Using XAFS in Unusual Ways

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Abstract

Barium tantalum oxynitride ($BaTaO_2N$) is an odd case. It is a non-polar, centrosymmetric crystal that nonetheless has a very high dielectric constant. This is curious because a truly centrosymmetric crystal cannot maintain the persistent dipole moment that is a characteristic feature of a dielectric. I will present the results of a temperature-dependent EXAFS study that will explain this apparent contradiction. What makes this more interesting than "just another EXAFS talk" is the tight integration of the results of first-principles theory into the analytic approach. I will show how a clever analysis strategy results in a far more detailed understanding of the local structure of $BaTaO_2N$ and of the relationship between the local structure and its material properties. I will speculate on how this link between EXAFS measurement and first principles theory can be further developed. I will also consider how this theory-based approach to EXAFS analysis, which works so well for problems of materials physics, can be applied to systems of interest in other disciplines.

In the second part of this presentation, I will shift gears from a hard-core application of EXAFS to the application of absorption spectroscopy to an unusual subject. The Chandra X-Ray Observatory is NASA's *Great Observatory* dedicated to measurements at soft x-ray energies. The x-ray spectra of certain distant x-ray sources show features consistent with absorption by iron and silicon species in the solid state. The Astro-E2 facility will be launched in 2005 and will measure a broader energy range than Chandra at higher resolution. I will speculate on the possibility of using astronomical x-ray measurements along with techniques developed for synchrotron x-ray spectroscopy to determine the chemical species of materials in the interstellar medium.

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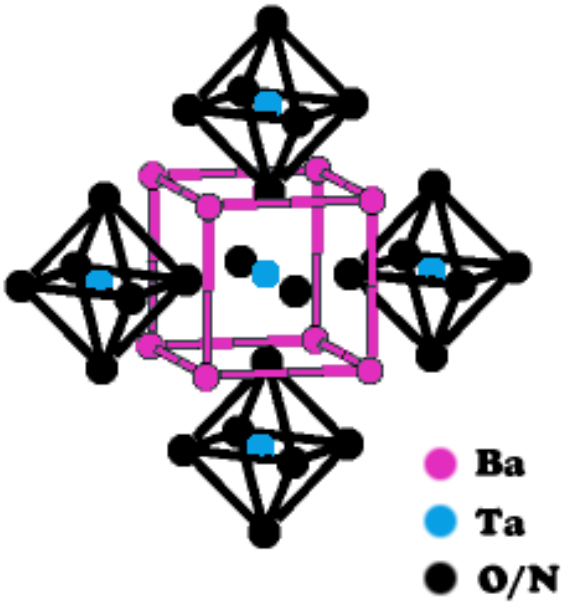
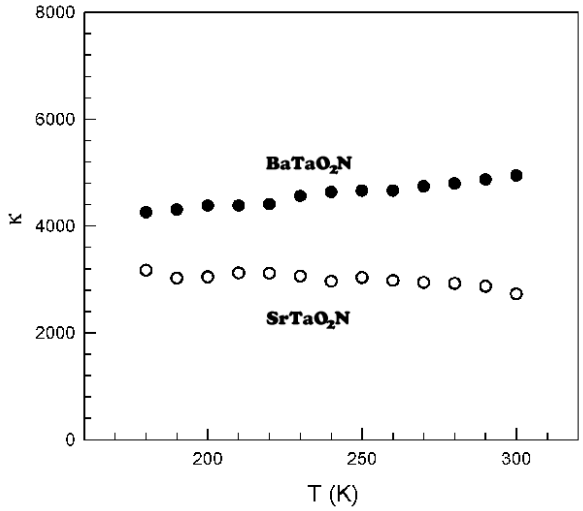
The Material

$BaTaO_2N$ is a cubic perovskite with the anion site randomly occupied by $\frac{2}{3}$ O and $\frac{1}{3}$ N.



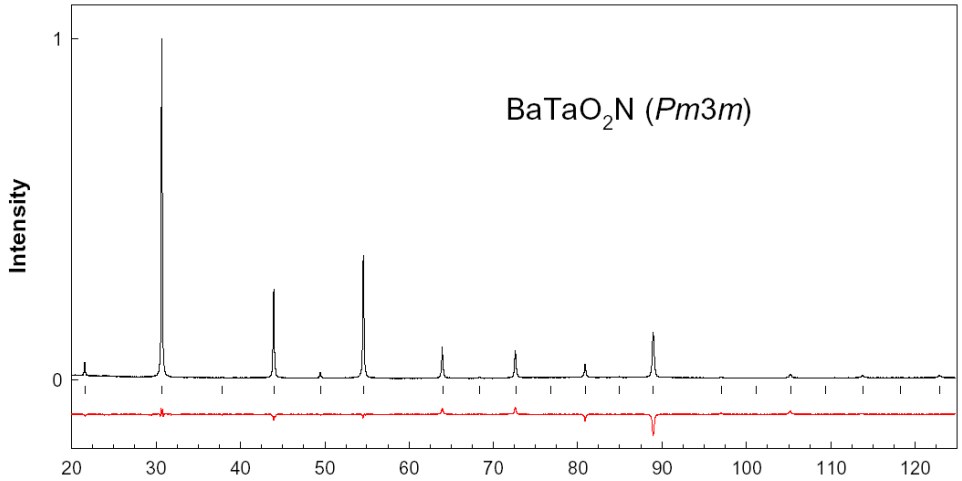
Relative permittivity from impedence spectra



Dielectrics store electrical energy, thus are used in electrically driven devices such as capacitors, resonators, switches, and so on.

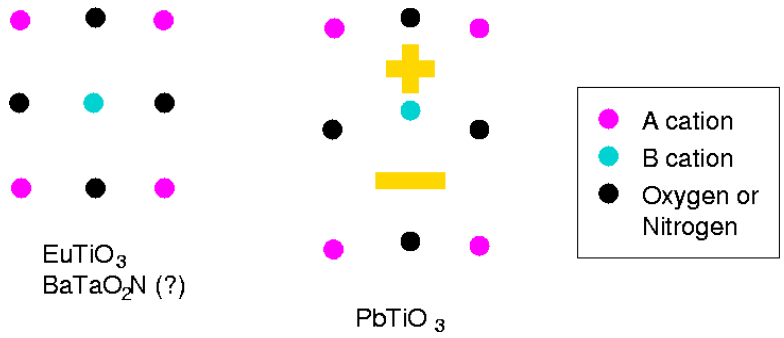
Materials design goals are a high dielectric constant, low dielectric loss, and a low temperature coefficient.

The Problem



$BaTaO_2N$ is of the $\mathtt{Pm\bar{3}m}$ space group — a non-polar, centrosymmetric group.

Y.-I. Kim et al. *Characterization of the Structurel, Optical, Dielectric Properties of Oxynitride Perovskites AMO_2N (A=Ba,Sr,Ca; M=Ta, Nb)*, Chem. Mater. **16**, (2004), pp. 1267–1276



In a crystal with atomic centrosymmetry, the charge distribution will also be centrosymmetric, thus incapable of supporting a persistent dipole moment.

Broken atomic symmetry implies broken charge distribution symmetry.

A portion of the unit cell will slightly positive and another slightly negative.

Two Possible Solutions

Boundary layer dielectric

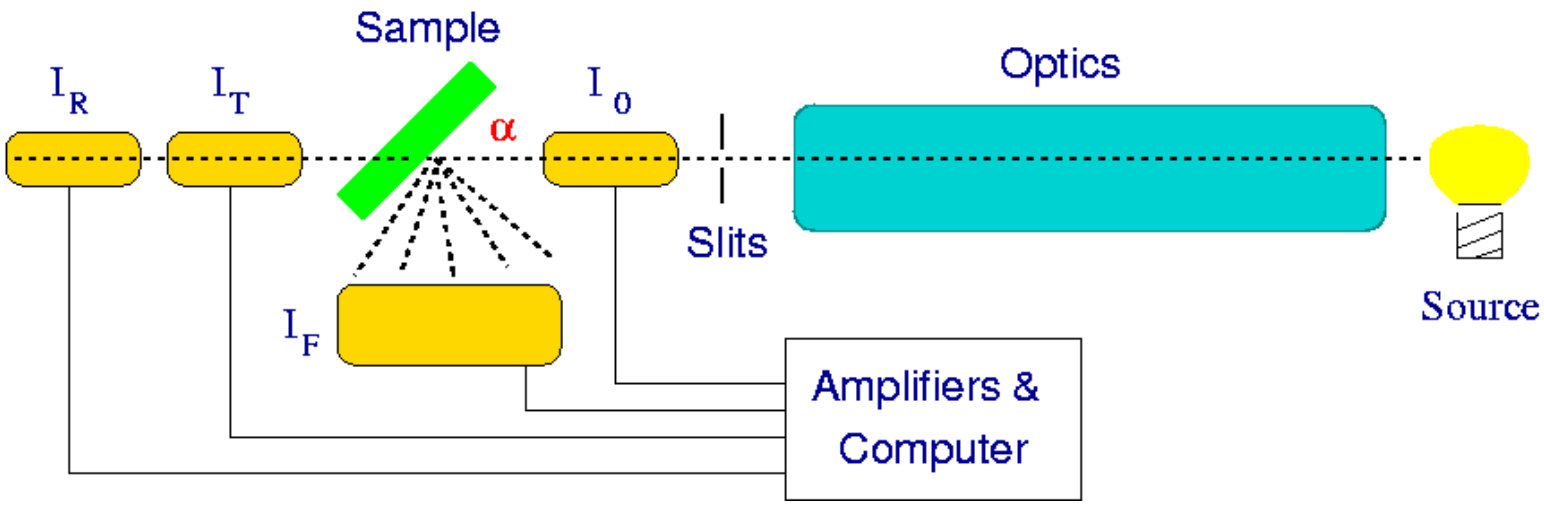
Grains might be bounded by a polarizable TaO_x or BaO_x oxide layer. This explanation is consistent with the large dialectric loss due to poor sintering, but is not consistent with impedence measurements.

Local disorder

The size and electronegativity difference between O and N could lead to local distortions which are uncorrelated over large length scales. These local distortions could support persistent dipole within the unit cells.

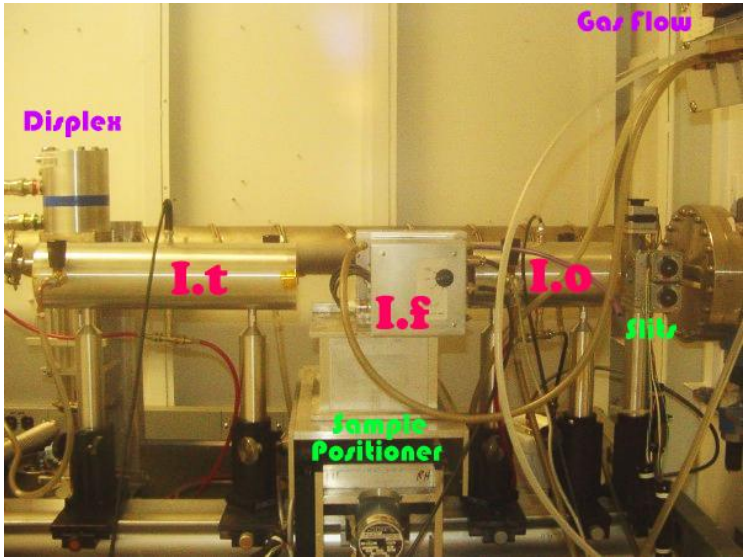
EXAFS is exactly the right tool to explore the second possibility.

The Experiment



For the $BaTaO_2N$ experiment, the sample was measured in transmission and was mounted on a Displex cryostat.

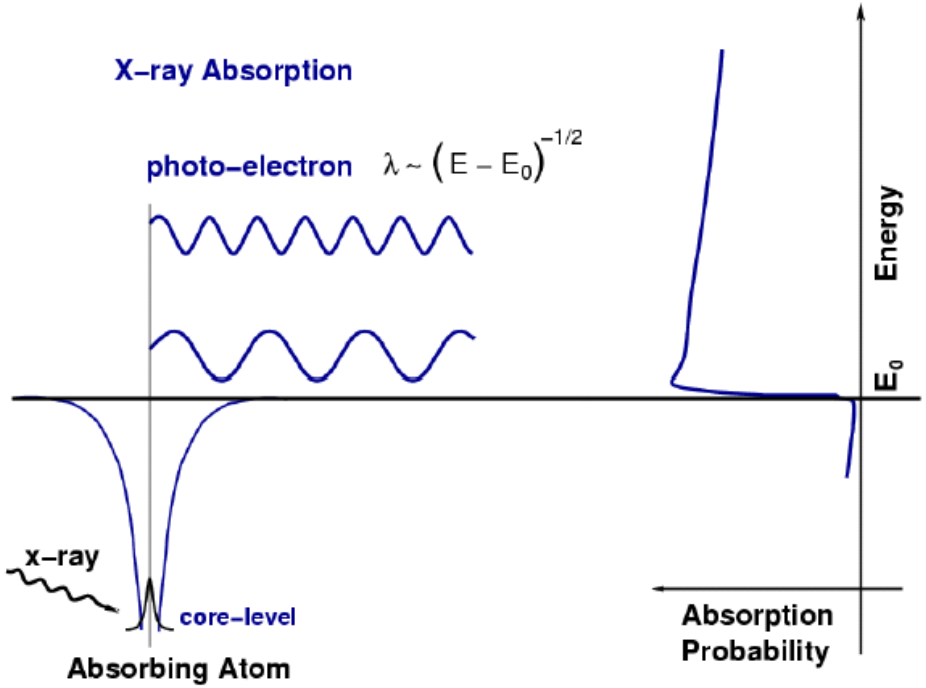
Care was taken to make a uniform sample of an appropriate thickness for the Ta L_{III} edge.



This is NSLS X11A's hutch.

X-ray absorption by a free atom

An atom absorbs an x-ray of energy E, destroying a core electron with energy E_0 and emitting a photo-electron with kinetic energy $(E - E_0)$. The core state is eventually filled, ejecting a fluorescent x-ray or Auger electron.



An empty final state is required.

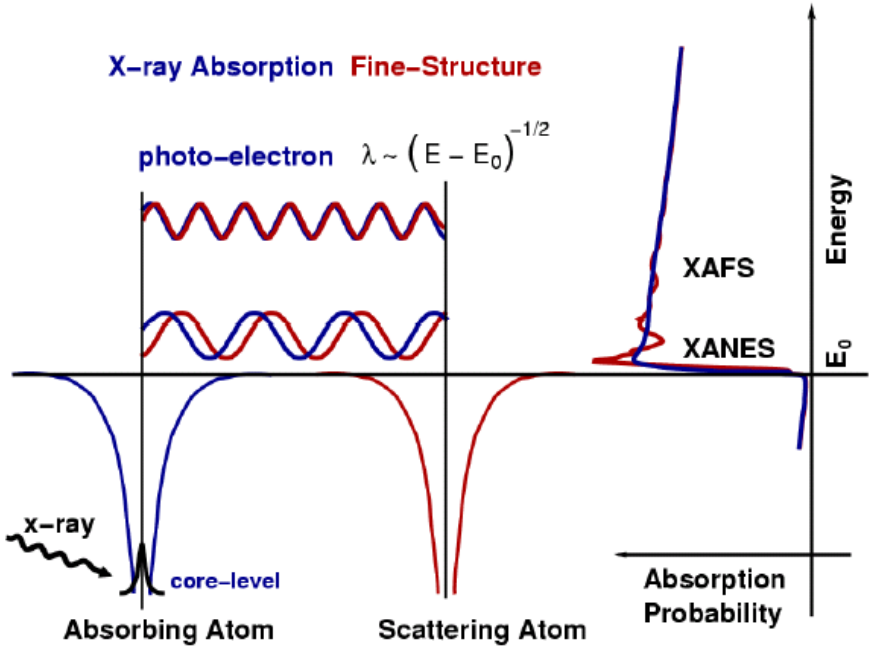
No available state,
no absorption!

Once the x-ray energy is large enough to promote a core electron to the continuum, there is a sharp increase in absorption.

For an isolated atom, $\mu(E)$ has a sharp step at the core-level binding energy and is a smooth function of energy above the edge.

X-ray absorption with photo-electron scattering

The ejected photo-electron can scatter from neighboring atoms. R has some relationship to λ and there is a phase shift associated with the scattering event. Thus the outgoing and scattered waves interfere.



The scattering of the photo-electron wave function interferes with itself.

$\mu(E)$ depends on the density of states with energy $(E - E_0)$ at the absorbing atom.

This interference *at the absorbing atom* will vary with energy, causing the oscillations in $\mu(E)$.

The EXAFS Equation

$$\chi(k,\Gamma) = \mathrm{Im}\left(\frac{(N_\Gamma S_0^2) F_\Gamma(k)}{k R_\Gamma^2} e^{i(2kR_\Gamma + \Phi_\Gamma(k))} e^{-2{\sigma_\Gamma}^2 k^2} e^{-2R_\Gamma/\lambda(k)} \right)$$

$$R_\Gamma = R_{0,\Gamma} + \Delta R_\Gamma \qquad k = \sqrt{2m_e(E - E_0)/\hbar^2}$$

$$\chi(k) = \sum_\Gamma \chi(k,\Gamma)$$

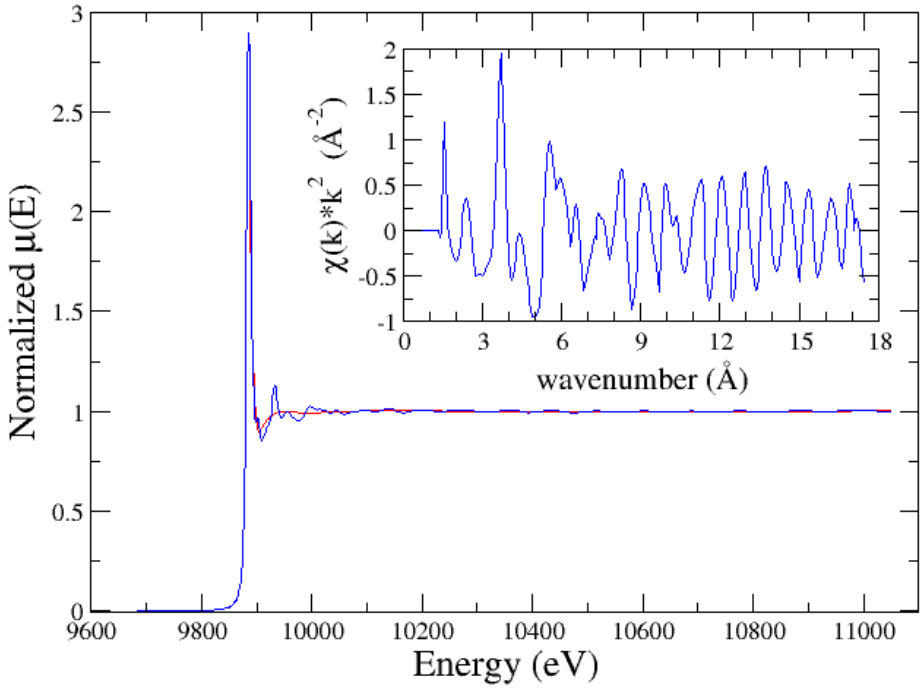
Multiple scattering theory is used to generate the brown terms

- $R_{0,\Gamma}$ nominal path length
- F_Γ effective scattering amplitude
- Φ_Γ effective scattering phase shift
- λ mean free path

Structural and electronic information is determined from the blue terms

- ΔR_Γ change in half path length
- σ_Γ mean squared displacement
- N_Γ path multiplicity
- S_0^2 passive electron reduction
- E_0 overall energy shift

The Data



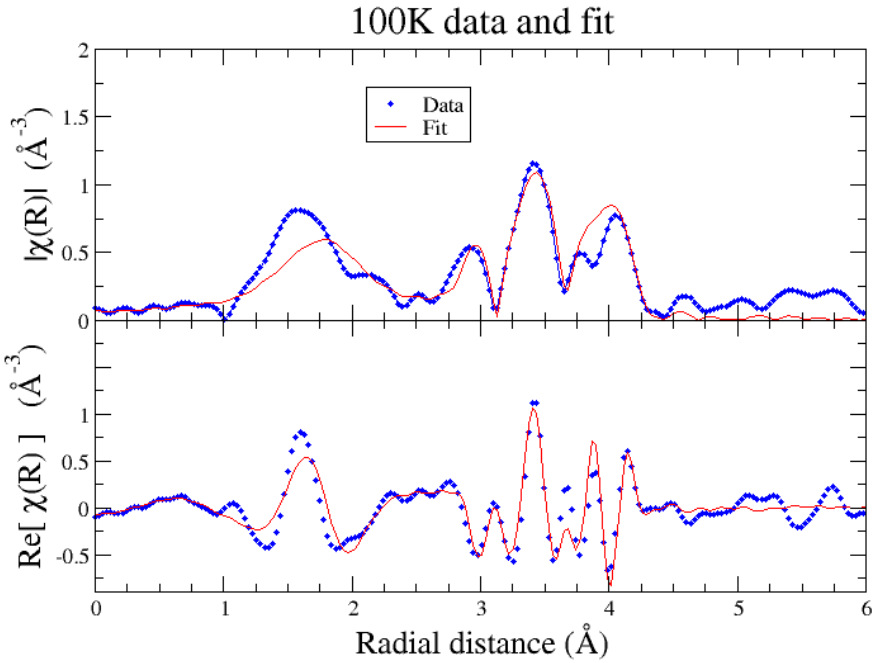
Data were collected in transmission at 10, 100, 200, 300 K.

The $\chi(k)$ fine structure was isolated from the $\mu(E)$ spectrum using the AUTOBK algorithm and the ATHENA program.

How hard can it be to analyze data this good?!?!

The Cubic Perovskite Model

In this model, I assume that the local structure is well-described by the perovskite structure and cumulant distributions about the absorber–scatterer pairs.



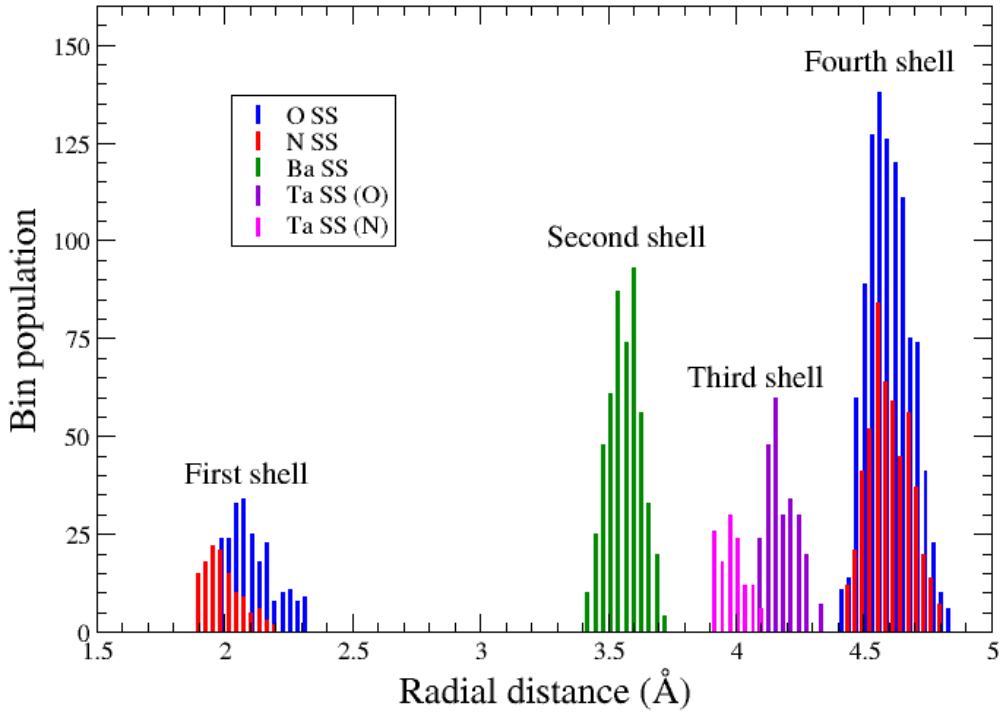
parameter	value
α	0.024(5)
E_0	14.6(6)
E_0(MS)	10.4(4)
σ^2_{O}	505(20) K / 0.0181(2) Å^2
σ^2_{Ba}	261(45) K / 0.0065(6) Å^2
σ^2_{Ta}	249(4) K / 0.0032(1) Å^2
σ^2_{O4}	very large
C_3(O)	-0.0005(1)
C_3(Ba)	0.0008(2)
C_3(Ta)	0.0002(2)

Not so great!

Significant misfit in the 1st shell & at 3.5 – 3.9 Å. Very large static σ^2, two E_0's, large α.

Something is missing from this model.

Local Distortion Model: Single Scattering



The total energy was minimized for a box of $4 \times 4 \times 4$ unit cells, with 320 atoms and periodic boundary conditions. I found all pairs involving at least one Ta and collected them into bins 0.02 Å wide.

Bimodal distributions in 1^{st} and 3^{rd} shells due to O/N. Note that the 4^{th} shell is **not** bimodal.

C.M. Fang et al. *Local structure and electronic properties of $BaTaO_2N$ with perovskite-type structure*, J. Phys. Chem. Solids **64**, (2003), pp. 281–286

Revisiting the EXAFS Equation

The EXAFS equation fits well with the concept of a histogram.

$$\chi(k,\Gamma) = \mathrm{Im}\left(\frac{(N_\Gamma S_0^2) F_\Gamma(k)}{64\, k R_\Gamma^2} e^{i(2kR_\Gamma + \Phi_\Gamma(k))} e^{-2{\sigma_\Gamma}^2 k^2} e^{-2R_\Gamma/\lambda(k)} \right)$$

$$R_\Gamma = R_{0,\Gamma} + \Delta R_\Gamma \qquad k = \sqrt{2m_e(E - E_0)/\hbar^2}$$

$$\chi(k) = \sum_\Gamma \chi(k,\Gamma)$$

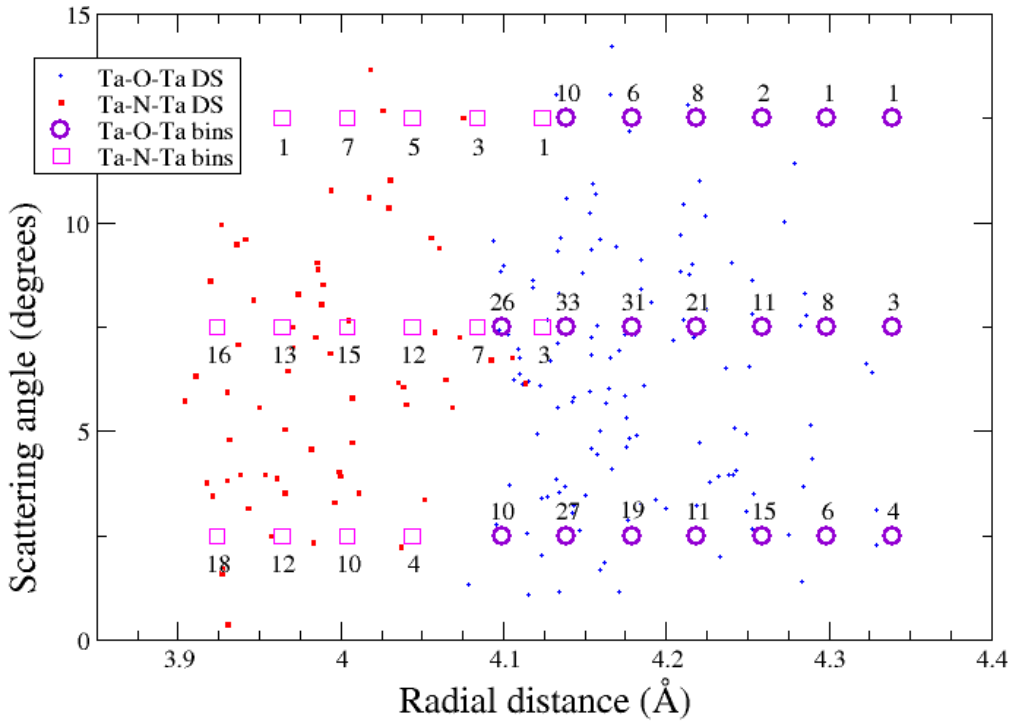
Multiple scattering theory and the cubic perovskite structure are used to generate the brown terms for the SS paths

R_0	from the cubic perovskite
F_Γ, Φ_Γ, λ	from FEFF

Details of the histogram representation the RDF are expressed using the blue terms

ΔR_Γ	$(R_{\mathrm{bin}} - R_0) \times (1 + \alpha)$
σ_Γ	like cubic model
N_Γ	bin population

Local Distortion Model: Multiple Scattering



Also found all nearly-collinear, 3-body distributions Ta–N–Ta or Ta–O–Ta, around the 3rd shell distance. These are spread over some dstribution of length and angle.

There is no simple way to parameterize the dependence on scattering angle of $F(k)$ and $\Phi(k)$ in the EXAFS equation.

Collect paths into bins of $5° \times 0.03$ Å. Run FEFF specially for each bin.

The Scary Details of How FEFF was Coerced into Computing the MS Bins

'paths.dat'

```
BaTaO2N, data from Kim, Woodward et al preprint
Rmax  6.5000,  keep limit  0.000, heap limit  0.000  Feff 6L.02  paths 3.05
Plane wave chi amplitude filter   2.50%
-----------------------------------------------------------------------
  101    3  20.000  index, nleg, degeneracy, r=  4.0990
    x          y          z     ipot  label      rleg    beta      eta
  2.049744    0.000000    0.000000   3 'O     '
  4.097537    0.089409    0.000000   2 'Ta    '
  0.000000    0.000000    0.000000   0 'Ta    '
  102    4  10.000  index, nleg, degeneracy, r=  4.0995
    x          y          z     ipot  label      rleg    beta      eta
  2.049744    0.000000    0.000000   3 'O     '
  4.097537    0.089409    0.000000   2 'Ta    '
  2.049744    0.000000    0.000000   3 'O     '
  0.000000    0.000000    0.000000   0 'Ta    '
```

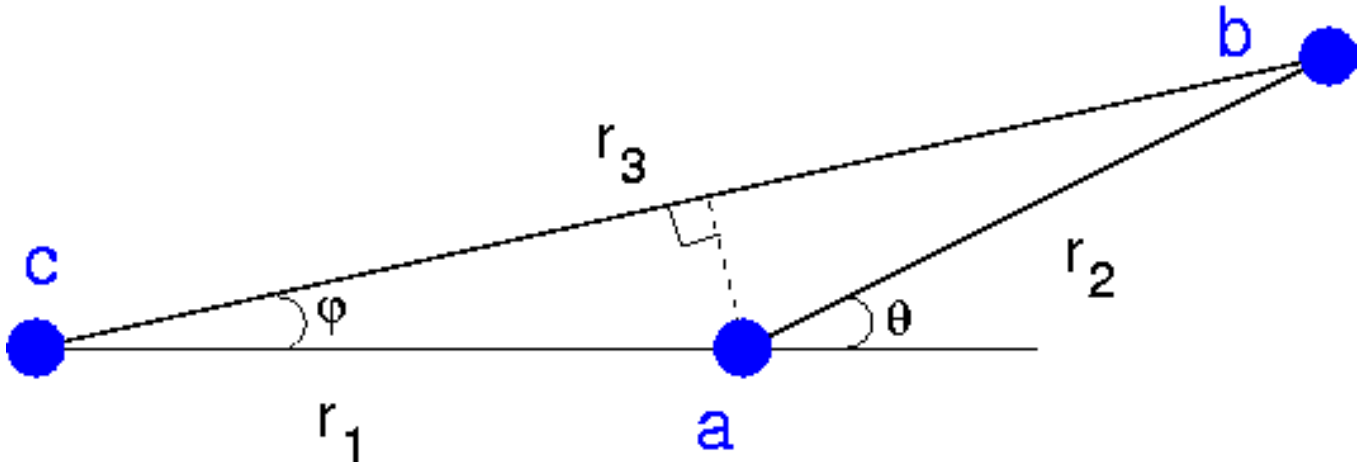
```
TITLE BaTaO2N, data from Kim, et al Chem. Mater. 16 (2004) 1267

HOLE 4 1.0 *  Ta L3 edge (9881.0 eV), 2nd number is S0^2

*         mphase,mpath,mfeff,mchi
CONTROL   0      0     1     1
PRINT     0      0     0     0

RMAX        6.0
                          *  the rest of the file is unchanged...
```

Run FEFF using the cubic perovskite structure to get the scattering amplitudes and phase shifts for the Ta, O, and N atoms, which are contained in the 'phase.bin' file.

Construct DS and TS paths in 'paths.dat' for each three-body bin with the **correct length, angle, and population**.

Run FEFF **again**, this time with only the second two CONTROL values set to 1. This will produce 'feffNNNN.dat' files for each entry in the specially constructed 'paths.dat'.

The Scary Details of Creating the Three-Body Paths



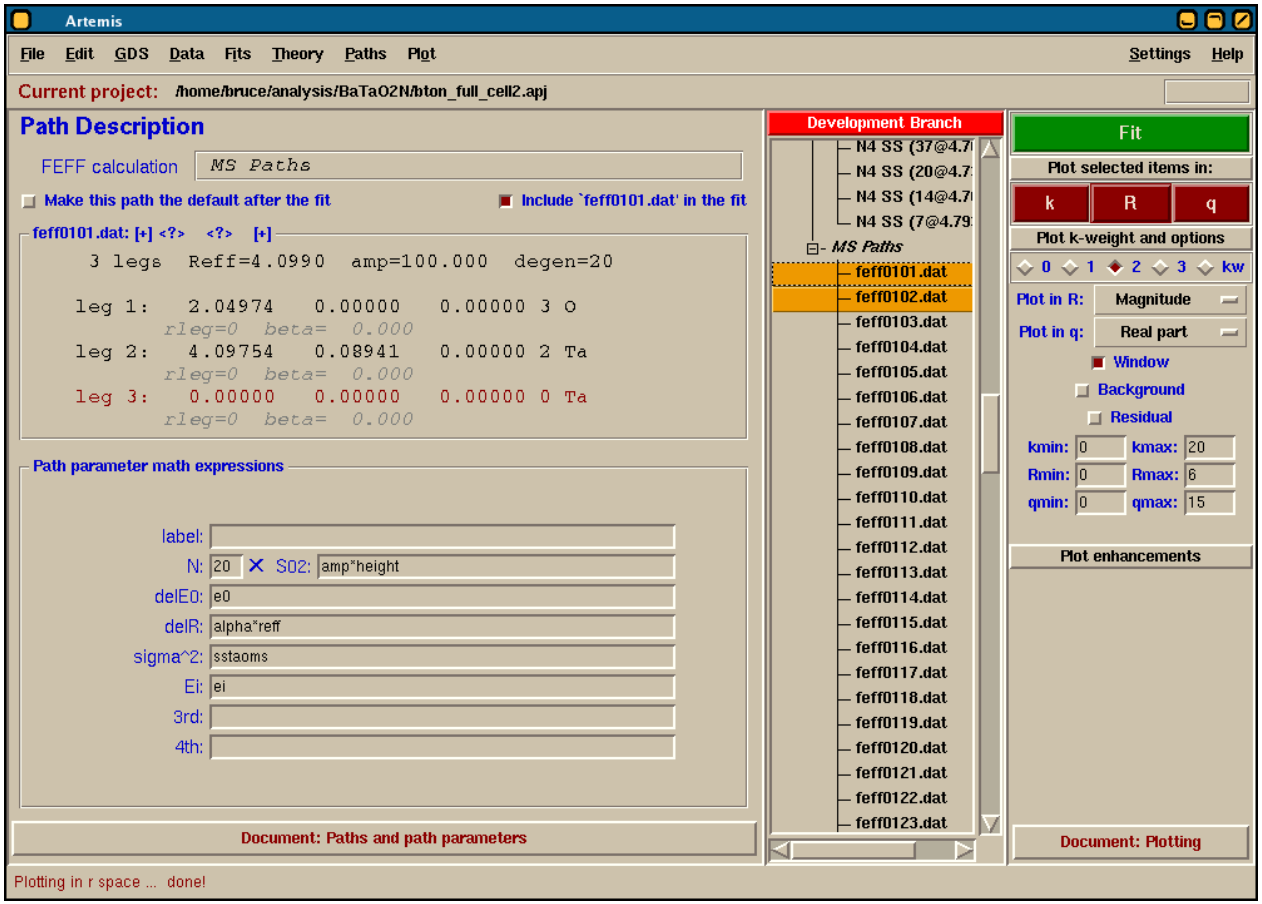
R and θ are the values for each three-body bin.

C is at $(0,0,0)$
A is at $(x,0,0)$
B is at $(x\big(1+\cos(\theta)\big), x\sin(\theta), 0)$

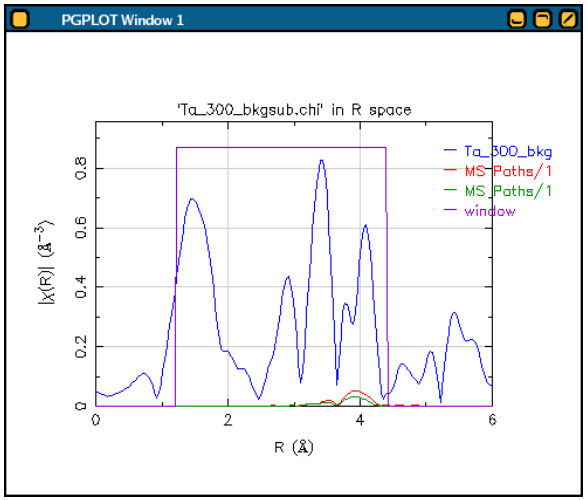
$$r_1 = r_2 \equiv x$$
$$R = 2x + r_3 \quad (1)$$
$$\phi = \frac{\theta}{2} \quad (2)$$
$$\cos(\theta/2) = \frac{r_3}{2x} \quad (3)$$
$$r_3 = 2x\big(1+\cos(\theta/2)\big) \quad (1\&3)$$
$$x = \frac{R}{2\big(1+\cos(\theta/2)\big)}$$

The positions A, B, and C are printed to the '`paths.dat`' file shown on the previous page.

The Scary Details Continued

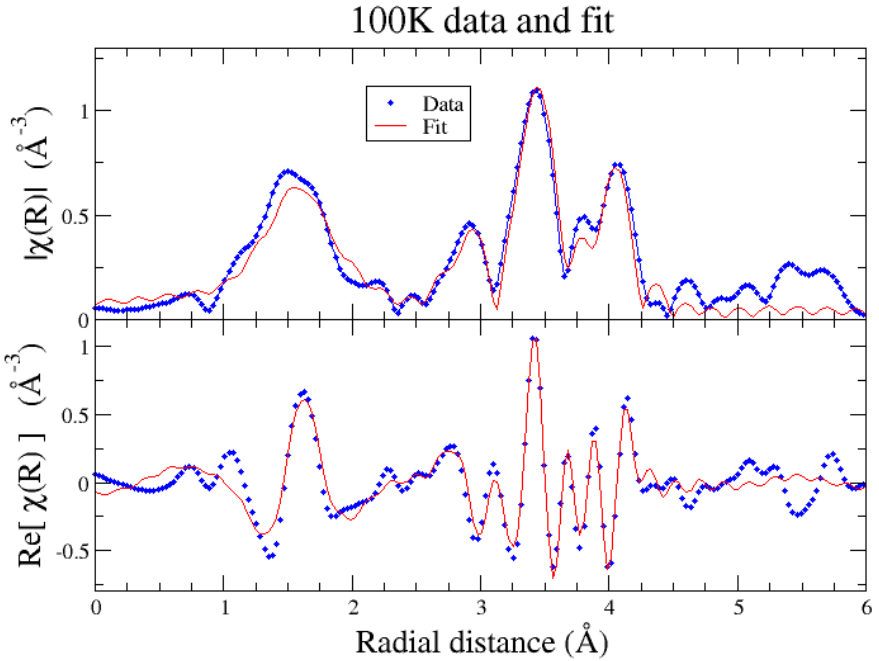


N is set to the bin population, The S02 parameter is the product of S_0^2 and a normalization constant. delR is modified by the lattice expansion coefficient α, sigma2 is constrained to be the same as the σ^2 parameter for the Ta–Ta SS path.



Local Distortion Model: Fit to the Data

79 SS bins + 138 nearly collinear DS and TS bins



parameter	value
α	0.0034(5)
E_0	10.2(1)
σ^2_{O}	441(85) K / 0.0039(12) Å^2
σ^2_{Ba}	249(25) K / 0.0010(3) Å^2
σ^2_{TaO}	302(42) K / −0.0008(3) Å^2
σ^2_{TaN}	577(89) K / −0.0026(7) Å^2
σ^2_{O4}	343(39) K / 0.0051(12) Å^2

Much better!

Closer fit in 1$^{\mathrm{st}}$ shell and at 3.5 – 3.9 Å. Reasonable, σ^2 & α, E_0 parameters, no C_3.

Implications of this work for $BaTaO_2N$

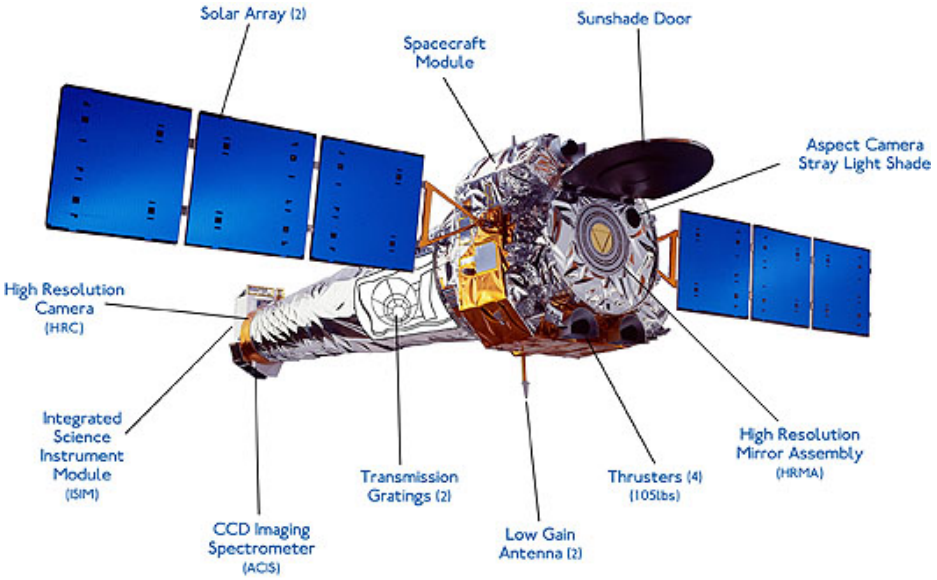
- The results of Fang et al. are consistent with these data.
- Local distortions explain the dielectric properties of $BaTaO_2N$ by providing a mechanism for storing electrical energy in the crystal.
- Fang's results suggest that the correlation length of the local distortions is around 1 unit cell length. This explains the XRD results.
- Shortcomings of the model:
  - There seems to be slightly too little disorder in Fang's results, judging from the non-zero σ^2 offsets.
  - Due to the large white line, the background removal was challenging and highly correlated to the 1^{st} shell parameters. σ^2_O and σ^2_N could not be independently measured.
  - A single calculated scattering function was used for each SS bin.
  - The MS bins subtend a rather large range of angles.
  - There is no convenient way to parameterize the details of the distributions from the energy minimization.

Future Work

- Other oxynitrides, ABO_2N, A $\in$ {Ba, Sr, Ca, B $\in$ {Ta, Nb. $SrTaO_2N$, for instance, is tetragonal but polar. Presumably it's dielectric properties are explained the same way as $BaTaO_2N$.
- The histogram approach to data analysis needs to be better integrated into the data analysis procedures and software.
- An $\mathcal{R}$-factor from a fit to the EXAFS data can be used as an entropy term in the energy minimization. Thus the experiment can help drive the energy minimum solution of the structure.

How is this Materials Physics Problem Relevant to other Disciplines?

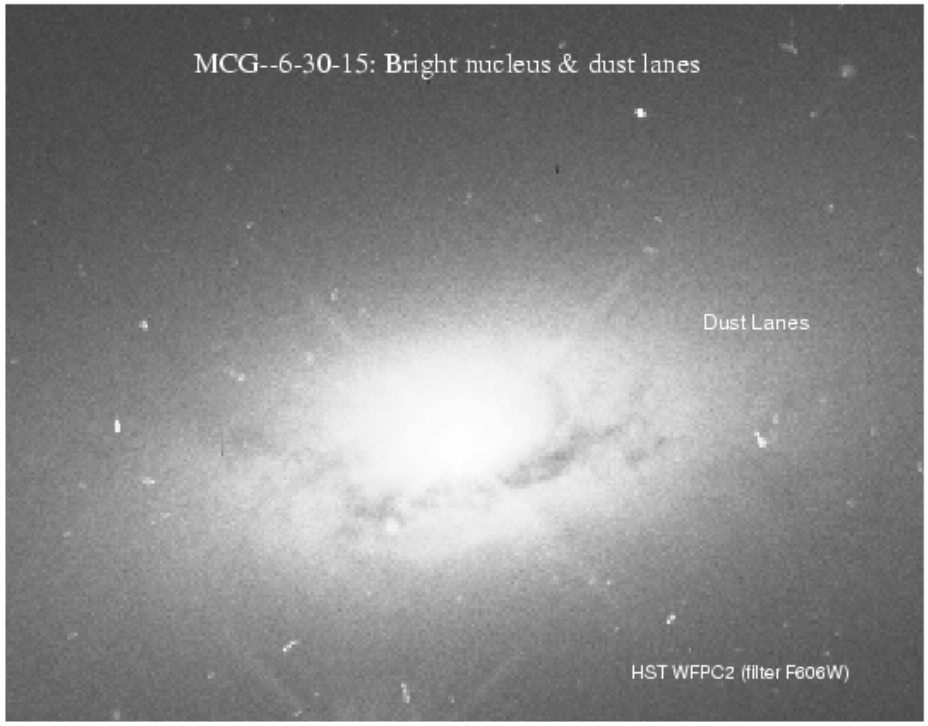
The Chandra X-Ray Observatory

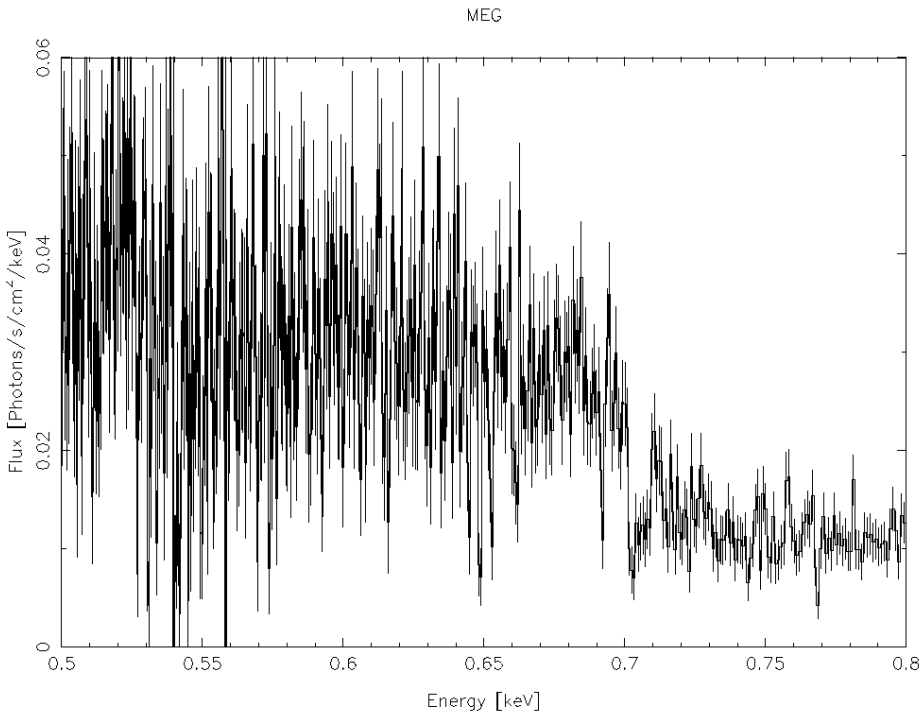


Chandra was launched July 23, 1999. It's x-ray spectrometer has $\Delta E/E \simeq 10^{-3}$ over the range of what synchrotron folk call soft x-rays.

Iridium coated mirrors form a conical array focusing on a CCD at the rear of the satellite.

Seyfert galaxy MCG-6-30-15





This x-ray source is a brightly emitting black hole. The data shown is from one of two 60 kilosecond observations in 2000. A variety of features in the spectra are attributed to relativistic effects or to absorption of highly ionized atoms, e.g. the feature near 690 eV is attributed to absorption of helium-like oxygen, O^{VI}.

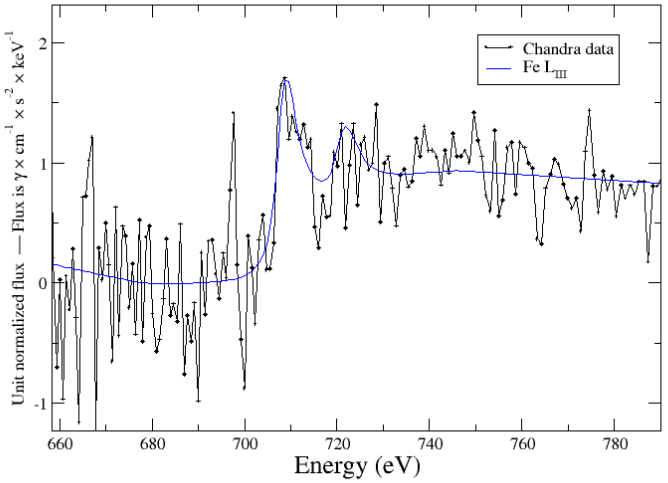
The Worst "Beamline" You've Ever Seen

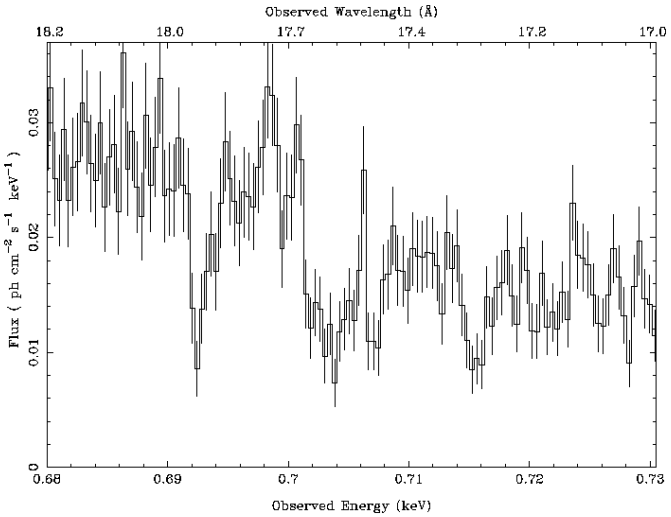
This is not an ideal XAS experiment!

synchrotron	$\Longrightarrow$	pulsar
10s of meters from the source	$\Longrightarrow$	mega light years from the source
carefully prepared sample	$\Longrightarrow$	miscellaneous dust along the flight path
$\Delta E/E \sim 10^{-4}$	$\Longrightarrow$	$\Delta E/E \sim 10^{-2}$ or 10^{-2}
$> 10^6$ counts per second	$\Longrightarrow$	$\mathcal{O}(10^2)$ counts per bin
conveniently located	$\Longrightarrow$	in space
easy to get more beamtime	$\Longrightarrow$	limited lifespan, limited duty cycle

But it **is** a way of measuring an absorption spectrum. If the neutral atom absorption edges can be disentangled from excited atom lines and the issues of noise and resolution can be dealt with, these spectra might have something to say about the nature of the interstellar medium.

The ~ 17 Å Spectrum from MCG-6-30-15



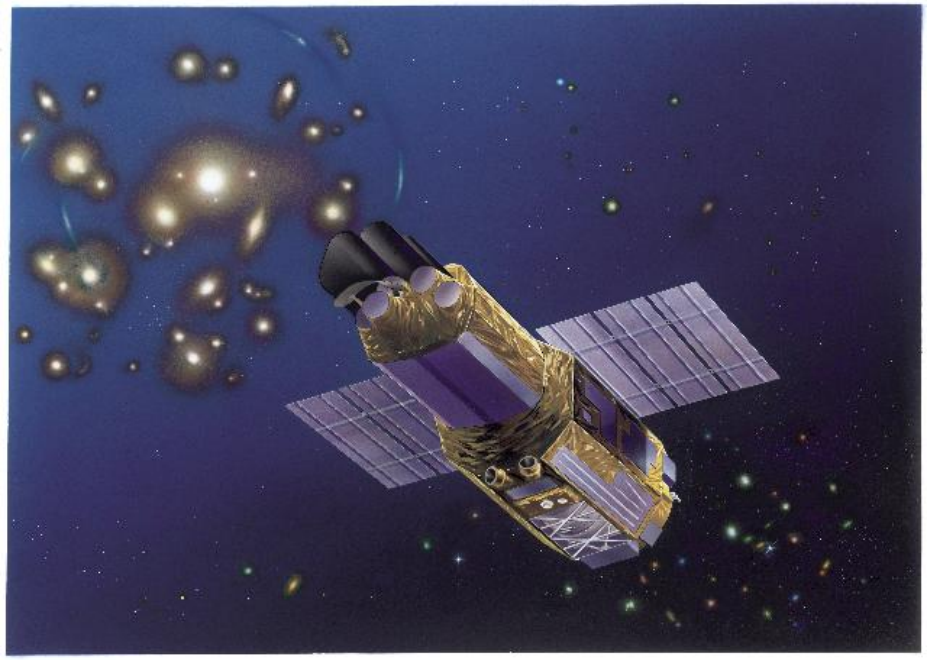


The left is a snippet of the 120 kiloseconds of observation of the MCG-6-30-15 signal around the Fe $L_{3,2}$ edges just above 700 eV plotted with an artificially broadened iron foil spectrum. Each point represents about 25 counts.

The right is a subsequent 540 kilosecond observation of MCG-6-30-15. Each point represents about 120 counts.

This makes a 10 ppm environmental sample seem positively chock-full of signal!

The Astro E2 Observatory

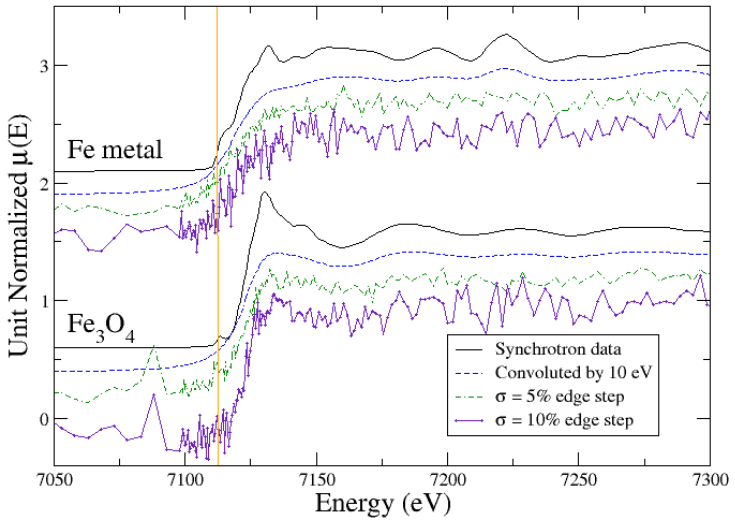


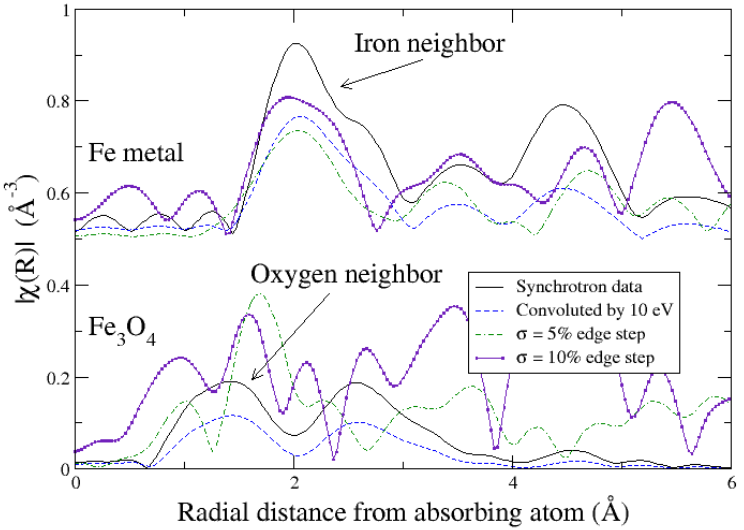
This will carry an X-ray Spectrometer, a calorimeter with 0.3-12 keV energy range, and 6 eV FWHM resolution. resolution

It is a Japanese/US joint effort with a scheduled early 2005 launch. (Astro E failed in February 2000.)

We have applied for 200 kiloseconds (about 2 days, $7\frac{1}{2}$ hours) of observation time — that's a lot!

The Effect of Noise on the Astro E2 XAFS Measurement



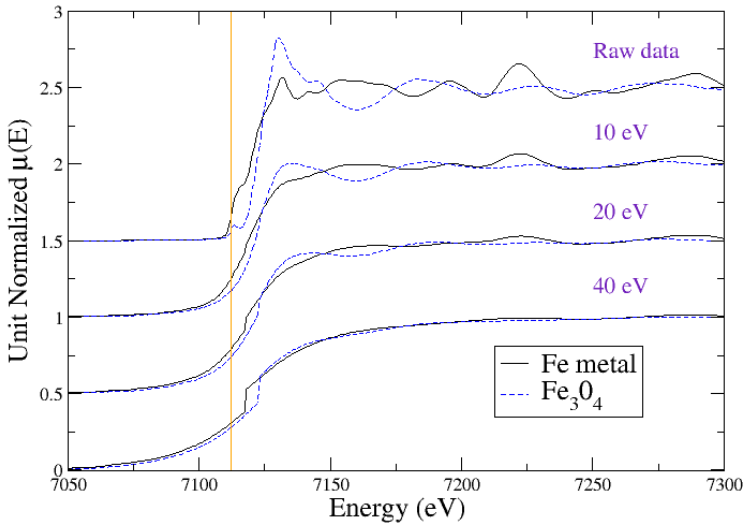


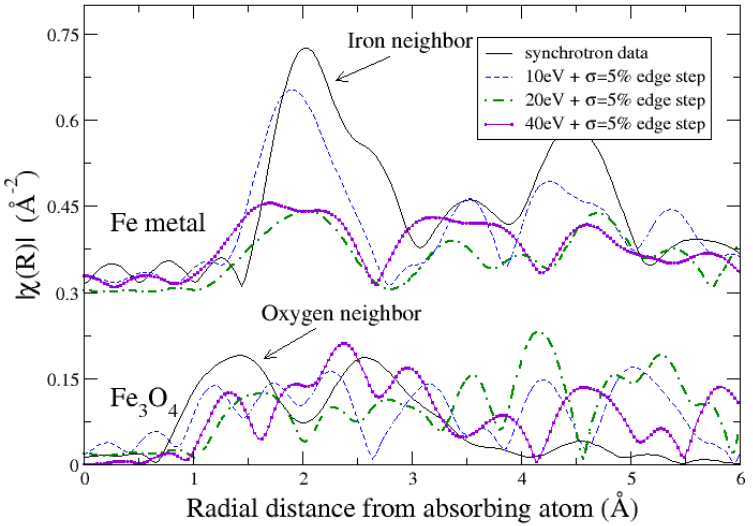
We have convolved measured synchrotron data by 10 eV to conservatively simulate the resolution of the calorimeter. We then add noise with σ as a fraction of the edge step.

The metallic spectrum can tolerate a high level of noise (10% of the edge step) and still be recognizable as metallic iron.

The oxide spectrum is much more sensitive to the noise. Even 5% noise renders the spectrum unidentifiable. So noise is a very serious problem to doing *extended* XAFS with the satellite.

The Effect of Resolution on the Astro E2 XAFS Measurement



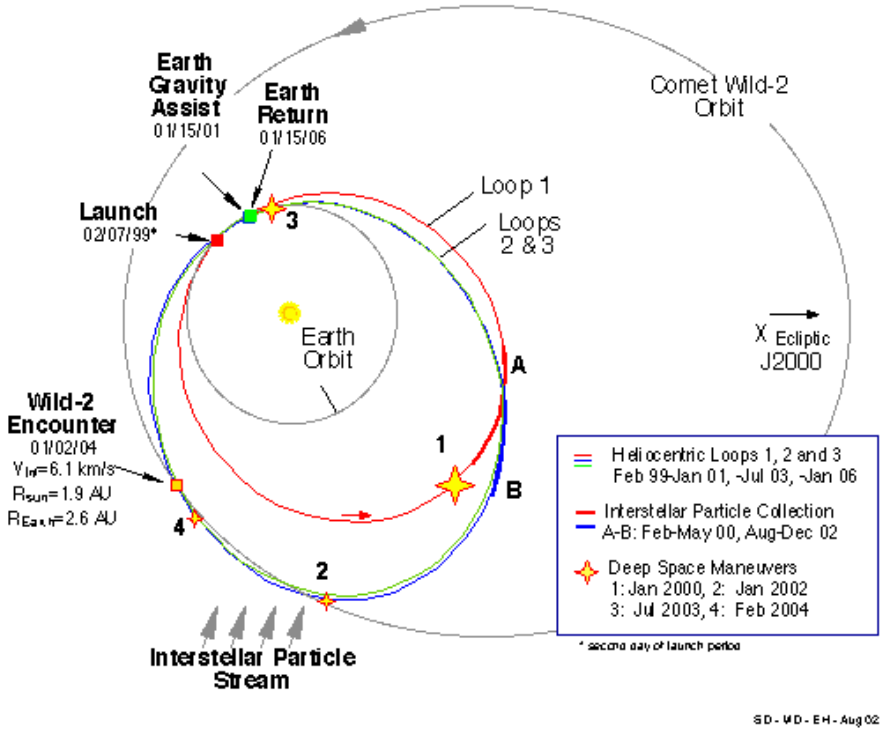


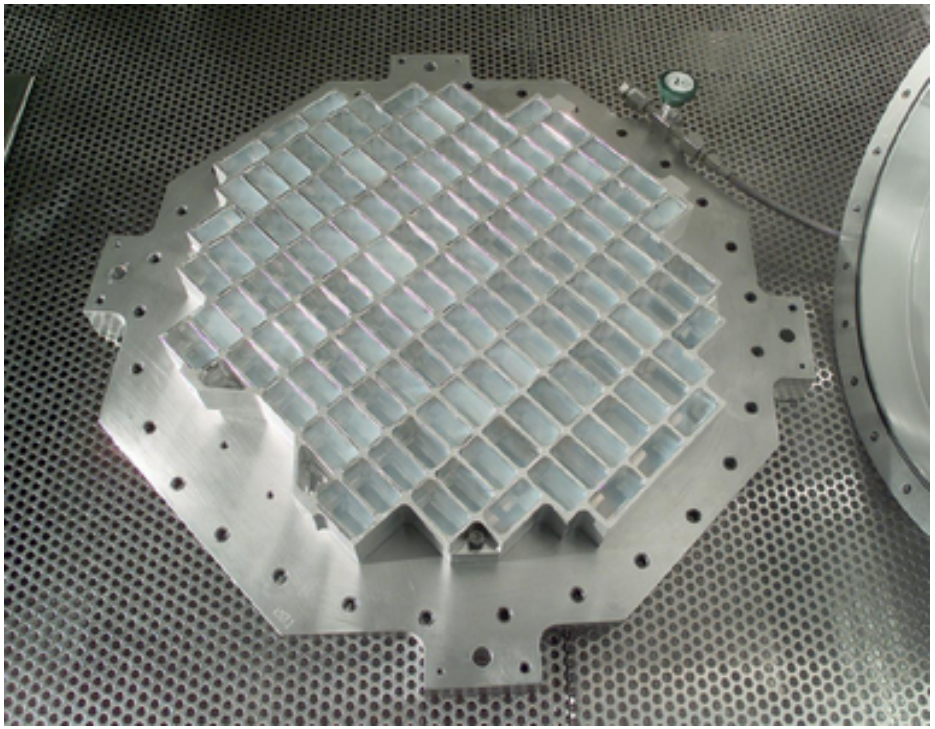
A common way of increasing signal-to-noise in the satellite business is to rebin the data into larger bins.

Here we simulate the effect of rebinning by convolving the data by 10, 20, and 40 eV. The largest convolutions render the XANES spectra essentially indistinguishable. Larger convolution also makes the EXAFS data more susceptible to noise.

Rebinning is not an acceptable method of increasing signal-to-noise. Counting longer is only real solution.

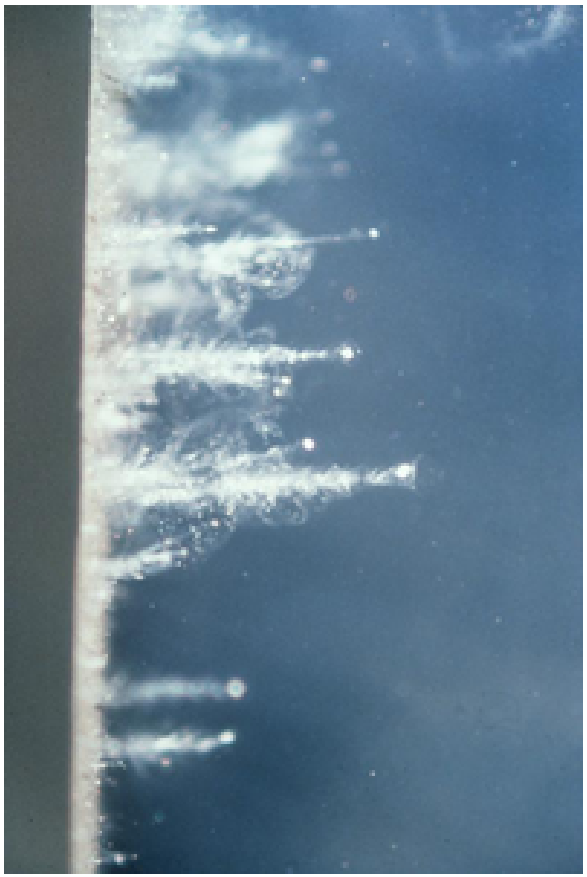
The Stardust Flight Path and Collector





7 February 1999: Launch. **February-May 2000**: 1st Interstellar dust collection. **15 January, 2001**: Earth gravity assist. **April 18, 2002**: Aphelion. **August-December 2002**: 2nd Interstellar dust collection, **November 2, 2002**: Asteroid Annefrank flyby. **January 2, 2004**: Comet Wild 2 encounter. **January 15, 2006**: Earth return.

Cool Aerogel Pix



The pic to the left shows the result of using an airgun to fire dust motes into the aerogel to simulate the passage through the comet tail.

The pics to right are just kinda cool.

Materials and Experiments

In January 2006, Stardust will return to earth and land in the Utah desert via parachute, much like the recent failed XXXX mission. After retrieval, the materials will be available to researchers via proposal to NASA.

- Fluorescence tomography more 3d elemental maps of the particles. μ-fluorescence for 2d maps of larger particles.
- Absorption tomography or μ-XAS to speciate minerals in the particles.
- Cryo-STXM (NSLS X1A) for L-edge and water-window mapping of particles.

References

A link to a copy of this PDF file will be on my web site after I get home:
`http://feff.phys.washington.edu/~ravel/`

References relevant to this paper.

1. Kim, et al. Chem. Mater. **16** (2004) pp. 1267–1276
2. Fang, et al. J. Chem. Phys. Solids **64** (2003) pp. 281–286
3. Lee, et al. Astrophys. J. **554** (2001) pp. L13–L17
4. Lee, et al. Astrophys. J. **567** (2002) pp. 1102–1111
5. Woo, Astrophys. J. **447** (1995) pp. L129–L132
6. Woo, et al. Astrophys. J. **477** (1997) pp. 235–240
7. Forrey, et al. Astrophys. J. **505** (1998) pp. 236–243

URLs for the analysis software mentioned in this presentation:

1. FEFF: `http://feff.phys.washington.edu/feff/`
2. IFEFFIT: `http://cars.uchicago.edu/ifeffit/`
3. ATHENA, ARTEMIS: `http://feff.phys.washington.edu/~ravel/software/exafs/`

URLs for the space missions mentioned in this presentation:

1. Chandra: `http://chandra.harvard.edu/`
2. Astro E2: `http://heasarc.gsfc.nasa.gov/docs/astroe/astroegof.html`
3. Stardust: `http://stardust.jpl.nasa.gov/`

About this document

This document covers research performed during 2004 in collaboration with Patrick Woodward of Ohio State University, Changming Fang of Eindhoven University of Technology, and Julia Lee of MIT and Harvard.

This document was created using a variety of free software tools, including PDFLaTeX, the XEmacs text editor and the excellent editing mode AUCTeX, xmgrace, xfig, and rasmol. Screenshots were made using KSnapshot. Some image editing was done with the gimp and with ImageMagick. KGhostView and the Adobe Acrobat Reader (which is free of cost, but is not really free software) were used to view the document as I was writing it.

The text and layout of this document is just LaTeX, pure and good! The source files are available from my web page, as is a PDF file of this document.

The image of $BaTaO_2N$'s dielectric constant and diffractogram were taken from the paper by Kim et al. The images explaining absorption by a free atom and absorption in a solid were taken from a talk by Matt Newville. The image of and data from the Seyfert galaxy was provided by Julia Lee. The various images of the Chandra, Astro E2, and Stardust missions were taken from the press sections of the respective web sites.

Notes