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In situ high-pressure wide-angle hard x-ray photon correlation spectroscopy: A versatile tool probing atomic dynamics of extreme condition matter

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ABSTRACT

With the advent of new synchrotron radiation x-ray sources that provide a significantly enhanced coherent flux, high-energy x-ray photon correlation spectroscopy measurements can be performed on materials in a diamond anvil cell. Essential information on atomic dynamics that was previously inaccessible can be obtained for various novel phenomena emerging under extreme conditions. This article discusses the importance, feasibility, and experimental details of this technique, as well as the opportunities that it offers to address critical scientific challenges.

I. IMPORTANCE AND LIMITATIONS OF HIGH-PRESSURE DYNAMICS RESEARCH

Over recent decades, thanks to remarkable progress in static pressure generation and *in situ* high-pressure probing, many breakthroughs have been achieved with otherwise inaccessible novel phenomena, and exotic materials have been discovered at extreme conditions.[1,2] However, high-pressure studies to date have mainly focused on the static (time-averaged) atomic structures of materials and their relationship with the properties of those materials. Besides static structures, how the structure of a material evolves with time, i.e., its dynamics, also plays a critical role in deepening our understanding of materials. Previous experimental investigations of material dynamics under pressure have relied mainly on measurements of dielectric constants, rheology, dynamic light scattering (DLS), or nuclear magnetic resonance (NMR). However, these techniques are usually limited either to a specific class of materials, states, or compositions (insulators, liquids/solutions, or transparent macromolecules) or to relatively low pressures or dynamic ranges. Therefore, developing a versatile technique for studies of the high-pressure dynamics of various materials is desirable.

II. ADVENT OF HIGH-BRILLIANCE X-RAY SOURCES OFFERS A NEW APPROACH TO ATOMIC DYNAMICS UNDER EXTREME CONDITIONS

When a coherent light beam is scattered by a sample with disorder, a grainy diffraction pattern with inherent random intensity fluctuations, termed speckle patterns, can be obtained. Speckle patterns carry information on the exact positions of all scatterers in the sample, representing a microstructural "fingerprint" of the sample. Therefore, the structural dynamics of materials can be studied by tracking the changes in a series of speckle patterns over time using intensity autocorrelation functions (for steady dynamics) or higher-order correlation functions (e.g., the two-time correlation function for heterogeneous dynamics). Based on this concept, light photon correlation spectroscopy (LPCS) (also called DLS) using optical lasers has been well established for decades. However, LPCS is limited to optically transparent systems and a quite small wavevector transfer q (at length scales larger than the wavelength of visible light, i.e., hundreds of nanometers).

To overcome the limitations of LPCS, an x-ray counterpart, namely, x-ray photon correlation spectroscopy (XPCS), was

proposed. The first x-ray speckle pattern was observed in 1991 with coherent synchrotron x-rays, opening up the possibility for measurements of collective atomic motions in various condensed matter systems with high resolution in reciprocal space and broad coverage in the time scale.[3] Since then, XPCS has been extensively used to explore, among other things, atomic diffusion and phase transformations,[4] magnetic domain fluctuations,[5] and relaxation dynamics in metallic glasses.[6]

The speckle contrast depends strongly on the coherence of the incident x-ray beam. Third-generation synchrotron sources are only partially coherent. Spatial filtering using collimation slits or pinholes and temporal filtering using a monochromator are needed to obtain coherent x-rays within a limited coherence volume (the volume within which the scattering is coherent), which leads to a considerable loss of total flux. The coherence flux in the coherence volume is proportional to the square of the x-ray wavelength,[7] and therefore a relatively low x-ray energy (e.g., ~8 keV) is usually chosen at most XPCS beamlines. However, such low-energy x-rays cannot effectively penetrate the two thick (typically a total thickness of ~5 mm) diamond anvils in a high-pressure diamond anvil cell (DAC),[1] owing to the severe absorption of x-rays with energy below 10 keV. Thus, XPCS measurements might seem impossible for high-pressure samples. However, *in situ* high-pressure XPCS experiments should become feasible if the experimental setup can be optimized by increasing the x-ray energy above 10 keV or even above 20 keV (available at many XPCS beamlines), for which the transmission through 5 mm thick diamond anvils will be significantly increased (from ~0.4% at 8 keV to ~53% at 20 keV), by decreasing the thickness of the diamond anvils, and by choosing heavy-element samples with strong scattering ability. Moreover, with the advent of fourth-generation "diffraction-limited" synchrotron storage rings, the coherent flux in the hard x-ray regime will be of the order of a 100 times higher than before, which will allow XPCS measurements at much higher energies than are possible today, thus significantly benefiting *in situ* high-pressure XPCS experiments using DACs in the wide-angle mode for atomic dynamics studies under extreme conditions.

III. KEY FACTORS FOR SUCCESSFUL *IN SITU* HIGH-PRESSURE HIGH-ENERGY XPCS MEASUREMENTS

For the typical setup of a high-pressure XPCS experiment (a schematic of which is shown in Fig. 1), besides the sample, the x-ray beam also goes through diamond anvils and a pressure medium, which may generate extra scattering signals. To avoid such signals, single-crystal diamond anvils and noncrystalline light-element pressure media are preferred. Possible Bragg or diffuse scattering signals from single-crystal diamond anvils could be removed by slightly changing their orientation (i.e., by changing the rotation angle of the DAC). In addition, some factors that do not matter in other high-pressure measurements could severely affect the correlation function in XPCS measurements. First, the sample spatial stability will be critical. To ensure an identical probing volume of the sample, the DAC should be firmly mounted on the stage, and the sample position must be scanned before each exposure. Second, special attention should be paid to the pressure stability in the sample chamber during exposure. To stabilize the pressure, a long waiting time can be adopted after the pressure increase before each exposure. Gasket flow will also cause severe pressure instability and sample position drift, which can be avoided by reducing the initial size and thickness of the sample chamber. Moreover, the effect of shear stress will be non-negligible when the pressure goes beyond the hydrostatic limit of the pressure medium.[8]

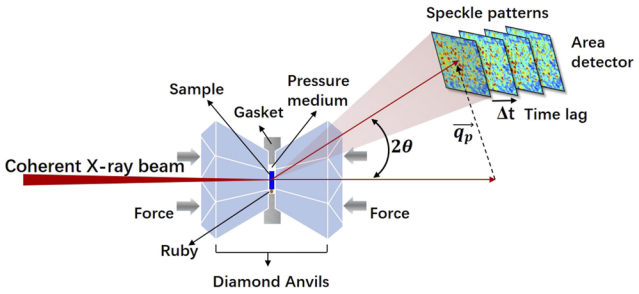

FIG. 1. Schematic of experimental setup for *in situ* high-pressure high-energy XPCS experiments using a DAC.

IV. PERSPECTIVES FOR *IN SITU* HIGH-PRESSURE HIGH-ENERGY XPCS IN GLASS SCIENCE AND BEYOND

With this technique, one of the most intriguing problems to tackle is related to the elusive nature of glasses and the glass transition.[9] With compositions consisting of heavy elements and with relatively high resistance to damage caused by intense x-ray radiation, metallic glasses could constitute ideal glass systems to study glassy dynamics with pressure tuning through phase transitions such as liquid-to-glass (glass transitions) and glass-to-glass (polyamorphic) transitions. Under pressure, previously proposed dynamics-sensitive structural indicators and critical parameters, such as the local atomic packing (cluster distribution and density), free volume, and internal stress level/state, could be gradually and effectively altered, while being separated from changes in thermal energy. Furthermore, unique information could be acquired regarding the atomic mechanisms underlying the dramatic (exponential) slowing down of dynamics through glass transitions, and, in combination with x-ray diffraction data, the relationship between dynamics and structure in glass and glass-forming liquids could be revealed.[9] With external resistive heating, studies could also be extended into a wider, previously unexplored, pressure–temperature space. Moreover, with high-energy x-ray free-electron lasers, *in situ* high-pressure XPCS could even probe atomic dynamics on time scales extending down to sub-microseconds.

In addition, the application of pressure can significantly change the structure and properties of any material, and the atomic dynamics information obtainable by *in situ* high-pressure high-energy XPCS is by no means limited to a specific topic or system: it could also be used to gain essential insight at the atomic length scale into various novel phenomena emerging under extreme conditions, such as the glassy nature of pressure-induced amorphous phases (ice, silicon, etc.) and their relationship to liquid polymorphism,[10] to confirm the existence of novel superionic states under conditions like those at the Earth's core,[11] and to investigate the atomic mechanisms underlying pressure-induced phase transitions,[4] charge/spin ordering dynamics in quantum materials,[5] etc.

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AUTHOR DECLARATIONS

Conflict of Interest

The author has no conflicts to disclose.

Author Contributions

Qiaoshi Zeng: Conceptualization (lead); Funding acquisition (lead); Writing – original draft (lead); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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