

# Highly efficient gaseous sample loading technique for diamond anvil cells

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A clean and highly efficient technique has been developed to load diamond anvil cells (DACs) using a small amount of gaseous samples. The loading process consists of two steps. First, gas is condensed on a designated cold surface in a pre-evacuated system; second, the solidified sample is loaded into a DAC at liquid-nitrogen temperature. A hundred milliliters of gas at ambient condition is typically required to produce a solidified sample. The use of solid sample material for DAC loading is beneficial to a clean loading process. We demonstrated this technique by loading isotopically enriched (99.925%  $^{83}\text{Kr}$ ) krypton into a DAC. 200 ml of this rare and expensive gas were solidified with 99.6% efficiency and almost completely recovered. © 2004 American Institute of Physics. [DOI: 10.1063/1.1813111]

## I. INTRODUCTION

There are several methods for loading gaseous samples into a diamond anvil cell (DAC), e.g., the so-called “pressure bomb loading method,”<sup>1</sup> which creates a high-density gas such that, in some cases, the density of the gas is nearly the same as that of liquid; and the “cryogenic loading method,” which requires at least part of or the entire DAC to be submerged in the liquified gas sample.<sup>2</sup> Both methods require a large amount of gas to form either the high-density gas or the large amount of liquid and are clearly unsuitable to prepare samples from rare or expensive gases. In the method of Pravica and Remmers,<sup>3</sup> the required amount of gas is probably much smaller because the gas is first condensed onto a cold surface and then transferred to a gasket hole of the DAC. But still, the suggested condensation process, i.e., blowing warm gas through a capillary tube onto an open, cold surface, requires larger amounts of gas than necessary and is therefore not sufficiently efficient to work with very rare, expensive, or hazardous gases. Furthermore, the residual solidified sample cannot be recovered from its open system. We propose an improvement of the solidification process by avoiding the flow of warm gas which is responsible for a significant amount of gas escaping during solidification. To get it solidified from a small amount of gas, the gas can be efficiently condensed in a confined volume. We have developed such a system to condense gaseous samples onto a well-controlled cold surface that is part of a leak-free system. The system is evacuated prior to sample condensation to obtain a solid sample with high purity. Condensation is very efficient because the small vapor pressure of the gas (e.g., krypton) at liquid-nitrogen temperature produces very little amount of

residual gas in the system. The condensed solid sample is then cryogenically loaded into a DAC in a glove box. After the sample loading, the residual solidified sample can be preserved in the condensation chamber at low temperature sealed with a metal plug. The details of the system design and loading process are reported in this article.

The behavior of rare-gas solids under high pressure in DACs is a research area enjoying continuous interest.<sup>4</sup> One of them is the study on the vibrational dynamics of krypton (Kr) under high pressure by means of nuclear resonant inelastic x-ray scattering (NRIXS).<sup>5</sup> The study utilizes the 9.4035 keV nuclear transition of the  $^{83}\text{Kr}$  isotope. The NRIXS signal is typically weak, and experimental capabilities would definitely benefit from an increase in abundance of  $^{83}\text{Kr}$  nuclei in the sample. Since the natural abundance of Kr in air is only 1.14 ppm, of which 11.5% is the  $^{83}\text{Kr}$  isotope, isotopically enriched  $^{83}\text{Kr}$  gas is rare and expensive. Using the method reported in this article, we have successfully loaded a pure krypton sample into a DAC by using about 200 ml of ambient  $^{83}\text{Kr}$  gas. We were then able to perform NRIXS measurements on compressed Kr with much improved counting rates. In the future, the loading technique presented here is expected to allow similar high-pressure experiments on more challenging systems, e.g., Kr clathrates.

## II. GAS CONDENSATION

The design criteria of the gas condensation system include: (1) gas condensation takes place in a pre-evacuated leak-free system to obtain high purity of the solidified sample; (2) only a small portion of the system is cooled so that the condensation is concentrated and more efficient; (3) the system is easy to operate in a glove box so that the solidified sample can be taken out of the condensation sys-

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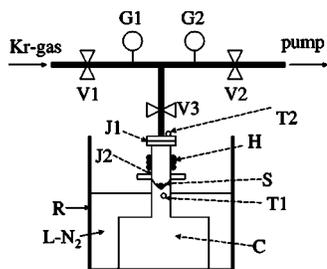


FIG. 1. Apparatus for gas condensation. V1, V2, V3: vacuum valves; G1, G2: vacuum/pressure gauges; J1: vacuum joint; J2: soldering joint; H: heater; C: sample container; S: condensation surface; T1, T2: temperature sensors; R: LN<sub>2</sub> reservoir.

tem for sample loading; and (4) the system can sustain both vacuum and positive pressure, since the gas supply generally comes from pressurized cylinders.

The melting temperature of krypton is 115.95 K, and the boiling temperature is 120.2 K at standard atmosphere (1.013 bar), therefore, liquid nitrogen (LN<sub>2</sub>) is used as thermal reservoir to condense the krypton gas around 78 K. We use VacuSeal components<sup>6</sup> with a metal-to-metal seal since they are leak free for both vacuum and positive pressures (up to 350 bar for a  $\frac{1}{4}$  in. tube). The VacuSeal connector is also easily handled in a glove box.

A sketch of the sample condensation system is shown in Fig. 1, and pictures of it are shown in Fig. 2. The compact system is made of a  $\frac{1}{4}$  in. stainless-steel tube with a VacuSeal tube fitting. In Fig. 1, V1, V2, and V3 are high-purity stainless-steel diaphragm valves, and G1 and G2 are gauges to monitor the vacuum and positive pressure, respectively. The sample container (C) is made of solid brass with half-spherical, concave shape (S) on its top, the radius of S is about 8 mm. Brass is chosen because of its high thermal conductivity. The whole container can be cooled down to LN<sub>2</sub> temperature (78 K) within several minutes when placed in a LN<sub>2</sub> reservoir (R). The container is kept cold during sample condensation. To prevent components other than the sample container being cooled down to LN<sub>2</sub> temperature, the top of C is soldered to a heated neck made from a stainless-steel gland (0.75 in. in diameter and 1.5 in. in length). The

open end of the gland (J1) serves as the opening of the sample container. By disconnecting J1 inside a glove box when the sample condensation is done, the solidified sample can be taken out while the whole sample container is kept cold in a LN<sub>2</sub> reservoir. The soldering joint between the gland and the sample container (C) is J2. H is a Pt wire heater. Stainless-steel is chosen as the neck material because of its low thermal conductivity. Instead of the standard wall thickness ( $\sim 1.2$  mm) of the  $\frac{3}{4}$  in. gland, it is thinned to about 0.2 mm. The heating power of H can be easily transferred to the inner wall of the neck through such a thin wall. By properly choosing heating power of H, S can be the only area with a temperature lower than krypton melting temperature. S then becomes the gas condensation area of the system. T1, T2 are thermocouples (type K) to monitor temperatures during condensation process. The krypton gas used in our sample loading is 99.925%-enriched <sup>83</sup>Kr (Chemgas, France).

Figure 2 shows pictures of the sample condensation system: Fig. 2(a) shows the whole system, Fig. 2(b) shows the sample container and Fig. 2(c) shows the solid Kr sample being taken out of the sample container.

During the loading process, the whole system was pre-evacuated by a turbo pump with valves V2 and V3 opened and V1 closed. When the vacuum became better than  $10^{-3}$  Pa, generally within 10 min due to the small volume of the system, V2 was then closed. LN<sub>2</sub> was introduced in R to cool down the sample container (C) to about 80 K. A direct current heating power of 18 W was applied via H. When both T1 and T2 reached the desired temperatures, (T1  $\sim 80$  K and T2  $> 200$  K), V1 was opened to let the krypton gas flow into the system. The condensation started immediately and finished within several seconds. The condensation process was monitored by G1 and G2. When G1 indicated a pressure of about 4 mbar, the condensation was complete because this pressure represents the vapor pressure of krypton at LN<sub>2</sub> temperature. The solidified sample was then ready to be loaded into a DAC.

### III. SAMPLE LOADING AND MEASUREMENT

The most challenging part of the cryogenic sample loading is to keep all parts of a DAC (including gasket, diamonds and DAC frame) and loading tools colder than the sample melting temperature (116 K for Kr) and, at the same time, prevent moisture condensing on the surfaces of these parts. Our sample loading was carried out in a glove box with careful water vapor removal and monitoring. At first, the glove box was flushed by continuously flowing dry nitrogen gas in, while both nitrogen gas and moisture were taken out by a pump. The moisture-removal system of the glove box was then kept running by circulating the gas through its desiccant dry-train. The moisture level, measured by a H<sub>2</sub>O analyzer,<sup>7</sup> was generally around 15 ppm after 2 h. When LN<sub>2</sub> in plastic coolers was introduced in the glove box, the dry N<sub>2</sub> gas supply was closed, since the evaporating N<sub>2</sub> gas from LN<sub>2</sub> was sufficient to keep positive pressure in the glove box. Several moisture condensers made of copper

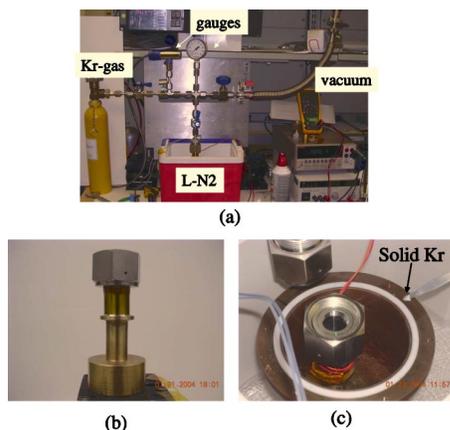


FIG. 2. (Color online). Pictures show (a) the sample condensation system, (b) sample container, and (c) solid Kr sample removed from the opened sample container.

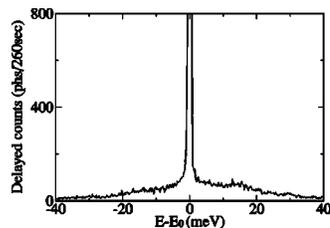


FIG. 3. NRIXS spectrum of  $^{83}\text{Kr}$  under a pressure of 34 GPa. The horizontal axis is the energy deviation from resonant energy ( $E_0=9.4035$  keV) in units of meV. The vertical axis represents the intensity of delayed nuclear resonant signals. The sharp peak at  $E_0$  represents elastic nuclear resonant scattering from  $^{83}\text{Kr}$ .

poles were placed in  $\text{LN}_2$ . This could further reduce the moisture level in the glove box to about 5 ppm.

The two halves of a DAC were separately placed in brass containers with lids on their top to avoid moisture condensation during the cooling period. The brass containers were placed in the  $\text{LN}_2$  reservoir. The DAC was not directly placed in the  $\text{LN}_2$  to avoid strong vibration of the boiling  $\text{LN}_2$  during cooling and sample loading. This also avoids possible splashing of  $\text{LN}_2$  into the predrilled hole of the gasket. The temperature of the DAC was monitored during the loading process. Once all the parts were cold enough, the sample container *C* was opened at J1, and the solidified krypton sample was scraped with cold tweezers and put on the gasket in the DAC. The sample was further loaded into the gasket hole under a microscope using a precooled sharp needle. The two halves of the DAC were immediately assembled, and the sample was sealed by tightening the screws of the DAC.

Pressures of Kr were measured using the fluorescence<sup>8</sup> from ruby pieces that were placed in the gasket hole prior to sample loading. The solid Kr sample was studied by means of x-ray diffraction and NRIXS. Figure 3 shows the NRIXS spectrum of  $^{83}\text{Kr}$  under a pressure of 34 GPa. The central peak at  $E-E_0=0$  is the elastic peak resulting from the recoilless nuclear resonant excitation of  $^{83}\text{Kr}$ , where  $E_0=9.4305$  keV is the nuclear transition energy. The side bands around the elastic peak correspond to the phonon creation/annihilation process. It shows a successful loading of  $^{83}\text{Kr}$  sample in a DAC by our sample loading technique. The details of the experimental results will be analyzed and published later.<sup>9</sup>

#### IV. DISCUSSION

The efficiency of the system can be estimated by checking the amount of residual gas in the system after condensation. The amount of residual gas depends on its vapor pressure at certain temperatures. In the case of krypton, the vapor pressure is 4 mbar at 80 K and 730 mbar at 115.95 K.<sup>10,11</sup> The total volume of our system is about 0.027 l, which is negligible compared with the cylinder volume (1 l in our loading). The total volume before and after the condensation

is about the same ( $\sim 1$  l). The condensation efficiency then depends merely on the pressure difference, 1 bar before and 4 mbar after the condensation takes place. At a temperature of 80 K, the residual gas is about 0.4% ( $=4$  mbar/1 bar) of the total krypton gas, meaning that an efficiency of 99.6% of gas condensation is achieved. Since the density of solid krypton at 80 K is about  $2.97$  g/cm<sup>3</sup>,<sup>12</sup> 1 l of ambient krypton gas should form approximately  $1.25$  cm<sup>3</sup> of solid, which is more than enough for a DAC sample. Assuming the gasket hole to be  $100$   $\mu\text{m}$  in diameter and  $20$   $\mu\text{m}$  in thickness, about  $10^{-6}$  cm<sup>3</sup> of solid krypton are required to fill the sample chamber. In our sample loading, about one-fifth of the solidified Kr made from 1 l ambient Kr gas was used for several loading attempts. One can see that with our sample loading technique, a fraction of 1 l of gas would be sufficient for loading a DAC. Since the gas vapor pressure increases with increasing temperature, the condensation temperature should be kept as low as possible to obtain a high efficiency of solidification.

After the sample loading, the remaining Kr solid in the sample container can be preserved by sealing the sample container with a 3/4 in. VacuSeal plug and left in a  $\text{LN}_2$  dewar for later use.

In our current setup, the sample condensation system was placed outside of the glove box, and the sample container was moved with the  $\text{LN}_2$  reservoir into the glove box after the condensation was finished. This process brought some moisture into the glove box. It took extra time and efforts to reduce the moisture level before sample loading could be performed. To improve the current system, vacuum ports to pump the condensation system inside the glove box and direct  $\text{LN}_2$  filling into the glove box are planned.

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