On-sample Containment for High-energy X-ray Scattering Studies of Hydrogen Fluoride

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Introduction

Fluoride-based materials are among some of the most interesting systems available. They display a wide range of structural, chemical, and bonding properties that lead to their application in industry and in synthesis and more fundamental academic studies. Current fluences and new instruments recently built at third-generation x-ray sources have significantly widened the range and complexity of chemical samples for which these types of scattering can provide detailed structural information. In addition, information from elastic neutron scattering experiments is often complementary to that from the x-ray scattering analog. The complementary nature of the two techniques is due to the differing nature of the neutron-matter interaction and x-ray-matter interaction. High-energy synchrotron x-ray diffraction shares many of the features of neutron scattering in terms of the level of penetration possible in condensed matter [1].

In order to apply high-energy x-ray scattering to chemically ambitious samples, sample environmental equipment that satisfies chemical and experimental constraints must be designed and built. The work herein contributes to this effort through its design, construction, and preliminary results, by using sample cells that allow the structural properties of anhydrous liquid hydrogen fluoride (HF) to be measured while conserving chemical integrity. HF is an exceptionally dangerous material to handle. It has a very high chemical toxicity and causes severe and highly dangerous burns when it comes in contact with human tissue, even when it is in aqueous solution. In the equipment design, chemical containment must therefore meet very severe safety constraints.

Materials and Methods

Design Constraints

There are several commercially available materials that can safely contain fluoride-containing samples. Among them are polytetrafluoroethylene (PTFE) and alloy 400 ($Ni_{1.86}Cu$). Of these, PTFE has the greater general resistance to fluorides at low temperatures and pressures, especially in the presence of traces of water. Copper and nickel are also both largely resistant to attack by fluorides. They can be treated with F_2, which passivates the surface by forming a fluoride coating that renders these materials resistant to further attack. The constraint of chemical resistance is required in experiments such as these in order to preserve the chemical purity of the sample. PTFE is a partially crystalline material that produces a diffraction pattern containing Bragg peaks, which arise from the periodic crystalline lattice, together with a diffuse component that arises from the local and intermediate range atomic correlations [2, 3]. Alloy 400, on the other hand, is a polycrystalline material, the scatter from which is predominately Bragg in nature, with low levels of diffuse scatter. Figure 1a) shows the diffraction pattern of alloy 400 recorded at the BESSRC 11-ID-C beamline, and Figure 1b) shows the corresponding pair distribution function.

The samples for which this suite of sample environment (SE) equipment was designed were liquids. As such, they exhibit a complete absence of Bragg scatter because of the absence of any lattice. The diffraction intensity is confined to diffuse scatter. The choice of material is therefore crucial if the subtraction of background signal is to be successful. In the subtraction of a diffuse background from diffuse sample scatter, there is no simple *a priori* method for determining from what source the diffuse signal is recorded — sample or cell. In this respect, the material most suitable for sample containment in a liquid diffraction experiment of this type is alloy 400, even though Cu and Ni both exhibit large scattering intensities. $Z_{Ni} = 28$ and $Z_{Cu} = 29$ therefore have Bragg peaks of very large intensity. However, subtraction of the prominent Bragg intensity is possible through both standard analysis procedures and empirical subtraction [5].

Sample Cell Design

All parts of the diffraction cells, with the exception of the valves and the 'o'-rings, are machined from alloy 400. All consist of two separable parts: a cell head that allows for transfer of hydrogen fluoride via the vacuum line described below, and a sample cell body in which the sample is contained during the diffraction experiment. The two parts are joined by using a 1-in. SwageLok® nut and a PTFE 'o'-ring seal. The sample cells constructed for the diffraction experiments are shown in Fig. 2.
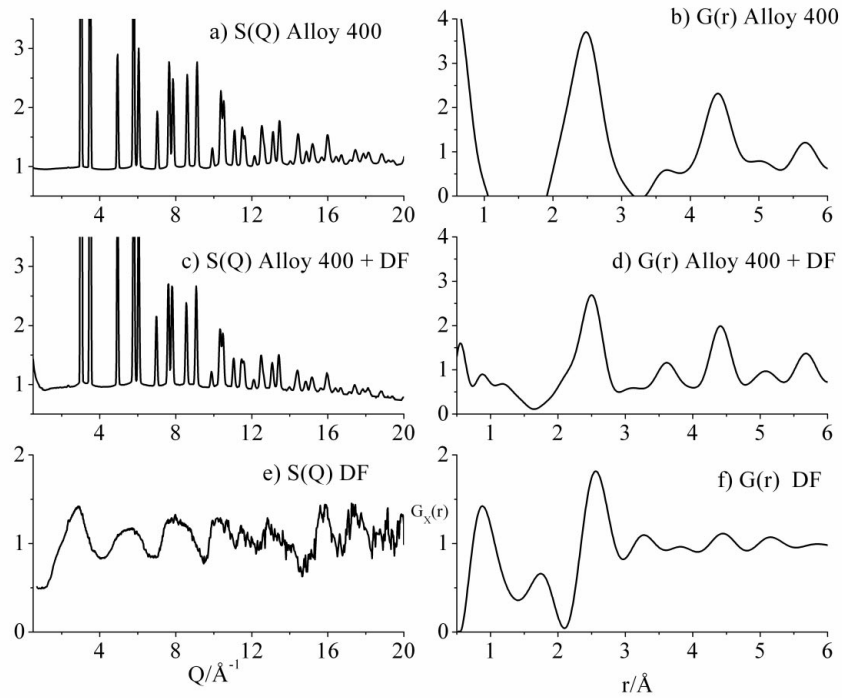
FIG. 1. a) Diffraction pattern for alloy 400. b) Fourier transformation of alloy 400. c) Diffraction pattern for alloy 400 plus DF. d) Fourier transformation of alloy plus DF. e) Corrected DF diffraction pattern. f) Corrected DF Fourier transformation.
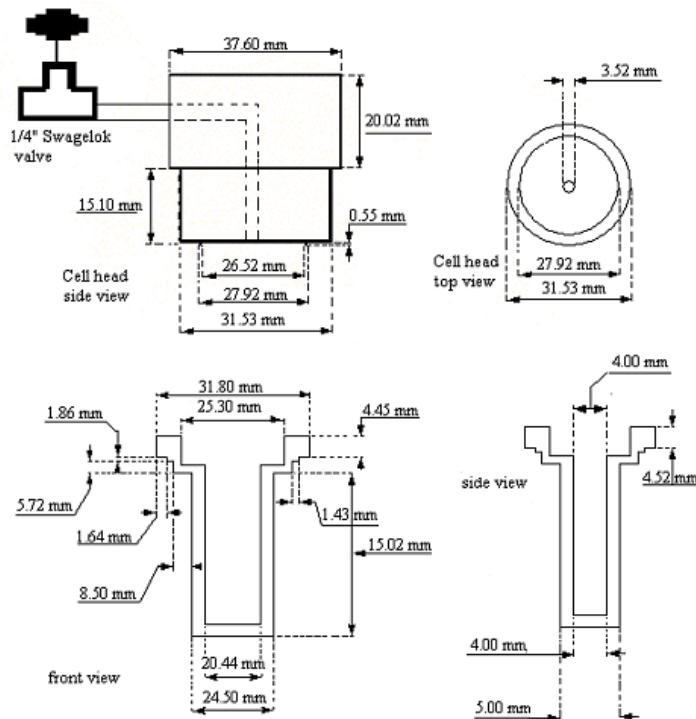

FIG. 2. Diffraction sample cells.

The body of the sample cell head was machined from alloy 400 bar stock. In order to load the samples into the body of the cell, the top portion of the cell head was drilled with a 6.35-mm bore that turns 90° in approximately the middle of the head. A piece of 6.35-mm o.d. alloy 400 seamless tubing was welded onto the outside top of the cell in order to connect the needle valve. The lower portion of the head was additionally machined with threads to fit a SwageLok 1-in. nut, which allows for the connection with the body of the sample cells. At this interface, a knife edge was machined to present a sealing surface to the 'o'-ring. Appropriately sized PTFE 'o'-rings were machined to cause the vacuum seal.

In order to minimize background container scattering, the wall thickness of each cell body was machined to be as thin as possible yet still maintain the integrity of the container. The cell bodies were machined as large as possible within the wall thickness. This allowed a sample to be 4 mm in thickness in the high-energy x-ray experiments.

Results

Figure 1 shows the diffraction pattern of the sample can for deuterium fluoride (DF), with and without the presence of the sample. Whereas in Fig. 1c), the presence of the sample is not immediately noticeable, in the Fourier transform of the diffraction pattern, the structure due to DF can be clearly seen overlain by the local structure of alloy 400 [Fig. 1d)]. This figure shows the advantage of using a crystalline material as the material from which to construct the cells. The background intensity is confined to the pair correlation function expected from a cubic crystalline system, and subtraction of the diffraction pattern of the cell in both the high-energy x-ray experiments and the neutron experiments proved to be tractable, as stated above. The DF sample data, after corrections for x-ray diffraction measurements, are shown in Figs. 1e) and 1f) [4]. Previous, unpublished neutron diffraction data from using PTFE cells proved to be far less tractable, with structural results that were less reliable [5].

Discussion

Although the intensity of the background in a crystalline sample container is dramatic in reciprocal space, it is the source of the diffracted intensity that is important when considering a sample container. For a crystalline system, almost all of the background intensity, beyond that from the ubiquitous local structure, is confined to Bragg intensity, whereas for a partially or completely amorphous cell, this is not the case. The periodicity in a crystalline system, inherent because of the presence of a lattice, limits the local structure to a minimum. As required in the presence of a lattice, only a small number of unique distances are required to describe the structure in real or reciprocal space. For liquid samples, it is clear that minimization of diffuse scatter, beyond the local structure, is the most important consideration.

Acknowledgments

References

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