33eV and 1846.87 eV for Cu with oxidation state of 0, +1 and +2, respectively, which aligns simulated Cu, Cu₂O and CuO spectra to their corresponding EELS experimental spectrum. For the small subset of materials that were classified as mixed valence, they were aligned based on whichever integer oxidation state they were closest to.

It is important to note that this alignment procedure is not aligning the edge to the exact location of the Cu/Cu₂O/CuO edges for all Cu 0, +1 and +2 spectra (i.e. forcing every Cu(II) spectrum to start at 930.2 eV, where the CuO edge is located). This alignment procedure computes a correction based on FEFF9's Fermi energy prediction and then uses the energy gap between the simulated spectrum of either Cu metal, Cu₂O and CuO, post Fermi correction, and the corresponding experimental spectrum to scale all spectra with that oxidation state. For example, not every Cu(II) spectrum is at the same edge energy, and many of them are quite different based on their initial location post Fermi energy correction. The relative energy alignment from FEFF9 within an oxidation state is often preserved, particularly for Cu(I) and Cu(II) materials, and this scaling using the experimental spectra is done to bring the energy

axis to experimental relevance. Without this correction, the energy axis for the FEFF9 spectra is misaligned by multiple eV and any experimental prediction is impossible. An example of this alignment procedure is shown in Figure S15.

Our spectral dataset was then augmented by generating simulated mixed valence samples (see step III in Figure 1, Figure S16). To accomplish this, 300 random sets of spectra were drawn from the integer dataset, each draw taking a random Cu(0), Cu(I) and Cu(II) site averaged spectrum. Each of these 300 sets of 3 integer spectra were then linearly combined to mimic mixed valence structures. For each set of three spectra, 20 random fractions of each material were combined to produce a simulated mixed valence spectrum. To ensure an even spread of mixed valences, 100 sets were combinations of Cu(0) and Cu(I), 100 were combinations of Cu(I) and Cu(II), and 100 were combinations of Cu(0), Cu(I) and Cu(II). This mixture produced a final dataset of roughly 9500 spectra with data well distributed from Cu(0) to Cu(II) (step III in Figure 1, Figure S16). Our training and test sets were generated by separating classes of mixtures, rather than a random 75/25 split across the full 9500 spectra dataset. To accomplish this, we tracked the compositions of each random mixture, and ensured each composition was fully placed in either the training or test set. For example, an arbitrary mixture of Cu(0), Cu(I) and Cu(II) would have 20 random proportions of each material in our full dataset, and our train/test split ensured all 20 of these were either in training or test. This ensures the model is not biased by seeing a 0.3 0.3 0.4 mixture of the above materials in training and then tested on a mixture of 0.2 0.3 0.5 of the above compounds, which results in a very similar spectrum.

To achieve the best ML model performance, we have tested different spectral representations, including the spectrum itself, its first and second derivative, and the cumulative integral of the spectrum. We found that the best model performance was achieved with the cumulative integral with intensity normalized to 1. In addition, using the cumulative integral, referred to as a cumulative spectrum in this work, as input feature can ensure consistency in the absolute scale of the EELS spectrum. This representation can simplify intensity scaling, as experimental post processing decisions and noise can create a high degree of variability in spectral intensity. The cumulative spectrum approach is insensitive to the absolute scale of the spectrum, although it does require an accurate identification and subtraction of the baseline for experimental spectra.

Random Forest Modeling

Random forest (RF) models for this work were trained using Scikit-learn’s Random-ForestRegressor model [54]. The number of trees was fixed at 500, with all features available and max depth unfixed. The dataset was split into train and test components using a 75/25 random train test split function from Scikit-learn. The structure of this model allows for the input of a raw spectrum of arbitrary min and max energy and energy scale. The model then takes the input spectrum and interpolates it to a 0.1 eV resolution from 925 to 970 eV to ensure the consistency of the energy grid used in the training data. Spectral smoothing is then applied using a Savitzky-Golay filter from scipy [55]. The smoothing step is done before the interpolation provided that the inputted spectrum is on an evenly spaced energy scale. The cumulative operation

on the spectrum is then performed and this spectrum is the input of the model. The trained RF model is an ensemble of 500 individually trained decision trees, and returns the predictions of each decision tree. A simple average of inferred valence values from each tree is taken as the final prediction, although median and mode predictions can be returned as well. The mode prediction is determined by finding the highest count on a histogram with bin widths of 0.2. The mode is determined by finding the center of the highest bin, meaning integer valence predictions will be returned as 0.1 higher than the integer valence (ie a prediction of Cu(0) will have a mode of 0.1 assigned to it, as the bin will range from 0.0 to 0.2). The standard deviation of these 500 predictions can approximate the model’s internal confidence in its prediction, and is visualized in the prediction histogram in Figures 1, 3 and S4, the last of which illustrates the entirety of the processing steps performed on an input spectrum.

Experimental EELS

To validate the utility of this model on experimental data, experimental EELS spectra of standard reference samples were measured, including Cu metal, Cu₂O and CuO. Cu metal was purchased from Sigma-Aldrich with 99.999% purity. Cu₂O and CuO were purchased from Sigma-Aldrich with 99.99% purity. The Cu₂O sample was measured using a vacuum holder to prevent oxidation. However, the Cu metal sample was not delivered in a vacuum sealed container, and under the assumption that surface oxidation had already occurred, a vacuum holder was not used for this sample. Using the TEAM I microscope, a double-corrected Thermo Fisher Titan microscope, we acquired monochromated reference data for these samples at roughly 0.2 meV resolution. Data were collected at 300kV with a semi-convergence angle of 17 mrad and a collection angle of 82 mrad. All data was collected using a Gatan Continuum spectrometer equipped with a K3-IS detector operated in electron counting mode. Spectra were baseline subtracted using the GMS Digital Micrograph software package, and spectra were taken using dual EELS to dynamically remove shifts in the reference elastic energy and deconvolved with the simultaneously measured zero-loss region to mitigate artifacts from electrons experiencing multiple scattering events. The deconvolution of multiple scattering is essential to ensure the experimental EELS spectra are comparable to XAS.

Data and Code Availability

The spectral dataset and the code to generate and analyze the random forest model presented in this study can be found in the GitHub repository https://github.com/smglsn12/ML_XAS_EELS.

Author Contributions

SPG took the experimental data, generated the simulated XAS dataset, conducted the machine learning training and analysis and wrote the manuscript. DL provided

training and expertise necessary to generate the simulated dataset. JC provided experimental EELS knowledge, microscope training, led the collaboration and designed the scope of this work. All authors read, edited and approved the final manuscript.

Competing Interests

The authors declare no competing interests.

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Fig. 1 A flow chart containing the four components of constructing the training data and random forest model. I, data is extracted from the Materials Project and scaled, aligned and processed to ensure internal consistency and accuracy to experiments. The colored boxes in I show how the materials project classifies the materials extracted and simulated by this work. II, the spectra are labeled by their oxidation state using the Materials Project oxidation state function “average oxidation states”. III, the dataset is augmented by creating mixture spectra made up of linear combinations of integer valence spectra. IV, the random forest model is trained and validated using test simulated data and experimental reference samples [40].

Fig. 2 The performance of the random forest model on the test set of simulated data. (a) R^2 plot, where each spot’s size is proportional to the number of spectra at that point and its color corresponds to the prediction’s standard deviation. (b) histogram of the absolute errors, with the vertical green line showing the location of the root mean square error (RMSE) and the vertical red line showing the location of the mean absolute error (MAE). (c) feature importance of the random forest model plotted on the same energy axis as the spectra.

Fig. 3 The performance of the random forest model on experimental Cu oxide EELS standards collected in this work. The top row (a, b, c) shows the raw spectrum with the cumulative spectrum as an insert. The bottom row (d, e, f) shows the prediction histograms for each spectrum, where the grey bars correspond to the number of decision trees predicting values over that range. The formal oxidation state is shown by the vertical blue line in each plot, while the predictions generated by the mean and median of the decision tree predictions are shown in red and orange, respectively. The standard deviation of the decision tree’s predictions is shown as a green horizontal line.

Fig. 4 The impact of energy misalignment on the prediction for EELS spectra taken in this work and XAS spectra extracted from the literature. Experimental EELS spectra are shown in (a-c) and literature XAS spectra are shown in (d-f) [21]. The spectra are shifted horizontally on the energy axis by the amount indicated in the x axis but are not changed in any other way. The scatter plot color corresponds to the prediction's standard deviation. The horizontal orange dashed lines show the location of the formal oxidation state of each material. The dashed black line indicates the location of the raw spectrum without any energy axis shifting. The red dashed line indicates the amount of energy axis shifting required to bring the experimental spectrum's onset energy to the same value as its corresponding simulated spectrum in our dataset.

Fig. 5 Performance of the random forest model on experimental mixed valence spectra. (a) shows mixtures of Cu(0) and Cu(I), while (b) shows mixtures of Cu(I) and Cu(II). The scatter plot color corresponds to the prediction's standard deviation. The dashed line indicates the location of a perfect prediction, while the vertical lines indicate the standard deviation of each prediction. The vertical lines show one standard deviation in the negative and positive direction.

Fig. 6 Random forest model performance on simulated data augmented by Poisson noise. The standard deviation of the Poisson distribution used to generate the noise is shown in the x axis of each plot. The error bars denote the standard deviation of the RMSE/R² across 100 random states for that noise standard deviation value.