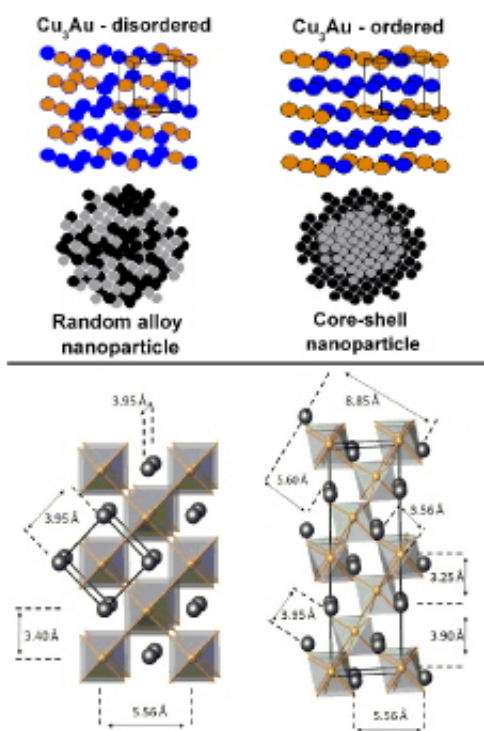


Extending resonant diffraction to very high energies for structural studies of complex materials

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Systems investigated using the high-energy resonant PDF method: the (dis)ordered phases of Cu_3Au , PtPd random-alloy and core-shell nanoparticles (upper part), and the BiFeO_3 perovskite structure (undistorted and distorted; lower part).

(PhysOrg.com) -- Researchers utilizing the U.S. Department of Energy's Argonne Advanced Photon Source (APS) have added a twist to the high-

energy x-ray pair-distribution-function (PDF) technique by conducting measurements near heavy-element K absorption edges. This exploits resonant scattering to render it selective to the environment of the resonant species. A view of the atomic surroundings from a specific element's vantage point can be simpler to interpret. This approach can be used to gain structural insight into the intrinsic disorder in complex materials, and has been applied to PtPd core-shell nanoparticles relevant to fuel cell catalysis and the multi-ferroic BiFeO₃ perovskite of interest in microelectronics applications. Both are examples of nanostructured materials exhibiting disorder that is relevant to their potential applications.

The well-known atomic pair-distribution function method is a combined diffraction and analysis technique that treats Bragg and diffuse scattering in a unified manner that is well-suited for high-spatial-resolution studies of [complex materials](#) with intrinsic disorder. The PDF method's strength lies particularly in the use of high-energy x-rays (60-120 keV), which provide penetration into contained environments; improved validity of the so-called Born approximation (i.e., single-scattering) that is almost always assumed in extracting structure from scattering data; and accessibility to high momentum-transfers, giving fine real-space atomic resolution upon Fourier inversion. This fairly routine technique provides information via a result called the total atomic PDF, which is a weighted sum of elemental pair-correlation functions in real space, one for every pair of chemical species in the material.

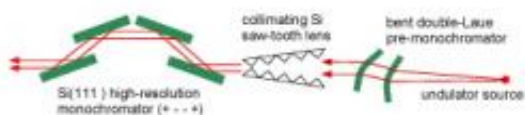
Researchers from the APS and Central Michigan University have taken the high-energy PDF technique a step further by making the diffraction measurements near heavy-element K edges, taking advantage of resonant (i.e., anomalous) scattering. When possible, this offers the added strength of elemental environmental selectivity by providing the differential atomic PDF that gives the distribution of distances to neighboring atoms relative to a central atom of the resonant species only,

similar to the result from the extended x-ray absorption fine structure (EXAFS) method. Unlike EXAFS, which yields atomic ordering information out to 5-6 Å, the differential PDF will show such correlations up to the longest interatomic distances to which they extend. Instead of being faced with the superposition of all pair-correlations in a total PDF (which can be difficult to interpret), differential PDFs can offer unambiguous insights because the PDF is composed of fewer pair-correlations associated only with the coordination about a single element that could play a relevant role in the behavior of the material being studied.

Obtaining a differential PDF involves the challenge of making a reliable subtraction of two nearly identical diffraction data sets taken in the vicinity of an atomic K-edge resonance whose scattering factor f' contrast or variation is relatively weak at high atomic number due to core-hole broadening and the large number of non-resonant electrons. This low contrast, combined with the specialized high-energy-resolution x-ray optics required (uniquely available at the X-ray Science Division high-energy beamline 1-ID at the APS) has been responsible for resonant scattering at heavy element K edges to be considered quite difficult, leaving it unexploited and even questionable in regard to feasibility. The researchers in this study, working at beamline 1-ID, first validated the approach of combining high-energy resonant scattering with PDF analysis by examining the structurally well-known Cu₃Au alloys (chemically ordered and disordered) using x-rays near the Au K edge (~81 keV).

Next, this method was applied to more complex materials of interest in fuel cell catalysis. Pt-differential PDFs for PtPd alloy and core-shell nanoparticles (NPs) were obtained by scattering near the K absorption edge of Pt (~78 keV). The data show how the atomic ordering of the catalytically active Pt atoms is related to the NPs' design. Catalytic properties of NPs with different alloy structures are substantially

different, making desirable a detailed understanding of their structure, particularly with regard to disorder. Standard (non-resonant) PDF measurements show that pure Pt and random-alloy PtPd NPs are dense and highly ordered, whereas the core-shell NPs are not. However, the disorder in the latter is better understood through the insight of resonant (Pt-differential) PDF analysis, which shows that in the Pt-core/Pd-shell NPs the Pt core is ordered, whereas the Pd shell is loosely packed and disordered. The differential PDFs also indicate that for the Pd-core/Pt-shell NPs the disorder is present in both the Pd cores and Pt shells.



Optics at APS beamline 1-ID, which deliver high-energy resolution at high x-ray energies.

The researchers also turned their attention to the multiferroic distorted perovskite BiFeO_3 in nanosized state. BiFeO_3 has attracted much attention recently due to its display of a coexistence of antiferromagnetic and ferroelectric order over a wide temperature range above room temperature, allowing for the manipulation of magnetism by electric fields and vice versa. Of particular interest to technological applications (e.g., data storage and spintronics) is the question of maintaining the multiferroic behavior in nanosized BiFeO_3 particles. Bi-differential PDFs, measured near the Bi K edge (~ 91 keV), indicate that with decreasing particle size, the Bi sublattice (responsible for ferroelectricity) loses structural coherence faster than, and becomes uncorrelated with, the Fe-O sublattice (responsible for magnetic order) at sizes less than ~ 18 nm. This "melting" of the Bi sublattice offers

structural insight into the size-dependent aspects of ferroelectricity in BiFeO_3 and is consistent with other evidence of the disappearance of ferroelectricity below a certain nanosize length scale. Once the ground-state structure of free-standing nanoparticles is known in satisfactory detail, the technologically important ferroelectric properties of ABO_3 -type perovskites are easier to understand and, hence, take control of in fabrication towards applications.

This work demonstrates the feasibility of very high-energy K-edge resonant scattering for obtaining atomic differential-PDFs and is a step forward in expanding the limits of nontraditional (i.e., beyond purely Bragg-peak-based) x-ray diffraction to the rapidly growing area of materials of unusual structural complexity.

More information: -- "Element-Specific Structure of Materials with Intrinsic Disorder by High-Energy Resonant X-Ray Diffraction and Atomic Pair-Distribution Functions: A Study of PtPd Nanosized Catalysts", V. Petkov and S. D. Shastri, *Phys. Rev. B.* 81, 165428-1-8 (2010)

-- "Melting of Bi Sublattice in Nanosized BiFeO_3 Perovskite by Resonant X-Ray Diffraction", V. Petkov, et al, *Phys. Rev. Lett.* 105, 185501-1-4 (2010)

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