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An Apparatus for Molecular Beam Scattering from Single Crystal Surfaces in Ultra High Vacuum

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ABSTRACT

A system which combines molecular beam scattering with low energy electron diffraction is described. The apparatus is used to study molecular and atomic beam scattering from single crystal surfaces and to investigate reactive scattering of gases from surfaces. The detector is a quadrupole mass spectrometer which may be rotated about the target crystal both in and out of the plane formed by the incident beam and the surface normal. Through the use of differential pumping techniques, the sample is maintained in an ultra high vacuum environment ($<10^{-8}$ torr) during the course of the molecular beam scattering experiment. The use of UHV permits the experimental investigation of gas-solid interaction parameters which are unobtainable with more conventional techniques. Low energy electron diffraction (LEED) provides information on surface conditions while Auger spectroscopy may be used to identify surface contaminants.

INTRODUCTION

Scattering experiments with crossed molecular beams have long been used to probe the dynamics of gas phase reactions. The investigation of molecular beam-surface interactions, although initiated in the late twenties,[1] has only recently begun to yield valuable information concerning the dynamics of scattering from surfaces and of surface reactions.[2,3] Theoretically, such studies can be used to obtain the angular distribution of the scattered beam and products, the partition of reaction energy among translational, vibrational and rotational modes, the surface residence time,[4] and the reaction probability as a function of surface and gas temperatures. To date, only a few of these possibilities have been realized and reported in the literature. Due to recent advances in molecular beam, electronic detection and ultra high vacuum techniques, however, several research groups are now pursuing such studies.

Interpretation of the early experimental results obtained in surface scattering studies was difficult due to the unknown surface properties and polycrystalline nature of the targets then employed. Recognition of this problem has led recent experimenters to use single crystal targets[5] and to devise methods to insure surface cleanliness during the course of the scattering experiment. The most widely used of these methods are: (1) high surface temperatures so that the rate of desorption of the background gas is greater than its rate of adsorption,[6] and (2) continuous deposition of the solid substrate at a rate exceeding that of the impinging background gas.[5] The first of these methods is restricted to

the thermally stable faces of a few refractory metals and does not permit the study of a reaction's dependence upon surface temperature. Method (2) permits only limited temperature variation due to the restricted conditions necessary for the epitaxial growth of single crystal surfaces on a substrate. Such studies must be limited to only those crystal faces which can be deposited with a dominant orientation, thus excluding the investigation of high index faces. Currently, the only faces that have been deposited are those of the (111) orientation of Ag, Au and Ni.[7]

We have developed an apparatus which permits one to study the scattering of molecular beams from single crystal surfaces at any temperature (either high or low), under ultra high vacuum ambient conditions ($<10^{-8}$ torr). In our apparatus, using almost any high purity single crystal commercially available, one may investigate the effect on the gas-solid interaction of varying the following parameters: the surface temperature, the incident angle of the beam, the crystallographic orientation of the target plane or the surface order. We can also carry out low energy electron diffraction (LEED),[8] Auger spectroscopy,[9] ellipsometry,[10] and ion bombardment[11] studies to concurrently probe the surface.

This paper describes the apparatus constructed to permit the study of beam scattering under the conditions described above. The sample may be bombarded by either continuous (d.c.) or pulsed (a.c.) thermal atomic or molecular beams. LEED may be used to monitor surface conditions before, during, and after scattering studies. The combination of these techniques is used to provide information on the energy transfer between the incident molecules and the surface during chemical reactions. Such data should be of great importance in the fields of surface reaction

kinetics and heterogeneous catalysis.

APPARATUS DESCRIPTION

Fig. 1 shows a schematic diagram of the major components of the entire apparatus while Fig. 2 gives a more detailed view of the scattering chamber. The apparatus consists of three separate parts: (I) a specially constructed ultra high vacuum scattering chamber coupled by a bakeable gate valve to two other differentially pumped chambers, (II) and (III), where the molecular beams are generated. The UHV portion is pumped entirely by sorption and ion pumps and is bakeable to 250°C while the other two chambers are pumped by conventional liquid nitrogen baffled oil diffusion pumps. The actual scattering experiment from the single crystal surface is carried out in the UHV chamber. This chamber also houses the mass spectrometer used as a beam detector and the LEED optics used to monitor the surface structure. Chamber (II) contains the beam chopper or a rotating disk velocity selector and chamber (III), the oven source used to generate the beam.

I. Scattering Chamber

The ultra high vacuum chamber itself consists of a type 304 stainless steel sheet, 4.8 mm thick, welded into a cylinder 30 cm in diameter and 50 cm in height. Thick plates (25.4 mm) welded to the top and bottom of this cylinder prevent buckling due to the external and internal pressure differences. Various size copper sealed access ports (Fig. 2) are situated in convenient locations about the cylinder's circumference as well as in its top and bottom. Total pressures are measured with a nude ionization gauge mounted directly in the chamber. In the absence of a molecular beam, the gate valve between the scattering and selector

chamber is kept closed, thus allowing the UHV chamber to be used independently for low energy electron diffraction experiments.

The molecular beam enters the scattering chamber along a fixed line intersecting the axis of the cylindrical chamber by traversing a bakeable gate valve (Whittaker Model SVS-3) which has been fitted with a (changeable) collimating orifice 1.5 mm in diameter. The target, an oriented single crystal disk (7 mm in diameter and 1 mm thick) is suspended from a Varian multipurpose electromechanical feedthrough at the point where the LEED, ion bombardment, and molecular beams intersect the axis of the scattering chamber. This mounting permits the crystal to be rotated approximately 300° on the UHV chamber's cylindrical axis for use in either LEED or scattering experiments. Sample temperatures above room temperature are attained through resistive heating while low temperatures may be reached by the use of a special liquid nitrogen cooled holder.[12]

In order to study molecular beam scattering from a surface in an ultra high vacuum ambient, differential pumping techniques must be used to avoid flooding the scattering chamber with non-directional gas molecules effusing through the collimating orifice. Even so, vigorous pumping of the scattering chamber is necessary to keep the ambient as gas free as possible. Ideally the pump should be located directly opposite the beam source so that the beam molecules pass directly into the pump unless scattered by the target surface. For this work, a 500 liter/second vacuum ionization pump (Varian Noble VacIon) was chosen. The large speed is desirable because, even for such "noble gas" pumps, the pumping speed falls to roughly 30% of the maximum rate observed for N_2 when one pumps He or Ar. A bakeable gate valve connects the pump to

the UHV scattering chamber. This allows the pump to be isolated and left operating when the main chamber is opened to change the sample, thus facilitating later pump-down. Evacuation is initiated by an air aspirator (Varian GASP Roughing Pump) to a pressure of roughly 200 torr and followed by the serial application of two sorption pumps (Ultek Model 50-135) to 10^{-3} torr or lower. At this pressure the gate valve to the ion pump may be opened. Use of the aspirator considerably shortens the pump-down time. Pressure below 10^{-7} torr are regularly achieved within two hours. Following a 200°C bakeout, pressures on the 10^{-10} torr scale (as indicated by a nude ion gauge) have been measured in the scattering chamber. Fig. 3 shows a mass spectrum of the residual gas background in the isolated scattering chamber (i.e. no parent beam present).

Before, during, or after scattering by the molecular beam, the surface may be studied by low energy electron diffraction. The LEED optics are located perpendicular to both the beam line and the cylindrical axis of scattering chamber (Fig. 2). Back diffracted low energy electrons (energies of 5 to 500 ev yield wavelengths between 5.5 Å and 0.5 Å) are well suited to probe the surface structure during a molecular beam scattering experiment because their strong coulomb repulsion by the substrate permits penetration of only a few atomic layers.[8] LEED can also be used to identify the presence of contaminant surface structures. For example, Fig. 4a and 4b show the diffraction pattern of a clean Pt (100) surface and a platinum surface yielding a ring-like diffraction pattern caused by surface carbon.[13] The beam scattering properties of the platinum surface may be markedly changed in the presence of a layer of graphitic carbon.

LEED techniques have demonstrated that heating the sample in vacuum is usually insufficient to prepare a clean surface. While some contaminants (i.e. carbon and hydrocarbons on Pt or Ni) may be removed by heating in oxygen (followed by heating in hydrogen to reduce excess oxygen), cleaning is best accomplished in situ for most species by alternate cycles of sputtering with noble gas ions followed by high temperature annealing of the specimen. A Varian ion bombardment gun is used to provide low energy ions of Ar^+ or Xe^+ (140 to 375 volts) at current densities up to two microamps per square centimeter. These conditions have been found to yield a minimum of disordering of the surface structure coupled with an optimal removal of surface impurities.

The scattering of reactive gases (CO, hydrocarbons, etc.) may induce the formation of ordered surface structures due to the adsorption of gas molecules incident on the surface during the scattering experiment.[14] Thus, one may observe a transient change in the scattering properties of the surface as a function of time due to the formation of a new structure. This can be ascertained and studied by simultaneous beam scattering and LEED experiments.

Other gases which may be used in molecular beam studies adsorb in a disordered manner on the single crystal surface. LEED is not particularly sensitive to the presence of amorphous deposits on the surface in concentrations less than 10% of a monolayer.[15] Auger spectroscopy, however, can be used to monitor the surface composition. This technique involves the energy analysis of the back-scattered low energy electrons.[9] The observed signal is independent of surface order but proportional to the concentration of contaminant surfact atoms. This measurement can

also be carried out in the scattering chamber using the LEED optics either during or after a scattering experiment.

To detect the angular distribution of the scattered parent beam and the scattered products of a surface reaction, a quadrupole mass spectrometer (Electronic Associates Inc. Model 250-A) is used. Its versatile mounting, pictured in Figure 5, is built from a commercial rotary motion feedthrough (Ion Dynamics Corp.) with the normal length 9.5 mm diameter shaft replaced by one extending 30 cm beyond the flange face. This feedthrough is attached to a specially built linear motion drive containing the electrical connections necessary for the quadrupole's operation. Alignment of the rotating shaft is maintained by a ball bushing located on the axis of the scattering chamber. One advantage of this mounting system is that the mass spectrometer may be easily inserted or removed from the chamber with all its internal connections intact. The mounting allows study of the scattered beam both in and out of the incident plane and rotation from -10° to $+190^{\circ}$ relative to the parent beam line. A 5° acceptance angle at a distance of 5 cm from the target was obtained by modifying the Pierce gun ionizer as shown in Figure 6. The vertical profile of a d.c. Xenon beam is presented in Figure 7. Due to the low resolution at the time this curve was obtained, the half width is somewhat exaggerated.

In order to reduce the ambient pressure as well as help in pumping condensable gases, a liquid nitrogen cold finger can be installed below the viewing port opposite the LEED optics.

II. Selector Chamber

This chamber acts primarily as a buffer between the source chamber containing the oven which generates the beam and the scattering chamber.

During an experiment using an oven pressure of several torr, the pressure in the selector chamber is 3×10^{-7} torr. A tuning fork beam modulator (American Time Products Type L40 Light Chopper) with a frequency of 150 hertz is used to generate an a.c. molecular beam. Alternately, a rotating disk velocity selector[16] is placed in the chamber to prepare monochromatic beams for use in scattering and surface chemical reaction studies.

A 10" oil diffusion pump (MCF-1400 with Dow Corning-704 fluid) trapped by a liquid nitrogen baffle and protected by an air operated gate valve (Temescal Metallurgical Corp.) is mounted to one side of this chamber. A large access port is opposite the pump port.

III. Source Chamber

A glass multichannel effusive source (Bendix Mosaic Fabrications) consisting of a .8 mm by 4.8 mm rectangular array of tubes (length to diameter ratio 100) is used to generate a thermal molecular beam of some noncondensable gas. The capillary array is held between gold O-rings in a stainless steel oven that can be heated to +400°C and cooled to -196°C. A detailed description of this oven (shown in Figure 8) is given elsewhere.[17] These sources have been used by other authors for molecular beam studies[18] and their characteristics have been fully investigated.[19]

The source chamber is separated from the selector by a collimating orifice having the same dimensions (.8 mm by 4.8 mm) as the beam source. It is pumped by a diffusion pump which is identical to that used to pump the selector chamber. To handle the large gas load during operation of the beam, both pumps are backed by a rotary blower (Rootes model RS 120).

In order to insure that the crystal, gate valve collimator, and oven collimator were all collinear, a laser beam was used to align the last

slit (oven collimator) with the first two positions. The main body of the oven chamber was then welded in place to the tube in which the oven resides. The laser beam can also be used to optically determine the angle of the mass spectrometer detector and the crystal surface with respect to path of the incident molecular team.

The gas handling system for the oven is a glass line external to this chamber. Precise gas flow conditions from a high pressure reservoir to the oven and the ballast flask used to damp out pressure fluctuations are maintained by a variable saphire leak valve (Varian). In order to minimize contamination of the beam gases and saphire leak by stopcock grease, single O-ring sealed Teflon needle valves (Fisher and Porter Co.) have been used in place of high-vacuum stopcocks in this manifold.

INTERLOCKS

With an apparatus of this size and complexity, any electrical or vacuum failure can damage parts of the system, especially components of the ultra high vacuum chamber. Consequently, a system of "fail-safe" safety devices was designed to isolate the damaged part from the rest of the apparatus.

Power input to the diffusion pump heaters is controlled by water flow, water temperature, and fore-vacuum pressure sensors. All valves, except those leading to the scattering chamber, are air operated and wired such that they are normally closed. Thus a sudden loss of electrical power causes all air operated valves to close and remain so if any conditions unfavorable to their opening still exist when the electric power returns. Additionally the valves are interlocked to one another so that they can only be operated in a set sequence to further protect the system. Finally, the valves between the diffusion pumps and the source and selector

chambers are connected to pressure sensors that close them when the pressure in either chamber exceeds a preset value.

Both the mass spectrometer and LEED power supplies are interlocked to line voltage through a relay that requires manual resetting after a power failure. In this way, current surges through the spectrometer ionizer and LEED electron gun filaments can be averted. The ion pump on the scattering chamber is self protected. Automatic shutdown results from the high ion currents due to high pressures.

SUMMARY

An apparatus has been built to study molecular beam scattering from clean single crystal surfaces under ultra high vacuum conditions. By successfully isolating the differentially pumped beam source and velocity selector chambers, and by the use of high speed pumps in all three chambers, the target crystal may be maintained in an ultra high vacuum environment during the scattering experiment. Low energy electron diffraction (LEED) and Auger spectroscopy may be used during the scattering studies to monitor the crystal surface. Cleaning of the surface is accomplished by *in situ* ion bombardment sputtering. The angular distribution of the scattered a.c. or d.c. molecular beam is obtained with a quadrupole mass spectrometer that can be rotated about the crystal. During the scattering experiment, the surface temperature may be varied between -196°C and the crystal's melting point.

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FIGURE CAPTIONS

Fig. 1. Schematic diagram of molecular beam scattering apparatus.

Fig. 2. Detailed view of Scattering Chamber. Ion pump (not shown) located on port below LEED optics.

Fig. 3. Scattering chamber background mass spectrum in absence of molecular beam. Total pressure 9×10^{-10} torr.

Fig. 4a. Diffraction pattern of clean Pt(100) sample yielding characteristic (5x1) structure, E = 124 V.

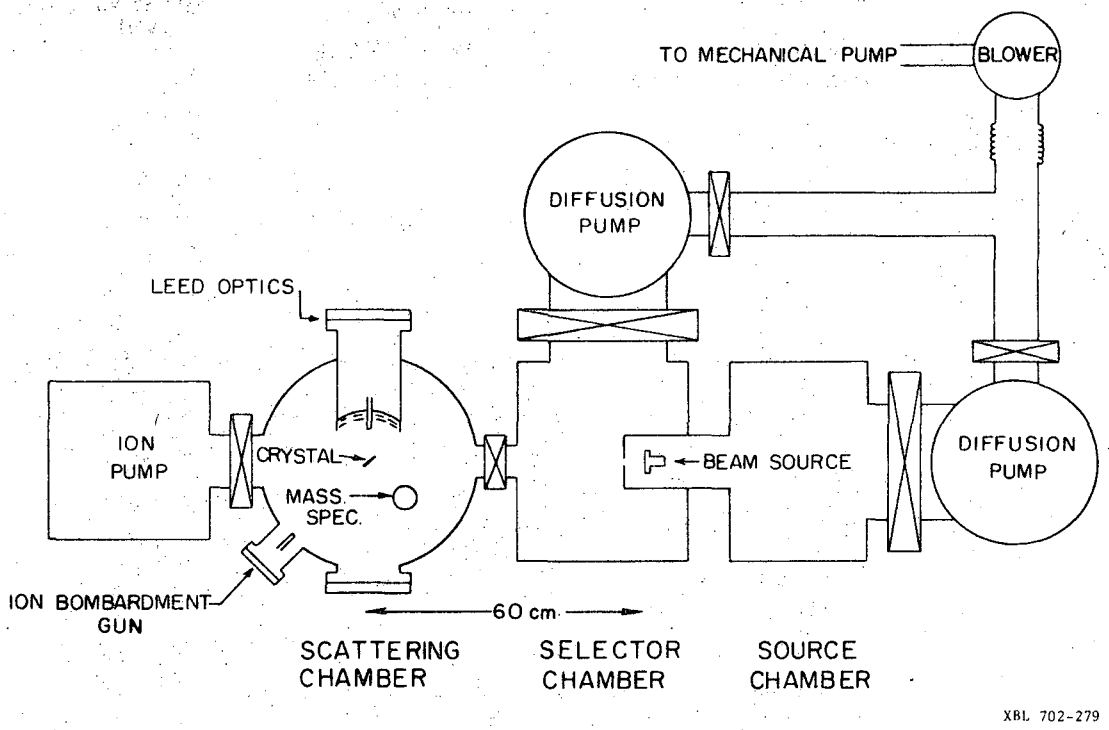
Fig. 4b. Ring-like diffraction pattern due to presence of surface carbon on Pt(100), E = 98 V.

Fig. 5. Mass spectrometer and linear-rotary motion feedthrough.

Fig. 6. Modified mass spectrometer ionizer.

Fig. 7. Vertical profile of D.C. xenon molecular beam.

Fig. 8. Multichannel molecular beam source.


TO MECHANICAL PUMP
BLOWER
DIFFUSION PUMP
LEED OPTICS
ION PUMP
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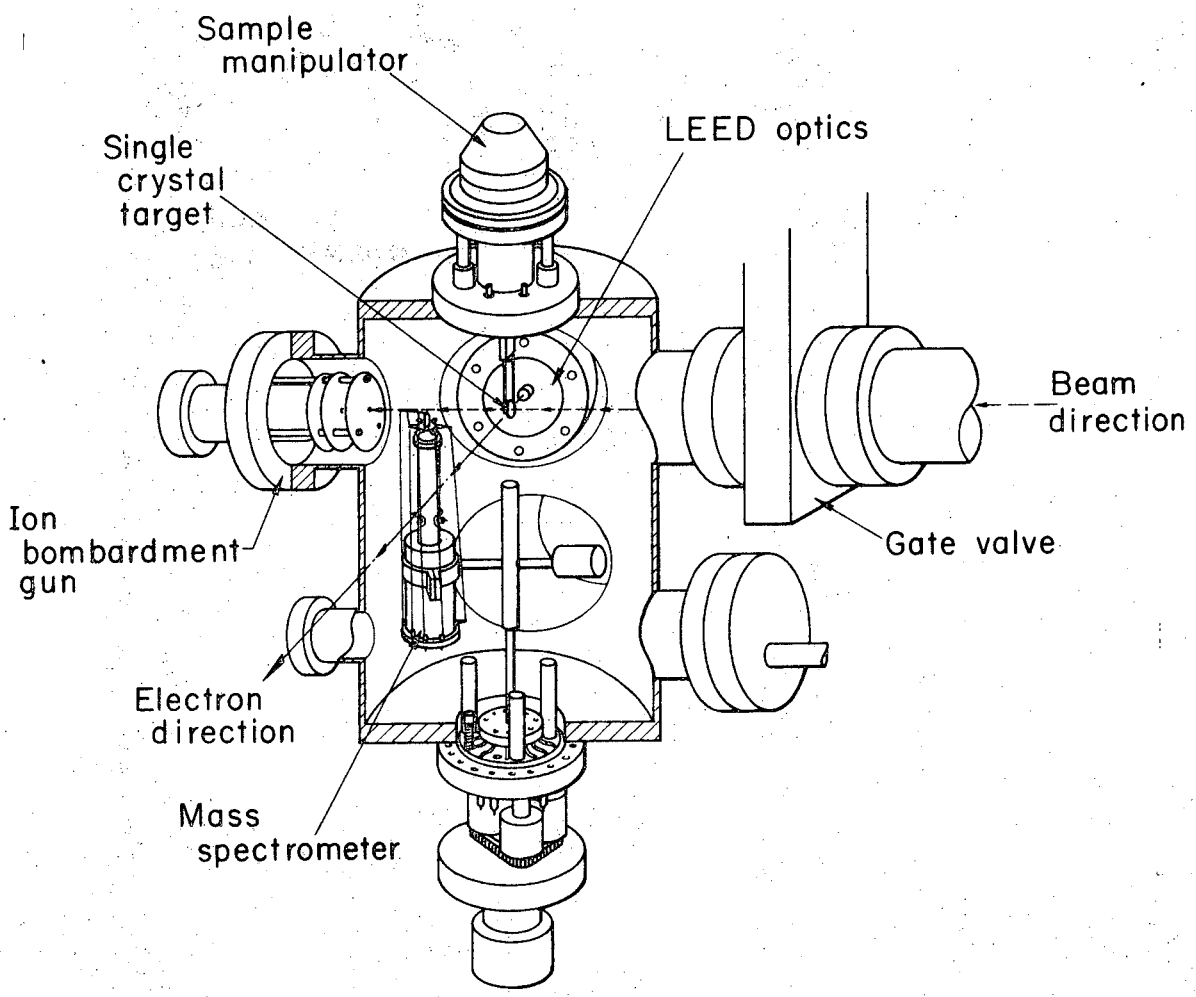
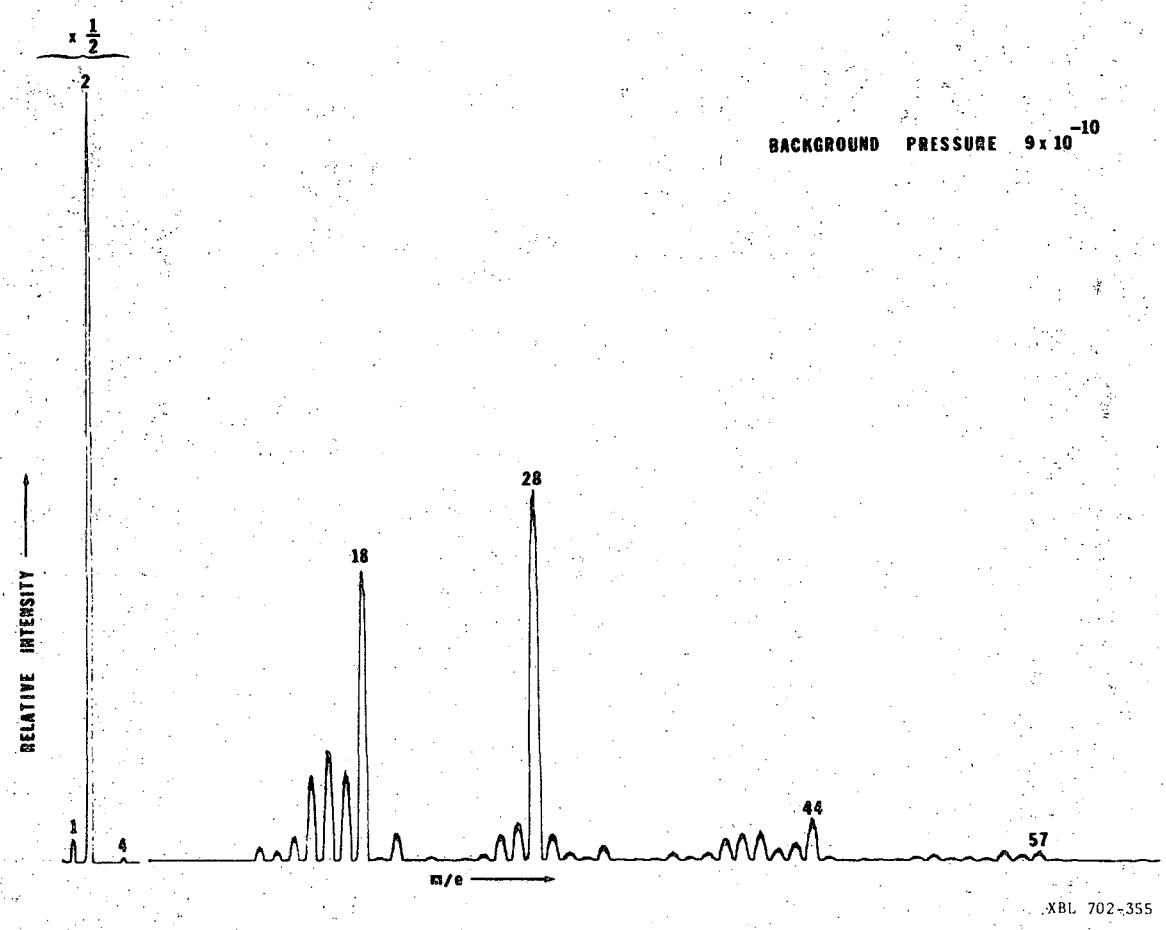
BEAM SOURCE
DIFFUSION PUMP
ION BOMBARDMENT GUN
60 cm
SCATTERING CHAMBER
SELECTOR CHAMBER
SOURCE CHAMBER
XBL 702-279

Fig. 1



SCATTERING CHAMBER

Fig. 2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RELATIVE INTENSITY
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18
44
57
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4
m/e
XBL 702-355

Fig. 3

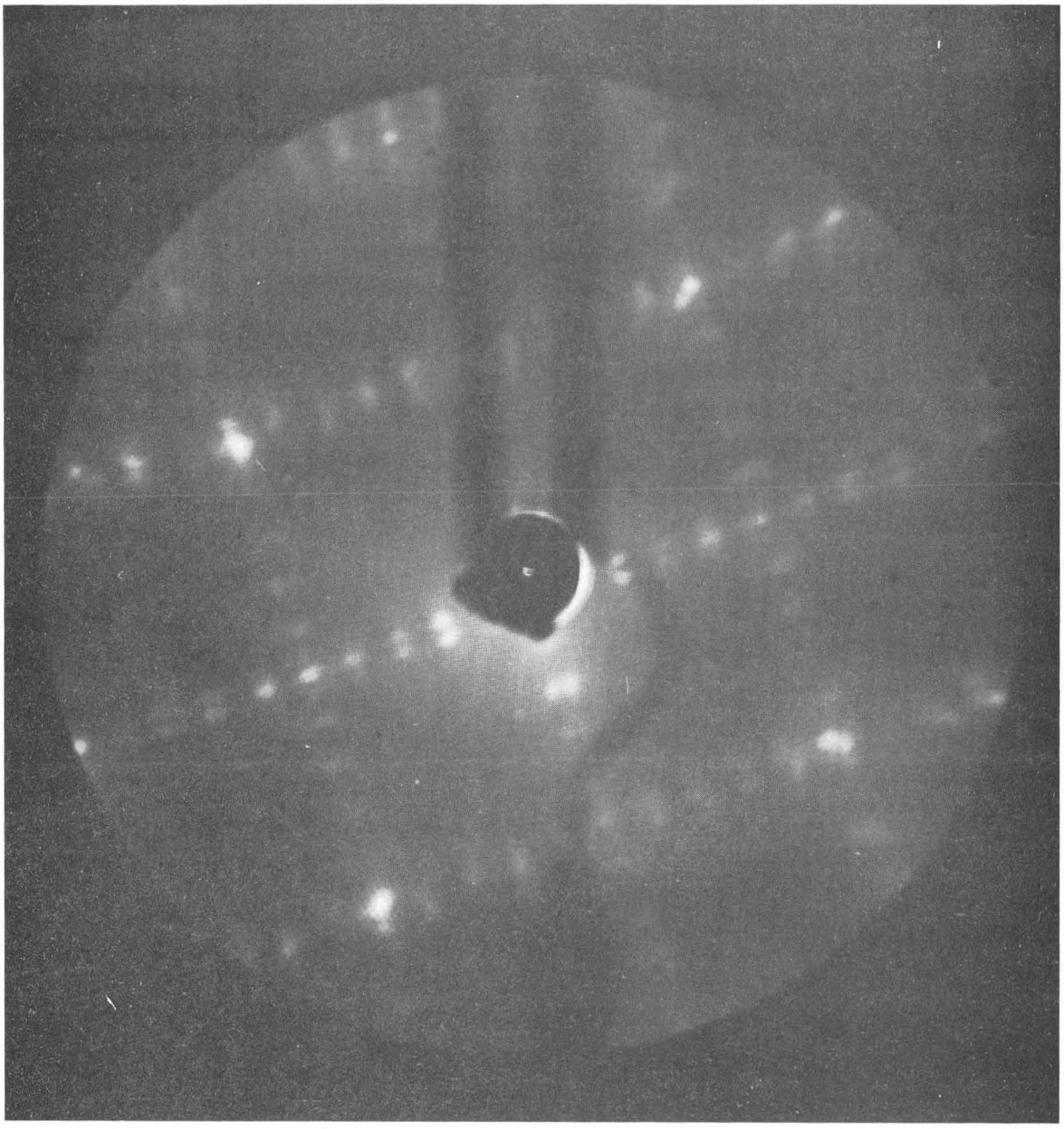

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Fig. 4a

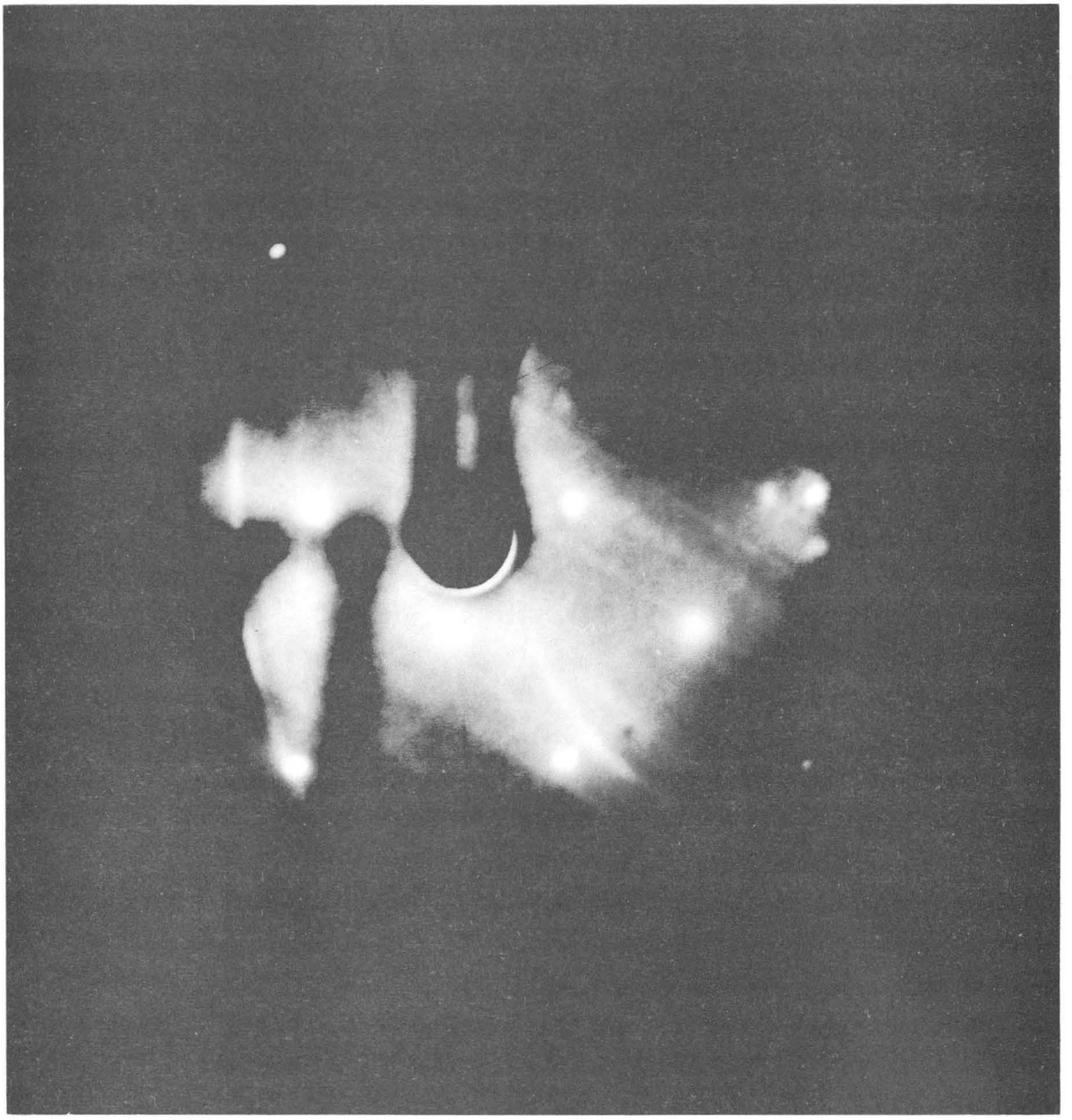

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Fig. 4b

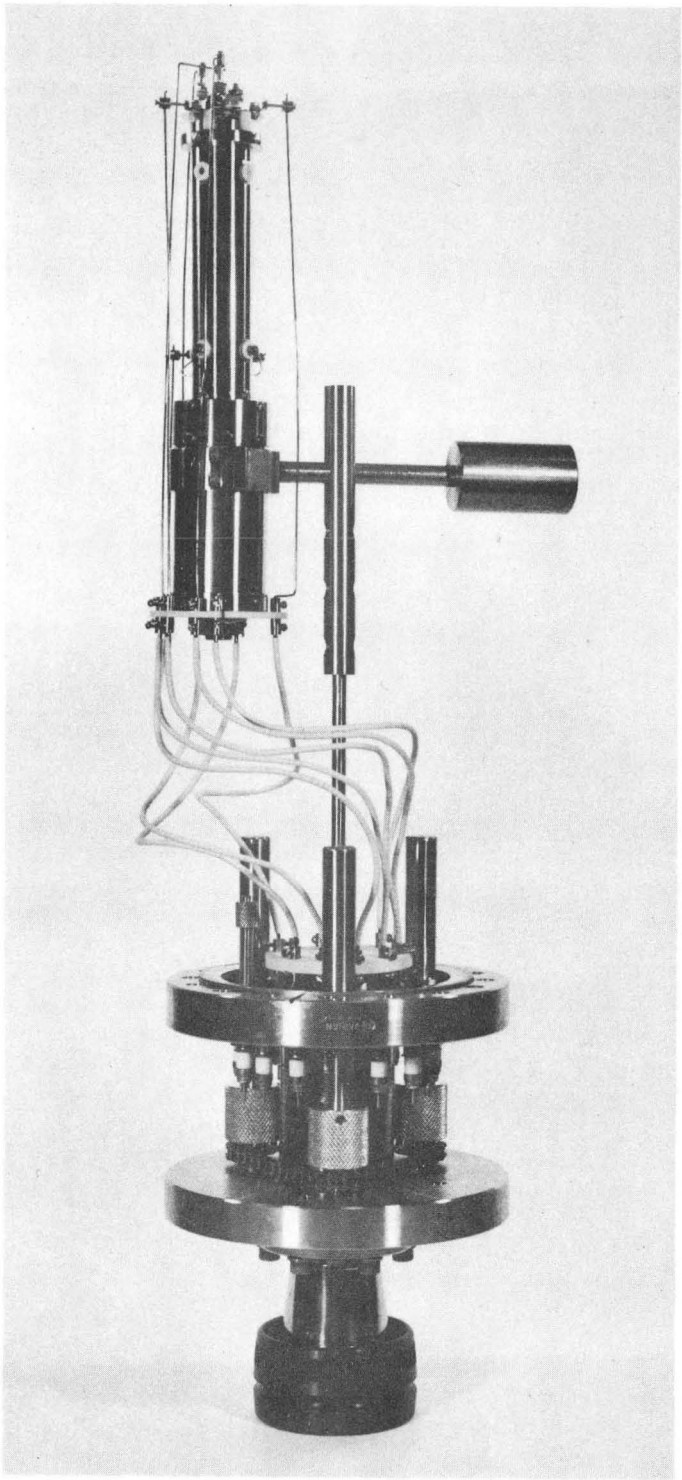

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Fig. 5

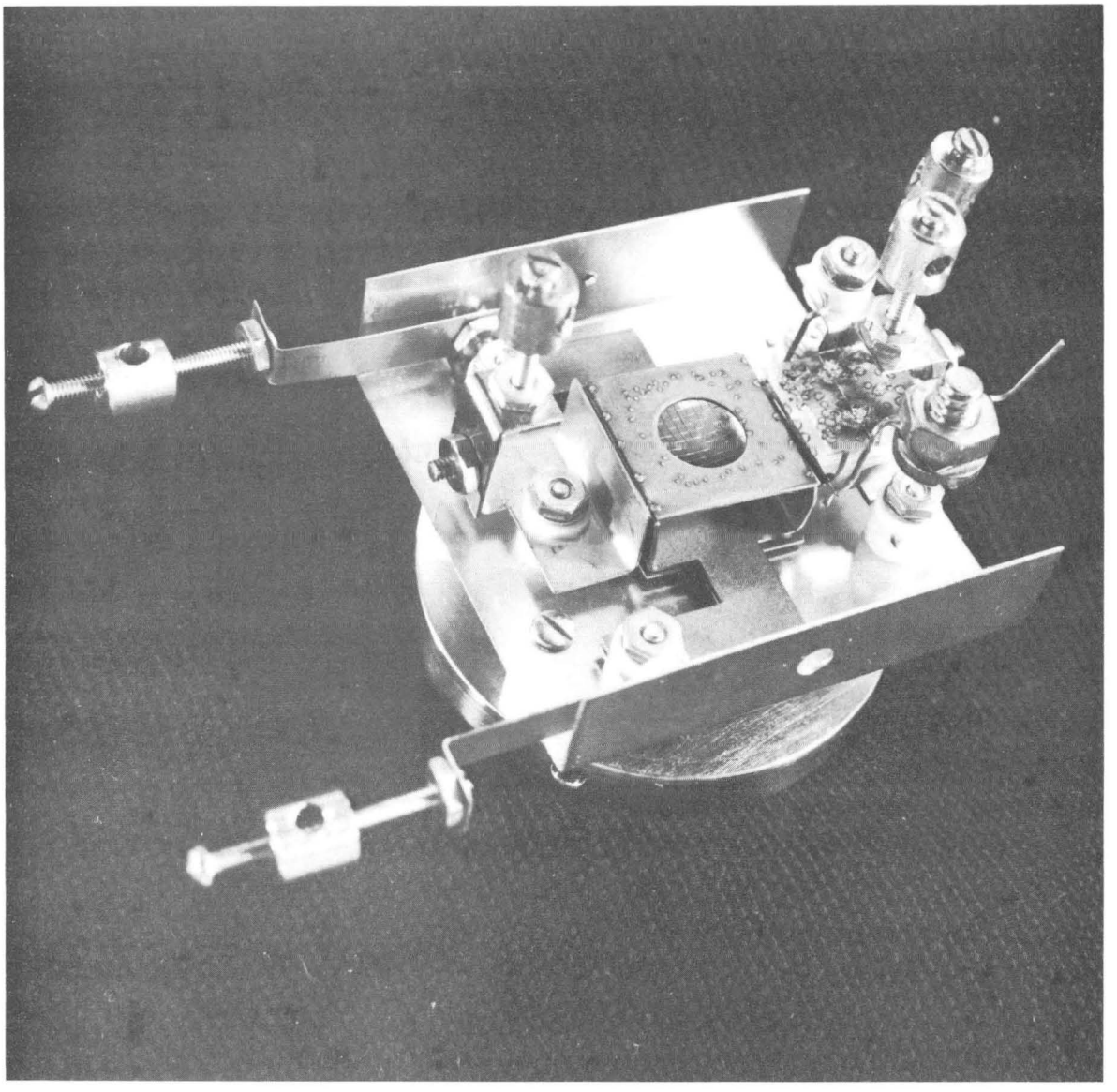

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Fig. 6

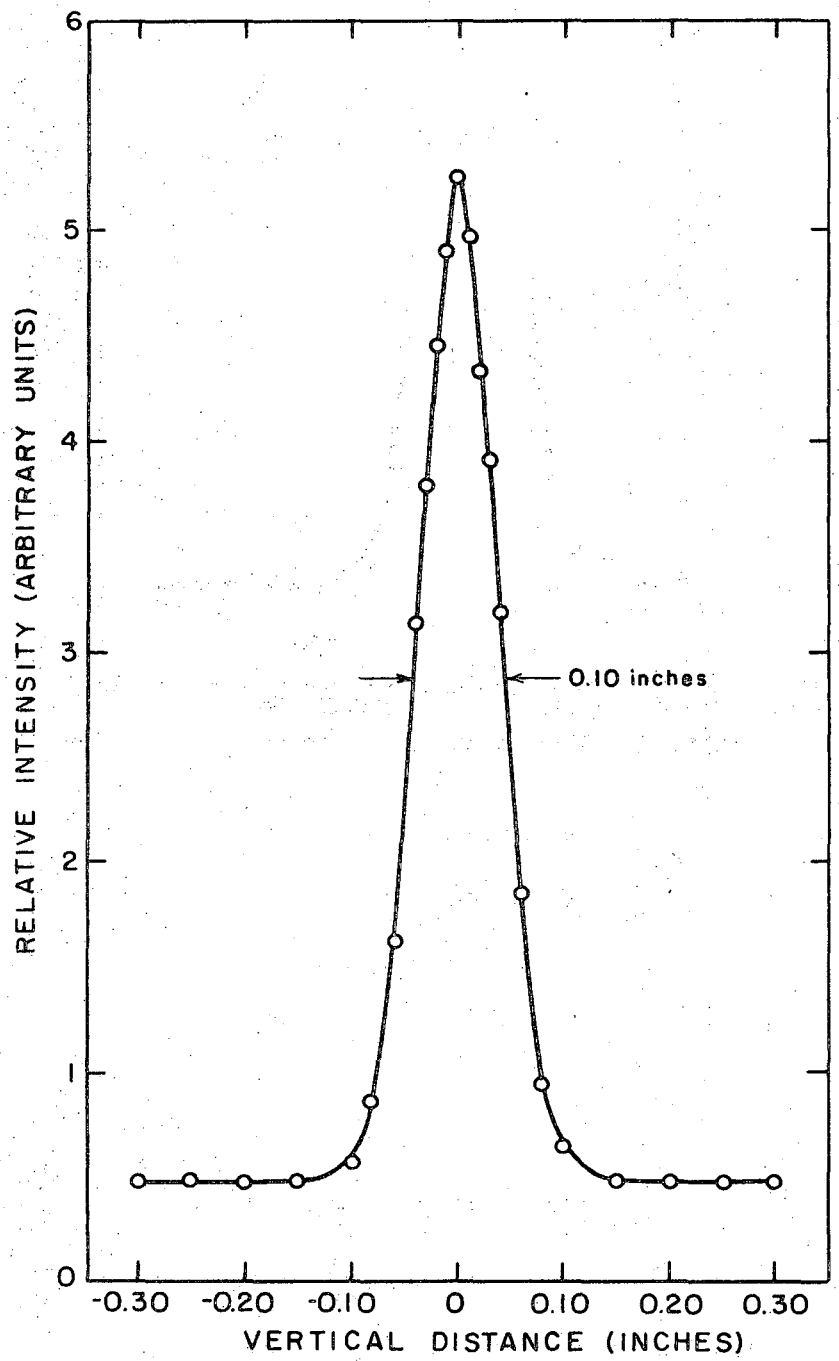

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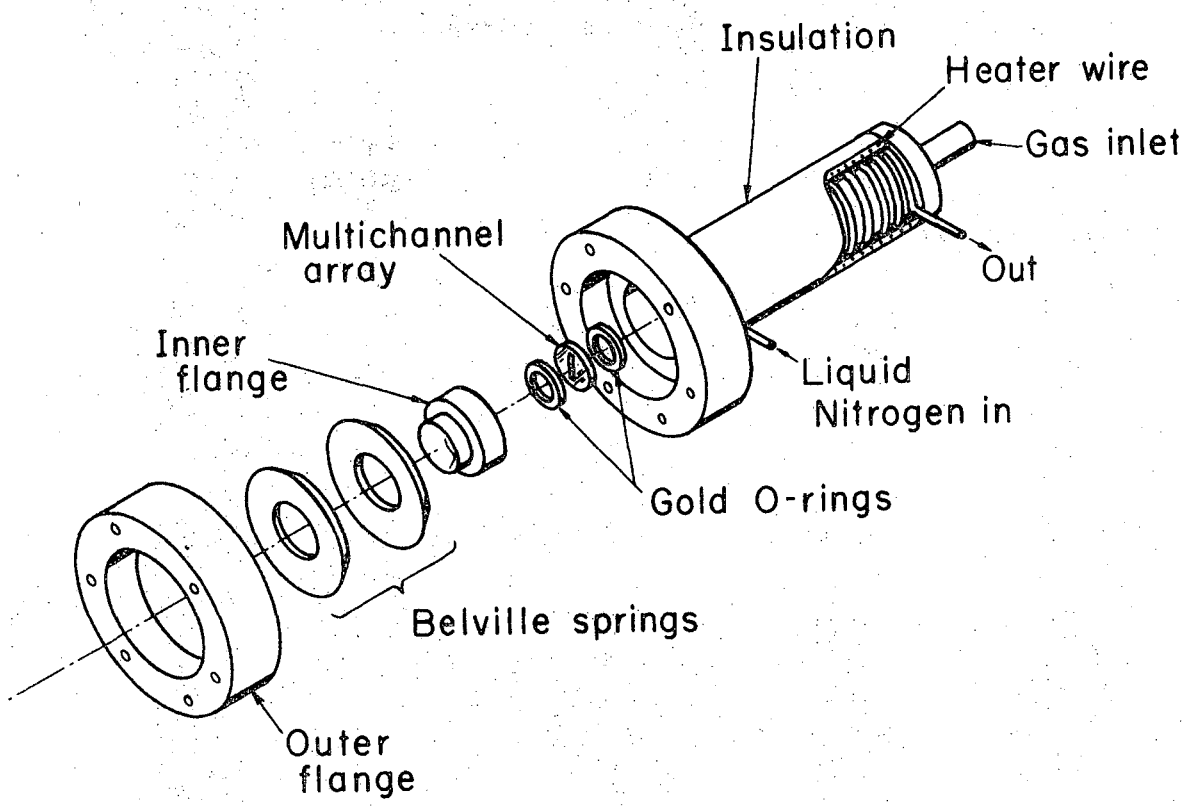
Fig. 7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Heater wire
Gas inlet
Multichannel array
Out
Inner flange
Liquid Nitrogen in
Gold O-rings
Belville springs
Outer flange
XBL 704-2669

Fig. 8

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