The Use of a Diamond Anvil Cell for Spectroscopic and
Electrical Conductivity Studies of Some Semiconductors[*]

by

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ABSTRACT

A diamond anvil cell(DAC) permits pressure studies to be conducted on compounds while the effects are observed through the diamond windows. The cell allows for analysis of very small samples as well as air sensitive samples. In this work, a DAC was used to study chalcogenides (CaS, MgS, SrS, and EuS) in the visible, near-IR, and far-IR regions of the spectra and a shift of absorption with pressure was observed for the transverse lattice optical mode. The calculated values of $\partial \nu / \partial p$ are then related to the type of bonding in the crystal structure. The study showed that MgS is the most ionic and SrS is the least ionic.

A solid electrical conductivity probe was developed for the DAC to allow for screening of compounds for possible conductors. The probe works well for the purpose it was developed, but it is no substitute for a single crystal measurement.

The work described in this paper involves two major studies utilizing the diamond anvil cell. In the first study a group of chalcogenides were studied spectroscopically under pressure. In the second study a solid conductivity probe was developed and used to determine the bulk conductivity of several platinum and iridium compounds.

TABLE OF CONTENTS

INTRODUCTION

This research explored methods of utilizing a diamond anvil cell (DAC) for the studies of some semiconductor properties under high pressure conditions (0-40kbars). These studies included spectroscopic observations in the near infrared(NIR), far infrared(FIR), and visible regions, microscopic observations, and electrical conductivity measurements. Semiconductors chosen for the spectroscopic studies included MgS, CaS, SrS, and EuS chalcogenides. Semiconductors chosen for the conductivity studies included several new platinum chain compounds and iridium carbonyl halide compounds.

A. Background of the Diamond Anvil Cell (DAC)

There are several types of high pressure cells, but the most versatile for optical studies is the DAC, developed by Weir and associates.[1] A good discussion of the different types of high pressure cells now available is given by Ferraro and Basile.[2] The details of the diamond anvil cell are shown in Figure 1, and Figure 2 shows a picture of an assembled cell. The diamond anvil cell is called that because it uses diamonds as a pressure transmitter, a sample holder, and an optical window. The diamonds are mounted in plaster on stainless steel pistons, which are placed in the holder cylinder so that the diamond faces press against one another. It is very important that the diamonds are properly aligned, because improper alignment of the diamonds could cause breakage.

All loadings of the DAC must be monitored by a light microscope to assure that there is adequate sample to cover the face of the diamond. The DAC is used mainly with solids, although liquids can be used if a gasket (usually metal) is used to hold the liquid in place. A screw and spring apply pressure to one end of a lever,

Side view

Front view

Detail of diamond cell
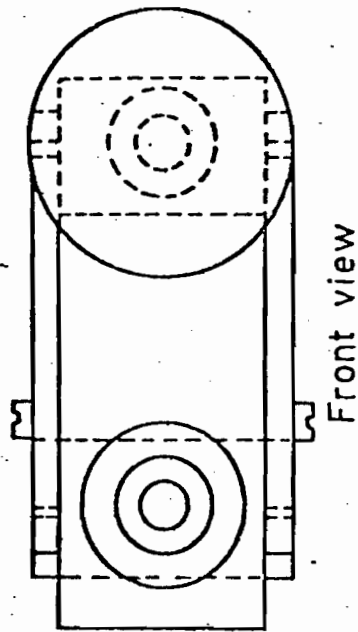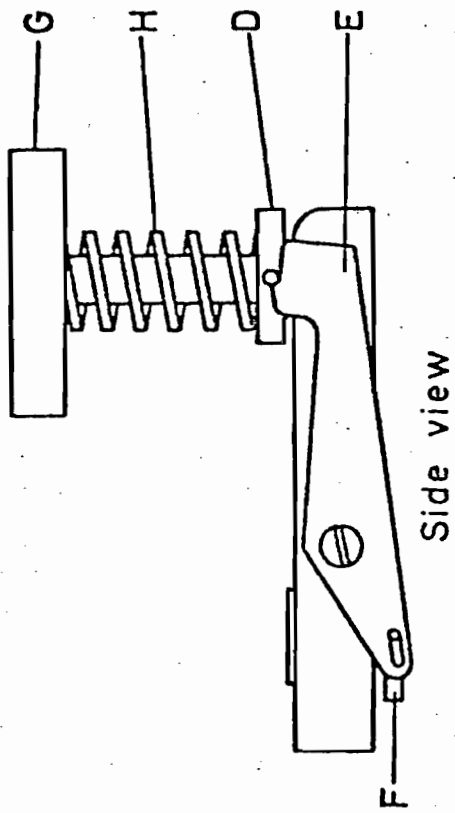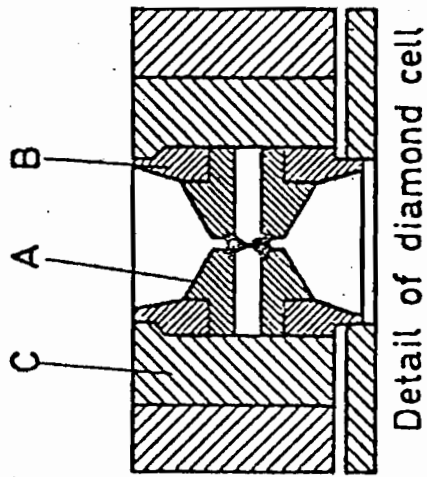
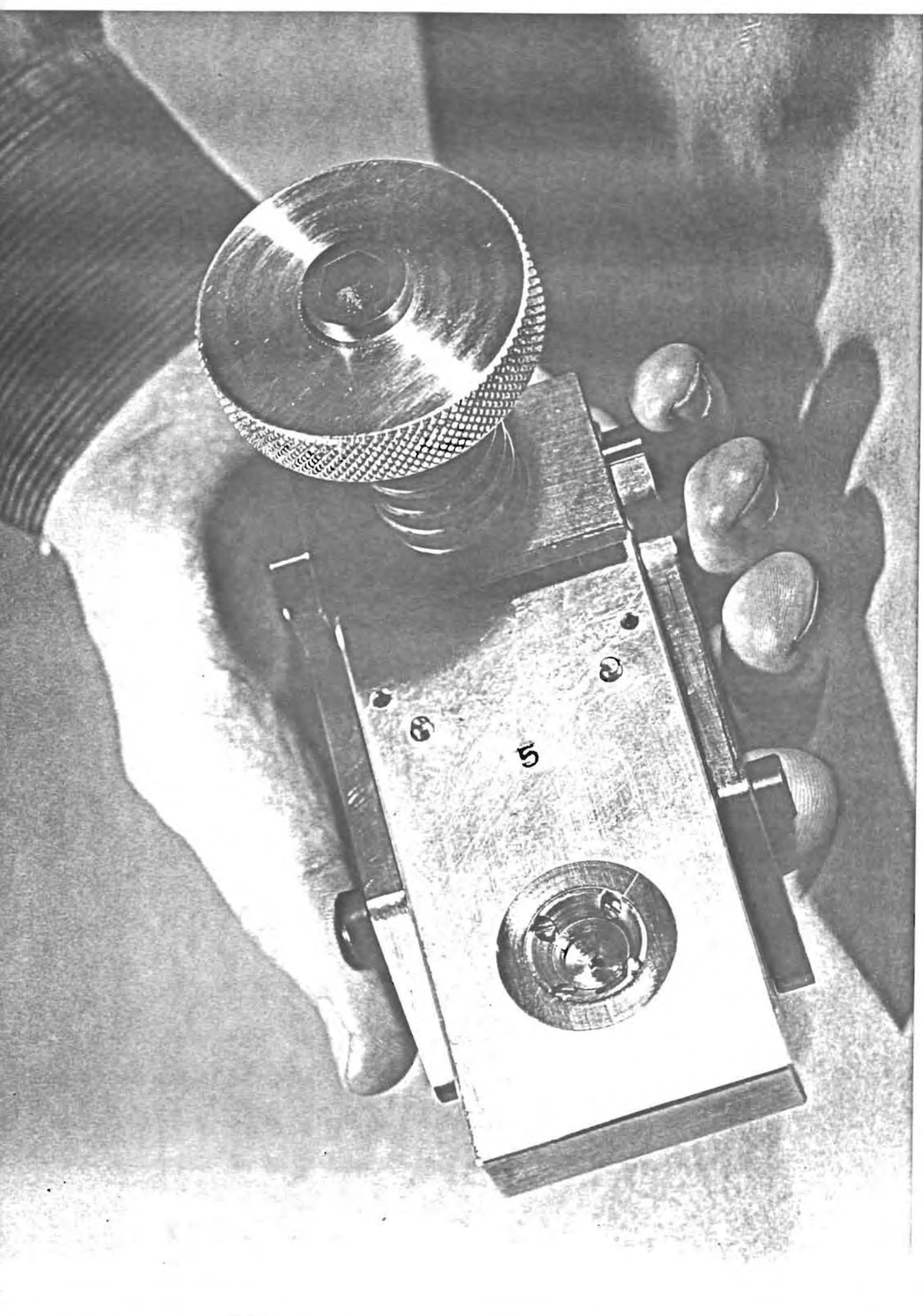Diamond anvil high pressure optical cell. A and B, parts of piston; C, hardened steel insert; D. presser plate; E, lever; G, screw; H, calibrated spring

Figure 1. Diamond anvil high pressure optical cell.

Fig. 2

Picture of the Diamond Anvil Cell

transmitting pressure to a plate, which in turn presses on the piston. This forces the diamonds together and allows for pressure studies to be conducted.

One of the major drawbacks of the DAC is the lack of hydrostatic pressure across the diamond faces. This pressure gradient, which may give pressures 1.5 times greater at the center than the edges, is not entirely disadvantageous.[2] Phase changes may be readily identified in the DAC by microscopic detection of changes in color and the sharp demarcation between the phases. A primary requirement for a phase change is the appearance of a Becke line of demarcation.[2] This is the method of identification of phase changes in solids that do not undergo color changes.

Pressures close to 100 kbars can be easily reached depending on the diamonds. (The use of bar and kbar in this paper follows the current common practice of workers in this field.[3] Note 1bar = $10^5 N/m^2$ = $10^6 dyn/cm^2$ = 0.9869atm. The international (SI) unit of pressure is the pascal (N/m^2).) Smaller diamonds will generate higher pressures since pressure is force per unit area. Today cells are available which generate pressures near the magabar range. The DAC has been used at temperatures grater than 900K and down to 0.03K.[2,4]

B. Pressure calibration

Calibration of the DAC can be done by several methods.[2] Any calibration of pressure will only represent an average since it has been mentioned that a pressure gradient exists across the face of the diamonds. In one method the spring compression is measured by

a Dillon force gauge, and the contact area of the diamonds is deter-
mined by means of microphotographs. One can then calculate the force
per unit area or pressure. Alternatively, solids that undergo phase
transitions at known pressures may be used to calibrate the cells.
For example, KBr shows a phase transition at 18 kbars; KCl at 20 kbars;
HgI_2 at 13 kbars. These can be observed either using a light micro-
scope or spectroscopically. A third calibration method utilizes
the change of wavelength absorption (λ_{max}) in nickel dimethlyglyoxime
(NDMG) in the visible absorption region. These changes have been
related to pressures by the National Bureau of Standards (NBS).

The research which utilized the DAC can be divided conveniently
into two seperate areas: spectroscopic examinations and conductivity
studies. These areas will be described in a sequential manner.

Part I. Spectroscopic studies using the DAC

Introduction

A. DAC as a spectroscopic sample cell

When used as a spectroscopic sample cell, a DAC places very
strict requirements upon the spectrophotometer source beam. The
DAC has a small surface area (approximately 0.25 mm^2 or larger),
and the critical angle of diamond is 26°. Because of these restrictions
some means of condensing the sample beam is necessary. In the case
of a grating double beam spectrophotometer a beam condenser is used
(usually about 6X condensation). A beam condenser should ideally
condense the light to a cone having an angle less than 52°, and the
focus should lie between the two diamonds in the DAC. For descrip-
tions of the beam condensers used with the Cary 14 and the Beckman
IR-11 see Appendices 1 and 2.

B. Spectroscopic Observations

The methods used in the spectroscopic observations included
direct observation of the compound in the DAC with a light microscope,
and examination of the FIR, NIR, and visible spectra under conditions
of ambient and non-ambient pressures. These studies were performed
on a small group of chalcogenides which included MgS, CaS, SrS, and
EuS.

Of major interest in this research is the transverse optical
lattice mode (ν_{TO}), which is a fundamental vibration of the crystal
structure. Most of the frequencies for the T.O. lattice modes in
ionic salts are found below 300 cm^{-1},[5,6] therefore lying in the FIR
spectral region. With the beam condenser on the Beckman IR-11 it
is possible to study these vibrations in the FIR under pressure in
the diamond anvil cell. The longitudinal mode has only weak absorption
in the infrared, therefore these bands are not typically observed.[5]

In more covalent solids ν_{TO} is very close to ν_{LO} and is not shifted much with pressure.

The relationship between the change in frequency with pressure for a simple ionic solid, where the crystallographic axes are equal, is given below[6]

$$\gamma \chi \nu = (\partial \nu / \partial p)$$

where γ is the Gruneisen parameter, χ is the isothermal compressibility of the solid, and ν is the frequency of the lattice mode. For solids which are of mostly covalent character the compressibility would be small and therefore the shift of the lattice mode absorption would also be small.[7]

At ambient pressure and temperature the chalcogenides studied have the NaCl type structure (C.N.=6). As the pressure was increased the T.O. lattice mode shifted toward higher frequencies as expected.[7] Eventually under higher pressures these compounds would be expected to convert to a CsCl type structure which has a C.N. of 8, while at still higher pressures one would expect a metallic phase to appear.[7]

EXPERIMENTAL

A. Materials

The chalcogenides used in this study were purchased from Cerac/ Pure Incorporated, Memonomee Falls, Wisconsin. They were 200 mesh and typically 99.9%.

B. Optical observations

Direct observation of the compounds under pressure is often the best way to tell if a phase change is occuring. The compounds to be observed were loaded into the DAC inside a glove box under a dry nitrogen purge. After removal from the glove box the DAC was then placed on the stage of a light microscope. The compounds were observed under varying pressures up to 35 kbars to see if any change occured.

C. NIR and visible spectra

The near IR and visible spectra were recorded on a Model 14 Cary spectrophotometer. The samples were again loaded in the drybox to prevent them from reacting with oxygen or water. Once loaded the DAC is placed in the sample compartment of the Cary along with the associated beam condenser. The spectra were recorded at ambient pressure at at incremental higher pressures. For a description of the beam condenser used with the Cary 14 see Appendix 1.

D. Far-IR Studies

The FIR spectra were recorded on a Beckman IR-11. The amount of material loaded into the DAC had to be extremely thin because the transverse optical mode absorption of the compounds are very strong in the FIR. Also the bands are located at approximately 200 cm^{-1},

at which point the energy coming through the DAC is very small. In
this region there is a constant fight between slit width and instru-
ment gain in order to get energy through the cell. These spectra
were recorded at ambient pressure, then recorded in increments up to
approximately 35 kbars of pressure. The instrument is calibrated
for frequency accuracy with yellow HgO.

RESULTS AND DISCUSSION

The transvere optical lattice mode frequencies for the chalcogenides and the calculated $\partial\nu/\partial p$ are listed in Figure 3. The results show that the T.O. lattice modes studied all fall in the $200 cm^{-1}$ range and shift toward higher frequency with pressure. The value of $\partial\nu/\partial p$ will give some idea of the degree to which the compound is ionic. Covalently bonded compounds show no change in the T.O. absorption with increasing pressure.[7] From the results obtained it appears that MgS is the most ionic compound studied and SrS is the least ionic in character.

The FIR spectra of SrS showed a second band at $190\ cm^{-1}$, but due to lack of time the exact cause of this band is not known. It is possible that this band might be attributed to the T.O. mode of the CsCl structure. It is also possible that this band could be due to a reaction of the SrS with water in the air.

The error on the location of the peak is estimated to be possibly up to $2cm^{-1}$ in this region with the DAC. Because of the small sample area the beam coming through the DAC is sometimes very weak, which requires that the instrument's slits be opened wide and the gain be increased. The combination causes increased noise in the recorded spectra.

The microscopic observation of the samples in the DAC did not yield any phase changes that could be observed. It can be noted that EuS is a rose colored compound, although in bulk it appears to be black. The MgS, CaS, and SrS all have the appearance of a yellow-ish brown powder. Because these compounds react with water in the air to form H_2S and some oxide of the compound, all the work concerning

them must be done in a dry box and the cells transported in a dessi-
cator to the spectrophotometer. EuS was the only compound to show
any absorption in the visible region. It had only one rather broad,
weak absorption centered around 470nm. This band shifted toward
higher frequency with the application of pressure.

Fig. 3 Table showing transverse optical mode frequencies (cm^{-1})

for the compounds studied. Note-one turn $\cong$ 5.7 kbars.

(Pressure) Turns	MgS	CaS	EuS	SrS
0	248	245	190	211
1	256	246	193	213
2	262	252	194	215
3	265	254	196	215
4	267	256	198	217
5	270	258	201	219
6	273	263	204	220

calculations

	MgS	CaS	EuS	SrS
$\Delta\nu$ $(\gamma_{hp}-\gamma_{lp})$ cm^{-1}	25	18	14	9
ΔP kbars	34	34	34	34
$\partial\nu/\partial p$ (cm·kbar)$^{-1}$	0.74	0.53	0.41	0.26

Part II. Electrical Conductivity Studies in the DAC

INTRODUCTION

A. Background

Recently there has been an interest in the electrical conductivity properties of organic, organometallic, and transition metal coordination compounds.[8] The study of these properties has been slowed by the notion that a large single crystal must be available for measurements, and the fact that many compounds to be studied are air sensitive. Although a single crystal is required for ultimately precise conductivity measurements, an initial rapid screening of materials could be obtained from a polycrystalline material. Such a screening should be available for the chemist which would give at least some information on the order of magnitude of the electrical conductivity for a particular material.

Cahen, Hahn, and Anderson described a four probe conductivity cell that places the sample between two pieces of boron nitride.[8] These pieces are brought together by the action of a piston. Their system uses a spring loaded system for the electrodes to assure good contact with the sample. The setup allows for studies up to about 2 kbars and uses a rather large sample size(about 1g). The system developed by Hottman and Pohl[9] uses about the same system but allows for studies at increased temperature also. Both of these methods use a large sample size that is often unavailable to the synthetic chemist.

B. The DAC as a Conductivity Cell

Only recently have electrical conductivity measurements been made in the DAC. Mao and Bell[10] developed a method for measuring electrical conductivity in an ungasketed system, and more recently Block and Piermarini[3] have developed a method for measuring electrical resistance

in a gasketed DAC. They use a methanol-ethanol mixture as a pressure transmitting fluid and claim hydrostatic pressures up to 104 kilobars. Their electrical circuit consists of a metal gasket, an insulating ceramic layer, and a very fine tungsten wire laid across the gasket hole. The sample makes contact with both the gasket and the wire the cir-cuit is complete. They have carried out studies on semiconductor to conductor transitions and have found that an abrupt change of optical absorption does correlate with the order-of-magnitude changes in con-ductivity.

At the Naval Research Laboratory a diamond pressure cell has been designed that operates down to temperatures of 0.03 K and pressures up to 100 kbars.[4] In their setup the sample is sensed magnetically using a SQUID magnetometer to detect changes in magnetic moment. Dave Grubser and Alan Webb[11] have used this equipment to study the superconducting transition temperature of aluminum up to 62 kbars. At 62 kbars the transition temperature was reduced to 0.075K from the ambient value of 1.8K.

In this research a four point solid electrical conductivity probe for use with the DAC was developed so that bulk conductivity of semi-comductors could be measured under conditions of ambient and non-ambient temperature and/or pressure. The probe was to be used mainly as a screening process whereby the members of a group of compounds could be ranked as to conductivity, and a rough order of magnitude of conductivity could be assigned. The probe also allows for examination of air sensitive compounds by loading the cell in a dry box.

EXPERIMENTAL

A. Materials

The platinum chain compounds were supplied by Dr. Jack Williams, Argonne National Laboratory - Chemistry Division. The compounds were long lustrous gold colored crystals which were ground in order to make the powdered conductivity measurements.

The iridium compounds were supplied by Drs. A. Reis and S. Peterson, ANL - Chem Division. These compounds were also long gold needlelike crystals.

B. Design of the probe for the DAC

Several variations of designs were tested to find which would perform best with the DAC. It was decided that the way to hold the probes in place would be with a plastic disc. The first design used was a cross wire arrangement (shown in Figure 4A) which allowed for a direct four probe measurement of the sample. The disc was made in a pellet press with the wires embedded in the polypropylene plastic melt. Once removed from the press the disc had to have a hole drilled through the inter-section of the wires. This procedure required the use of a Dremel tool fitted with a #20 syringe tip as the drill, but since the plastic is very soft, in comparison to the wire, the drill would often slip aside and not cut the wires. Other times the wires would be cut off short, therefore not making contact with the sample. This procedure proved to be too time consuming for its worth, so it was abandoned.

The second method also was a cross wire design, but this time the plastic (0.01 inch mylar) was punched out of a sheet with a $\frac{1}{2}$ inch punch. Then a 1/16 inch hole was drilled in the center of the disc. Once the

disc was prepared two 0.002 inch tungsten wires were melted into the mylar using a soldering iron, then the wires were cut with a surgical knife under a microscope. This method proved better than the first, although it still had its problems. It was much quicker than the first method, but often upon applying pressure to the sample, the wires would bend and slip out from between the anvils of the two diamonds. Once this happened it became impossible to get a good reading of resistance.

The third design tested was a parallel wire arrangement, shown in Figure 4B. Again the precut Mylar disc was used with the 0.002 inch tungsten wire, but this time the wires were cemented to the mylar using Bond All Purpose Cement No. 527, manufactured by Bond Adhesives, P.O. Box 406, Jersey City, NJ. The wires were not cut in this procedure, but were rather run parallel to each other so the resistance is measured between the two wires. The reading is just a two probe measurement to the sample, however four probes are used to the wires leading into the cell to eliminate the resistances of the leads. Once the disc was in place the pistons are placed in the holder to make sure that the wires are under the face of the smaller diamond. The sample is then loaded into the cell and the measurement is made using the Fluke 8800A digital multimeter. In the case of air sensitive species the loading and measurement was done entirely in the dry box.

The arrangement of the discs for measuring conductivity is shown somewhat in Figures 4C and 4D. The plastic disc with the probes were taped on the face of the piston, while the wires extended through holes in the piston. The holes in the piston were insulated with plastic shielding in order to prevent shorting of the wires against the steel piston.

The electrical resistance in this section were measured using a Fluke model 8800A digital multimeter which was calibrated with NBS standard resistors. This instrument does the four probe resistance measurement automatically. Two of the leads apply a current (I) and the two other leads measure the voltage drop (V) across the sample. The resistance is then calculated by the instrument as R=V/I and then shown on a digital display. The currents applied by the meter will vary from 1mA in the 0-200 ohm range to 0.25 A in the megaohm range.

C. Calculations

The resistivity can be calculated by the formula derived by Van derPauw[12] when the sample assumes a symmetrical shape. Van derPauw's formula for calculating resistivity is given by

$$\rho = \frac{\pi \, t}{\ln 2} R$$

where t is the thickness of the sample and R = V/I across the sample. This method of calculating resistivity has been used by others with similar types of conductivity cells.[8,9] By simply taking the reciprocal of the resistivity the conductivity, σ , can be obtained.

It should be noted that to properly define the specific conductivity, σ_o, conductivities at several different temperatures would have to be determined. The equation for conductivity at a specific temperature is given as:

$$\sigma = \sigma_o \exp^{(-E/kT)}$$

where E is the thermal activation energy.[13] To calculate specific conductivity a plot of $\ln\sigma$ vs. 1/T would have to be prepared then extrapolated to where 1/T=0. At that point the intercept would be the $\ln\sigma_o$. Using this method would also result in an experimental value for the thermal activation energy.
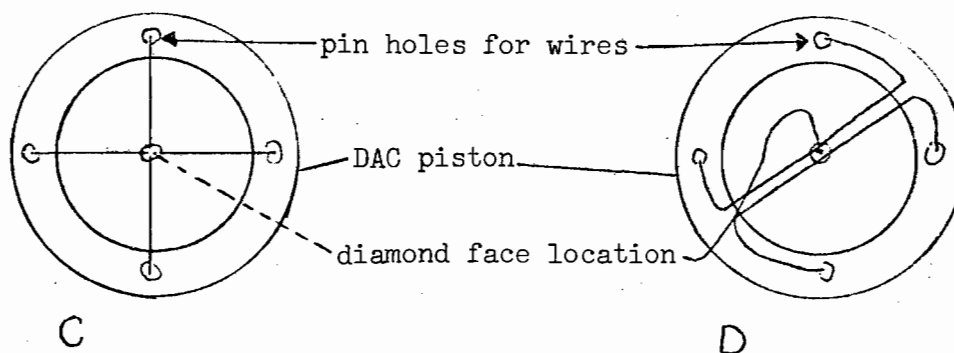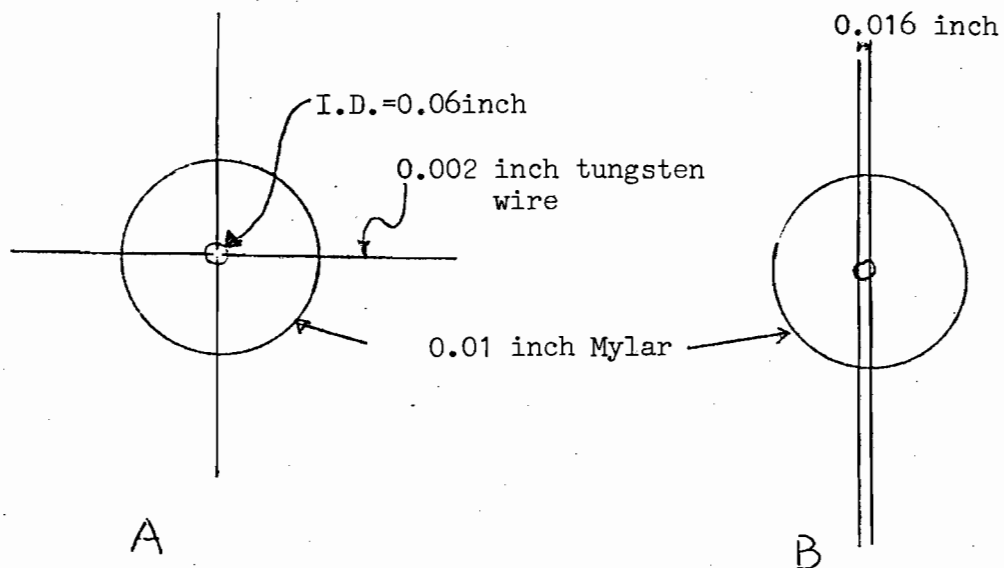
18.

Figure 4: Details of the conductivity cell (A) four probe conductivity
disc for DAC (B) Parallel wire arrangement for conductivity
(C)(D) Arrangement of the discs on the DAC piston.

The conductivity cell was tested using Ag_2HgI_4 which has been studied for conductivity under pressure by others.[14,15] The results of the measured conductivity for the Ag_2HgI_4 agreed favorably with those reported in the literature.

RESULTS AND DISCUSSION

Figures 5 and 6 show the results for the conductivity studies.
The conductivity values for the platinum chain compounds do not agree
well with the single crystal conductivities as reported by Jack Williams
at ANL. In fact variations of several orders of magnitude are observed.[16]
This is thought to be caused by the fact that when measuring bulk con-
ductivity of the compounds the crystals are arranged in random position,
while these compounds are one-dimensional semiconductors (i.e. the resist-
ance to current is much less in one direction than in a direction 90°
from the first). Generally there was no significant increase in con-
ductivity up to pressures of 15 kbars.

The conductivities of the three iridium compounds have been shown
as a function of pressure in Figure 6. It is noted that an increase
in conductivity is observed up to 5-8 kbars then the conductivity either
levels off or decreases somewhat. The Cl compound shows higher con-
ductivity than the others which is predicted because of the smaller
size of the chlorine atom allowing for tighter packing of the crystal
structure.

The probe works well for a screening process, but single crystal
measurements would have to be made if very precise values are needed.
The system is good for ranking a group of compounds as to the conduc-
tivity, but its most important asset is that it requires only a very
small sample.

Fig. 5. Conductivities of several compounds at ambient pressures[*]

COMPOUND	CONDUCTIVITY ($ohm^{-1} cm^{-1}$)
$Cs_2[Pt(CN)_4]\,FHF_{0.39}$	6.3×10^{-3}
$Rb_2[Pt(CN)_4]\,FHF_{0.40}$	8.5×10^{-4}
$K_2[Pt(CN)_4]\,FHF_{0.30} \cdot 3H_2O$	4.0×10^{-4}
$Ir(CO)_3Cl$	6.1×10^{-4}
$Ir(CO)_3Br$	1.6×10^{-4}
$Ir(CO)_3I$	6.4×10^{-5}
$K_{1.75}[Pt(CN)_4] \cdot 1.5H_2O$	1.1×10^{-4}
$[Pt(NH_3)_4][PtCl_4]$ (Magnus salt)	1.1×10^{-4}
Ag_2HgI_4	2.4×10^{-6} Lit value[14] 1.4×10^{-6}

[*] Pressed powder measurement

fig 6   Plot of pressure verses conductivity for the iridium compounds.

Note that each turn equals approximatly 2 kilobars
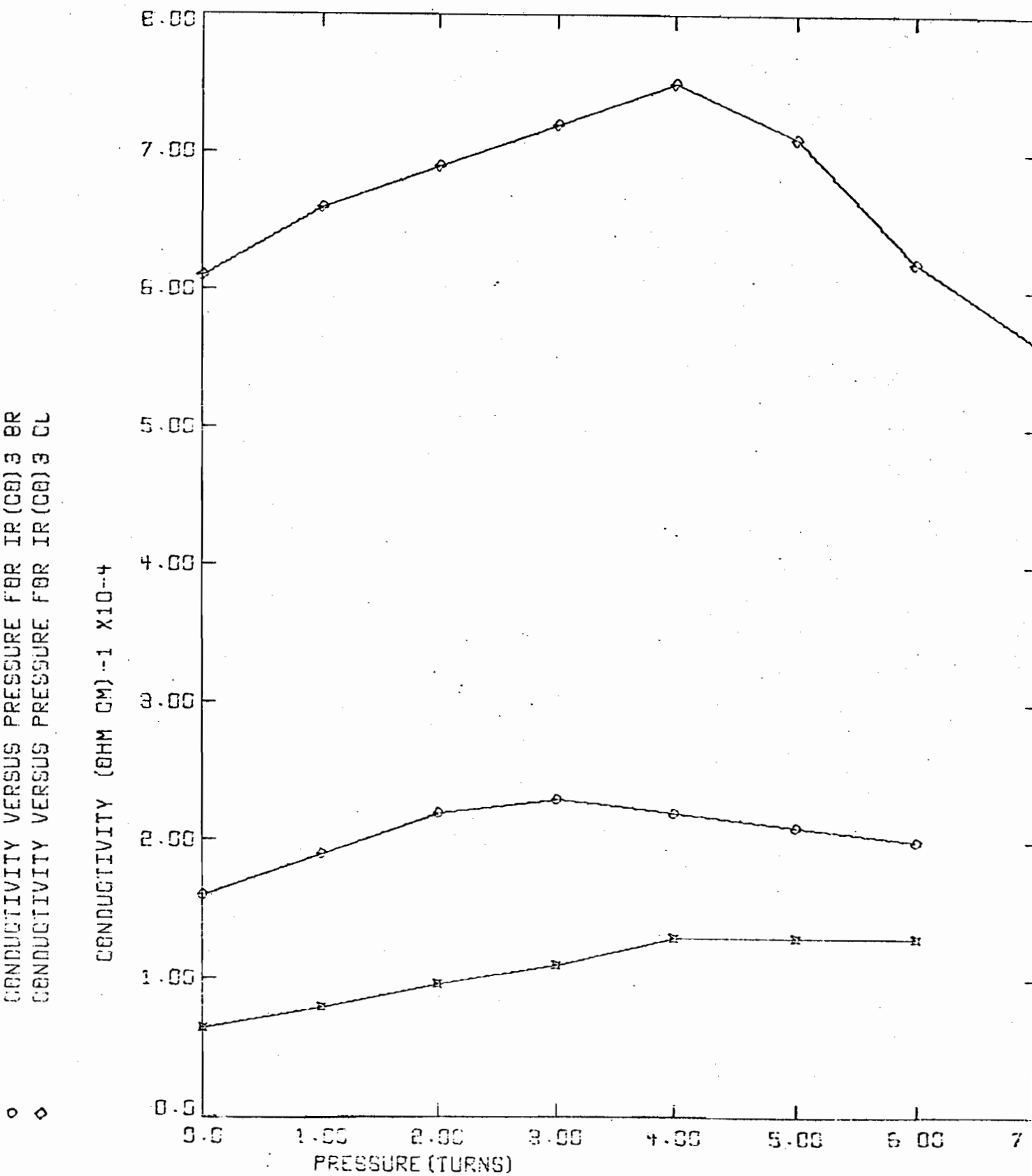
Appendix 1: Description of the Cary 14 Beam Condenser

The information for this section comes from G.L. Long, Grant Miles, and John R. Ferraro, Applied Spectroscopy, Volume 28, No. 4, page 377, 1974.

Because of the large size of the sample beam in the Cary 14 it is necessary to have a condenser system to utilize the diamond anvil pressure cell for spectroscopic studies. The condenser system was limited by the space in the sample compartment. Figure 6a shows the optical light path for the condenser. Element 1 focuses the radiation emerging from the Cary's entrance window to an image of the slit near the sample between the diamonds. Element 2 produces an image of the entrance window near element 3. Element 3 produces an image of the slit near element 4. Element 4 reimages the entrance window near the exit window.

The optics are made of quartz glass. The result of using the beam condenser is that approximately ten times more energy passes through the cell than without the condenser. This allows spectra to be recorded in the NIR and visible at low gain with little noise. Figure 7 shows a picture of the condenser in place in the Cary 14.

SPECTROPHOTOMETER
EXIT WINDOW

DIAMOND
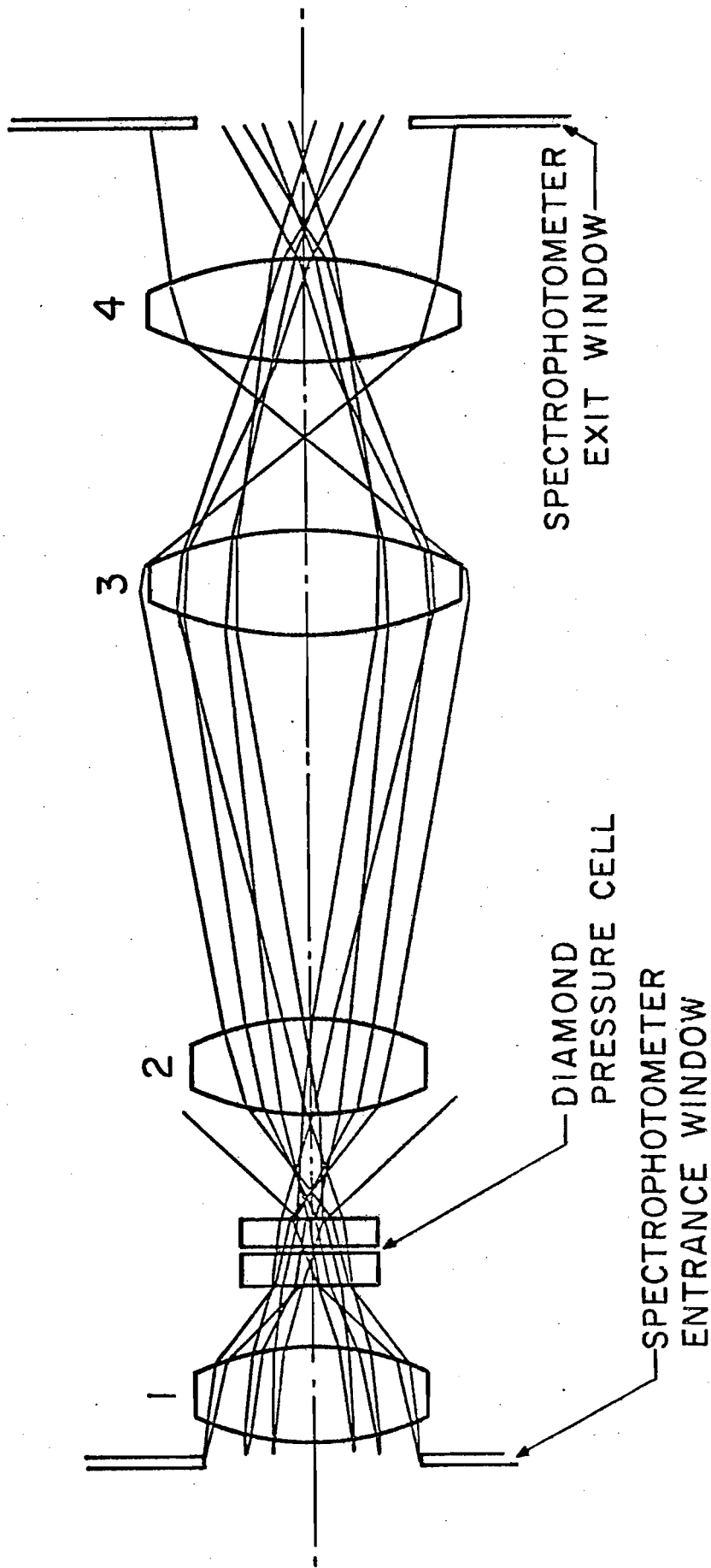PRESSURE CELL
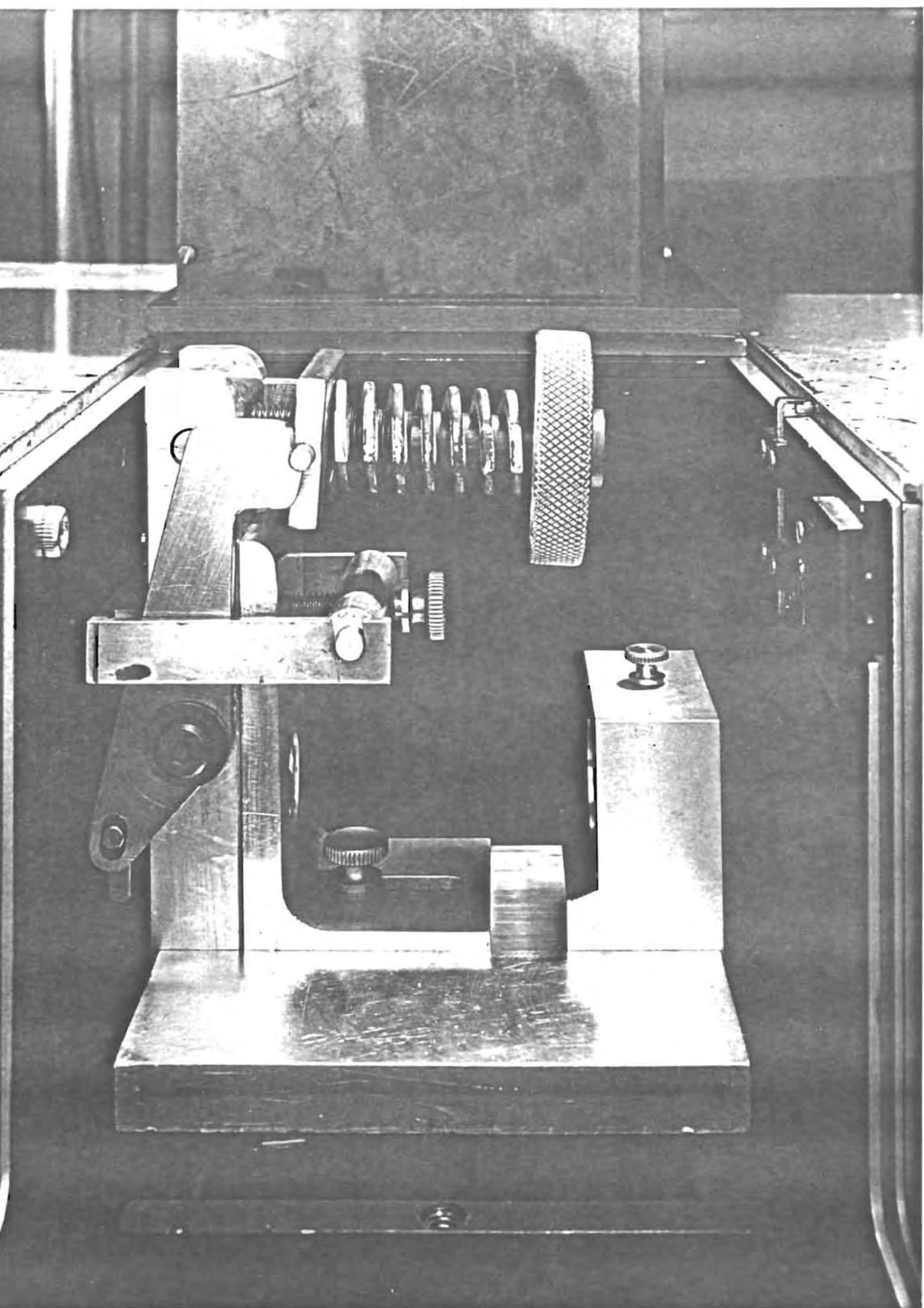
SPECTROPHOTOMETER
ENTRANCE WINDOW

Fig 6a. Optical light path diagram for the spectrophotometer beam condenser.

Fig. 7

The DAC in place in the Cary 14

Appendix 2:   Beam Condenser for Beckman IR-11.

The Beckman IR-11 is a specially built instrument having a ten inch sample compartment. The beam condenser for the IR-11 was also built by Beckman. Figure 8 shows the path of the radiation through the sample compartment of the IR-11. The condenser consists of all front reflecting mirrors, so that very little energy is lost. With the condenser system in place approximately 78% of the normal energy reaches the detector. However with the DAC in place the energy is cut much more causing a required increase of gain to approximately five times the standard gain in order to get a good signal. This of course also increases the noise level. Figures 9 and 10 picture the beam condenser of the IR-11. Since water has some very strong absorption bands in the far-IR the sample compartment must be enclosed and purged with nitrogen.
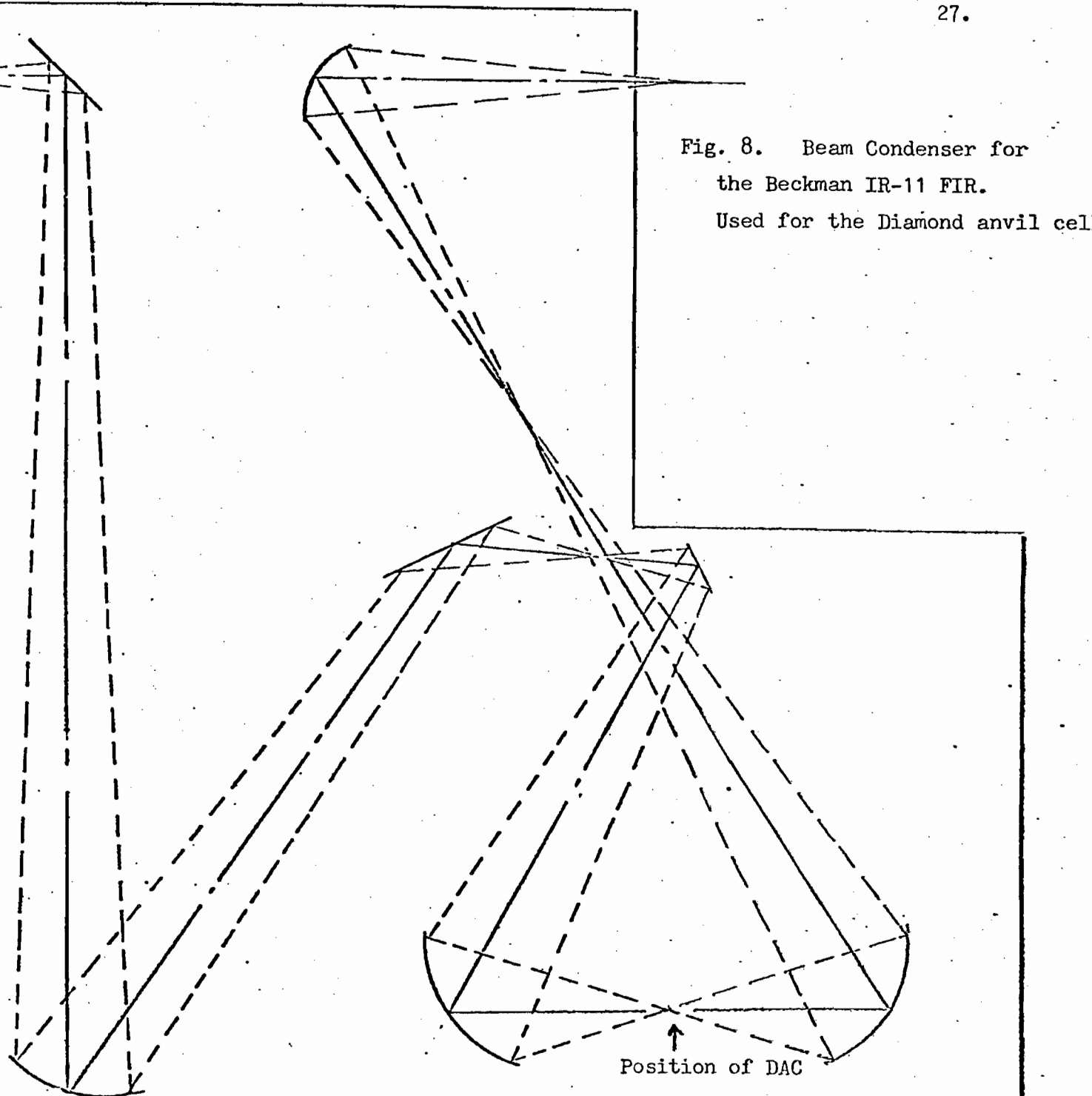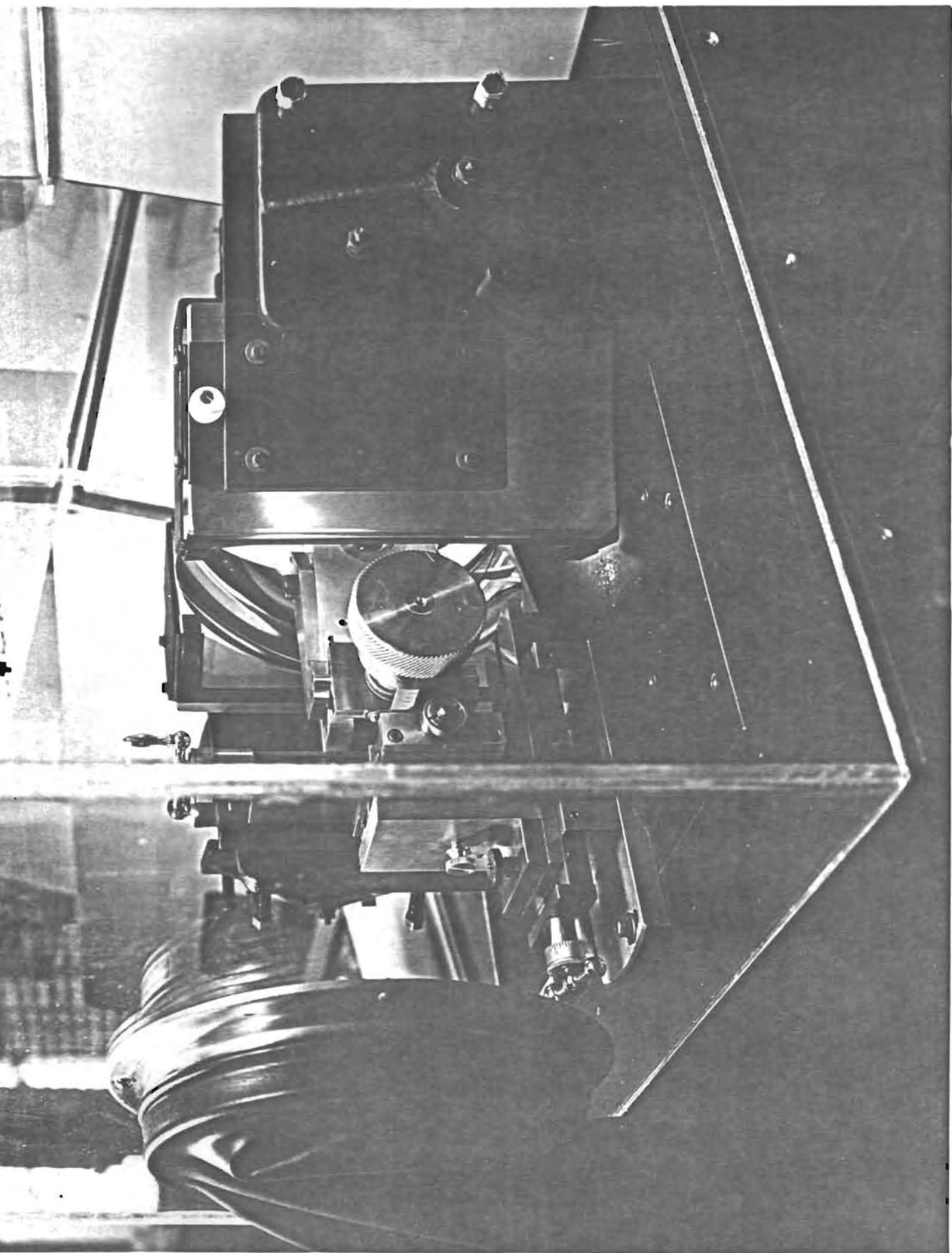
Fig. 8.   Beam Condenser for
the Beckman IR-11 FIR.
Used for the Diamond anvil cell

Position of DAC

Fig 9 and 10

Pictures showing the beam condenser on the Beckman IR-11

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