

Anomalous X-ray Scattering Studies of Nanophase Clusters in Confined Geometries

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Introduction: Materials containing small nanoclusters of semi-conductors confined with zeolitic frameworks are of great interest as a result of the host of unusual properties they display arising from quantum confinement effects due to the very small size of the clusters.¹ However, much uncertainty exists over the structure and bonding in these clusters due to their disordered and dynamical states, and their sometimes incommensurate nature with respect to the host lattice. Anomalous X-ray scattering (AXS) techniques are a powerful tool for obtaining structural information about these phases. In the AXS technique multiple diffraction patterns are recorded at different x-ray energies, both just below the absorption edge of a particular element e , and far from the edge.² The differences in scattering power of element e at each X-ray wavelength enables the unambiguous assignment of the identity of the species at each crystallographic site. AXS is therefore a site and element specific technique that can be used to distinguish the environment of nanocluster atoms from those of the host crystalline lattice, even in those cases where the nanoclusters are disordered with respect to the host lattice – a frequent occurrence in these type of materials which hampers conventional diffraction studies. It is therefore an extremely powerful technique for solving the structures of nanoclusters contained as a minority phase inside a macroscopic crystalline framework. We have prepared materials in which HgSe, ZnSe, and SnSe clusters have been incorporated into a variety of host materials of differing channel size and dimensionality, namely zeolites Na-A and Nd-Y (3D interconnected channels), the aluminophosphate $\text{AlPO}_4\text{-5}$ (1D channels), and the zeolite ZSM-5, and have begun anomalous X-ray scattering (AXS) studies of these materials.

Methods and Materials: Anomalous X-ray scattering (AXS) studies were performed on the HgSe/SnSe-NdY, HgSe/ZnSe- $\text{AlPO}_4\text{-5}$, and HgSe/ZnSe-ZSM-5 materials on beamline X7A of the NSLS. The samples were sealed in 1-2 mm capillaries and the experiments performed in Debye-Scherrer geometry using a Si111 monochromator and Ge220 analyzer crystal. Data was obtained on the Se edge for all materials, together with metal edge data where appropriate (i.e. on the HgSe and ZnSe materials). Off-edge data was also obtained for all of the materials.

Results: The refined structure for the HgSe-NdY material (composition $(\text{Hg}_{-5}\text{Se}_{-8})\text{Nd}_{19}\text{Al}_{56}\text{Si}_{136}\text{O}_{384}$) modeled in space group Fd-3m is shown in **Figure 1**. The material consists of an $\text{Hg}_{13}\text{Se}_{16}$ clusters located at the center of the zeolite supercage. The central atom was found to be a Hg atom, which is surrounded by a tetrahedron of Se atoms. Surrounding these atoms are two further shells of Hg and Se atoms. The Se in the outer-shell atoms lie close to the SIII sites in the 12-ring window of the supercage. The Hg atoms in the outer shell are coordinated by three framework oxygens. The Nd^{3+} cations are located exclusively in the SI' sites located within the sodalite cages. There is a high degree of disorder with respect to the host lattice with multiple possible orientations of the cluster. **Figure 1** shows the refined structure of the HgSe clusters within the supercage of zeolite Nd-Y, while **Figure 2** shows the final Rietveld plot of the Se edge data. For clarity only one of the orientations of the cluster is shown in **Figure 1**. For the HgSe- $\text{AlPO}_4\text{-5}$ material (composition $(\text{Hg}_{-3}\text{Se}_{-3})\text{Al}_{12}\text{P}_{12}\text{O}_{48}$) it appears that the material contains small chains of Hg_5Se_4 clusters, which are again highly disordered with respect to the host lattice. Analysis of the data for this and the other materials is continuing.

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References: ¹ G.A. Ozin, A. Kuperman, A. Stein, *Angew. Chem. Int. Ed. Engl.* **28**, 359 (1989); ² P. Armand, M.-L. Saboungi, D.L. Price, L. Iton, C. Cramer, M. Grimsditch, *Phys. Rev. Lett.* **79**, 2061 (1997).

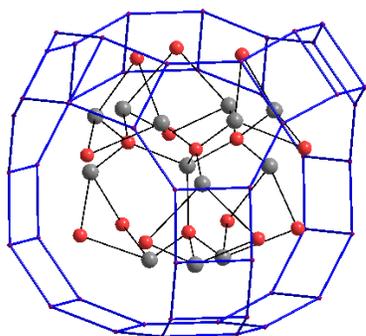


Figure 1: View of the structure of $\text{Hg}_{13}\text{Se}_{16}$ nanoclusters contained within the supercage of zeolite Nd-Y. Hg atoms are shown in gray, Se atoms in red, and framework Al/Si atoms in purple. For clarity, bridging framework oxygen atoms are omitted and only one of the

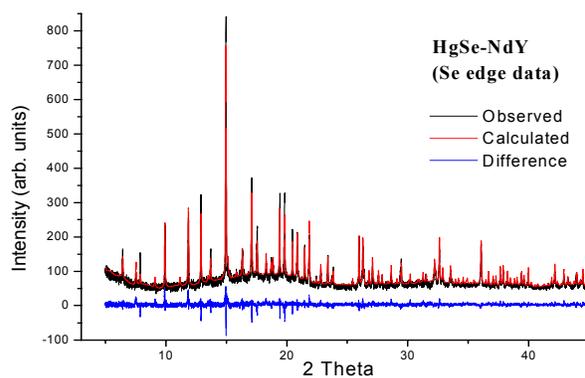


Figure 2: Rietveld plot for HgSe-NdY recorded at the Se edge ($\lambda = 0.981 \text{ \AA}$). The observed data is shown in black, the calculated pattern in black, and the difference curve in blue.