The Advanced Photon Source

Extending Resonant X-ray Diffraction to High Energies

Our understanding of how complex materials are tailored at the atomic level is driven by novel analytical techniques. Among these is resonant high-energy x-ray diffraction (XRD), which provides an element-specific snapshot of the way atoms are arranged inside materials having topological and/or chemical disorder. Until recently, such snapshots were overcrowded by the inherently large number of atomic coordination spheres appearing in the atomic pair distribution functions (PDFs) yielded by traditional XRD. But, thanks to optimized high-energy x-ray optics on X-ray Science Division beamline 1-ID at the U.S. Department of Energy Office of Science's Advanced Photon Source (APS) at Argonne, researchers have shown that coordination spheres related to a particular atomic species can be "highlighted" and others "dimmed" by exploiting high-energy *K*-shell resonances, thereby revealing the atomic arrangement in materials with both excellent spatial resolution and elemental specificity. This work, for which the APS is especially well suited given its high brightness at hard x-ray enrgies, paves the way to a greater understanding of the properties of many types of complex materials with a wide range of potential applications.

The technique of resonant XRD uses sharp changes in the atomic x-ray scattering factor near the characteristic *K*-absorption edge of an element to isolate the scattering associated with that particular type of atom. This yields information qualitatively similar to extended x-ray absorption fine structure (EXAFS) spectroscopy in that the data reflects only correlations involving the element whose absorption edge is probed. Unlike EXAFS, resonant high-energy XRD is capable of revealing correlations over very long interatomic distances. Resonant XRD entails measuring two diffraction data sets close to but below the absorption edge of an atomic species, taking the difference between these two data sets, and Fourier transforming the difference into a quantity called the differential atomic PDF. Achieving excellent spatial resolution and elemental specificity over very long interatomic distances involves probing the high-energy K-shell electrons of elements having relatively high atomic number (*Z*). In general, good quality differential atomic PDFs can be obtained for any material that contains elements with a *K*-absorption edge of 20 keV or higher.

To demonstrate the feasibility of this nontraditional experimental approach, the researchers from Central Michigan University and Argonne probed the *K*-absorption edge of gold (Au) atoms (~81 keV) in chemically ordered and disordered bulk Cu_3Au alloys. The resulting Au-differential PDFs showed very good sensitivity to the different ways Au atoms are known to occupy the sites of otherwise identical cubic lattices of those materials, confirming the feasibility of the high-energy resonant XRD approach. The technique was then applied to more complex materials—a PtPd nanosized alloy and core-shell nanosized (~2–4 nm) PtPd particles developed for catalytic applications—by probing the K-absorption edge of platinum (Pt) (~78 keV).

The resulting Pt-differential atomic PDFs revealed that Pt atoms in the nanosized alloy and core-shell PtPd particles exhibit a great deal of structural diversity, reflecting the different ways Pt and palladium (Pd) assemble at the nanoscale (Fig. 1). In particular, the core and shell of the nanoparticles were found to be structurally incoherent in respect to each other, something that has never been expected to take place in nanoparticles based on face-centered cubic metals. The resonant XRD-based results agreed with those of high-angle-annular-dark-field scanning transmission electron microscopy experiments, but went beyond the mostly qualitative picture yielded by imaging techniques by providing a firm, quantitative basis for rigorous modeling of the three-dimensional atomic ordering in the nanoparticles. Such models are a critical prerequisite to understanding the nanoparticles' properties, particularly when catalytic applications are involved. Nanosized materials based on Au and Pt are also being explored for high magnetic-density recording, bioimaging, and drug delivery. These research areas can also benefit significantly from high-energy resonant XRD experiments involving differential atomic PDF data analysis.

— Vic Comello (Argonne National Laboratory)

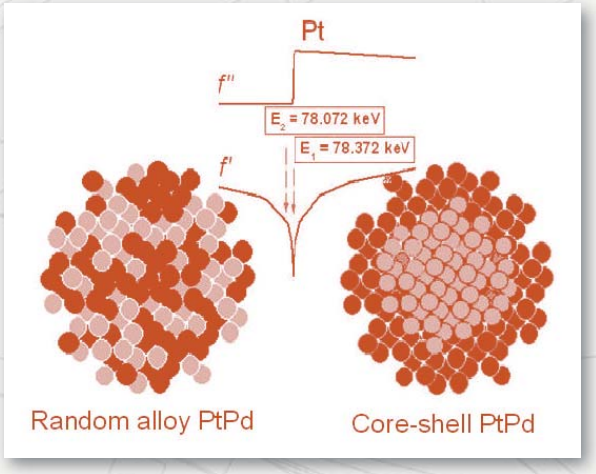

Fig. 1. Random alloy (left) and core-shell (right) PtPd nanoparticles. By probing the K-edge of Pt (central part), a "differential" atomic PDF is obtained that reflects correlations involving only Pt atoms, in this case Pt-Pt and Pt-Pd correlations. Thanks to its enhanced sensitivity, the Pt-differential PDF gives a very detailed snapshot of the atomic ordering in PtPd nanoparticles, and so provides a very precise structural basis for explaining their useful catalytic properties.

See: V. Petkov[1]* and S.D. Shastri[2]**, "Element-Specific Structure of Materials with Intrinsic Disorder by High-Energy Resonant X-ray Diffraction and Differential Atomic Pair-Distribution Functions: A Study of PtPd Nanosized Catalysts," Phys. Rev. B **81**, 165428 (2010); and V. Petkov, S.M. Selbach, M.-A., Einarsrud, T. Grande, and S.D. Shastri, "Melting of Bi Sublattice in Nanosized BiFeO3 Perovskite by Resonant X-Ray Diffraction," Phys. Rev. Lett. **105**, 185501 (2010).
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Call for APS General-User Proposals

The Advanced Photon Source is open to experimenters who can benefit from the facility's high-brightness hard x-ray beams.
General-user proposals for beam time during Run 2011-2 are due by Friday, March 4, 2011.
Information on access to beam time at the APS is at http://www.aps.anl.gov/Users/apply_for_beamtime.html or contact Dr. Dennis Mills, DMM@aps.anl.gov, 630/252-5680.
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