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APPARATUS FOR X-RAY DIFFRACTION IN ULTRAHIGH VACUUM

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We have constructed an instrument that allows a solid surface, prepared with established ultrahigh vacuum (UHV) procedures, to be examined by X-ray diffraction. The greatest advantage of X-ray diffraction as a surface probe lies in the high angular resolution attainable with a synchrotron source. Therefore, we have avoided compromising the precision of the diffractometer by isolating the sample from the vacuum chamber on a bellows and sliding teflon seal. A manipulator, built into the sample stage, ensures great flexibility of surface analytical and preparatory techniques.

1. Introduction to scientific problems

Since the first demonstration that reasonable X-ray diffraction signal rates could be obtained from a single layer of atoms at a surface [1], there has been considerable interest in the application of X-ray scattering measurements to surface structure and the associated two-dimensional (2-D) physics. The excitement over being able to perform X-ray scattering measurements is due to certain unique properties of this probe. First, the scattering cross sections for X-rays are very well understood and, to a very good approximation, are independent of chemical environment. Secondly, for most systems and certainly for 2-D systems, the scattering of X-rays can be interpreted in the kinematic approximation. Finally, a large body of sophisticated experimental and data analysis techniques is in place for use in X-ray analysis.

Before X-rays could be used to examine the surfaces of bulk materials, two basic problems were overcome. Firstly, the need for sufficiently bright X-ray sources was solved with the advent of synchrotron radiation sources and, for certain problems, high power rotating anode sources. Secondly, it was necessary to develop techniques to separate the surface contributions of the X-ray signal from those of the bulk: 1) by studying reflections from the surface which are crystallographically distinguishable from bulk reflections (e.g., superlattice reflections from reconstructed surfaces or incommensurate layers), or 2) by using total reflection to limit the penetration of X-rays into the bulk.

A wide range of problems has already been studied using these X-ray scattering techniques. These include: 1) X-ray crystallography of monolayers and inter-layer effects in thin films [1,2], 2) the study of long range correlations in monolayers via high resolution line shape analysis [3], 3) the study of 2-D phase transitions [3] and 4) the study of very disordered (e.g., amorphous) surface layers [4]. The potential systems of interest range from inert gases on substrates at low temperatures to high temperature materials processing.

A general purpose instrument for work in these areas would combine UHV protocols with the high precision of an X-ray diffractometer. In this paper, we review and critique the previous instruments used in surface diffraction studies, describe our design of such an apparatus and present a summary of its performance.

2. Introduction to technical difficulties

2.1. Basic scattering geometries

The essential technique in high resolution scattering is the precise orientation of the sample in the incident X-ray beam and of an analyzer with respect to it. The conventional 4-circle diffractometer achieves this by defining a "scattering plane" containing the incident and scattered beams. The analyzer moves only in this plane (2θ angle), while the sample rotates on three Eulerian axes (θ, ϕ, χ) [5]. The mapping of a 3-dimensional position in reciprocal space onto 4 angles leaves one redundancy, which is manifested in an arbitrary azimuthal angle of the sample about its scattering vector. This redundancy allows one additional geometric constraint to be imposed; the grazing incidence condition is an example of such a constraint.

An alternative diffractometer layout is often referred

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to as a "Z axis" machine [6]. Here the sample has two degrees of freedom (a vertical α axis followed by a horizontal θ axis). The detector then has two motions relative to the sample (a horizontal β axis and an orthogonal γ axis). The total number of motions is the same and there is again one redundancy.

2.2. Previous instruments

Because it is difficult to couple high resolution motions into a vacuum, the earliest surface diffraction measurements utilized a small portable sample cell which could either be mounted on a 2-circle diffractometer or a UHV sample preparation system [7]. X-rays reached the sample through two viton-sealed beryllium windows. The sample was rigidly attached to the cell wall for scattering measurements, but could be picked up with a manipulator and transferred through a gate valve interlock to the main chamber for surface characterization and preparation. The UHV compatible interlock had a long cycle time, which resulted in a delay between the X-ray measurements and other surface examinations. This delay restricted the application surface diffraction to relatively inert surfaces.

To overcome the time delay problem, a second generation "Z axis" system was constructed by Brennan and Eisenberger (BE) and is described in these proceedings [6]. This instrument rotates the entire vacuum chamber (X-ray window and surface probes) on a heavy-duty 2-circle diffractometer. The major advantage of this approach is that simultaneous surface diffraction and classic surface techniques (such as LEED and Auger analysis) can be performed. Also, because the sample is never moved from the X-ray scattering position, cryogenic and very high temperature sample holders are relatively straightforward to design.

When the sample cannot move inside the vacuum, as is the case with both these designs, a 360° beryllium X-ray window is needed for complete generality. This requirement significantly increases construction costs and limits the ultimate flexibility of the system (because a cylinder surrounding the sample must remain clear). A second disadvantage of the BE system is the limitations placed on surface probes and pumping capacity due to weight problems.

3. Basic instrument design

Our design of an apparatus for surface diffraction differs substantially from those previously mentioned.

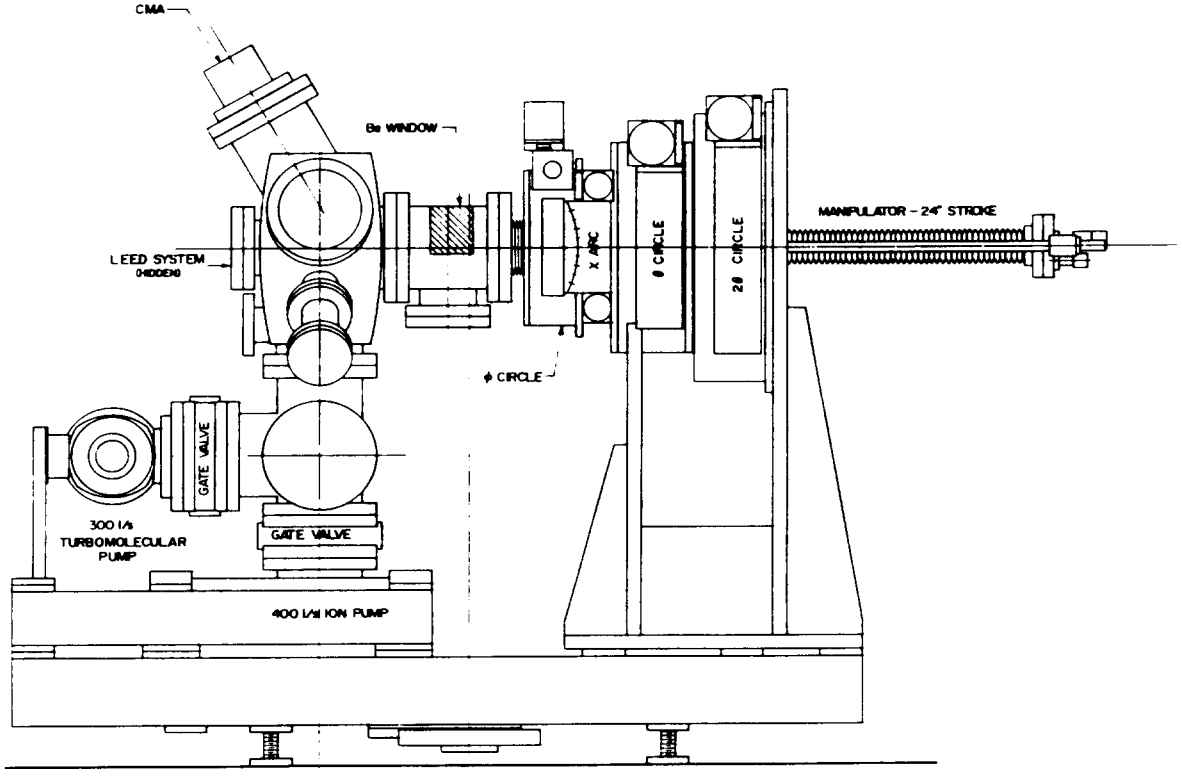

Fig. 1. Side view of the complete instrument viewed towards the source. The center of the beamline is bottom right in the beryllium window (shaded). The detector arm and its counterweight are not shown. The air pads at the bottom lie directly on the hutch table top.

The main difference is that direct coupling of the sample motion into a stationary vacuum chamber is accomplished with a differentially pumped, teflon sealed feedthrough and a welded bellows. This arrangement allows: 1) uncompromised X-ray scattering precision, 2) standard state-of-the-art surface preparation tools, 3) operation of the instrument as a 4-circle diffractometer with a restricted range and 4) a very flexible chamber arrangement that can easily incorporate future modifications. We will discuss each of these aspects in this section.

The apparatus (see fig. 1) consists of several major components. From right to left we have: 1) a sample manipulator, 2) the Huber diffractometer, 3) the beryllium window assembly and 4) the main vacuum chamber. Underneath the main vacuum chamber is the pumping system and the entire apparatus rests on a support structure based on optical tables. The system has two basic modes of operation shown in fig. 2. First, during X-ray scattering measurements, the manipulator is moved fully to the right, pulling the sample up against a pedestal (kinematic mount). This pedestal ensures that the sample is aligned reproducibly in the X-ray beam and couples it directly to the diffractometer motions. The sample is free to move inside the vacuum, because of the bellows and seal. In the second mode which allows the sample to access a full range of surface probes, the manipulator is extended into the main vacuum chamber by contraction of the long bellows and the sample is pivoted 90° on a knuckle joint so that its surface lies 3″ off-axis. Using the motions built into the diffractometer, the sample can then by precisely positioned in front of each of the surface science tools.

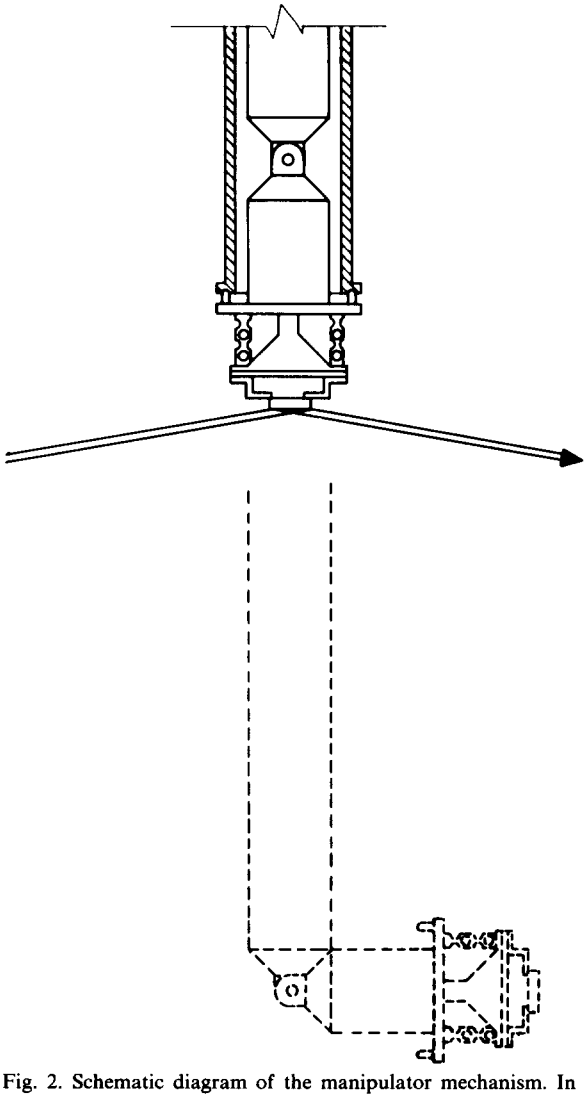

Fig. 2. Schematic diagram of the manipulator mechanism. In the scattering position (right), the sample is pulled tightly back against a pedestal (3 point contact). In the surface preparation position (left), it is turned 90° away from the axis by means of a knuckle joint and push-rod.

3.1. Surface preparation system

The vacuum chamber has three major analytical components: a Physical Electronics single pass cylindrical mirror analyzer (CMA), a Varian LEED system and a Vacuum Science Workshop quadrupole residual gas analyzer (RGA). A single pass CMA was chosen because we do not need the spatial resolution to make photoemission measurements. Provisions have been made for expansion to a double-pass unit by mounting the CMA on an 8″ flange. In addition, the horizontal ports are provided that look at the focus of the CMA. One of these ports is occupied by an ion sputtering gun and the other two are available for light sources, or they can be oriented such that the synchrotron beam can be focused at the CMA. The LEED system is viewed through an opposing 8″ port. The RGA has a mass range of 1–200 amu and is equipped with both a Faraday cup and a channel plate ion detector. The sample can be placed in close proximity to the RGA to facilitate desorption studies.

In addition to the main components, the vacuum chamber has two 6″, two 4 1/2″ and nine 2 3/4″ flanges that face the sample and five 2 3/4″ flanges that do not. One 6″ flange is directly in-line with the manipulator, allowing the addition of an auxiliary vacuum chamber for specialized (e.g. "dirty") sample preparations or for a sample exchange system.

3.2. Pump system

The pump column consists of a 400 l/s Varian ion pump isolated from the vacuum chamber by a 6″ ID Viton sealed gate valve, 300 l/s Balzers turbomolecular pump with a 6″ gate valve and a Varian "Mini Ti-Ball"

titanium sublimation source (TSP) in a custom pump housing with a copper spiral through which liquid nitrogen can be flowed. This TSP arrangement should allow efficient pumping while performing adsorbed noble gas experiments. The area of the copper insert exposed to the Ti source is 170 in^2, resulting in a pumping speed of ~ 7000 l/s for N_2 and H_2.

3.3. Beryllium window assembly

The Be window assembly was designed by us and fabricated by Electrofusion Corp. [8]. The basic structural unit (see fig. 3) is a 6″ OD 0.25″ wall stainless steel tube. The Be window is 3″ long, subtends 200° of arc and is brazed directly to the stainless steel tube using a high temperature braze. A destructive test of a similar Be window assembly was performed by Electrofusion. First a 0.020″ window was subjected to 4 atm external pressure and found to be safe. Then the window was etched to 0.015″ and again found to be safe. When thinned to 0.013″, it failed at 2.7 atm [8]. Consequently, we ordered windows of 0.015″ and 0.020″ thicknesses, in order to have a conservative back-up unit. The assembly also includes a 6″ port and two 1 1/3″ ports. The 6″ port allows the addition of extra pumping in the sample region or electron detectors for performing in situ SEXAFS and photoemission measurements. The two mini flanges can be used to connect the vacuum chamber directly to the beam line, or they can be used for liquid nitrogen cooled Be shrouds for low temperature studies.

3.4. Differentially pumped seal

The rotary seal (see fig. 4) is formed by three in-line teflon gaskets [9] separating two evacuated spaces. The seals mate with polished cylindrical surfaces on the inside (rotating) and outside (fixed with respect to the vacuum chamber). Differential pumping lines pass through the latter wall. Deflection of the seal is restricted by a high precision ball bearing, which clamps the inner and outer walls. The stationary side of the seal unit mates through a short welded bellows to the Be window assembly; the rotary side connects to the dif-

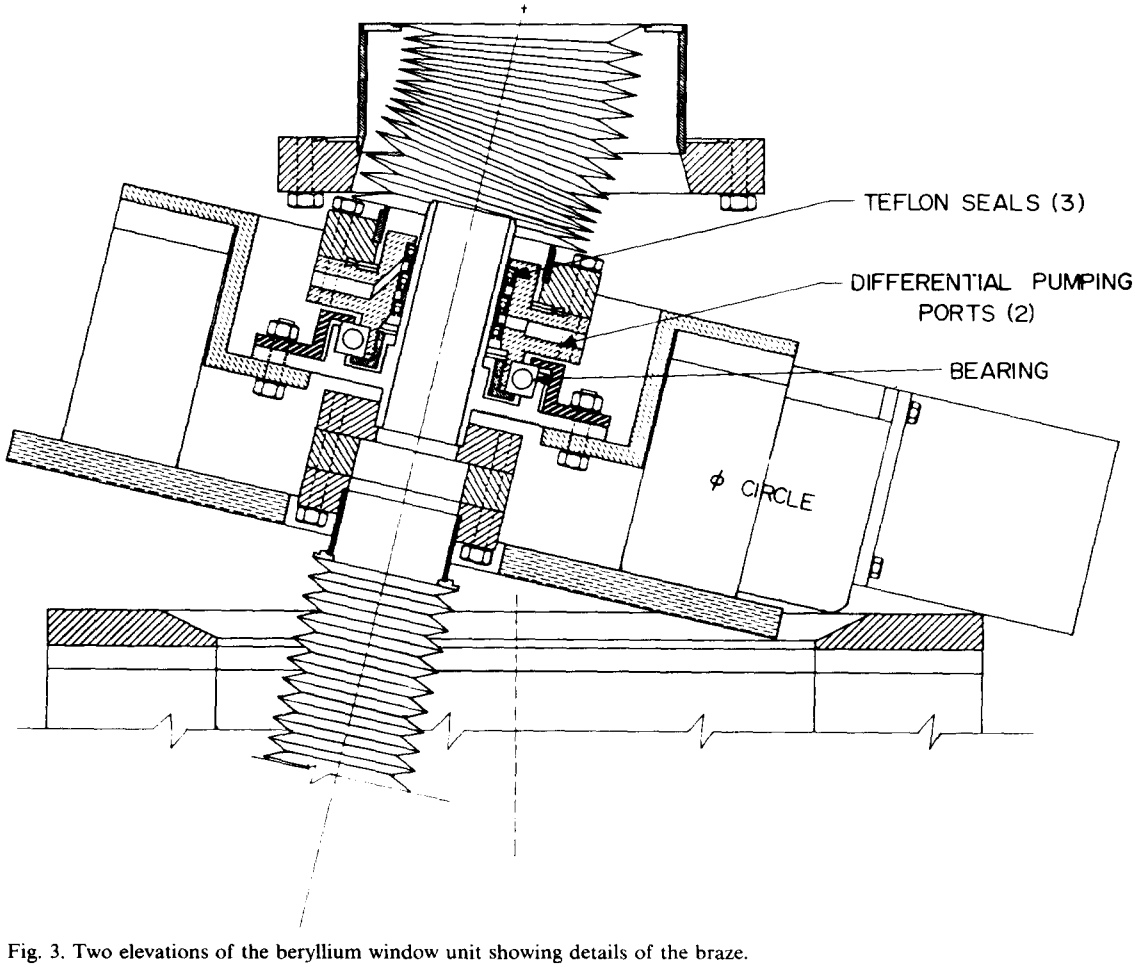

Fig. 3. Two elevations of the beryllium window unit showing details of the braze.

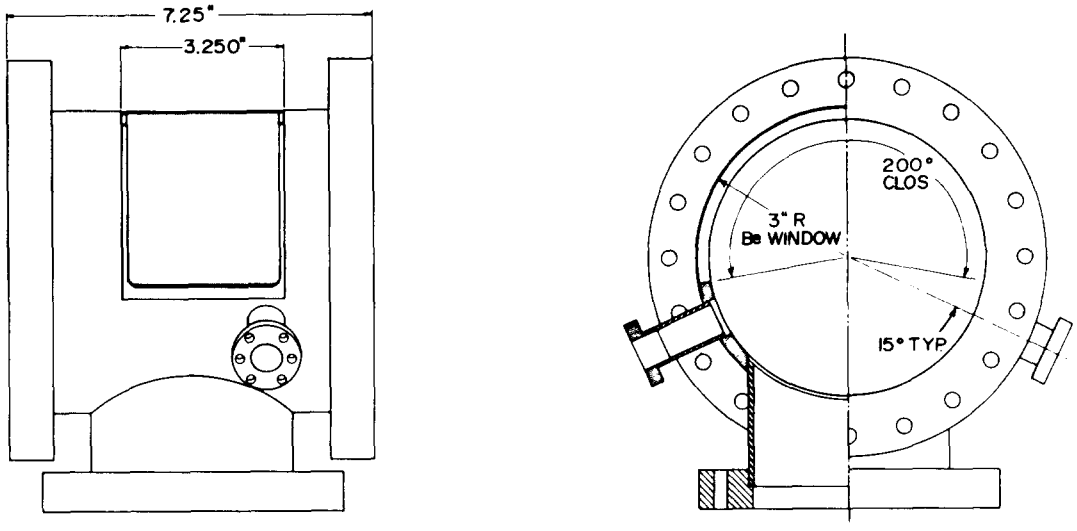

Fig. 4. Cross section of the seal/bellows unit and part of the diffractometer. The sample surface lies at '+' and is shown tilted to the maximum extent. The sample pedestal and the plumbing attached to the differential pumping ports are omitted for clarity.

fractiometer ϕ circle and sample manipulator.

The leak rate of this seal has been measured under several sets of conditions. If no differential pumping is used and the seal is not moved, the leak rate is $\sim 2 \times 10^{-5}$ Torr · l/s; this rises to $\sim 4 \times 10^{-4}$ Torr · l/s with the seal moving at ~ 5 rpm. With one pumping stage of the seal at ~ 200 mTorr and the other unpumped, the leak rate is $\sim 2.0 \times 10^{-7}$ Torr · l/s whether moving or not. In our vacuum system, this results in a base pressure of $\sim 1 \times 10^{-9}$ Torr (although the pressure in the seal region is probably higher). When both differential pumping stages are used, we anticipate base pressures limited by the outgassing of the chamber.

3.5. Sample manipulator

The manipulator is a crucial element in this design. It must: 1) hold the sample firmly against the kinematic mount on the goniometer, 2) support the sample rigidly enough in the main chamber for sample preparations and surface analysis, 3) have enough stroke to extend into auxiliary chambers and 4) provide heating and cooling (hopefully from 20 to 1400 K).

The basic element of the manipulator is a 1" OD stainless steel tube that slides inside a WS_2 lubricated [10] linear bearing located behind the rotary seal. This tube carries electric power to the sample, a push-rod to drive the knuckle and a 1/2" diameter conduit to a coolant reservoir. Since the manipulator end flange moves with the sample tip at all times, none of these connections flexes; a helium transfer line can therefore be inserted along the entire length. A long welded bellows surrounds this assembly to provide 24" of stroke. The whole unit rotates inside and slides along a pair of guide rods attached to the diffractometer between the χ and ϕ motions.

The details of the sample mount vary from one experiment to another, but the basic features are as follows. At the end of the transport tube is the knuckle which allows the sample to access the main chamber instruments and sufficient flexibility to pull solidly against the X-ray scattering pedestal. The mount contains sapphire electrical insulators and stainless steel thermal isolators. Contact to the liquid nitrogen reservoir is provided by a combination of OFHC copper braid and rod. The sample can be heated radiatively with a filament, with electron bombardment, or by passing a current through the sample.

3.6. Diffractometer

The X-ray diffractometer is based on the standard Huber 430/440 diffractometer combination. We replaced the χ circle of the standard Huber 5020 4-circle diffractometer by a pair of 5202 arcs, because of space limitations. A Huber 421 was used instead of a 410 for the ϕ circle to increase the bore size and to provide extra torque. The sample surface normal can be arbitrarily oriented within a 12° cone using this arrangement (limited by the bore of the 440). We found the use of orthogonal arcs to be inferior because they 1) would be substantially thicker and thus limited to smaller angles and 2) would place restrictions on the thickness of the manipulator in two directions instead of one.

3.7. Support and alignment structure

The entire surface scattering system is mounted on a $60'' \times 36'' \times 8''$ Newport Research Corp. (NRC) research grade optical table, which deflects < 0.01 mm under the weight of the system. This table is, in turn, floated by air bearings on a second NRC table to allow precise positioning of the entire surface system in the $X-Y$ plane and about the Z axis. The bottom NRC table can be tilted on a horizontal axis and translated vertically, providing all degrees of freedom for positioning our experiments.

4. Summary and conclusions

The surface diffraction chamber described here is a very flexible instrument designed to study a wide range of surface systems. Most components have been assembled and are waiting for installation on Beamline X16A at the NSLS. The line will be equipped with a toroidal focusing mirror [11] and a two crystal, parallel setting monochromator [12] optimized for use in the 4 to 12 keV energy range. We believe this combination of a dedicated high brightness X-ray source and a highly flexible UHV X-ray scattering system will lead to a better understanding of surface phenomena.

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