CONDENSED MATTER ASTROPHYSICS: A PRESCRIPTION FOR DETERMINING THE SPECIES-SPECIFIC COMPOSITION AND QUANTITY OF INTERSTELLAR DUST USING X-RAYS

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ABSTRACT

We present a new technique for determining the quantity and composition of dust in astrophysical environments using <6 keV X-rays. We argue that high-resolution X-ray spectra as enabled by the Chandra and XMM-Newton gratings should be considered a powerful and viable new resource for delving into a relatively unexplored regime for directly determining dust properties: composition, quantity, and distribution. We present initial cross section measurements of astrophysically likely iron-based dust candidates taken at the Lawrence Berkeley National Laboratory Advanced Light Source synchrotron beamline, as an illustrative tool for the formulation of our technique for determining the quantity and composition of interstellar dust with X-rays. (Cross sections for the materials presented here will be made available for astrophysical modeling in the near future.) Focused at the 700 eV Fe LIII and LII photoelectric edges, we discuss a technique for modeling dust properties in the soft X-rays using L-edge data to complement K-edge X-ray absorption fine structure analysis techniques discussed by Lee & Ravel. The paper is intended to be a techniques paper of interest and useful to both condensed matter experimentalists and astrophysicists. For the experimentalists, we offer a new prescription for normalizing relatively low signal-to-noise ratio L-edge cross section measurements. For astrophysics interests, we discuss the use of X-ray absorption spectra for determining dust composition in cold and ionized astrophysical environments and a new method for determining species-specific gas and dust ratios. Possible astrophysical applications of interest, including relevance to Sagittarius A*, are offered. Prospects for improving on this work in future X-ray missions with higher throughput and spectral resolution are also presented in the context of spectral resolution goals for gratings and calorimeters, for proposed and planned missions such as Astro-H and the International X-ray Observatory.

Key words: ISM: abundances – dust, extinction – ISM: molecules – methods: data analysis – methods: laboratory – techniques: spectroscopic – X-rays: ISM

1. INTRODUCTION

Understanding dust is vital to our understanding of the Universe. Dust is a primary repository of the interstellar medium (ISM) and contributes to the chemical evolution of stars, planets, and life itself. A better understanding of the content of astrophysical dust has far reaching relevance and application to areas of astrophysics ranging from nucleosynthesis to planet formation. Dust is everywhere, and for many astrophysical topics, its presence hinders our studies in some way, be it to extinguish a UV part of a spectrum, or possibly affect Cosmology results, as, e.g., in the case of using Type Ia supernovae light curves (which are affected by line-of-sight dust) as a beacon for probing the dark energy content in the Universe. Therefore, at a minimum, a better understanding of dust will allow us to better isolate its effects (be it complicating spectra or light curves) to get at a cleaner study of topics from cosmology to black hole environments. There is a multiwavelength industry (mostly radio to IR) focused on the problem of astrophysical dust, and in recent years, Spitzer observations have significantly improved our understanding. Yet, despite good progress, there remains much to understand about dust properties (size, composition, and distribution) in astrophysical environments, from the colder ISM environs to the hotter environments near the disks and envelopes of young stars and compact sources. Our quest to address outstanding problems, therefore, can greatly benefit from additional complementary and/or orthogonal techniques.

There are several advantages of studying dust properties in the X-rays, the most significant of which is that we can directly measure its quantity (relative to gas phase), and composition. (“Dust” in this paper includes complex molecules). In the UV and optical wavelength, the presence of dust is generally inferred through depletion, rather than directly measured. Radio spectroscopy is able to probe the presence of certain molecules, and IR, some subset of ISM compounds (mostly polycyclic aromatic hydrocarbon or PAHs, graphites, certain silicates, and ice mantle bands). In these bands, spectral features come from probing the molecule as a whole through rotational or vibrational modes originating from, e.g., the excitation of phonons (rather than electrons). In contrast, both gas and ($\lesssim 10 \mu m$) dust are semitransparent to X-rays, so the measured absorption in this energy band is sensitive to all atoms in both gas and solid phase. Therefore, these high-energy photons can be used to facilitate a direct measurement of condensed phase chemistry via a study of element-specific atomic processes, whereby the excitation of an electron to a higher lying quantum level, band resonance, or molecular structure will imprint modulations on X-ray spectra that reflect the individual atoms that make up the molecule or solid. Therefore, in the same way that we can look at a given energy to identify ions, the observed spectral modulations near photoelectric edges, known as X-ray absorption fine structure (XAFS), provide unique signatures of the condensed matter that
imprinted that signature. For this reason, high-resolution X-ray studies, currently best enabled by X-ray grating observations (Chandra and XMM), provide a unique and powerful tool for determining the state and composition of ISM grains.

Lee & Ravel (2005) have discussed the viability of XAFS analysis and techniques for K-edge data with particular emphasis on iron in the hard >7 keV X-rays, in early anticipation of the launch of the Suzaku calorimeters. (See also Woo 1995, Woo et al. 1997, and Forrey et al. 1998 for early theory discussions relating to XAFS detections in astrophysical environments.) Due to the unfortunate in-flight failure of the instrument, the viability of astrophysical XAFS studies will have to focus on the softer <6 keV regime with existing instruments, until the Astro-H launch. While a more complicated part of the spectrum (due to the numerous ions that populate this spectral region), XAFS signatures in the soft X-rays have been reported in early papers based on Chandra and XMM spectral studies (Paerels et al. 2001; Lee et al. 2001, 2002; Ueda et al. 2005; Kaastra et al. 2009; de Vries & Costantini 2009; see also Takei et al. 2002; Schulz et al. 2002; Juett et al. 2004, 2006 for studies focused on the oxygen K edge for abundance determinations). It is the detection of these features in X-ray spectra of astrophysical objects that have motivated us to obtain laboratory measurements of likely ISM grain candidates to facilitate astrophysical modeling efforts. To date, no modeling of the magnitude we propose here has been undertaken. The ~0.1–8 keV energy coverage combined between the Chandra and XMM-Newton gratings will allow us to look in more detail to photoelectric edges near C K, O K, Fe L, Mg K, Si K, Al K, S K, Ca K, and Fe K, and therefore molecules/grains containing these constituents. We note, however, that for the K-edges of C, S, Ca and Fe, we are likely to be limited by signal-to-noise ratio (S/N) and/or spectral resolution, but are nevertheless well situated to study magnesium-, silicate, and aluminum-based grains using K-edge data, and iron-based grains/molecules can be studied using L-edge spectra at ~700 eV. Additionally, because X-ray absorption spectra are of some admixture of gas and dust, each having very different individual spectral signatures, we can separate their relative contributions through spectral modeling. Our proposed technique for doing so is discussed in Section 3, using cross section measurements of XAFS at Fe L as the illustrative example for our discussion points.

This paper presents dialog focused on the application of condensed matter X-ray techniques to the soft X-ray absorption study of astrophysical dust properties: composition and quantity. What knowledge we gain from this work will greatly complement current IR studies of dust. Ultimately, the questions we would strive to address in this study include: (1) the mineralogy of dust in different astrophysical environments, and perhaps (2) something of its nature (e.g., crystalline or amorphous). Since K-edge analysis has already been discussed by Lee & Ravel (2005), we focus on XAFS studies as applied to L-edges, where the spectral modeling of near-edge absorption modulations (XANES: X-ray absorption near-edge structure), rather than far-edge absorption modulations (EXAFS: extended X-ray absorption fine structure) play a primary role. While the emphasis is on the ~700 eV Fe L spectral region, the techniques presented will be widely applicable to all L-edge studies. Because condensed matter measurements are discussed in the context of astrophysics studies, we organize this paper into sections that would be of interest and useful to both condensed matter experimentalists (Section 2) and astrophysicists (Sections 3 and 4). For the experimentalists, Section 2.2 may be of particular interest for its discussion of an L-edge cross section normalization technique that is robust to laboratory synchrotron cross section measurements with relatively poor S/N. For astrophysics interests, Section 3 discusses a new method for determining interstellar dust quantity and composition through X-ray studies. This is followed in Section 4 with a brief discussion of some possible studies of interest and ability of this technique to separate out fractional contributions of different composition of dust in different regions. Prospects for improving on this work in the context of future missions are discussed in Section 5.

2. THE SAMPLES AND LABORATORY EXPERIMENT

UV, IR, and planetary studies of meteorites and dust have pointed to interstellar dust grains condensed from heavier elements such as C, N, O, Mg, Si, and Fe. With respect to using Chandra High Energy Transmission Grating Spectrometer (HETGS) spectra to enable detailed studies of absorption structure near photoelectric edges to determine grain composition, Fe-, Mg-, and Si-based dust would be the most relevant since the L-edge of Fe and K-edges of Mg and Si are all contained within the ~0.5–8 keV (~1.5–25 Å) HETGS bandpass, where the effective area is also highest. (The Fe K-edge is also encompassed by the HETGS, but the S/N there is usually too low to be useful for analysis.) For this paper, we compare cross section measurements for hematite (α-Fe2O3), iron sulfate (FeSO4), fayalite (Fe2SiO4), and lepidocrocite (γ-FeOOH). Cross section measurements at Fe L and Si K are nearing completion for the most astrophysically likely iron- and silicon-based dust, which will be presented in a future paper on XAFS standards for astrophysical use, while the data presented in this paper are used primarily to illustrate our proposed analysis techniques and methodology. Planned measurements are also being made for other interesting edges discussed previously.

The laboratory data presented in this paper were taken at the Lawrence Berkeley National Laboratory Advanced Light Source beamline 6.3.1. This is a bending magnet beamline with a Variable Line Spacing Plane Grating Monochromator (VLS-PGM) that is sensitive to 300–2000 eV energy range and has a resolving power E/ΔE ~ 3000. This resolution exceeds the E/ΔE = 1000 Chandra HETGS resolving power by factor of three.

The 6.3.1 detectors allow for a choice between total electron yield, photodiode (fluorescence), and transmission experiments. The latter would have been the ideal choice, since transmission measurements would be directly related to what we seek to understand, namely the transmission of X-rays through interstellar grains of comparable thickness. However, a nominal thickness estimate for 30% transmission would require film/foil thicknesses for our candidate samples in the range ~0.1–0.8 μm from the transparent to opaque side of the edge at Fe L, as calculated according to the formalism \( T = e^{-\rho t} \). (The density \( \rho \) for the compounds was taken from “The Handbook of Chemistry and Physics,” and the values for the attenuation length were obtained from the6 CXRO at LBL and7 NIST.) Preparation of pure-phase samples of that thickness was impractical. As such, we opted to obtain cross section measurements using both fluorescence and electron yield (Section 2.1).

6 http://www-cxro.lbl.gov/optical_constants/.
7 http://physics.nist.gov/PhysRefData/FFast/html/form.html.
2.1. Fluorescence and Electron Yield Experiments

In an X-ray-absorption spectroscopy (XAS) experiment, the incident X-ray photon promotes a deep-core electron into an unoccupied state above the Fermi energy. For the iron L edge experiments shown in this paper, that deep core state is a 2p state. As the incident photon energy is varied using a variable line spacing plane grating monochromator, the cross section of this absorption process is monitored by measurement of the decay of a higher-lying electron into the core hole. The fluorescence of a photon and emission of Auger and secondary electrons can be monitored in tandem. Because the mean-free path of the electron is limited to a few nanometers or less, the electron yield measurement is mostly sensitive to the surface of the sample. The fluorescent photon, on the other hand, has a larger mean-free path, and therefore is a better probe of the bulk of the sample.

The samples measured in this paper were fine powders, either purchased as such or prepared by grinding in an agate mortar and pestle. A portion of these fine powders was sprinkled onto the sample holder. The fluorescence measurement is made using a photodiode pointed at the sample. However, since all of our samples were thick compared to the penetration depth and highly concentrated in iron, the fluorescence data were significantly attenuated by the self-absorption effect (see, e.g., Booth & Bridges 2005). All data in this paper were measured in electron yield mode.

To measure the electron yield, an alligator clip was clamped onto the glass slide and electrical contact was made with the otherwise isolated carbon tape and indium strip, and used to carry the photocurrent into a current-to-voltage amplifier. This experimental arrangement provided for redundant measurements of each sample. Some samples proved more amenable to measurement on the carbon tape substrate and others to the indium. For every sample, each measurement was repeated three times. In each case, the measurement yielding the highest quality, most reproducible data was selected for presentation. The three scans for each sample have been calibrated in energy, aligned, and averaged.

Absolute energy calibration was attained by measuring an iron foil and calibrating it to the tabulated energies of the iron LII and LIII edges (Brennan & Cowen 1992). We had no capacity to prepare the surface of our foil, thus we relied upon the fluorescence measurement. Although the foil measurement is severely attenuated by self-absorption, the edge position can be reliably extracted. Iron-edge scans on other materials were aligned to the iron foil data using reproducible features in the spectrum of the incident intensity.

2.2. Absorption Cross Section Normalization Technique

In an XAS measurement, the absolute scale of the measured cross section is ambiguous. The size of the measured step at an absorption edge energy depends on a wide variety of factors, including the concentration of the absorbing atom in the sample, the electronic gains on the signal chains, and the efficiencies of the detectors. In order to compare measurements on disparate samples under differing experimental conditions, it is standard practice to perform a common normalization of every measured spectrum. In this work, we choose to perform this normalization by matching the measurements to tabulated values for bare-atom cross sections, as described in this section. In this way, we can directly and consistently compare measurements on our samples to one another as well as to astronomical observations.

The normalization of XAS L edge data is more complicated than for K edge data due to the close proximity of the LIII and LII edges in the soft X-ray regime. In order to properly normalize these spectra, we adopt the MBACK normalization technique of Weng et al. (2005) with modifications. Here, we describe the MBACK technique in brief, and our modification, which we found to be necessary for data with \( \gtrsim 0.2\% \) noise, as typical of each individual cross section measure. We note that the typical practice has been to first co-add all individual cross section measures to increase S/N, before normalization. However, we wished to be more rigorous in our methodology by first renormalizing the individually measured cross sections before averaging to create the final cross section to facilitate fitting purposes. The MBACK technique ensures better normalization for the more complex L-edge cross sections by calculating a smooth normalizing function over the entire measured data range, rather than extrapolating from independently pre- and post-edge linear fits as would be sufficient for the less complex K-edge cross sections. For our data, this normalizing function, \( \mu_{\text{norm}} \), is dominated by the Legendre polynomial term (in brackets) of the function

\[
\mu_{\text{norm}}(E_i) = \left[ \sum_{j=0}^{m} C_j (E_i - E_{\text{edge}})^j \right] + A \cdot \text{erfc} \left( \frac{E_i - E_{\text{em}}}{\xi} \right),
\]

where \( E_{\text{edge}} \) is the energy of the onset of the edge absorption, and \( m \) and \( C_j \) are, respectively, the polynomial order and coefficient. Weng et al. additionally note that a rapidly decreasing pre-edge shape, due to residual elastic scattering, is often seen in fluorescence experiments using energy discriminating detectors, and therefore include an additional error function component in the normalization as defined by the nonbracketed term of Equation (1); see Figure 1 for the shape of this function as determined from our sample fit to \( \gamma \)-FeO(OH)—lepidocrocite. Here, \( E_{\text{em}} \) and \( \xi \) are, respectively, the centroid energy of the X-ray emission line of the absorbing element and its width, with \( A \) as a scale factor. We note, however, that this function is adopted here solely as an effective way to model similar pre-edge feature shapes originating from experimental artifacts.

![Figure 1. Error function as defined in Equation (1), which accounts for any decreasing function in the pre-edge slope due to residual inelastic scattering.](image-url)
of uncertain origin. (Residual elastic scattering effects do not apply to our experiment, which measured total photocurrent.) In any case, our data do not show a large rapidly decreasing pre-edge slope, so this term has negligible effect on our overall normalization; nevertheless, we include it in our modeling efforts for completeness, since this would allow for a global prescription for the determination of $\mu_{\text{norm}}$ that is independent of experimental technique. See Figure 2(a) for an illustration of the components that make up the normalizing function for our sample $\gamma$-FeOOH compound. In general, the details of the normalization variables would clearly depend on the composition of the condensed matter.

To determine the best normalization (Figure 2(b)), we initially employ the prescribed minimizing function of Weng et al.

$$\frac{1}{n_1} \sum_{i=1}^{n_1} \left[ \mu_{bf}(E_i) + \mu_{\text{norm}}(E_i) - s \mu_{\text{raw}}(E_i) \right]^2$$

$$+ \frac{1}{n_2} \sum_{i=N-n_2+1}^{N} \left[ \mu_{bf}(E_i) + \mu_{\text{norm}}(E_i) - s \mu_{\text{raw}}(E_i) \right]^2,$$

where $N$ represents the total number of data bins, $i$ is the bin index, and $n_1$ and $n_2$ are, respectively, the total number of pre-edge and post-edge data bins, such that $N - n_2 + 1$ represents

\[\begin{array}{ccl}
\text{Wavelength (10^{-14} \text{ cm})} & & \\
17.97 & 17.71 & 17.46 & 17.22 & 16.98 & 16.75 & 16.53 \\
\text{Cross-Section } \sigma (10^{-18} \text{ cm}^2) & & \\
0.1 & 1 & 10 & 100 & 1000 & 10000 & 100000 \\
\text{Normalized Data (this paper, Eq1)} & & \\
\text{Normalized Data (Weng et al. 2005, Eq2)} & & \\
\text{Normalized Data (Weng et al. 2005, Eq3)} & & \\
\text{Normalized \gamma-FeOOH (Dataset)} & & \\
\text{Normalized \gamma-FeOOH (Average)} & & \\
\text{Deviation} & & \\
\end{array}\]

$\begin{array}{ccl}
\text{Energy (eV)} & & \\
700 & 720 & 740 \\
\text{Cross-Section (10^{-18} \text{ cm}^2)} & & \\
0.1 & 1 & 10 & 100 & 1000 & 10000 & 100000 \\
\text{Normalized Data (this paper, Eq1)} & & \\
\text{Normalized Data (Weng et al. 2005, Eq2)} & & \\
\text{Normalized Data (Weng et al. 2005, Eq3)} & & \\
\text{Normalized \gamma-FeOOH (Dataset)} & & \\
\text{Normalized \gamma-FeOOH (Average)} & & \\
\text{Deviation} & & \\
\end{array}$
modify Equation (2) by dividing $\sigma$ on simulated cross sections (considering a remedy for this, we tested Equation (2) based on our data which resulted in badly normalized cross sections. In $A = \sum_{i=1}^{n_1} \left[ \frac{\mu_{\text{tab}}(E_i) + \mu_{\text{norm}}(E_i) - s \mu_{\text{raw}}(E_i)}{s \mu_{\text{raw}}(E_i)} \right]^2$ and a polynomial of order 2 was deemed sufficient, i.e., the goodness of fit showed negligible improvement for higher polynomial orders. Postnormalization, cross sections of the highest quality were co-added to create the final cross sections of Figure 5. For the final cross sections, no fewer than nine (indium substrate) data sets were co-averaged per compound type. Figure 5 shows our measured cross sections post-normalization, compared against metallic (Kortright & Kim 2000), and what we assume for bound-free continuum absorption by iron (Brennan & Cowen 1992; Henke et al. 1993). For future fitting efforts to astrophysical data, we use the structure-less Fe L tabulated values of Brennan & Cowen (1992) to extrapolate the normalized XAFS data beyond the energy span of our measurements that extends from 0.4 keV to 10 keV.

We plan to avail the community of our cross section measurements for these and other compounds, as absolutely calibrated standards for interstellar dust studies, in the near future. Table 1

![Table 1](http://www.cfa.harvard.edu/hea/eg/isd.html)
lists details for a few of these, but as stated, the data shown here are intended merely as a vehicle to facilitate a presentation of our new techniques.

3. AN X-RAY METHOD TO DETERMINE THE QUANTITY AND COMPOSITION OF DUST IN INTERSTELLAR SPACE

Our ability to accurately measure the quantity of dust and elemental abundances in our Galaxy and beyond has far-reaching applications and consequences for a diverse range of astrophysical topics. Thus far, wavelength-dependent (IR to UV) studies of starlight attenuation as facilitated by $E(B−V)$ measurements and other extinction studies have been the primary technique by which we measure the amount of dust that is bound up in interstellar grains. Elemental depletion can be determined by UV absorption studies comparing the amount expected in gas-phase absorption from what is observed, and IR spectral studies can directly measure certain ISM dust. Here, we present an X-ray technique for directly determining the (element-specific) quantity and composition of interstellar gas (Section 3.1) and dust from within a single observation. What knowledge we gain from this technique, when combined with the wealth of knowledge from non-X-ray studies, will significantly increase our understanding of ISM dust and its effects on astrophysical environments.

3.1. Gas-phase ISM Absorption

Like condensed material, atomic transitions to higher quantum levels within an isolated atom will also give rise to multiplet resonant absorption. To give the example for Fe, these lines would consist of all possible discrete transitions to all possible configurations of the 3d-shell, since the electronic configuration of $Z = 26$ Fe is $1s^22s^22p^63s^23p^64s^23d^6$. Therefore, while the bound-free non-resonant transitions can be modeled by a simple step function as, for example, that of Brennan & Cowen (1992) for Fe L, additional discrete resonant features will have to be included to account for the bound–bound resonant component of absorption.

Figure 6 shows our calculations for the resonant transition for various Fe ions from Fe$^{+0}$ to Fe$^{+4}$, as evaluated based on the (Gu et al. 2006; Gu 2005) predictions for oscillator strengths, radiative decay rates, and autoionization rates for these lines. Based on the ISM ionization spectrum of Sternberg et al. (2002), the most prominent contribution from Fe ions in the L-edge region would come from neutral Fe$^{+0}$ (i.e., Fe t), or singly ionized Fe$^{+1}$ (Fe II). These lines are convolved with the Chandra HETGS spectral resolution ($R ∼ 0.9$ eV at FeL; blue), and the resolution of ALS beamline 6.3.1 is used for the XAFS measurements presented in this paper (red). At present, $R ∼ 3000$ is also the baseline spectral resolution for the IXO spectrometers.

Figure 5. X-ray absorption near edge structure in the vicinity of the Fe L photoelectric edge, postnormalization, reveals that structures known as XAFS are distinct for different states of condensed matter. Note also differences in edge structure between bound-free continuum absorption (the solid black step function) vs. metallic (the dashed black) and molecular (in color) states. Note that these are only preliminary measurements which we intend to improve upon before incorporation into astrophysical databases for common use. The inset illustrates the $ΔE$ values distinguishing condensed matter (red) from gas-phase (black) absorption at the Fe L$_{III}$ and L$_{II}$ photoelectric edge energies, for the different compounds which are tabulated in Table 1.
and hot \((T \sim 5 \times 10^5 \text{ K})\) phases of the ISM, the iron ions that contribute most strongly to the L-edge region are \(\text{Fe}^{10}\) followed by \(\text{Fe}^{11}\). At \(T = 8000 \text{ K}\), the peak ion fractions are \(\text{Fe}^{10} \sim 0.67\), \(\text{Fe}^{11} \sim 0.33\), \(\text{Fe}^{12} \sim 2.8 \times 10^{-3}\) and \(\text{Fe}^{13} \sim 1.9 \times 10^{-6}\), assuming the ISM ionizing spectrum defined by Sternberg et al. (2002). At the much colder temperatures of the cold ISM, only \(\text{Fe}^{10}\) contributes, and at the much hotter temperatures of the hottest phase of the ISM, it is \(\text{Fe}^{25}\) (at 6.7 keV) which contributes the bulk iron fraction.

3.2. A Prescription for Determining Species-specific Gas-to-Dust Ratios

As stated in Section 1, the cross sections we measure in the laboratory of astrophysically likely dust candidates (Section 2) will be applied to X-ray spectra showing structure near photoelectric edges to determine dust composition and quantity. We propose the following prescription to do so:

\[
F_{\text{final}} = F_0 T = F_0 \exp \left[ -\tau_{\text{LOS}}(Z) - \tau_{\text{ionized-gas}} - \tau_{\text{gas}} - \tau_{\text{dust}} \right],
\]

whereby the absorption contributions from gas (cold and ionized) and dust can be separately accounted for by each of the exponential terms. Here, \(F_{\text{final}}\) and \(F_0\) are respectively the detected and incident flux, and \(T\), represented by the exponential terms, is the transmission. The \(\tau_{\text{ionized-gas}}\) is determined through photoionization modeling to account for any additional lines arising from the plasma of the source, and should be treated on a source-by-source basis. However, in the Fe L \(\text{III}\) and L \(\text{II}\) edge regions, we note that additional line contributions would have to come from high-transition (low oscillator strength) lines of He-like O \(\text{VII}\) \((O^{\text{VIII}}) 1s^2 - 1snp\) for \(n \geq 4\), and Fe I–Fe \(\text{XII}\) (i.e., \(\text{Fe}^{10} - \text{Fe}^{13}\)). Any significant contribution from oxygen would have to come from very ionized optically thick plasma; for the iron, moderate temperature plasma would have to be present in large quantities to have any appreciable effect in this spectral region. Therefore, for many astrophysical situations, neither ionized oxygen nor iron from the source plasma is expected to contribute strongly (if at all) to the Fe L \(\text{III}\) and Fe L \(\text{II}\) spectral region. Nevertheless, as stated, these can be modeled out through photoionization studies, the discussion of which is beyond the scope of this paper. For the total line-of-sight (LOS) (gas + dust) ISM absorption from all heavy elements, excluding the species of interest,

\[
\tau_{\text{LOS}}(Z') = \sum Z' \sigma'_{A Z} N_{A} N_{\text{H}} A_{\text{Solar}},
\]

where \(\sigma'_{A Z}, A_{\text{Solar}},\) and \(N_{\text{H}}\) are respectively defined to be the cross section, abundance, and line of sight equivalent Hydrogen column summed over all heavy elements present in the broadband X-ray spectrum, with the exception of the element we are trying to measure. One reason for removing the species of interest from the broadband fitting is that we are interested in decomposing the gas and dust contribution specific to that species. For this, we include two additional exponential terms to describe the absorption by the gas and dust for the species of interest whereby

\[
\tau_{\text{gas}} = (\sigma_{hf} + \sigma_{bb-gas}) N_{A} \gamma_{A Z} = \sigma_{Z_{\text{gas}}} N_{A} \gamma_{A Z},
\]

and

\[
\tau_{\text{dust}} = (\sigma_{hf} + \sigma_{bb-dust}) N_{A} (1 - \gamma) A_{Z} = \sigma_{Z_{\text{dust}}} N_{A} (1 - x) A_{Z}.
\]
In these equations, $\sigma_{Z_{\text{gas}}}$ and $\sigma_{Z_{\text{dust}}}$ refer to the cross section of the gas and dust, respectively, for the species of interest. The determination of $\sigma_{Z_{\text{dust}}}$ has been discussed in Section 3.1. The $\sigma_{Z_{\text{dust}}}$ and our efforts to measure this for astrophysically viable dust candidates have been discussed at length in Section 2. Given enough S/N, the species-specific abundance $A_Z$ can be fitted for, with the condition that the total abundance should be a combination of both gas and dust, hence the additional multiplicative factor to $A_Z$ of $x$ and $(1-x)$. Figure 7 shows these components as separated out in a fit to the X-ray binary Cygnus X-1. Details about the dust in Cygnus X-1 will be separately discussed in J. C. Lee et al. (2009, in preparation).

4. DISCUSSION

The Chandra and XMM-Newton archives are rich with high-resolution spectra of X-ray bright binaries and active galactic nuclei (AGNs). A cursory look at these spectra reveal XAFS near resolution spectra of X-ray bright binaries and active galactic binaries. These uncertainties affect our ability to accurately use the Fe K of the gas and dust, respectively, for the species of interest. The determination of $\sigma_{Z_{\text{dust}}}$ has been discussed in Section 3.1. The $\sigma_{Z_{\text{dust}}}$ and our efforts to measure this for astrophysically viable dust candidates have been discussed at length in Section 2. Given enough S/N, the species-specific abundance $A_Z$ can be fitted for, with the condition that the total abundance should be a combination of both gas and dust, hence the additional multiplicative factor to $A_Z$ of $x$ and $(1-x)$. Figure 7 shows these components as separated out in a fit to the X-ray binary Cygnus X-1. Details about the dust in Cygnus X-1 will be separately discussed in J. C. Lee et al. (2009, in preparation).

4.1. A Gedanken Problem: Can We Differentiate Dust Content in Different Locations?

The path length along the line of sight to our illuminating sources, be they X-ray binaries in our own Galaxy or black hole systems in other galaxies, is complex. Consider, for example, the simplified scenario of only two components distributed in some manner along the path. This problem then has two parts: the identification of the chemical species of those two components and the determination of their distribution along the path length. Assuming we can identify the two species, can we distinguish a heterogeneous arrangement (dust of composition a in location A plus dust of composition b found in location B) from a homogeneous arrangement (dust of mixed composition AB distributed along the path)?

The interpretation of the X-ray spectrum passing along this line of sight bears a strong similarity to the well-established technique of XAS as performed at synchrotron facilities. The use of XAS to identify chemical species in a chemically heterogeneous sample is common practice in terrestrial laboratories (Lengke et al. 2006 is but one example among thousands in the XAS literature). The common strategy is to interpret the spectrum from the mixture of species as a linear combination of the spectra from its component species, i.e., $\sum_{i=0}^{n} \alpha_i c_i$, where $\alpha_i$ represent the different species and $c_i$ their respective fractional contributions as per Lengke et al. (2006). The best determined relative percentages for the linear combination are derived by fits based on minimal $\chi^2$, which we recast for our purposes to be

$$\sum_{j=1}^{m} \left[ \frac{\sum_{i=1}^{n} c_i \alpha_{i,j} - \beta_j}{\sqrt{\sum_{i=1}^{n} (c_i \Delta \alpha_{i,j})^2 + (\Delta \beta_j)^2}} \right]^2, \quad (8)$$

where $\beta_j$ and $\alpha_{i,j}$ are the normalized cross sections in the $j$th bin of respectively the mixture and pure forms of the individual compounds, $\Delta \beta_j$ and $\Delta \alpha_{i,j}$ are their respective uncertainties, and $n$ is the associated number of compounds and $j$th bins to sum over; $c_i$ has the condition that $\sum_{i=1}^{n} c_i = 1$. With careful sample preparation, the fractional content of the component species in the spectrum is directly indicative of their fractional content in the physical sample.

To demonstrate this using iron-bearing species of relevance to the ISM, we performed the following experiment in the controlled laboratory of the synchrotron facility. We prepared two samples containing the common terrestrial iron compounds hematite ($\alpha$-Fe$_2$O$_3$), ferrosilicate (Fe$_2$SiO$_4$), and lepidocrocite close to the Galactic center as possible (see, e.g., Munoz et al. 2008 for latest X-ray binary catalog based on Chandra ACIS-I imaging data). Given the relative X-ray faintness of many of these objects, however, such a comprehensive spectral study in the nearest regions of the Galactic center will have to await missions with higher throughput, and at least equal spectral resolution.
The first sample contained equal parts by weight of hematite and ferrosilicate and the second contained equal parts by weight of all three materials. Samples for measurement by electron yield at beamline 6.3.1 were prepared as described above and the XAS spectra were measured on both mixtures. The hematite and lepidocrocite were very fine-grained, commercially produced powders. The ferrosilicate was commercially produced, but was ground by agate mortar and pestle from a chunk several millimeters across. Consequently, the ferrosilicate component of each sample was much larger grained than the other two components.

Because equal parts by weight were mixed in our two samples, we might expect the measured spectra to be interpreted by equally weighted fractions of the spectra from the three pure materials. In fact, the nature of the interaction between the X-rays and the morphology of the sample must be considered. Because the ferrosilicate component of each sample was much larger grained than the other components, its surface-area-to-volume ratio was considerably smaller. Because the electron yield measurement is surface sensitive, a much smaller fraction of the iron atoms in the ferrosilicate contributed to the actual measurement than of the other two components.

The data on the two mixtures along with the results of the linear combination analysis are shown in Figure 8. The binary mixture proved to be 16 ± 2% ferrosilicate and 84 ± 2% hematite. As expected from particle size, the ferrosilicate is underrepresented in the measured spectrum. The ternary mixture was 8 ± 2% ferrosilicate, 51 ± 7% hematite, and 41 ± 7% lepidocrocite. The two components of similar particle size are evenly represented, while the ferrosilicate is underrepresented.

This careful consideration of sample morphology in the synchrotron measurement is directly relevant to the interpretation of the astrophysical X-ray spectra. The astrophysical measurement is akin to a transmission measurement at the synchrotron, while the examples shown in Figure 8 were measured in electron yield. Still, the correct interpretation of the XAS spectra requires consideration of the nature of the interaction of the X-rays with the material through which they pass. A ray interacting with a large particle in the ISM will be lost to the satellite measurement by virtue of being completely absorbed by the particle. Consequently, the satellite measurement will be dominated by the small particles in the ISM as those are the only particles that allow passage of photons for eventual measurement at the satellite.

Finally, we must address the topic of distinguishing the distribution of the chemical species along the path length. By itself, a transmission XAS measurement is incapable of distinguishing between a layered and a homogenized sample. In transmission, an XAS measurement on two powders will be the same whether you prepare the powders separately and stack them in the beam path or mix the powders thoroughly before making the measurement. Similarly, the X-ray satellite measurement by itself cannot address the distribution of the species it is able to identify, if co-located at similar redshifts. However, since an XAFS contribution to a photoelectric edge is scaled according to the optical depth of that particular species, we can reasonably conclude that the compound that best fits the astrospectra is the compound where we are seeing the bulk contributions from, even if there might be lesser (e.g., 10%) contributions from other compounds along the line of sight. Therefore, in combination with other astrophysical studies using photon wavelengths that interact differently with the ISM (e.g., IR), the X-ray measurement can play an important role in the full determination of the composition of the ISM.

**Table 2**

| Spectral Resolutiona | Gratings 0.25–6 keV FWHM | Calorimeter 6–10 keV FWHM |
|----------------------|--------------------------|--------------------------|
|                      | Chandra R = 500          | Suzakub R = 923          |
|                      |                         | SXS prototypec R = 1500  |
|                      | IDEALd R               |

| Distinguish gas from dust | difficult² | yes¹ | yes | yes | 3000⁶ |
| Differentiate dust | not possible | yes⁸ | ok⁸ | yes⁸ | 5000⁶ |
| Discern oxides | not possible | no | no | maybe¹ | 5000 |

Notes.

a Spectral resolution R = E/ΔE = λ/Δλ referenced to 1 keV for the gratings and at 6 keV for the calorimeters.
b The spectral resolution of the calorimeter on board Suzaku which has since failed in-flight.
c Reasonable expectation for spectral resolution to be achieved with SXS prototype detectors (HgCdTe absorbers and implanted silicon thermometers) planned for the Astro-H mission. The 4 eV resolution (R = 1500) at 6 keV has been achieved in laboratory measurements (Astro-H Team 2008, private communication). The IXO calorimeter baseline performance is 2.5 eV.
d Applies to the 0.25–10 keV range for both grating and calorimeter instrument considerations.
e Insufficient spectral resolution limits our ability to discern the component of the photoelectric edge due to dust versus gas.
f As stated in Section 1, the soft X-ray band is also complicated by ionized absorption lines imprinted by the hot plasma environment of the illuminating source (e.g., black hole or neutron star) that needs to be modeled out in order to isolate the XAFS features.
g Possible with adequate statistics obtained from either long observation time or large detector area.
h Different forms of iron (silicates, oxides, metal) distinguished, but not different oxide forms.
i Challenging measurement requiring measurement statistics approaching the level of synchrotron experiment.
5. XAFS SCIENCE: PRESENT AND FUTURE

The X-ray energy band has been slow to be exploited for dust studies largely due to instrumental requirements for both good spectral resolution \( R \gtrsim 1000 \), and throughput. Yet, *condensed matter astrophysics* (i.e., the merging of high-energy condensed matter and astrophysics techniques for X-ray studies of dust) as a new subfield can be realized in the present era of *Chandra* and *XMM-Newton*. As such, X-rays should be considered a powerful and viable new resource for delving into a relatively unexplored regime for determining dust properties: composition, quantity, and distribution. Present-day studies with extant satellites will set the foundation for future studies with larger, more powerful missions such as the joint ESA–JAXA–NASA *International X-ray Observatory* \(^9\) (*IXO*). Proposed spectral instruments such as the Critical-Angle Transmission grating\(^10\),\(^11\) (CAT; Flanagan et al. \(2007\)) and Off-Plane Reflection Gratings (Lillie et al. \(2007\)) are designed to provide *IXO*’s baseline resolving power of 3000 under 1 keV, and configurations are contemplated, which will boost this to 5000 or more. Similar baseline resolving power is also expected from the calorimeters for the hard (>6 keV) spectral region. *IXO*’s target spectral resolution \( R = 3000 \) in the 0.2–10 keV bandpass, in combination with planned higher throughput (10 times *XMM*, and 60 times *Chandra*), will allow us in the future to move beyond the realm discussed in this paper to being able to use XAFS to recreate the crystalline structure of interstellar grains and determine precise oxidation states. In the interest of providing information for the planning of future missions, we provide spectral resolution goals that are mapped to XAFS science hurdles, for gratings and calorimeters (Table 2).

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\(^9\) http://ixo.gsfc.nasa.gov/.
\(^10\) http://space.mit.edu/home/dph/ixo/.
\(^11\) http://space.mit.edu/home/dph/ixo/comparison.html.