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DEVELOPMENT OF INTERCALATED GRAPHITE MATERIALS

UNIVERSITY OF PENNSYLVANIA
MOORE SCHOOL OF ELECTRICAL ENGINEERING AND SCIENCE
PHILADELPHIA, PENNSYLVANIA 19104

AUGUST 1976

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AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
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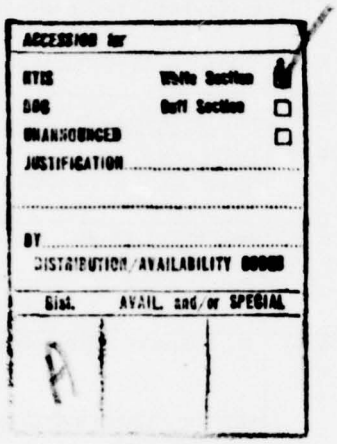
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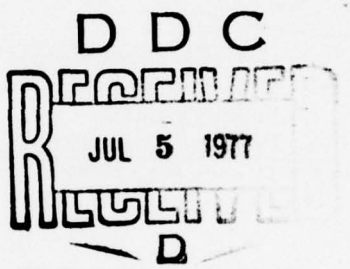
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20. High stage SbF_5 compounds were found to exhibit a reflectance of over 90% at wavelengths greater than 8 microns. These compounds also were relatively stable in air; lifetimes over 760 hours were observed several times. The highest electrical conductivity, 8 times greater than pure graphite, was observed for Stage 1 compounds; these are unstable in air. No significant differences were observed in the properties of SbF_5 and SbF_5-HF compounds.





PREFACE

This report was prepared by the Moore School of Electrical Engineering and Science, University of Pennsylvania, Philadelphia, Pennsylvania 19104, under USAF Contract F33615-75-C-5231. The contract was initiated under Project No. ILIR, "Laboratory Director's Funds". The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Mr. Paul W. Dimiduk, (AFML/LPJ) as Technical Monitor. Funds for this project were supplied to the AF Materials Laboratory by the Office of Aerospace Research.

Work covered by this report was carried out from 30 June 1975 through 31 July 1976. The report was submitted by the University of Pennsylvania in August 1976 for publication as an AFML Technical Report.

The Principal Investigators for this project were Dr. J.E. Fischer and Dr. F. Lincoln Vogel. Early work on HNO_3 compounds was performed by Dr. Frank L. Lederman, while the investigation of SbF_5 compounds was carried out by Dr. Lawrence R. Hanlon. The author is indebted to Dr. Arthur W. Moore of Union Carbide for providing the graphite from which our samples were made, Dr. Daniel Guerard and Dr. E. Robert Falardeau for preparation of the various intercalation compounds, and Dr. Thomas E. Thompson for allowing some of the results of his work on the conductivity of intercalation compounds under NSF Contract "DMR75-04954, to be included here for completeness. He would also like to thank Rich Greenberg for the x-ray analyses, Linda Taliaferro for typing the manuscript, and Renate Schulz for the drawings.

This technical report has been reviewed and is approved for publication.

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SECTION I

INTRODUCTION

The Air Force has expressed a need for graphite-based materials which exhibit higher electrical conductivity and infrared reflectance than pure graphite. Such materials would be most useful in the form of fibers because of potential applications in composite construction materials. In order to be practical, these new materials must of course be stable in a normal atmosphere of nitrogen, oxygen, and water vapor.

Graphite intercalation compounds are created when foreign molecules or atoms are inserted between the planes of carbon atoms in the graphite structure. The number of contiguous carbon layers between two successive intercalant layers is termed the "stage" of the compound. Many of these compounds are synthetic metals with a-axis or basal-plane (i.e. parallel to the carbon layers) dc conductivities of 1/6 to 1/2 that of copper.[1]

The largest conductivity increase yet observed occurred during some preliminary work using the strong acid SbF_5 as an intercalant.[2] The choice of SbF_5 resulted from the assumption that as the acid strength increases, so also does the charge transfer from the graphite lattice to the acid. If the attendant band structure changes are not insurmountably counterproductive, then the highest conductivity increases should be obtained.

In normal metals high infrared reflectivity accompanies high dc conductivity; so the highest conductivity graphite intercalation compounds are expected to exhibit the largest increase in infrared reflectivity. Therefore, in order to maximize the infrared reflectivity in a graphitic material, we proposed a study of graphite compounds prepared in strong Lewis acid fluorides, such as SbF_5.

Graphite fibers are the material of primary interest because of their usefulness as a construction material. However, fibers are replete with voids in the crystal structure; for example

typical fiber densities range from 1.6-1.9 gm/cm^3 while single crystal graphite has a density of 2.27 gm/cm^3. Thus an analysis of intercalation compounds would be greatly complicated if fibers were to be used at the outset in this investigation. It is better, indeed necessary, to first characterize the bulk properties of an intercalation compound so that the effects of intercalating fibers can be more readily analyzed. Therefore crystals of highly oriented pyrolytic graphite (HOPG) have been used for most of the experiments.

In the initial phases of this investigation, HNO_3 was often substituted for SbF_5 while the sample preparation techniques were being proven. This was done because of the extreme reactivity of SbF_5 -- upon exposure to moist air it reacts vigorously to produce copious quantities of toxic HF vapor. Therefore this report contains information on compounds prepared from both HNO_3 and SbF_5.

In this report we will discuss the graphitic materials which have been investigated, the experimental apparatus and procedures that have been used, and the results which have been obtained in the first year.

SECTION II

MATERIALS

A. Graphite

The graphite materials of interest in this investigation include cloths, foils, platelets, and fibers. Of these, only the platelets of hot-pressed highly-oriented pyrolytic graphite (HOPG) lend themselves readily to straightforward measurements of optical reflectance, because only with this material can large, smooth, freshly-cleaved surfaces be obtained. Therefore the strategy employed is to first study the relationship between intercalation and reflectance using graphite crystals in order to characterize the bulk material. With the information so gained, construction materials such as graphite fibers can be intercalated in a more predictable manner. A review of the work with each of the materials follows.

1. Cloth

A sample of type WCA poly-acrylonitrile based graphite cloth was obtained from Union Carbide.[3] This material is made by pyrolytic decomposition of a woven acrylonitrile cloth. The cloth is placed in tension to align the graphite crystallites, but because of the problems involved in tensioning both directions simultaneously the alignment of the crystal axes is not very good.

Reflectance measurements on graphite cloth are very difficult because the cloth is loosely woven and therefore has a very rough surface; furthermore the fibers themselves have a very low reflectivity. Nevertheless, a reflectance measurement was attempted. First a double layer of cloth was epoxied to a glass substrate, then aluminum was deposited over half of the area to provide a reference. Despite the aluminum reference, the scattering was so large that meaningful reflectance measurements were not possible. Therefore work on the graphite cloth was halted.

2. Foil

Samples of graphite foil were obtained from William Nystrom of Stackpole Carbon Co.[4] These pre-production samples were made by rolling vermiculated graphite into a foil. Vermiculated graphite is a low-density material obtained by rapidly heating H_2SO_4 and HNO_3 - saturated graphite powder above the boiling point of the acids. The rapid conversion of the liquid to vapor causes the graphite particles to expand tremendously and vermiculated graphite results. When it is rolled into a foil, the c axes of the graphite crystallites are aligned perpendicular to the plane of the foil.

The reflectance of the pristine foil was found to be approximately 15-20% in the visible and near-IR. When the foil was subjected to HNO_3 vapor at 25°C the individual graphite particles intercalated in differing amounts, and the resulting rough surface exhibited a lower reflectance than the pristine material. This is shown in Fig. 13. Because of the surface problem and the uncertain effect of the numerous graphite particles on the transport measurements, investigation of the graphite foil was suspended.

3. Highly-Oriented Pyrolytic Graphite (HOPG)

Highly oriented pyrolytic graphite, or aligned graphite, is created when carbon, obtained by pyrolytic decomposition of hydrocarbon gases, is simultaneously subjected to high temperature and uniaxial pressure. The resultant plates of graphite exhibit excellent alignment of the crystallographic c-axis. It has been established that with proper annealing the electrical and mechanical properties of HOPG approach those of natural single crystals.[5]

Single crystal graphite is rare, nevertheless it has been extensively studied and the band structure is well known. Since the properties of HOPG are so close to those of single crystal graphite, the effects of intercalation in compounds made from HOPG can be analyzed much more readily than in compounds made from other graphitic materials.

Because it is readily available and because it can be cleaved with razor blades, tweezers, or scotch tape to obtain smooth surfaces for reflectance measurements, aligned graphite is an excellent medium for determining the characteristic results of intercalation with a given substance, e.g. screening the effectiveness of the heavy metal pentafluorides. Most of our experiments have been performed with samples made from HOPG.

Pieces of aligned graphite were obtained from Dr. Arthur Moore of Union Carbide.[6] These are from Union Carbide's regular production of aligned graphite for x-ray monochromators, in which temperatures of 3000^{o}C and pressures of 500 kg/cm^{2} are used. The spread in c-axis orientation is typically 4^{o}.[7]

4. Fibers

Graphite fibers can be produced in several ways. "Thornel" type fibers are derived from polyacrilonitrile fibers by pyrolytic decomposition. Pitch-and coal-based fibers are spun from a carbon-rich liquid derived from pitch or coal. In all cases, the raw fiber is heated and placed in tension, causing graphitization to occur. Simultaneously, the graphite crystallites align themselves with their a axes along the longitudinal axis of the fiber. Pitch and coal derived fibers yield the best alignment.[8]

Samples of UC-307 graphite yarn were obtained from Union Carbide.[9] This yarn is composed of 1000 pitch-based fibers, each 10μ in diameter, and it exhibits a slight sheen. In a promising preliminary experiment, several strands of this yarn were affixed adjacent to each other on a flat substrate with small dabs of silicone grease. This mat of fibers exhibited a substantial reflectance when illuminated with a He-Ne laser. Although the reflected photons are scattered over a wide angle, with suitable optics they can be collected and measured. Because the reflectance measurements are promising and because of the preference for fibers as a construction material, work involving mats of intercalated fibers will be emphasized in the months ahead.

B. SbF_5

Antimony pentafluoride is a liquid at room temperature. It freezes at 7°C and boils at 150°C. In the initial phase of this work the SbF_5 was used as received from the manufacturer, Ozark-Mahoning," by simply pouring some from the steel storage cylinder into a teflon container.[11] Subsequent discussions with the manfacturer uncovered the fact that small (1-2%) but uncontrolled amounts of HF were present in their product. It was also discovered that the SbF_5 leaches iron from the walls of the steel cylinder, and that it should properly be stored in teflon containers. This information made it evident that all of our SbF_5 would have to be purified before use.

The decision to purify the SbF_5 triggered a literature search on the physical and chemical properties of this material. Perhaps the most significant is the fact that pure SbF_5 is an extremely viscous liquid. It will not pour; if inverted it slowly creeps down the walls of the container. This high viscosity results from polymerization of the SbF_5 molecules into extremely long chains. The polymerization in turn arises from an extremely strong tendency to form fluorine bridge bonds between adjacent SbF_5 molecules (Figure 1). This bridging tendency is so strong that SbF_5 vapor is dimeric at temperatures below 350°C.

By forming the fluorine bridge, each molecule can achieve its favored octahedral structure. The fluorine bridges are resonant, so the chain of molecules is continually changing its members. This behavior provides an additional contribution to the high viscosity of the liquid. However, the addition of small amounts of impurities breaks down a sufficient number of the fluorine bridges to markedly reduce the viscosity. Therefore, simply observing the viscosity is a sufficient operational test for determining the purity of the SbF_5.[32-34]

SECTION III

EXPERIMENTAL PROCEDURES

A. Sample Preparation

A wire saw equipped with a .010" diamond blade is used to cut samples of the desired size from the 4 mm thick aligned graphite plates. Typical sizes are 5x8 mm for samples used for optical reflectance and 5x15 mm for samples destined to be Hall bridges. These rough blanks are then razor cleaved into pieces approximately .35 mm thick. Optical samples are carefully cleaved with scotch tape until a surface smooth enough for reflectance measurements is obtained. The others are clamped between halves of a stainless steel pattern block for a 5-arm Hall bridge. The graphite is air abraded with 1μ alumina until the bridge shape is obtained. Then 3 mil diameter gold wires are wrapped around the arms and covered with Cermalloy #4350L gold paste[10] as shown in Figure 2. The sample is baked at 500°C for 15 min. to sinter the gold paste, then the conductivity of the sample is checked. Only those that show a value of 25,000 $(r\text{-}cm)^{-1}$ are used for intercalation.

B. Liquid Intercalation

Liquid intercalation of graphite has been carried out with pure HNO_3, SbF_5 and a 2:1 $HF\text{-}SbF_5$ superacid. The procedure for each of these acids will be described individually.

1) HNO_3

Liquid intercalation with pure HNO_3 is straightforward. The weighed sample is placed in a small beaker of the acid at room temperature, and a second stage compound is obtained in about 3 minutes. Because the reaction is so rapid the sample generally self-cleaves. This is helpful for optical measurements because a smoothly cleaved surface is obtained, however it is obviously unsuitable for conductivity measurements.

2) SbF_5

Liquid intercalation with SbF_5 has been done by two different techniques. Initially, the weighed sample of graphite was loosely wrapped with gold foil and placed in a teflon container. In a N_2-flushed glovebox, SbF_5 was poured into the container, which was then capped. The SbF_5 was used as received from the manufacturer, Ozark-Mahoning.[11] The teflon container was then placed in an oven at the desired temperature. The sample was periodically weighed in air until the weight uptake remained constant. It was then removed from the SbF_5 and the gold foil and used in reflectance or conductivity measurements.

Although the open containers of SbF_5 were handled in the glovebox it rapidly became apparent that the atmosphere was not sufficiently free of oxygen and water vapor. Therefore the synthesis of these SbF_5 compounds was lacking in repeatability. Because of this and additional problems with self-cleaving at elevated temperatures this procedure was abandoned for vapor phase intercalation.

Recently we have returned to liquid intercalation in order to reduce the time necessary for reaching first stage. In the present technique, the sample is suspended by platinum wire a few millimeters from the bottom of a pyrex ampoule, as shown in Figure 3. The whole assembly is heated to ~500°C while being pumped in order to remove water from the inner surfaces of the pyrex. Then pure SbF_5 is distilled from a Kel-F storage tube through a glass vacuum line to the pyrex ampoule. The distillation is done at room temperature; the pyrex ampoule is immersed in liquid nitrogen. When the proper amount of SbF_5 has transferred (enough to cover the sample), the nitrogen dewar is replaced by a 0°C ice bath. After about 10 minutes, the teflon valve[12] (Figure 3) is closed and the ice bath is removed. As the ampoule warms slowly to room temperature the SbF_5 melts and the reaction begins. After room temperature is reached, the whole pyrex apparatus is placed in a uniform-temperature oven at the desired intercalation temperature. Starting the intercalation slowly like this

has greatly reduced problems with self-cleaving and contact failure, however, if the reaction is not terminated after the sample reaches first stage self-cleaving will still occur.

3) $HF + SbF_5$

Liquid intercalation at room temperature has been carried out with a 1:1 $HF + SbF_5$ superacid. This experiment was done under conditions similar to the early SbF_5 liquid intercalations -- i.e. with small but uncontrolled amounts of O_2 and water vapor present.

Recently we have done several room temperature intercalations with a 2:1 $HF + SbF_5$ mixture. The procedure is similar to that just described for SbF_5. The sample ampoule is made from Kel-F tubing and employs a stainless steel Swagelok valve.[13] Using a stainless steel vacuum line, HF (obtained from Matheson)[14] is first condensed into the tube at -196°C, then the SbF_5 is transferred in. The HF is done first so that the two acids will mix when they melt. Otherwise, the less dense HF simply floats on top of the SbF_5. The rest of the procedure is identical to that employed for SbF_5.

C. Vapor Intercalation

Vapor phase intercalation was adopted early as the preferred technique because it produced less self-cleaving, cleaner sample surfaces, and more controllable results. Vapor intercalation has been attempted with HNO_3, SbF_5 and $HF + SbF_5$.

1) HNO_3

Three different systems have been used for vapor intercalation with HNO_3. Each new system was adopted because it offered the possibility of creating lower stage intercalates under more precisely controlled conditions. The three systems can be classified as a) room temperature red fuming nitric acid (RFNA); b) low temperature (RFNA); and c) <u>in situ</u> pure HNO_3. Each will be described in turn.

a) Room Temperature RFNA

Room temperature vapor intercalation with RFNA[15] is accomplished using the apparatus depicted in Figure 4. After weighing, the graphite samples are placed in the horizontal side arm of the apparatus. A small amount of heat applied in the immediate vicinity of the sample keeps this region free of condensed HNO_3 and assures that the sample is subjected only to vapor. The samples are weighed periodically; when the weight increase stabilizes they are removed from the apparatus. This system produces third stage graphite nitrate in 24 hours.

b) Low Temperature RFNA

In an attempt to create first stage nitrate compounds, the method developed by Fuzellier[16] was adopted. Essentially, this technique consists of maintaining the sample and the nitric acid at different low temperatures; the temperature difference between the two drives the intercalation process. The apparatus is shown in Fig. 5. Intercalation was attempted with sample temperatures ranging from $-25^{o}C$ to $0^{o}C$ and RFNA temperatures as much as $20^{o}C$ higher. We were unable to obtain first stage graphite nitrate; additional information from France confirmed the necessity of using pure HNO_3. Our efforts were then directed toward constructing a still for pure HNO_3 and finishing the <u>in situ</u> apparatus.

c) <u>In situ</u> Pure HNO_3

i) System Description

In order to obtain the most accurate characterization of an intercalated sample, all of the various measurements should be done with the sample still in the intercalating environment. This avoids unnecessary contact with the atmosphere and eliminates the possibility of decomposition occuring before the measurements are started. We have designed and built a system which allows the measurement of conductivity, thickness, and weight gain during a vapor intercalation. Once a desired

stage has been achieved the sample may be subjected to any desired atmosphere to test its environmental stability. The conductivity and thickness can also be monitored while the sample is de-intercalating, thus yielding additional information about the nature of intercalation compounds.

The apparatus is shown in Figure 6. In operation, the sample's leads are first connected to the proper platinum feed-through, then the sample is carefully positioned on a thin teflon disc on the fritted glass seal. Another teflon disc, also with cutouts to clear the leads, is placed on top of the sample. Next is a glass disc, then a glass-encased lead weight. The weight, usually between 4-8 oz., prevents self-cleaving or exfoliation of the sample. A vacuum system is connected at the top and a capillary tube of pure HNO_3 frozen in liquid nitrogen is attached to the bottom. After evacuation the system is sealed, the liquid nitrogen is removed, and the apparatus is mounted such that the capillary tube of HNO_3 is immersed in a constant temperature bath, usually $-30^{o}C$. As the intercalation proceeds the temperature of the bath is increased until the desired stage is achieved. Information about the stage of the sample is obtained by monitoring the decrease in acid level in the capillary tube. In preliminary trials with pure HNO_3, first stage was achieved with the temperature bath at $-20^{o}C$.

The use of HNO_3 is a result of its docile behavior compared to SbF_5. SbF_5 is highly reactive; if it is exposed to water vapor it produces HF. HF etches glass and in so doing produces more H_2O, as shown,

$$2SbF_5 + 2H_2O \rightarrow 2SbOF_3 + 4\ HF$$

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O,$$

therefore traces of H_2O in the *in situ* apparatus would result in its destruction. Thus HNO_3 was substituted during the initial runs while bugs in the *in situ* vapor intercalation procedure were uncovered and eliminated. Concurrent with the completion of this apparatus was the finding that self-cleaving is not a

problem for vapor-phase SbF_5 samples. Therefore less complex mounting techniques have been used for *in situ* conductivity measurements on SbF_5-graphite compounds.

ii) Preparation of Pure HNO_3

Pure nitric acid is distilled from RFNA using the technique developed by Potier.[17] The special distillation apparatus for this procedure is shown in Figure 7. In operation, the RFNA is boiled so that a vapor temperature of 85°C is achieved. Dry nitrogen flowing slowly into the other arm of the apparatus carries the vapor up to the condenser at the top of the central column. Condensed HNO_3 flows down into the collection flask while residual NO_x vapors are carried off with the N_2 stream. Typically, 600 ml of RFNA are needed to produce 100 ml of pure HNO_3. Once obtained, the pure HNO_3 must be stored in darkness at -20°C to prevent it from decomposing.

2) SbF_5

Two different methods of producing vapor intercalated SbF_5-graphite have been used. In both techniques the commerical SbF_5 is first purified by trap-to-trap distillation, followed by transfer to a working container. Initially the container was a special pyrex ampoule containing a fragile joint; at present it is the sample ampoule itself. The present technique is more streamlined and thus far less time-consuming. The purification and intercalation procedures will be discussed separately.

a) Purification

A schematic diagram of our original distillation apparatus for purifying commerical SbF_5 is shown in Figure 8. The apparatus was constructed of pyrex, with Halocarbon Corp. #25-20M

grease[18] used on all ground joints. We experienced no problems from SbF_5 attacking the glass or the grease.

In operation, the system was evacuated and the manifold heater energized. The manifold was maintained at ~100°C. The temperature of the cold trap at D was obtained from a mixture of acetone and solid CO_2. It was chosen to be well below the 7°C freezing point of SbF_5 but above the -90°C freezing point of HF. Thus solid SbF_5 was obtained at D and solid HF at E.

When the stopcock on the initial volume of SbF_5 was slowly opened, dissolved HF came out of solution. After the bubbling stopped, the SbF_5 was heated to ~80°C. Solid SbF_5 condensed at D while any remaining HF was trapped at E. When the initial container had boiled dry, it was replaced by a special ampoule containing a fragile joint (see inset, Figure 8). Other such joints had previously been placed at B & C. The stopcock F was then closed off, the vacuum pump disconnected, and the cold trap D heated to ~80°C. The SbF_5 was then distilled into the ampoules at A, B, and C. When the desired amount had collected, the stopcocks were closed and the necks on the ampoules carefully sealed. The result was a small quantity (typically ~.3 ml) of pure SbF_5 sealed under vacuum in a glass container.

An important precaution should be noted here. All SbF_5 ampoules were baked at 500°C under vacuum before they were allowed to come into contact with SbF_5. The baking drove absorbed H_2O off from the glass and eliminated the etching of the glass tube and the buildup of dangerous pressures of SiF_4 which would otherwise have occurred as the ampoule was heated during intercalation. The fact that we have stored such ampoules for several months with no degradation of the SbF_5 testifies to the success of this technique.

In our present procedure the distillation is done at room temperature. This became possible as a result of the installation of better vacuum equipment. The improved vacuum in the line allows

the distillation to proceed at a reasonable rate without using elevated temperatures. In addition, the anticipated use of HF to make superacid solutions required the elimination of all glass from the system, so we replaced the pyrex line with stainless steel and Kel-F components.

Working in the dry N_2 atmosphere of a glovebag or glovebox, about 20-25 ml of commerical SbF_5 are put into a Kel-F tube. The tube is capped with a Swagelok valve, then connected to the vacuum line. As before, dissolved HF is first slowly pumped out; then the SbF_5 is distilled into a second Kel-F tube suspended in a dewar of liquid nitrogen. (See Figure 9). The pure SbF_5 is stored in the Kel-F tube and used as needed for intercalation.

b) Intercalation

Experience with the first distillation apparatus established that pyrex is a suitable material for a sample cell as long as it is properly dried. Since it is highly desirable to be able to observe the samples during intercalation, pyrex has been adopted as the sample cell material. As in the last section, we will first describe the initial procedures, then the present techniques.

Initially, 3x9 mm (inside) rectangular pyrex tube was adopted as a standard sample cell for both reflectance and conductivity measurements. As shown in Figure 10 one end of the rectangular tube was joined to a 7 mm ID pyrex tube. If only a reflectivity measurement was desired, an 8x9x.5 mm (typical) sample of cleaved pyrolitic graphite was inserted diagonally into the rectangular end (see cross-section in Figure 10) and the tube was sealed. If both reflectivity and conductivity were desired, a Hall bridge mounted on a special lead frame of pyrex capillaries (Figure 11). was inserted into the rectangular end. The rectangular tube was then sealed around the capillaries and the platinum wires.

The sample and SbF_5 ampoules were joined, then a third piece of 7 mm pyrex tubing was added to make a tee. The glassware was baked at 500^{o}C under vacuum (except the sealed SbF_5 end) to drive

off water. The tee was then sealed off, the fragile joint was broken, and the intercalation started. See Figure 12. The ultimate extension of this method is the "tube a deux boules" technique in which the sample and the SbF_5 are maintained at different temperatures.

The present procedure employs the same apparatus as is used for liquid intercalation (Figure 3). Reflectance samples are supported in the upper portion of the straight tube by a spiral of .020" platinum wire. Conductivity samples (bridges) are suspended by their lead wires. Four .013" holes drilled in a teflon Swagelok plug pass .010" platinum wires which are spot-welded to the gold lead wires of the sample. When the Swagelok fitting is tightened on the end of the vessel, a compression seal is formed between the teflon plug and the platinum wires. This has proved to be an effective high-vacuum electrical feedthrough, and it is far easier to use than glass-metal seals.

Using a gas flame, the reactor is heated under dynamic vacuum to drive off water. The lower end of the apparatus is then immersed in liquid nitrogen, and the appropriate amount of SbF_5 is transferred from the Kel-F storage tube. After the teflon valve is closed, the apparatus can be removed from the line and placed in an oven.

3) $HF + SbF_5$

A vapor-phase superacid intercalation was attempted using a Kel-F tube as the sample cell. Because of the enormous difference in vapor pressures, achieving a ratio of ~4:1 $HF:SbF_5$ or less (by mole) in the vapor would require large amounts of liquid SbF_5 and only a trace of HF in the cell. We therefore attacked the problem indirectly. A sample was first intercalated with SbF_5, then the excess SbF_5 was transferred out of the cell. Gaseous HF was then introduced while the conductivity was closely monitored. As this technique did not produce a further conductivity increase, when we return to "superacid" compounds in the future we will

attempt a vapor intercalation using measured amounts of the two acids.

D. Stage Determination

The stage achieved by an intercalated sample can be determined by several methods. The simplest is just an observation of the sample's color. First stage HNO_3 and SbF_5 compounds are deep blue; first stage alkali metal compounds are gold while second stage ones are blue. Compounds less concentrated than these three samples retain the silvery color of the HOPG.

Measurement of the weight uptake provides an accurate indication of the sample's composition and therefore of its probable stage. For example first stage SbF_5 compounds have a composition between $C_{6.1}SbF_5$ and $C_{6.8}SbF_5$, while second stage is characterized by compositions near $C_{13.3}SbF_5$. This technique also indicates when a mixture of stages is present. The increase in weight is generally measured at the end of a reaction by transferring the sample to a teflon "pillbox" with a tightly-sealed lid. The transfer is performed in a dry N_2 atmosphere so that the sample is not exposed to O_2 or water vapor and the possibility of decomposition is minimized.

X-ray analysis is the most accurate way of determining stage. By measuring the angle at which Bragg reflection from the layers of carbon atoms occurs, the interplanar spacing can be determined. In pristine graphite the spacing is 3.35 Å; in the first stage SbF_5 graphite, for example, it is 8.46 Å. X-ray analysis is performed in a special aluminum holder into which the sample is placed while in a dry N_2 atmosphere. The holder has a plastic-wrap window[19] and is airtight; the small volume and captive N_2 atmosphere almost completely eliminate decomposition of the sample. When a mixture of stages is present, analysis of the x-ray data is extremely difficult. In such a case, the sample is cleaved with scotch tape and x-rayed again until a unique stage appears. Typical curves are shown in Figures 13-16.

E. Measurements

The purpose of this investigation is the development of intercalated graphite compounds with high infrared reflectance and good stability in air. In this context, the most significant characteristics of an intercalated sample are its IR reflectivity and its electrical conductivity. Knowledge of the conductivity is valuable not only for an understanding of the details of intercalation but also as an additional method for gauging the stability of an intercalation compound. The degradation in conductivity upon exposure to various atmospheres can be used to screen the stability of the different compounds.

Samples that exhibit promising stability are stored in air and their reflectance remeasured periodically. As discussed later, three samples of SbF_5 graphite have shown high reflectance at wavelengths greater than 8μ for more than 750 hours.

1) Optical Reflectance

Reflectivity measurements have been performed on HNO_3, SbF_5, and HF + SbF_5 intercalation compounds in the range .07-2.5 eV (17.7μ-.5μ). The instrumentation and the sample mounting techniques will be discussed separately.

a) Instrumentation

Three different spectrometers have been employed in the course of these measurements. Initially, a Perkin-Elmer #421 spectrometer[20] fitted with the appropriate specular reflectance accessories was used for measurements in the 2.5-20μ region. Since it was necessary to make measurements with the samples exposed to the atmosphere, or at best in a large box of flowing nitrogen, the lower stage compounds were decomposing as they were being measured. This technique is obviously unsuited for precise measurements.

An automated spectrometer available in our laboratory was used next. It is a single-beam instrument employing an evaporated aluminum reference mirror, and it covers a range of .6 eV (~2μ) to 5 eV (~.25μ). It is controlled by a programmable calculator and the reflectance spectra are automatically plotted after each sample is measured. It has been thoroughly described elsewhere.[21]

Reflectance measurements were performed through the walls of a pyrex ampoule (as in Fig.10 but without the KBr window). The Drude edge in several low-stage SbF_5 samples was observed in this manner, however the transmission characteristics of pyrex prevented IR measurements. This instrument is still available if measurements between 2.0 and 5.0 eV become necessary.

A second automated spectrometer, very similar in design to the first, was assembled for the purpose of investigating the reflectivity in the infrared. It has a shorter path length, and is fitted with a CsBr prism. It covers a range of .07 eV (~18μ) to 2.0 eV (~.62μ) at present; this can be extended to ~24μ. Reference mirrors made by depositing 4000 Å of gold on float glass substrates are used.

b) Measurement Ampoules

The standard sample holder for optical measurements is shown in Figure 17. It is constructed by joining a piece of 2x6 mm (ID) rectangular pyrex tubing to a female 14/35 standard taper joint. The end is sealed off, then a hole pattern of scotch tape is attached to one of the broad faces. The tube is dipped into molten Halocarbon #8-00 wax,[18] then the scotch tape pattern is pulled off. The result is an exposed area (about 3x6 mm) of glass. The assembly is dipped into 50% HF at 25°C for about 1½ hours until the section of glass is completely etched away. Then the wax is removed, and the hole is covered with a 1 mm thick window of KBr[22] attached with Halocarbon #12-00 wax.[18] When the ampoule passes a leak test, it is ready to be used.

The use of 2x6 mm tubing allows smaller pieces of graphite to be used as samples. As mentioned earlier, the typical size is

5x8x .35mm. The use of KBr as the window material allows reflectance measurements to be done within the range 25μ - .25μ. Samples are loaded into the ampoules under an atmosphere of dry nitrogen, and, unless otherwise noted, it may be assumed that these ampoules were employed in all of the optical measurements.

2) Conductivity

The conductivity can be measured with two different sets of instrumentation. A low frequency a.c. system based on a PAR 128 lock-in[23] is used for general conductivity measurements and for in situ measurements. In this technique the reference channel of the lock-in supplies a 400 Hz current to the sample. The voltage leads on the sample are connected to the signal channel of the lock-in, and the measured voltage is displayed on the output meter. Typical signal levels are on the order of tens of microvolts with 100 mA passing through the sample. A strip chart recorder is available to monitor changes in conductivity with time.

DC conductivity measurements are available through the cooperation of other members of the graphite group. This information is obtained as a result of their Hall effect and magnetoresistance measurements. Because of its complexity this apparatus is more useful for measuring the temperature dependence of the conductivity than for rapid, general purpose conductivity measurements, so most of the measurements are done with the ac system.

SECTION IV

RESULTS

In this section the results obtained during the first year will be presented. We will cover sample preparation, conductivity and reflectance measurements, and comment on the stability of the intercalated compounds.

A. HNO_3 Compounds

Graphite samples have been intercalated with HNO_3 using both liquid and vapor techniques. These compounds were made while the various sample handling and intercalation techniques were being checked out, as nitric acid is easier to work with than SbF_5.

For the nitrates, room temperature exposure to RFNA produces a third stage compound in two days, room temperature liquid intercalation in pure HNO_3 produces a second stage compound in three minutes, and vapor intercalation at room temperature above a $0^{o}C$ reservoir of pure HNO_3 produces a first stage compound in two days or less.

The near-IR reflectance of a second stage compound of graphite intercalated in pure HNO_3 is shown in Figure 18. The existence of a well defined plasma edge suggests that the IR reflectance will be high; this is confirmed by recent results shown in Figure 19.

The stability of nitrate compounds is, in general, not very good. However, other members of our graphite group have found that if a freshly intercalated compound is cooled to $77^{o}K$ and then allowed to warm to room temperature, the stability in air or in vacuum is greatly improved. This fact, coupled with the knowledge that higher stages (i.e. third or fourth) are intrinsically more stable and better conductors than the lower stages, makes it interesting to investigate the IR reflectivity of the higher stage nitrates. This will be done as time permits.

Since graphite fibers are of primary interest because of their utility as a construction material, an interesting result concerning changes in mechanical properties upon intercalation will be mentioned. Vogel[24] has recently measured resistivity, tensile strength, and elastic modulus for some Thornel 75 fibers intercalated by immersion in 25°C red fuming nitric acid. He observed conductivity increases of approximately 8 times, an average 21% decrease in the tensile strength, and an average 69% increase in the elastic modulus. The increase in modulus is explained by the increase in perfection of the graphite lattice as the carbon layers accomodate themselves to the intercalant.[25]

B. SbF_5 Compounds

We have prepared several compounds using SbF_5 as the intercalant. Both liquid and vapor phase techniques have been used. While early samples were prepared under conditions that were not entirely controlled (2-digit sample numbers), present procedures (3-digit sample numbers) allow precise control of the intercalation environment. Even so, the resulting compounds are not entirely predictable. This most likely results from the tendency of SbF_5 to polymerize as well as from varying impurity levels in the starting graphite.

1) *Optical Samples*

Two 9x9 mm optical samples, I-20 and I-21, were placed in liquid SbF_5 at room temperature. I-20 stabilized at a weight uptake corresponding to a $C_{39}SbF_5$ composition while I-21 stabilized at a $C_{30.5}SbF_5$ composition. This was our first indication of the unoredictable nature of SbF_5 intercalations, although at the time it was attributed to the procedures used.

The IR reflectance of each was measured in air on the Perkin-Elmer #421, both exhibited similar behavior ("initial"curve for sample I-20, Figure 20). After 5 days in air, the weight uptake

of I-21 stabilized at a composition $C_{39}SbF_5$ (same as I-20); both have remained the same ever since (approx. 4000 hours). As shown in Figure 20, the reflectivity of I-20 beyond 8μ remained high for 1050 hours (834 hr. for I-21). At that time the Perkin-Elmer #421 broke down and no further measurements were made until our IR spectrometer was completed. By then I-20 was over 4100 hours old, and the reflectivity had dropped to ~80%, as shown. The behavior of I-21 (3900+ hours) was essentially identical.

X-ray analysis initially showed these compounds to be a mixture of high stages (4 and 5 predominant). At an age of 1050 hours I-20 was x-rayed again, this time only graphite peaks were present. Since the sample had lost no weight, it had therefore rearranged into a residue compound. (A residue compound is one in which the intercalant resides in defects such as grain boundaries instead of between the carbon layers.) Since the reflectance remained high during and after the rearrangement, this has interesting implications for the intercalation of fibers.

Sample I-22 was intercalated in liquid SbF_5 at 45°C for 8 days. When removed it was a bright blue and showed a 265% weight increase, corresponding to a $C_{6.8}SbF_5$ composition. It was cleaved and measured in a nitrogen atomsphere, nevertheless the bright blue color gave way to a deep blue. This was later determined to be characteristic behavior for lst stage SbF_5 compounds; the darker blue presumably results from interaction with the atmosphere.

Acting upon information from Prof. Herold of the University of Nancy, France,[26] we had been associating the dark blue color with a second stage compound and the brighter blue with first stage. We have recently developed the ability to x-ray samples in a controlled environment, and the results so obtained indicate that both shades of blue are associated with a first stage compound. Therefore, the first and second stage IR reflectance curves previously reported and shown again in Figure 21 in reality simply reflect a first stage surface with varying amounts of chemical

debris. The true magnitude of the reflectance is uncertain because of the rough sample surface, and the structure in the curve probably results from absorptions in the thin layer of liquid SbF_5 on the surface of the decomposing sample.

Sample I-100 is the first intercalated in a well-controlled environment. It was intercalated and measured in the same pyrex ampoule, so no contact with the atmosphere occurred. The intercalant was also known to be pure SbF_5. The reaction took place in SbF_5 vapor for 2½ days at 80°C. Approximately half of the surface area turned dark blue, the rest assumed a silver color brighter than that exhibited by the initial HOPG.

The reflectance of both regions was measured, it is shown in Fig. 21. After two weeks the blue region had reverted to silver, when remeasured its reflectance was the same as the initial silver region. This strongly suggests decomposition from one stage to another; recent x-ray results indicate that the transition is from stage 1 to stage 2.

The plasma edge of the blue region was scaled to 100% reflectivity and then fit to the theoretical Drude model using a four-point minimization computer program. The value obtained for the conductivity, $\sigma_{opt} = 1.04 \times 10^4 (\Omega\text{-cm})^{-1}$, is lower than that of pristine graphite. Subsequent work[27] has shown that the solid-state parameters are so sensitive to the shape of the curve that a scaling procedure, such as that used here, completely invalidates the fit. Also, if the magnitude of the reflectance below the Drude edge is less than ~80%, the single-particle Drude model will not converge to the data.

It is extremely difficult for us to determine the true magnitude of the reflectance for 1st and 2nd stage SbF_5 compounds because their surfaces are very rough. However, the highest value we have observed just below the edge (~60%) is sufficiently low as to imply that the simple single particle Drude model cannot be applied to these compounds.

Samples I-101 and I-102 were prepared simultaneously in separate pyrex ampoules. They were intended to be intercalated at 75°C in SbF_5 vapor, but because of an unexpected temperature gradient in the oven some of the SbF_5 distilled into each of the sample ampoules. The net result was a 75°C liquid intercalation. Both samples had turned the characteristic blue color after 11 hours, and their reflectance was the same as that observed on I-100. I-102 was sealed off, I-101 was left connected to the ampoule of SbF_5. After 4 days I-102 had turned a dirty silver color; its reflectance then matched that observed on the silver part of I-100. Separate curves are not shown for these samples because they are so similar to those shown in Figure 22 for the blue and silver regions of I-100.

I-101 was stored at room temperature, still in an atmosphere of SbF_5 vapor. After two weeks it has reverted to a silver color. After two months (late May) it was placed in an oven for 3 days at 60°C and 1 day at 100°C. The dark blue color returned, and the weight indicated a first stage compound of $C_{6.9}SbF_5$ composition. The sample was ruined during an attempt to cleave it, however the interior was observed to be a bright blue. This was another indication that the dark blue does not indicate a different stage, for the surface is expected to have the greatest concentration of intercalant. It was also at this time that we discovered the great resistance to cleaving exhibited by 1st stage SbF_5 compounds.

In mid-April, two samples of SbF_5-graphite were hurriedly prepared at AFML's request for reflectance measurements using their Willey diffuse spectrophotometer. Two forms of graphite were used -- a 1"x1"x3/32" piece of HOPG and about 2 ml of Fisher #G-67 graphite powder.[28]

Because we had not previously intercalated samples of such geometry we had no idea how long the reaction would take or how far towards completion it would proceed. Intercalation was attempted at 75°C in SbF_5 vapor. After two days the powder most directly exposed to the SbF_5 had turned a very dark blue

while particles near the interior of the volume remained dark gray. The powder was mixed by agitation and replaced in the oven. After 3 days the powder appeared to be uniformly dark blue. The ampoule was removed from the oven and sealed for shipment. At this time (3 days) the large platelet still showed no sign of intercalation. The oven temperature was increased to 150°C for 3 hours, at which time it was necessary to remove and seal the ampoule for shipment. The platelet had turned the characteristic blue color all over, and it was assumed that a second stage sample had been made.

Measurements at AFML were done in air on the Willey spectrometer. They showed a reflectance for the Fisher powder of approximately 10% between 2 and 20μ. The reflectance of the intercalated powder was identical. The large platelet showed structure similar to that previously observed for compounds decomposing in air (Figure 21), however the magnitude of the reflectivity was larger (~85% at 2μ). The plate was cleaved and the interior surface measured; its reflectance was that of pure graphite. This was our first indication that surface color could not be used as an indicator of stage in SbF_5 compounds.

Using the new style of reactor shown in Figure 2, samples I-103 and I-104 were intercalated in SbF_5 vapor for 5 days at 80°C. Both turned the usual dark blue on the surface, but since the weight uptake indicated only fourth stage the samples were inhomogeneous -- i.e. the reaction had not gone to completion. The blue surface of I-104 was x-rayed and found to be first stage, a day later it had turned silver and was x-rayed as second stage. The surface was too rough for reflectance measurements, so the sample was tape cleaved, x-rayed again (3rd stage now), and the reflectance measured.

After 15 days in the measurement ampoule, the compound was removed, tape cleaved in air, and remeasured. Although it was not x-rayed, the surface was likely a mixture of stages 3 and 4.

The reflectance was measured again the following day and some small changes were noticed, probably as a result of an even larger proportion of fourth stage. After an additional 3 days in air, the sample was tape cleaved and x-rayed twice before a uniform fourth stage surface was achieved. The reflectance was measured and is shown in Figure 23-25. The high value of 97% for the reflectance beyond 6μ was especially noteworthy. The sample was remeasured periodically; after two days no change was observed. After nine days, the reflectance in that region had decreased to approximately 90%. After a total of 32 days (766 hr.) very little additional change had occurred; the reflectance in the same region was still ~89% (Figure 22).

At this point a word concerning the cleave-x-ray-measure procedure is in order. The intensity of the x-ray diffraction peaks obtained from these compounds was very low, so a calculation of the capture cross section was performed. The value was found to be so large that the x-ray penetration depth for the first few stages ranges from 20-60μ. It is therefore possible to obtain useful optical data from inhomogeneous samples, because 60μ thick slices of the sample can be characterized with x-rays and then measured optically. (Optical penetration depth is at most ~1μ). This was a fortuitous occurrence because the vapor phase compounds usually were inhomogeneous. Unfortunately, sample I-103 was discarded before the value of this technique was appreciated.

Samples I-105 and I-106 were intercalated in SbF_5 vapor at 80°C for 25 days. Their surfaces turned blue, however the weight uptake only corresponded to approximately second stage. The surfaces were very rough, essentially unusable for optics. I-105 was x-rayed as stage 1, so it was stored in a tightly sealed teflon container to await decomposition of the surface to stage 2. Unfortunately, the flow of events was such that when I-105 was next x-rayed it was predominantly stage 3, so it was discarded.

An attempt to measure the reflectance of I-106 was made, but the surface was too rough to get any truly useful data. Experience with conductivity bridges had shown that first and second stage compounds cannot be cleaved with scotch tape, so the sample's surface was scraped with a razor blade until a silver color was obtained. X-ray analysis showed a mixture of stages 2 and 3, so the sample was then tape cleaved. This time the x-rays showed a uniform third stage, so the reflectance was measured. The results are shown in Figures 26-28.

The sample was then exposed to air and measured periodically. After 20 hours its reflectance matched that observed for fourth stage in I-104. Because of scheduling problems with the diffractometer, it was not possible to x-ray the sample to confirm the presence of fourth stage. Over the next week, the behavior of I-106 was essentially the same as that of I-104, i.e. a slow decrease in IR reflectance to a value of approximately 90%.

2. Conductivity Samples

Concurrent with the above investigation of optical properties of SbF_5 compounds was an investigation of the dc conductivity of these compounds. This work was done by Dr. T.E. Thompson under NSF Grant #DMR 75-04954. All of these samples were intercalated using the latest of the techniques described earlier.

The four-point bridges for the a-axis electrical conductivity measurements typically measured 17 mm in length and 2 mm in width, with a thickness along the c-axis of 0.5 mm. The voltage arms were 10 mm apart. Electrical connections were made by wrapping 0.005 in. gold wire around the bridge arms and then thoroughly covering these contacts with gold paste. The bridge was heated to 500°C to drive off volatile materials and sinter the gold. This process produced a sturdy mechanical bond and good electrical contact to all the graphite layers. These gold wires were then spot welded to the platinum wires of the reaction vessel.

As described earlier, resistance measurements were made using a phase-sensitive detector operating at 210 Hz. The voltage developed across the sample was compared to that across a calibrated resistor in series with the sample. Currents between 1 and 10 mA were applied. The voltage scaled linearly with the current, and the two were always in phase to better than 1^{o}. The room-temperature a-axis conductivity for the graphite samples fell in the range 23-27 $(m\Omega\text{-cm})^{-1}$. These samples showed resistivity ratios between room temperature and 77K between 1.6 and 1.7.

While reactions were in progress the resistance of the bridge was monitored continuously to check on the rate and extent of the intercalation. At the same time thickness measurements were made on the sample at regular intervals. When no further changes in thickness or resistance had been observed for at least a day, the reaction was assumed to have ended.

The results of the electrical measurements are presented in Table 1.[29] The fractional thickness increase, $\Delta t/t_o$, represents an average over the length of the sample because of problems with fraying of the sample's edges. The x-ray data indicate that the ideal value for the stage-n thickness increase is given by

$$\Delta t/t_o = (8.44 - 3.35)\text{Å}/n\ 3.35\ \text{Å} \qquad (1)$$

Departures from these values are due to mixtures of stages and the self-cleaving which accompanies the large thickness increases of the lower stage compounds. The conductivity ratios σ_I/σ_o were calculated from the intercalated and starting resistances, R_I and R_o, making corrections for the thickness increase: $\sigma_I/\sigma_o = (R_o\ t_o)/(R_I\ t_I)$. One of the stage 1 samples had obviously over expanded. The ideal thickness increase, 1.52, was used for this sample. The implications of this data will be discussed later.

C. $HF + SbF_5$

Several intercalation compounds have been made using $HF + SbF_5$ "superacid" mixtures. The earliest of these was I-03, a 10x10 mm sample liquid intercalated at 25°C in a mixture of 1:1 $HF-SbF_5$. After four days a weight uptake of 115% was obtained. This corresponds to a composition of $C_{17.1}HSbF_6$, which should be approximately third stage. An almost identical result ($C_{17.0}HSbF_6$) was obtained for another sample intercalated at the same time (AGXCO501). When x-rayed, this sample indicated second stage, so I-03 was assumed to be second stage as well. In the light of our present knowledge, the samples were probably just inhomogeneous; predominantly third stage but with second stage surfaces.

The reflectance of I-03 from 2.5 to 25μ was measured in air using the Perkin-Elmer #337 spectrometer[20] and an aluminum reference mirror. The result is shown in Figure 29. When this information was reported previously (December), the curve was incorrectly drawn and showed a reflectance greater than 100%. In reality the data indicate a maximum value of 100%, as shown in the figure. Since this sample was measured in air it was undoubtedly decomposing, thus the true stage of the surface is unknown. Unfortunately, this sample was mishandled and destroyed by the x-ray technician.

Samples I-200 and I-201 were intercalated for 1.5 days at 26°C in a 2:1 $HF:SbF_5$ superacid mixture. The particular mixture was picked on the strength of some recently obtained information[30] which indicated that the strength of the $HF-SbF_5$ superacid system would be greater if the mixture were rich in HF. A conductivity bridge achieved first stage under the aforementioned conditions, however, when these samples were removed their weight uptake indicated third stage instead of the desired first stage. This discrepancy was attributed to the greater ratio of edge area to interior volume for the bridge than for the platelet. Sample I-201 was sent out for chemical analysis,[31] however the error in the

results was large enough to render the various possibilities of intercalated species indistinguishable.

Vapor intercalation with 2:1 HF-SbF_5 mixtures was attempted using conductivity bridges. No detectable reaction occurred when the sample was suspended over the acid. Furthermore, when HF vapor was added to a reactor containing an in-progress 25°C SbF_5 vapor intercalation, the reaction stopped and the sample resistance even increased. When the HF was removed, the reaction proceeded again. This seemingly deleterious effect of HF vapor is in marked contrast to the behavior of HF + SbF_5 liquid reactions. In the liquid phase, intercalation is already occurring at 0°C while with pure SbF_5 intercalation begins only above 14°C. The effect of HF on pentafluoride intercalations will be studied further using AsF_5.

Samples I-202 and I-203 were intercalated under the same conditions as I-200 and I-201. They were somewhat larger, 7x8 mm and ~59 mg vs 5.5 mm x 8 mm and ~29 mg for I-200 and I-201. They were removed from the acid after 8 days, but the weight uptake still indicated only a third stage compound. X-ray analysis also showed third stage, so the reflectance of a tape cleaved surface was measured. The results, shown on Figure 31, were essentially the same for both samples. In contrast to 3rd stage SbF_5 compounds, these compounds were stable in air for at least an hour. This was determined by repeated observation of the Drude edge, which is very sensitive to changes in the electronic properties. Long-term stability tests have not been done because the magnitude of the IR reflectance is not sufficiently large.

The results of the electrical measurements on the HF + SbF_5 compounds are presented in part B of Table 1. Comparison of the stage 1 sample with stage 1 SbF_5 shows that the addition of HF has not significantly improved the conductivity of the compound.

SECTION V

DISCUSSION

In this section the significance of the various results will be considered. The synthesis, reflectance, and conductivity of the compounds will be treated individually.

A. Synthesis

Several compounds have been made by intercalating graphite with SbF_5 and HF - SbF_5 mixtures. Compilations of sample geometry, reaction conditions, and resultant compound are presented in Tables 2 and 3 for SbF_5 and HF + SbF_5 compounds, respectively.

It is evident from the table that the reactions proceed more rapidly at higher temperatures and in liquid, as expected. It is also apparent that the long, narrow bridges intercalate more rapidly than the rectangular platelets. The most significant characteristic, however, is the variability of the end product. In several instances, both for SbF_5 and SbF_5+HF intercalants, two adjacent samples in the reactor vessel yielded different compounds. The difference seems to be random; in some cases the larger sample intercalated to a greater extent, in other cases the smaller one. This probably results from the local influence of impurities in the graphite on the polymerization of the SbF_5.

A synthesis problem not evident in the tables is the low predictability of the product. This is influenced by two factors -- the spatially nonuniform nature of the intercalation and the tendency of the sample's edges to fray. The nonuniform intercalation-outside faces rapidly reach first stage while the interior is a much higher stage - eliminates the possibility of using color as an indicator of stage. The fraying of the edges for lower stages coupled with the nonuniform intercalation reduces the usefulness of thickness measurements to simply a rough estimate of average stage. The sample could be x-rayed through the walls of the pyrex ampoule, but the small penetration depth in

SbF_5-graphite would preclude measurement of the sample's interior. Thus there is no straightforward way to recognize that the sample has reached a given stage and then stop the reaction. As a result, we have been unable to produce a cookbook for the preparation of SbF_5 intercalation compounds of other than first stage. For first stage, uniform compounds have been obtained most often after 5 days in 80°C liquid for both bridges and platelets, and after 3 weeks in 80°C vapor for bridges.

Another negative aspect of SbF_5 intercalation is the long reaction times involved. The sample preparation times in Table 2 are all on the order of weeks rather than hours. Even with the bridges 3 weeks are required to produce a first stage compound by vapor intercalation. By using liquid intercalation this can be shortened to 5 days, but removing the excess SbF_5 from the surfaces of the compound is a significant problem. In addition, the tendency toward self-cleaving is greatly increased.

The obvious step is to increase the temperature of the reaction, and this was attempted with bridge D2-8. It was intercalated in vapor at 120°C. After three hours the reaction terminated, however the bulk of the sample was not first stage but third. Only the surface was first stage. Lower temperatures (than ~80°C) were also employed. Here it was determined that the reaction does not proceed at a significant rate below ~45-60°C for vapor and ~14°C for liquid intercalation. The resulting compounds were mixtures of higher stages.

The addition of HF to the SbF_5 inhibits the reaction in the vapor phase, perhaps because of the large difference in vapor pressure between the HF and the SbF_5. In liquid, the presence of HF seems to catalyse the reaction. Liquid intercalation in 2:1 HF-SbF_5 proceeds readily at 0°C whereas, as mentioned above, for pure SbF_5 a temperature above 14°C is necessary. The "superacid" compounds do not turn blue before first stage is reached and there is only moderate fraying of the sample edges, so they may be

more predictable than pure SbF_5 compounds. There is still significant variability in the composition of the end product (Table 3), enough to preclude identification of the intercalated species from the weight uptake.

B. Reflectance

Room temperature optical reflectance measurements of stage 1 to stage 4 SbF_5-graphite have been performed over an energy range of 0.07 to 2.0 eV. The reflectance of all 4 stages exhibited a metallic edge; the curves are shown in Figure 30. The IR reflectance (2.5-17μ) for stage 3 and 4 SbF_5 compounds and stage 3 2:1 HF-SbF_5 compounds is shown in Figure 31.

A word of caution is needed concerning the stage 1 and stage 2 curves in Figure 30. Stage 1 and 2 compounds are possessed of very rough surfaces, therefore there is an appreciable uncertainty in the measured result. Absolute reflectance measurements are made with a He-Ne laser, however the reflectance is very low at 1.96 eV so a substantial error in scaling is possible. The curves as drawn represent the present best estimates for these two stages.

No such problem exists for the stage 3 and 4 compounds. Here smooth tape-cleaved surfaces are possible, and all of the reflected photons are captured and measured. Measurements of samples in the ampoules, including the KBr window corrections, agree with measurements in air to within the experimental error of the spectrometer ($\pm$ 1.5%).

As mentioned earlier, all four stages exhibit a metallic reflectance edge. In pure graphite this Drude edge is not observed because of the .02 eV threshold for interband transitions which arise from narrow overlapping bands near the zone boundaries.[35] The existence of metallic edges in these compounds therefore indicates a significant reduction in the strength of such transitions below 2 eV. The suppression of these transitions could result either from changes in the band structure or from a substantial decrease in the Fermi energy.

The location of the reflectance minimum increases monotonically with increasing intercalate concentration (Table 4). From the Drude model for optical reflectance of metals, it can be shown that the frequency of the minimum, ω_{min}, is related to the carrier density N by

$$\omega_{min} = \left[\frac{4\pi Ne^2}{m^*(\varepsilon_o - 1)}\right]^{\frac{1}{2}} \qquad (2)$$

where m* is the effective mass and ε_o is the core dielectric constant.

If intercalation were simply a doping process ω_{min} should increase as $X^{\frac{1}{2}}$, where X is the concentration of intercalate molecules. In fact, ω_{min} increases less rapidly than $X^{\frac{1}{2}}$, implying changes in the band structure (i.e. m* and possibly ε_o) as well as in carrier density. This has also been observed in alkali metal[27] and nitric acid-graphite compounds.[36]

For simple metals, the observed plasma edge can be fitted to the theoretical Drude expression for reflectivity. Values for the plasma frequency and the scattering time obtained from this procedure can be used to calculate the optical conductivity. In metals, the reflectance just below the edge is nearly 100%. For the SbF_5-graphite compounds, however, the low values of reflectance on the low-energy side of the edge made it impossible to fit the data to the simple, single-particle Drude model. Thus, it is clear that these compounds do not behave like simple metals.

The existing measurements for stage 1 and 2 reflectance in the IR do not pertain to surfaces of a unique stage, therefore they will not be discussed here. Good information does exist for stage 3 and 4, and for stage 3 compounds intercalated in a 2:1 HF-SbF_5 mixture. These are shown in Figure 31. As shown, there is no drastic difference between the reflectance of stage 3 SbF_5 and stage 3 HF+SbF_5, and the reflectance of each is similar in magnitude to that of pure HOPG. Fourth stage SbF_5-graphite

however, has a reflectance of approximately 97% (with respect to gold) at wavelengths beyond 8μ. Thus we see that dilute SbF_5 compounds will be the most important for this work. The high reflectance at fourth stage is probably a result of a beneficial mix of new carriers created by the intercalant and substantial remnants of the graphite band structure.

Another positive result involves the stability of these compounds. First, second, and third stage SbF_5 compounds are unstable in air; fourth stage is relatively stable. Although in time the Drude edge of the fourth stage compound degrades and becomes undefinable, the reflectance beyond 8μ remains high. This has been shown earlier in Figures 20 and 23. Three samples so far have retained this high reflectance after more than 760 hours exposure to air.

C. Conductivity

The conductivity data presented in Table 1 are shown in Figure 32 plotted as a function of $t_o/\Delta t$. Here t_o is the initial thickness of the bridge and Δt is the average thickness increase. The ideal values of $t_o/\Delta t$ for stages 1 to 4 given by Eq. (1) are also indicated. Samples with thicknesses corresponding to stage 1 were verified to be stage 1 by gravimetric and x-ray analysis. The conductivities indicated are, therefore, stage 1 conductivities. There appears to be no significant difference between the electrical conductivities of stage 1 compounds made with pure SbF_5 and those made with SbF_5-2HF mixtures.

For the other samples, caution must be exercised in using the thickness to associate a conductivity with a stage, because the measured thickness cannot be used as a stage indicator. However, some idea of the variation of conductivity with stage can be obtained from the figure. Samples containing a mixture of stages are equivalent to a network of resistors in parallel,

therefore the conductivity of the ith layer contributes to the average conductivity σ_I in proportion to its thickness, t_i:

$$\sigma_I = \sum_i (t_i/t)\ \sigma_i. \qquad (3)$$

For example, in a compound which is 1/3 stage 2 and 2/3 stage 1, the average conductivity is dominated by the stage 1 conductivity but is increased or decreased from that of stage 1 depending upon whether σ_2 is greater or less than σ_1. Since no measured conductivity is higher than that of stage 1, the conclusion is that the conductivity decreases for the higher stage compounds in a manner similar to that indicated in the figure. Thus we see that the maximum conductivity for compounds prepared in SbF_5 and SbF_5:2HF is approximately 8 times that of copper.

SECTION VI

SUMMARY

The first year's work on graphite intercalation compounds involving SbF_5 has established the following characteristics:

1. difficult synthesis. SbF_5-graphite intercalation compounds are characterized by a low predictability. Two adjacent samples in the same reactor yield different compounds; furthermore compounds of arbitrary stage cannot be produced on demand because the intercalation proceeds inhomogeneously. In addition, the reaction times are long, and the tendency of SbF_5 to polymerize complicates the analysis of the compounds.

2. high infrared reflectivity. Stage four compounds exhibit high infrared reflectivity (over 90%) between 8 and 17μ. The persistence of this behavior while the compound is rearranging into a residue compound implies that high-reflectance fibers may be obtained by inserting intercalants into pre-existing voids between graphite crystallites in the fiber.

3. stability in air. For SbF_5 compounds of stage 4 and higher, the high reflectivity mentioned above has persisted after exposure to normal air for a month.

4. complex Drude edges. The inability to fit the reflectance edge to the simple Drude model implies that these compounds are not simple metals and multiple carriers are involved in the conduction process.

5. same properties for superacids. Addition of HF to the SbF_5 alters the nature of the reaction (speed, uniformity), but the resulting compounds exhibit reflectance and conductivity properties very similar to those of SbF_5 compounds of the same stage.

SECTION VII

CONCLUSIONS AND FUTURE WORK

Graphite intercalation compounds made with SbF_5 can exhibit a conductivity 8 times that of HOPG or an IR reflectivity greater than 90%. The high reflectivity can persist in normal air for over a month. However, SbF_5 is a very difficult material to use as an intercalant. In fact, the synthetic difficulties are such that we recommend continued investigation of the SbF_5-graphite system only if no easily synthesized, stable, high reflectance compound can be found. Even if the addition of HF makes the intercalation predictable, the need to work with HF is industrially undesirable.

Accordingly, we are beginning an investigation of graphite intercalated with AsF_5. AsF_5 is a highly volatile gas at room temperature, only slightly less reactive than SbF_5, and easily moved about in a vacuum line. For intercalation of graphite, especially fibers, its physical properties are far more desirable than those of SbF_5. In a preliminary experiment, a sample of HOPG intercalated rapidly and retained its specular surfaces even at first stage. It was destroyed during an attempt to remove the excess AsF_5 from the reactor, so its reflectance was not measured. However, the brilliant silver color observed just before first stage is very encouraging.

SECTION VIII

TABLES AND FIGURES

Table 1

Thickness Increase, Resistance and Conductivity Ratios for SbF_5-Graphite

	$\Delta t/t_o$	R_o (mΩ)	R_I (mΩ)	σ_I/σ_o
a.	SbF_5			
	1.83	8.92	0.44	8.0*
	1.0	4.71	0.36	6.5
	0.67	2.40	0.22	6.5
	0.59	3.06	0.30	6.4
	0.43	4.85	0.63	5.4
b.	SbF_5-HF			
	1.52	8.33	0.43	7.7
	0.37	4.75	0.91	3.8

Ideal $\Delta t/t_o$: stage 1, 1.52; stage 2, .77; stage 3, .51; stage 4, .38.

Table 2
SbF_5 Compounds

Sample	Type	Initial Wt.	Reaction time, temp.	Stage by wt.	Stage from x-ray	% intercalate
I-20	platelet	111.1 mg	4 days, 25°C liquid	~6	-	31.5
I-21	platelet	81.2 mg	4 days, 25°C liquid	~4	-	44.7
I-22	platelet	149.2 mg	8 days, 45°C liquid	1	-	72.6
I-101	platelet	29.5 mg	3 days 60°C; 1d. 100°C liquid	1	-	72.6
I-102	platelet	41.5 mg	11 hr 75°C liquid	-	-	-
I-103	platelet	28.5 mg	5 days 79°C vapor	4	surface 1 interior 243	40.9
I-104	platelet	36.1 mg	5 days 79°C vapor	~4	-	44.2
I-105	platelet	29.5 mg	25 days 79°C vapor	~2	1 (surface)	61.7
I-106	platelet	34.7 mg	25 days 79°C vapor	~2	1 (surface)	54.8
C-04-8	bridge	22.4 mg	9 days 25°C vapor (sample 70°C)	6-7	-	29.1
C-06-6	bridge	36.2 mg	3 days liquid $\leq$ 65°C 4 days 75°C liquid	1	1	77.6
D-2-2	bridge	77.0 mg	20 days 78°C vapor	1	-	74.9
D-2-8	bridge	54.1 mg	3 hr 120°C vapor	3	1,2,3	51.

Table 3

$HF+SbF_5$ Compounds

Sample	Type	Initial Wt.	Reaction time, temp.	stage by wt.	stage from x-ray	% Intercalate
I-03	platelet	109.5 mg	4 days, 25°C 1:1 liquid	3	-	53.5
I-200	platelet	26.3 mg	2 days, 25°C liquid	3	-	47.7
I-201	platelet	28.1 mg	2:1 $HF:SbF_5$	3	3*	51.8
I-202	platelet	58.8 mg	8 days, 25°C liquid	3	3	49.8
I-203	platelet	48.9 mg	2:1 $HF:SbF_5$	3	3	45.1
G 002	bridge	20.4 mg	6 days, 25°C liquid 2:1 $HF:SbF_5$	1	-	74.1

Table 4

Reflectance Minima of SbF_5-Graphite

Stage	ω_{min} (eV)
1	1.8
2	1.4
3	1.18
4	1.13

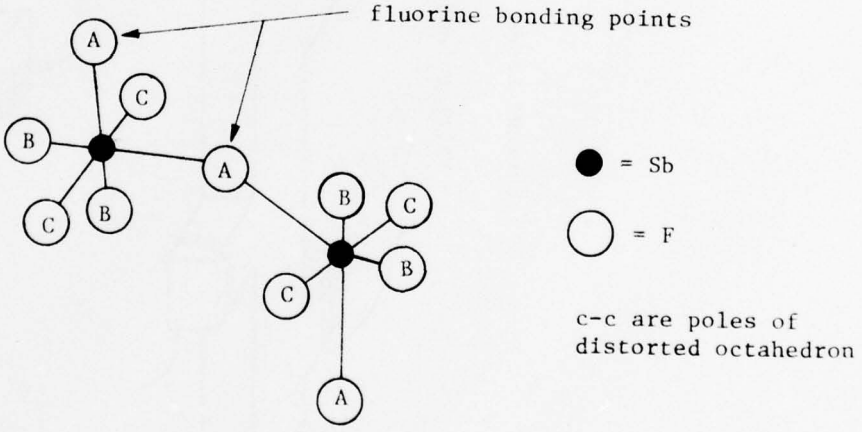


Fig. 1: POLYMERIZATION OF SbF_5

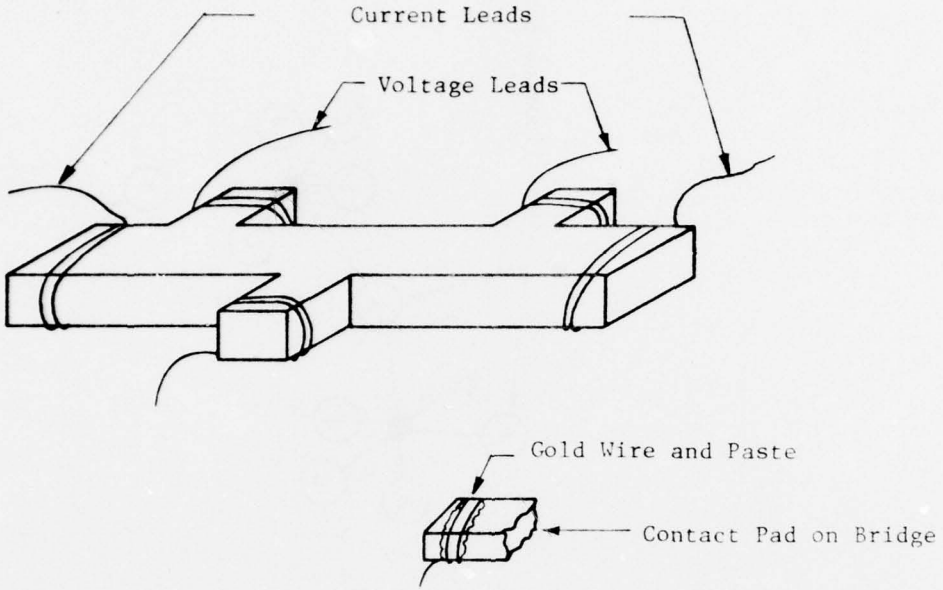


Fig. 2: HALL BRIDGE AND CONTACT DETAIL

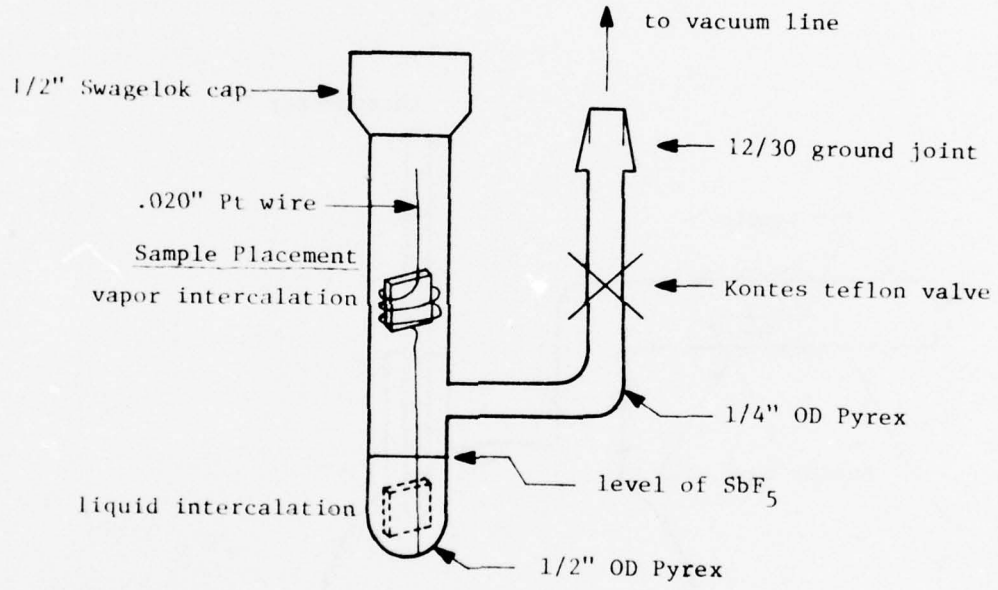


Fig. 3: SbF_5 INTERCALATION APPARATUS

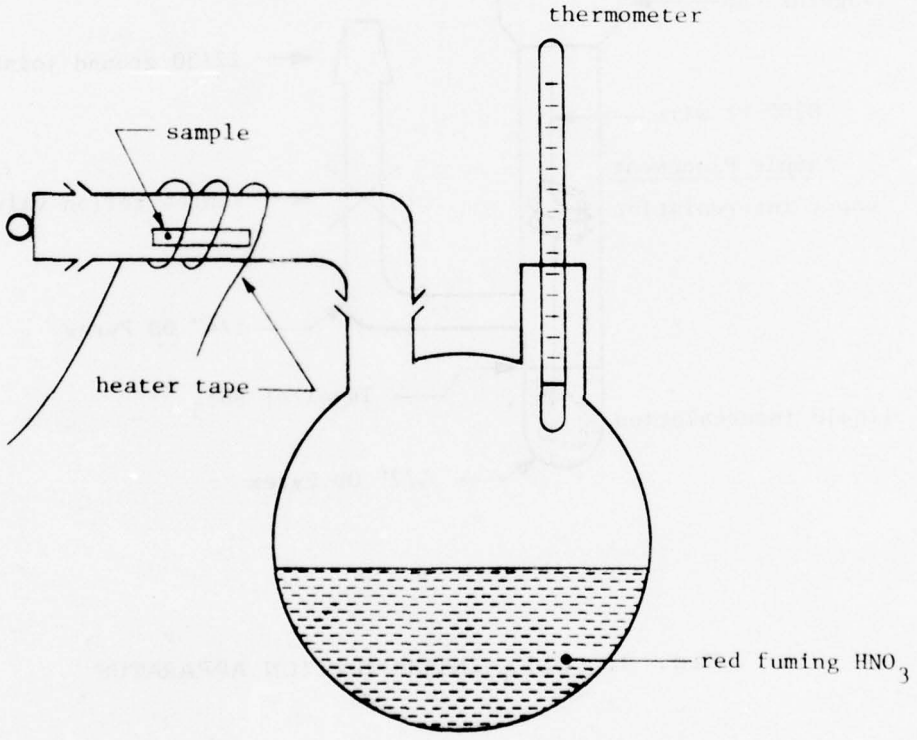


Fig. 4: ROOM TEMPERATURE VAPOR INTERCALATION APPARATUS

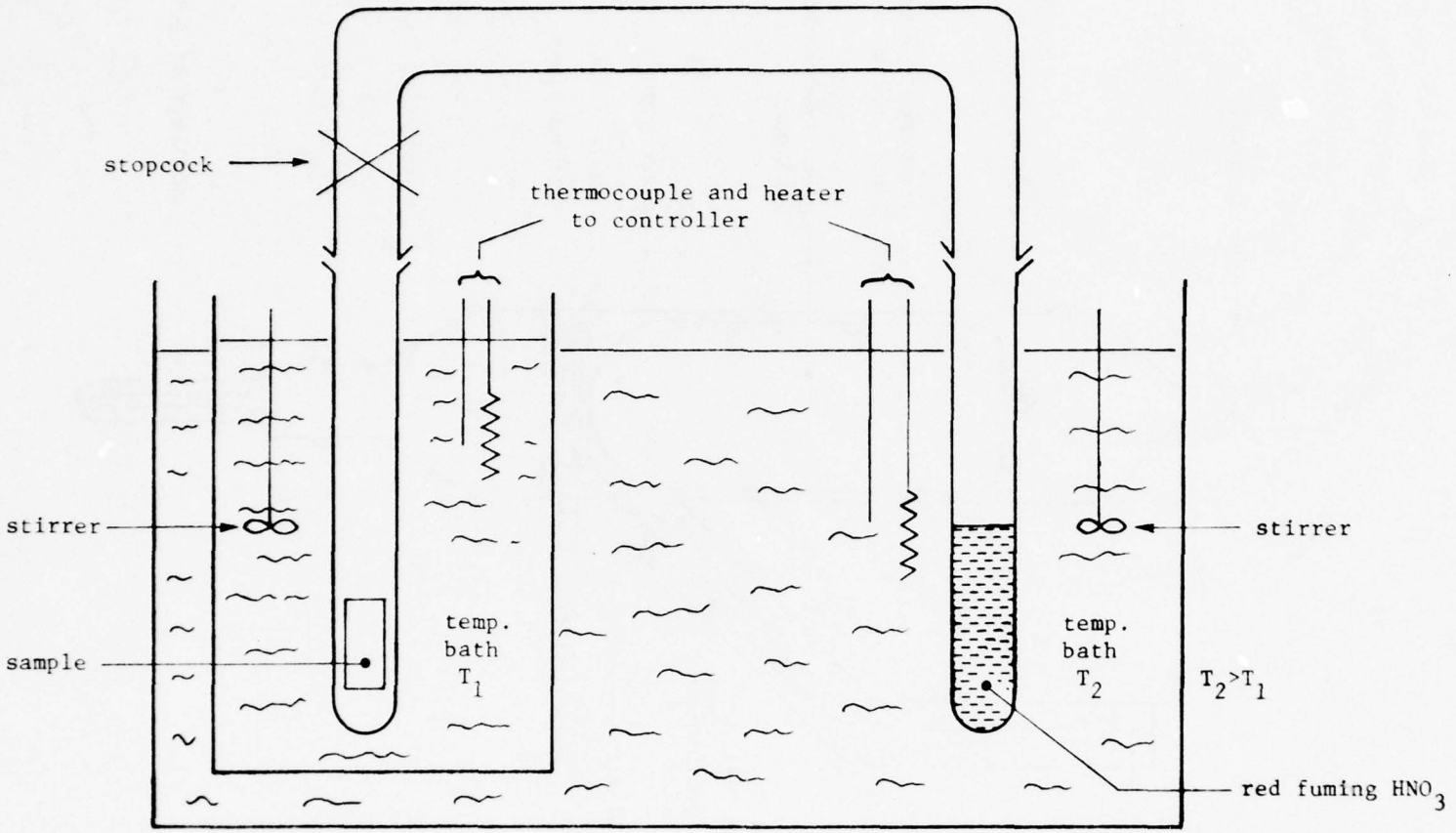


Fig. 5: LOW TEMPERATURE VAPOR INTERCALATION APPARATUS

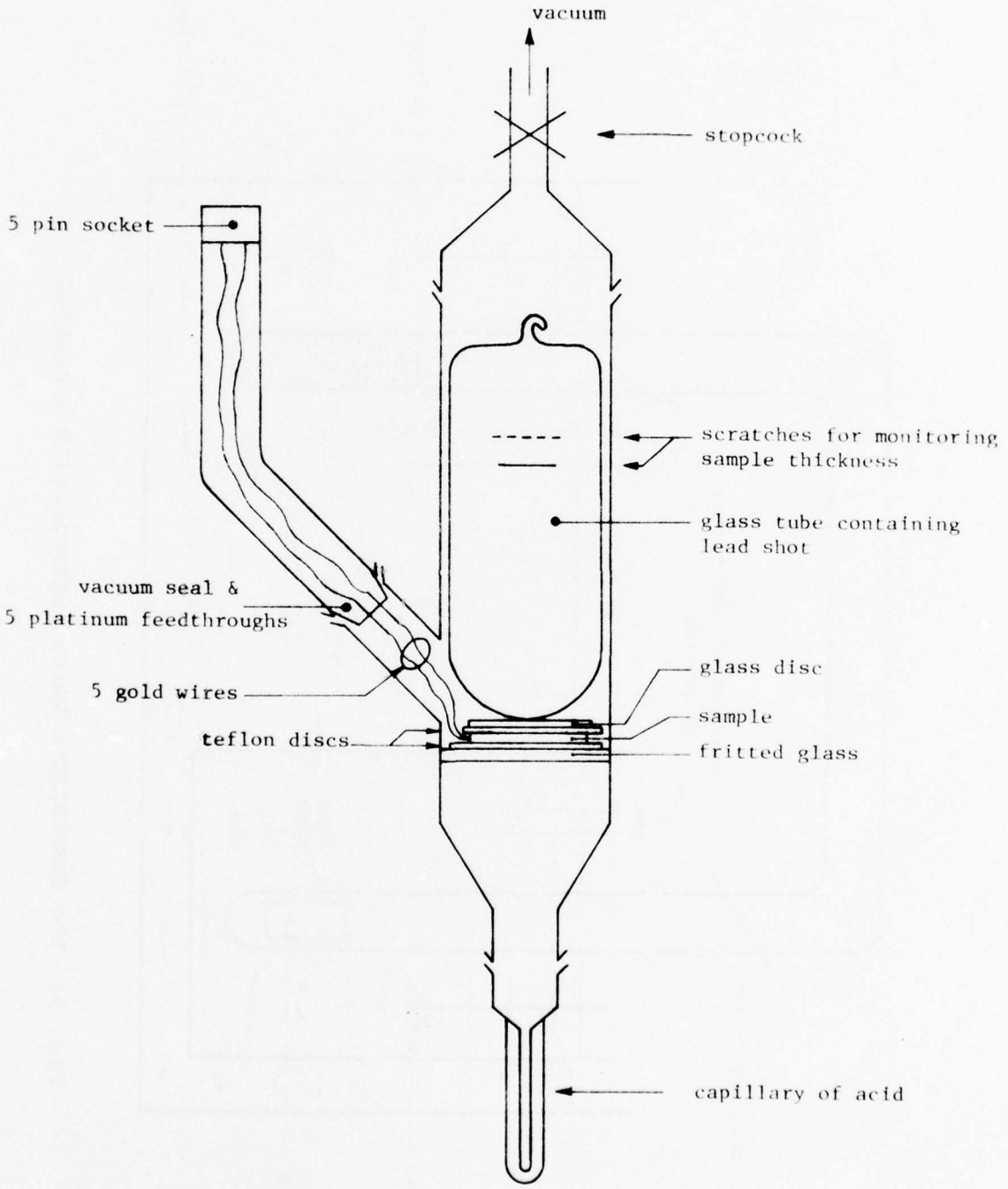


Fig. 6: IN SITU VAPOR INTERCALATION APPARATUS

PREPARATION OF PURE HNO_3

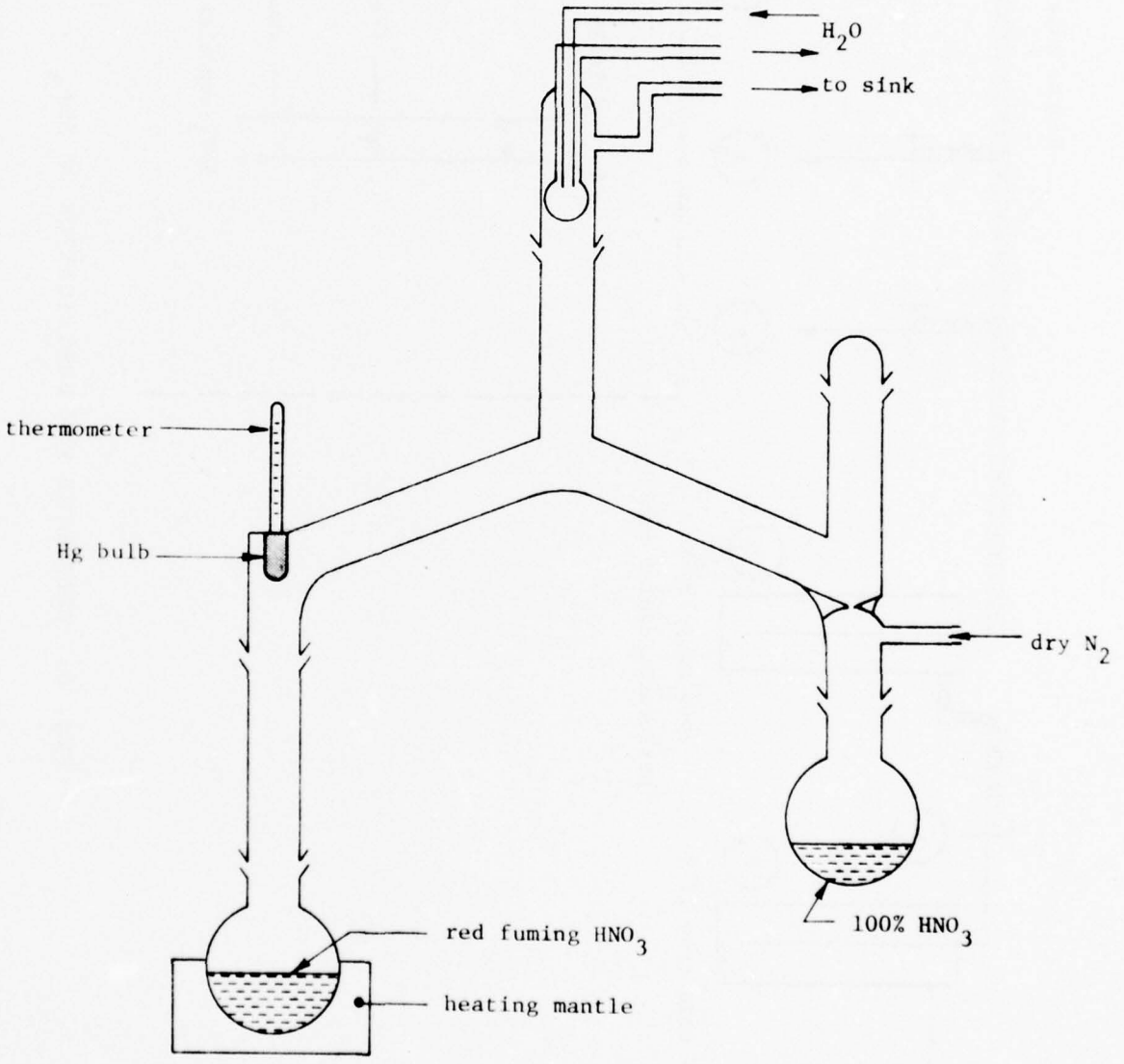


Fig. 7: PREPARATION OF PURE HNO_3

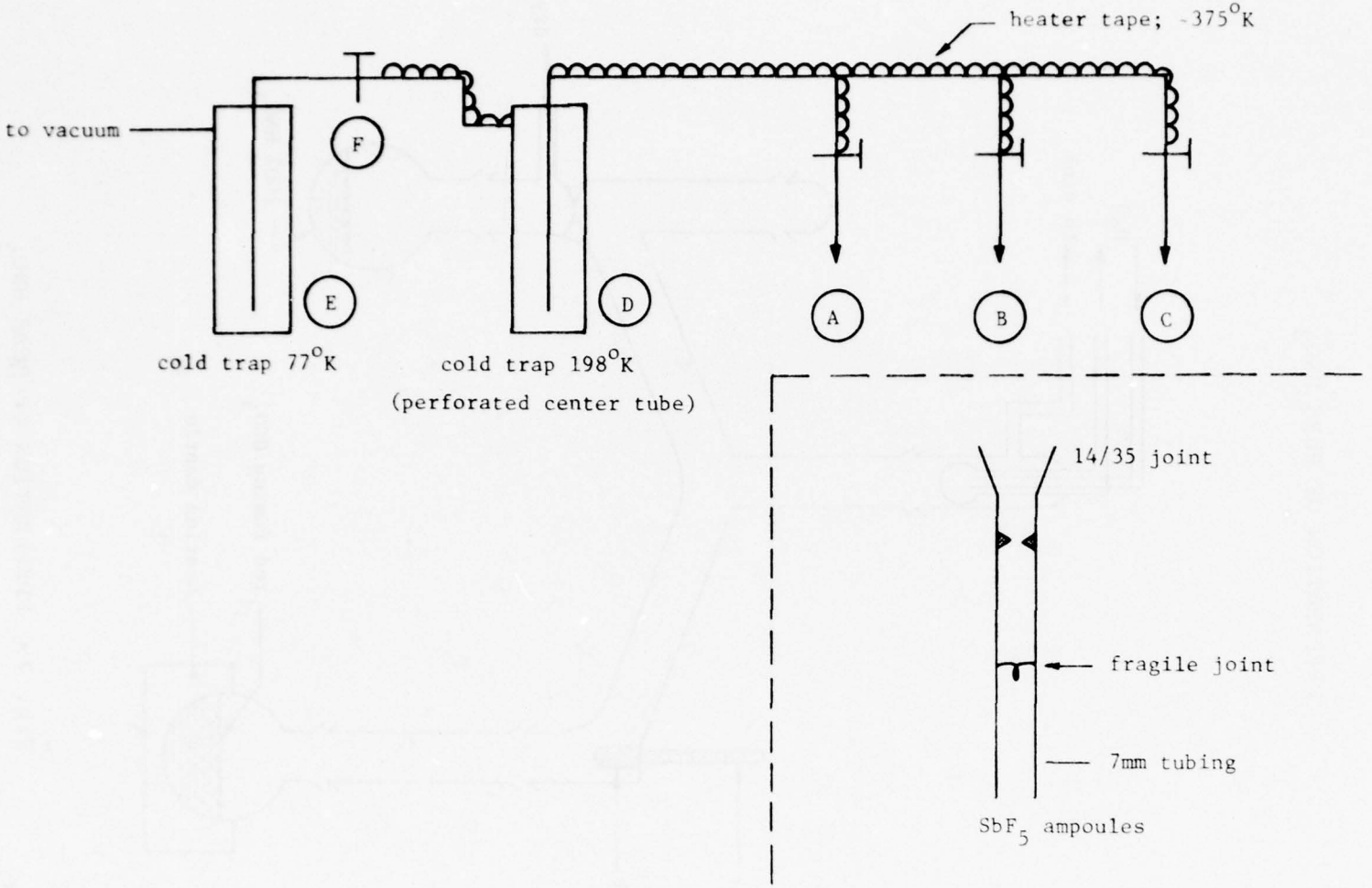


Fig. 8: APPARATUS FOR PURIFICATION OF SbF_5

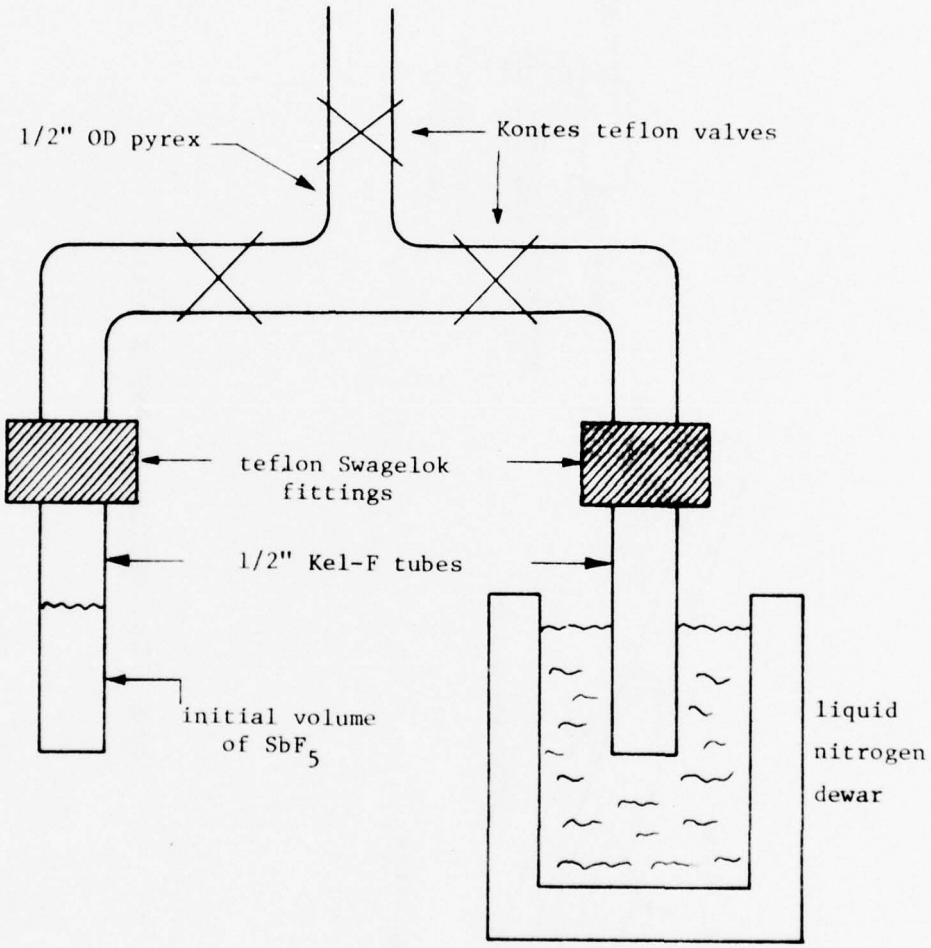


Fig. 9: SbF_5 DISTILLATION

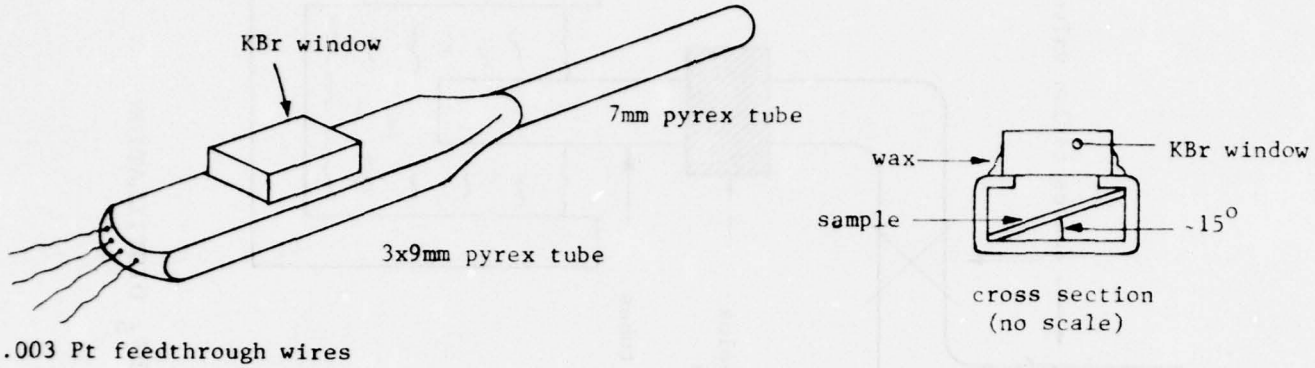


Fig. 10: ORIGINAL SAMPLE CELL

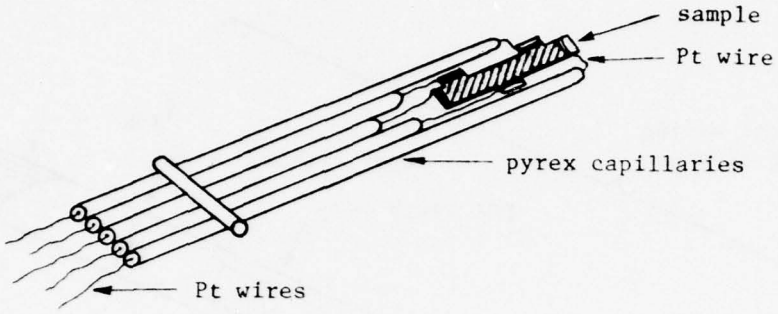


Fig. 11: SAMPLE MOUNTING FOR CONDUCTIVITY MEASUREMENTS

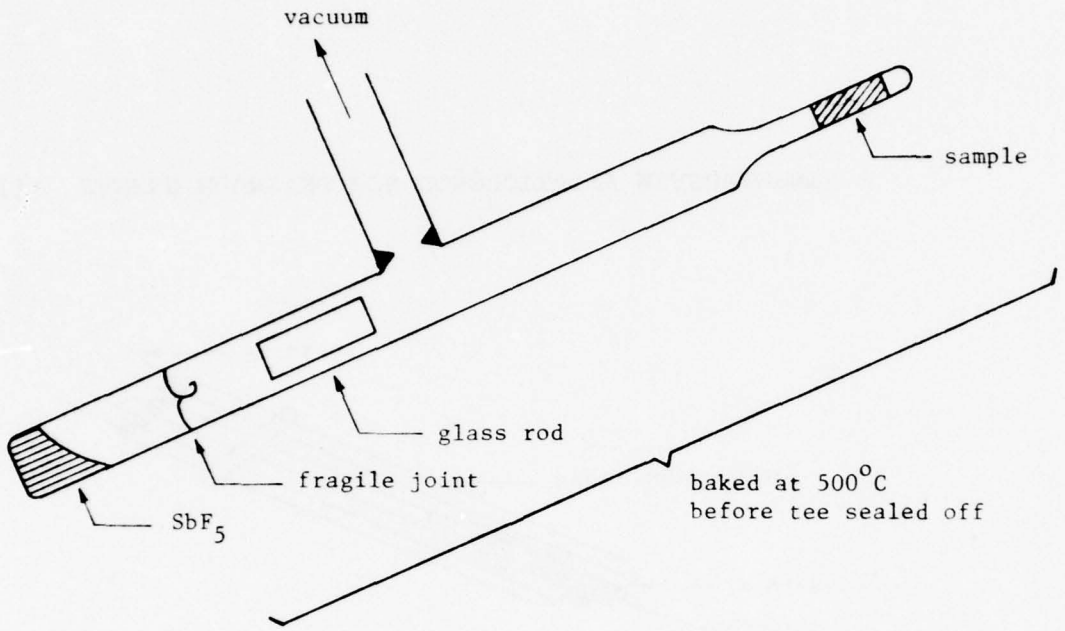


Fig. 12: ORIGINAL SbF_5 VAPOR INTERCALATION

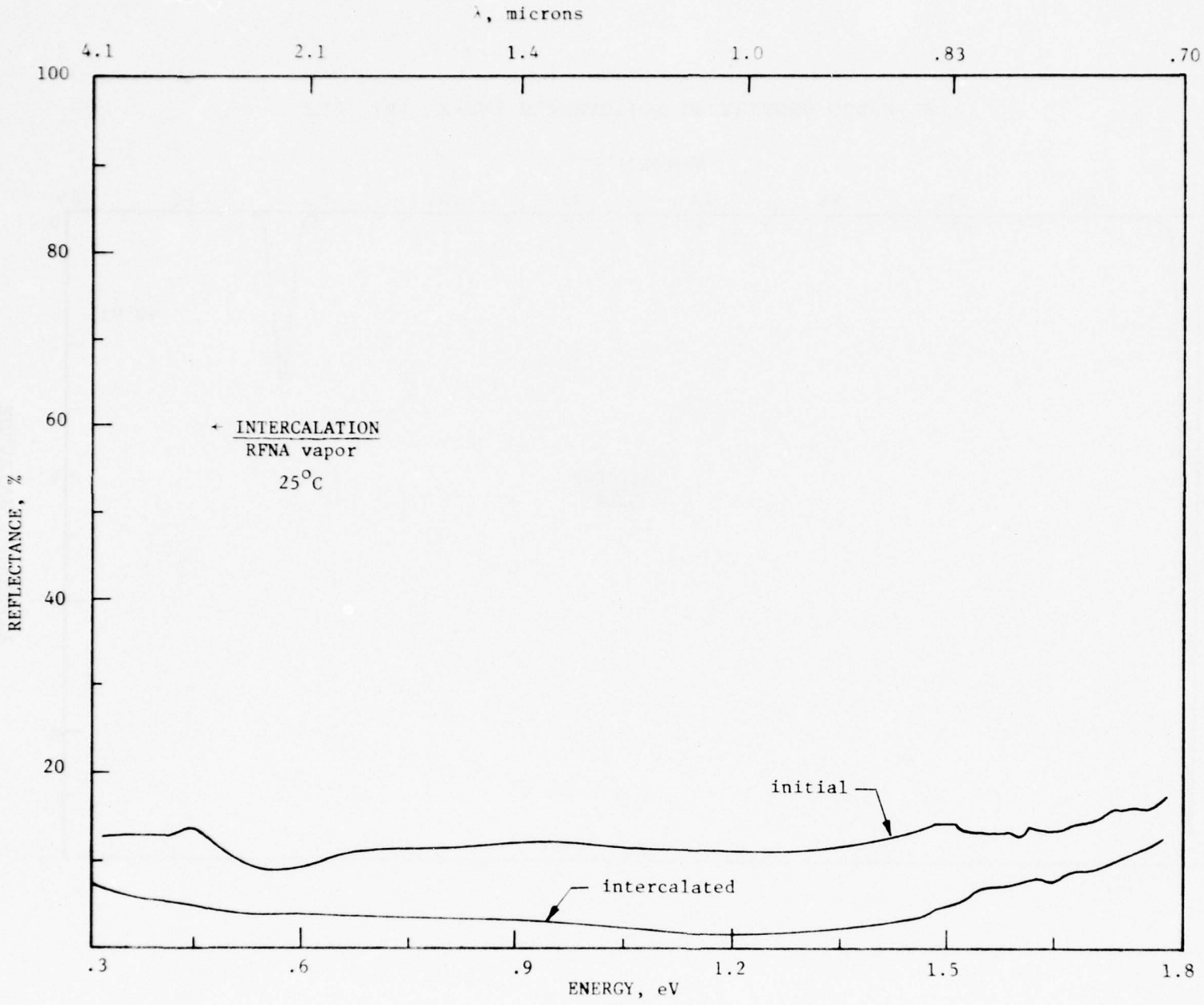


Fig. 13: REFLECTANCE OF HNO_3-GRAPHITE FOIL

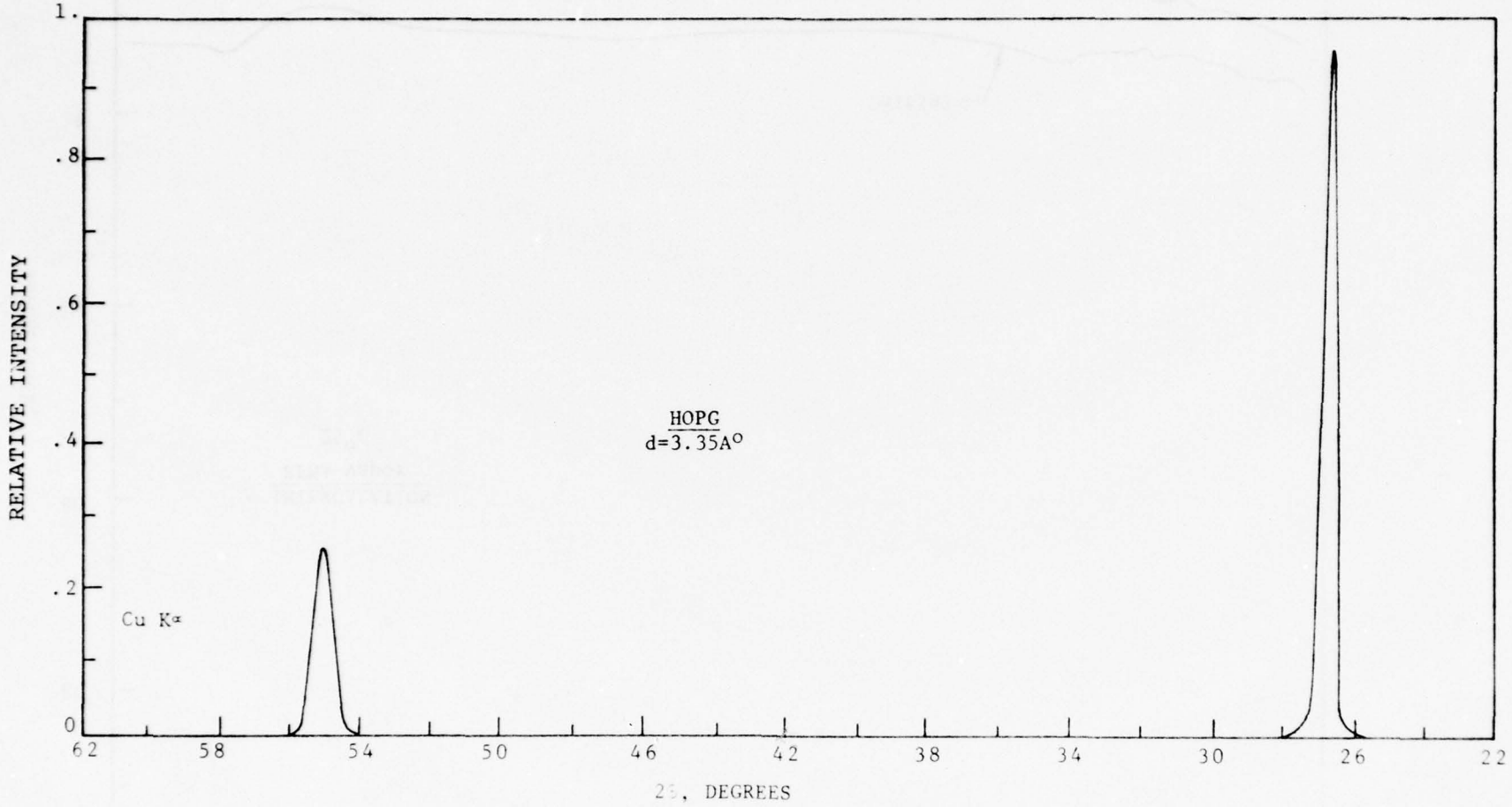


Fig. 14: X-RAY DIFFRACTION OF ALIGNED GRAPHITE

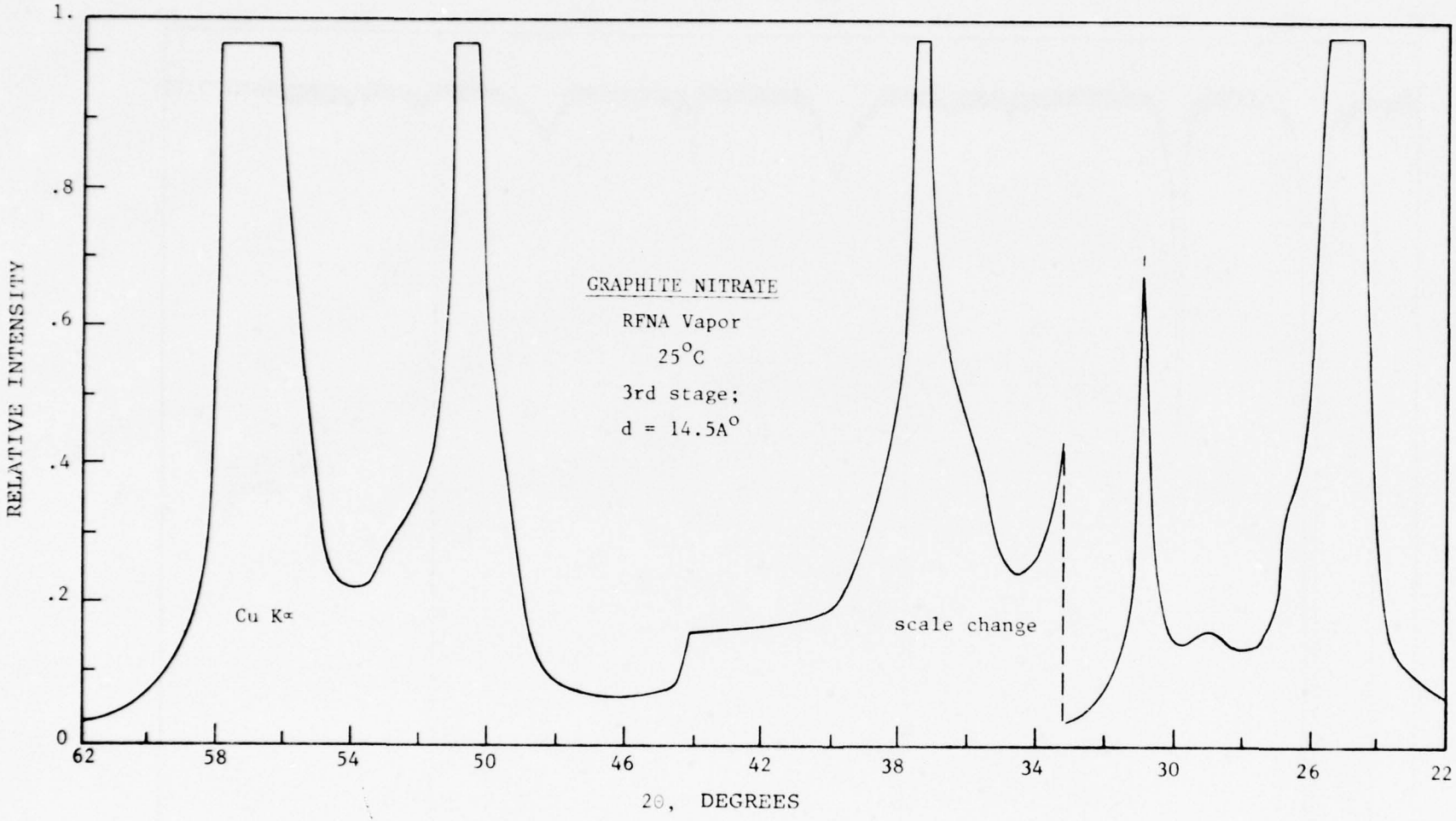


Fig. 15: X-RAY DIFFRACTION OF GRAPHITE NITRATE

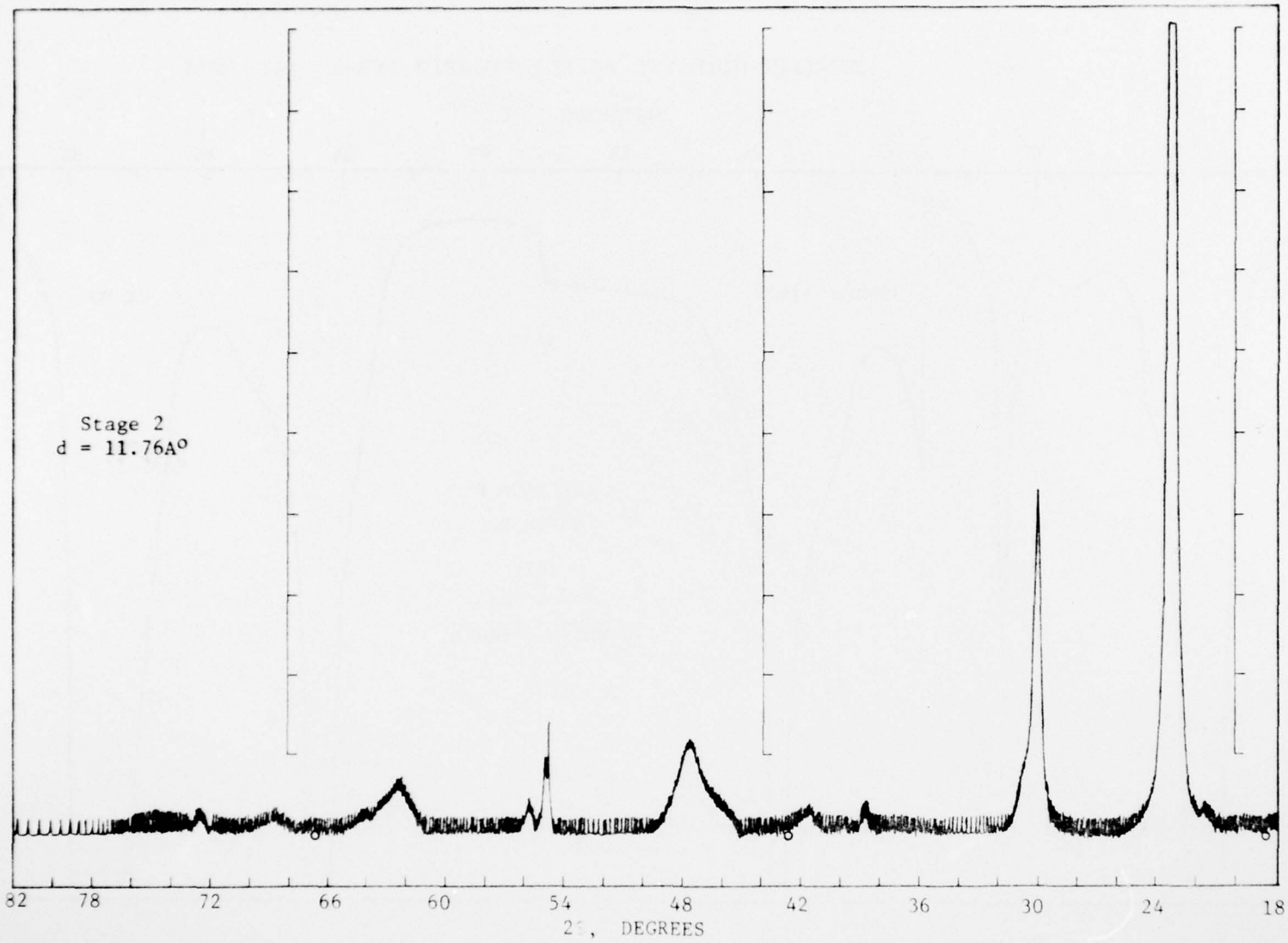


Fig. 16: X-RAY DIFFRACTION OF SbF_5 GRAPHITE

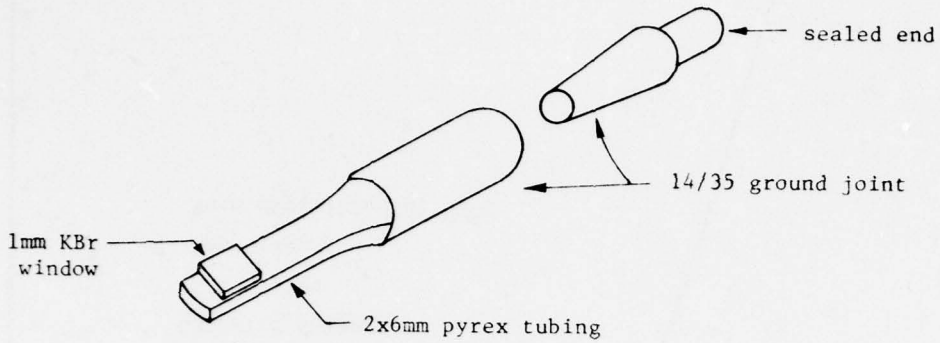


Fig. 17: OPTICAL MEASUREMENT AMPOULE

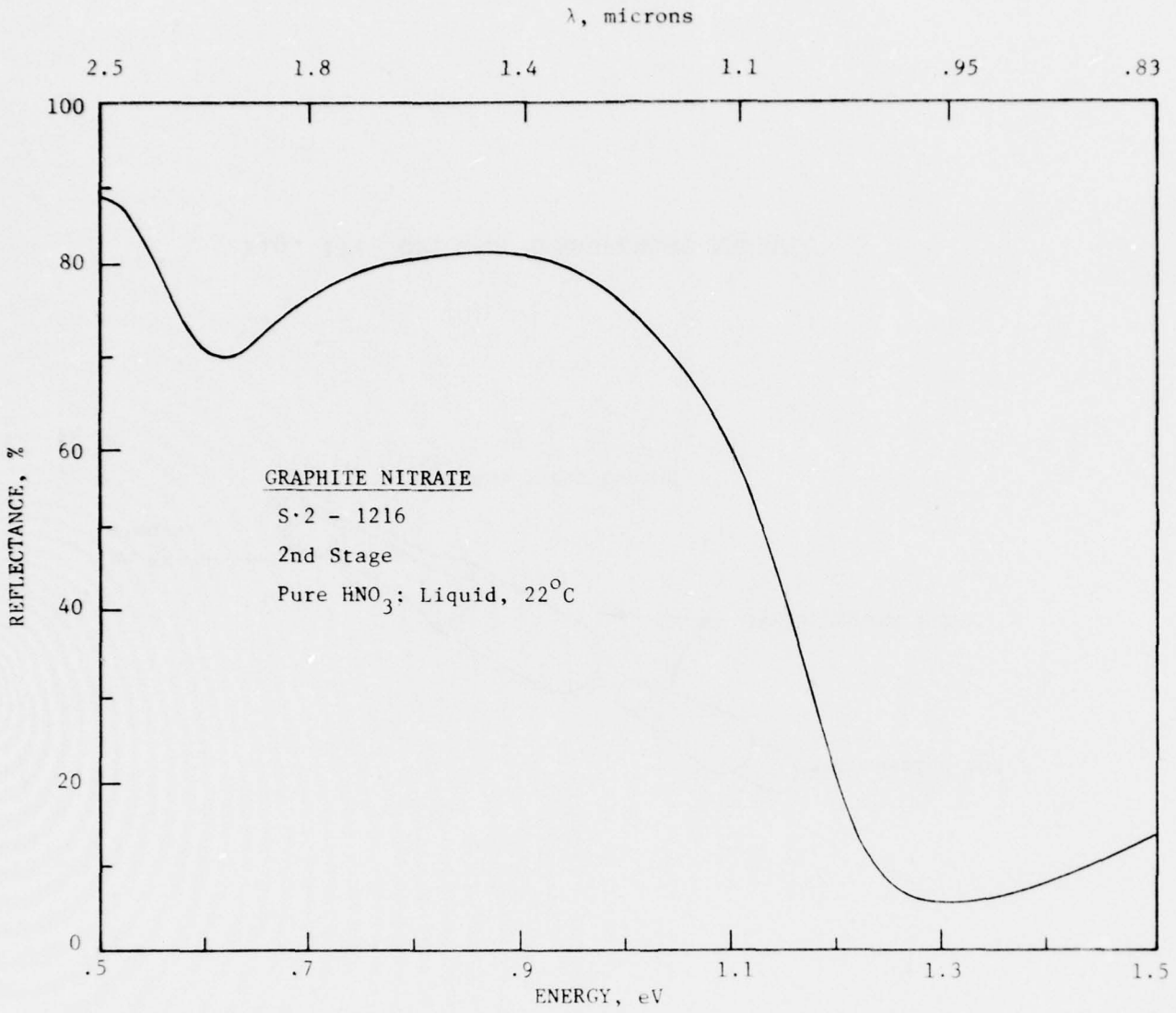


Fig. 18: REFLECTANCE OF GRAPHITE NITRATE

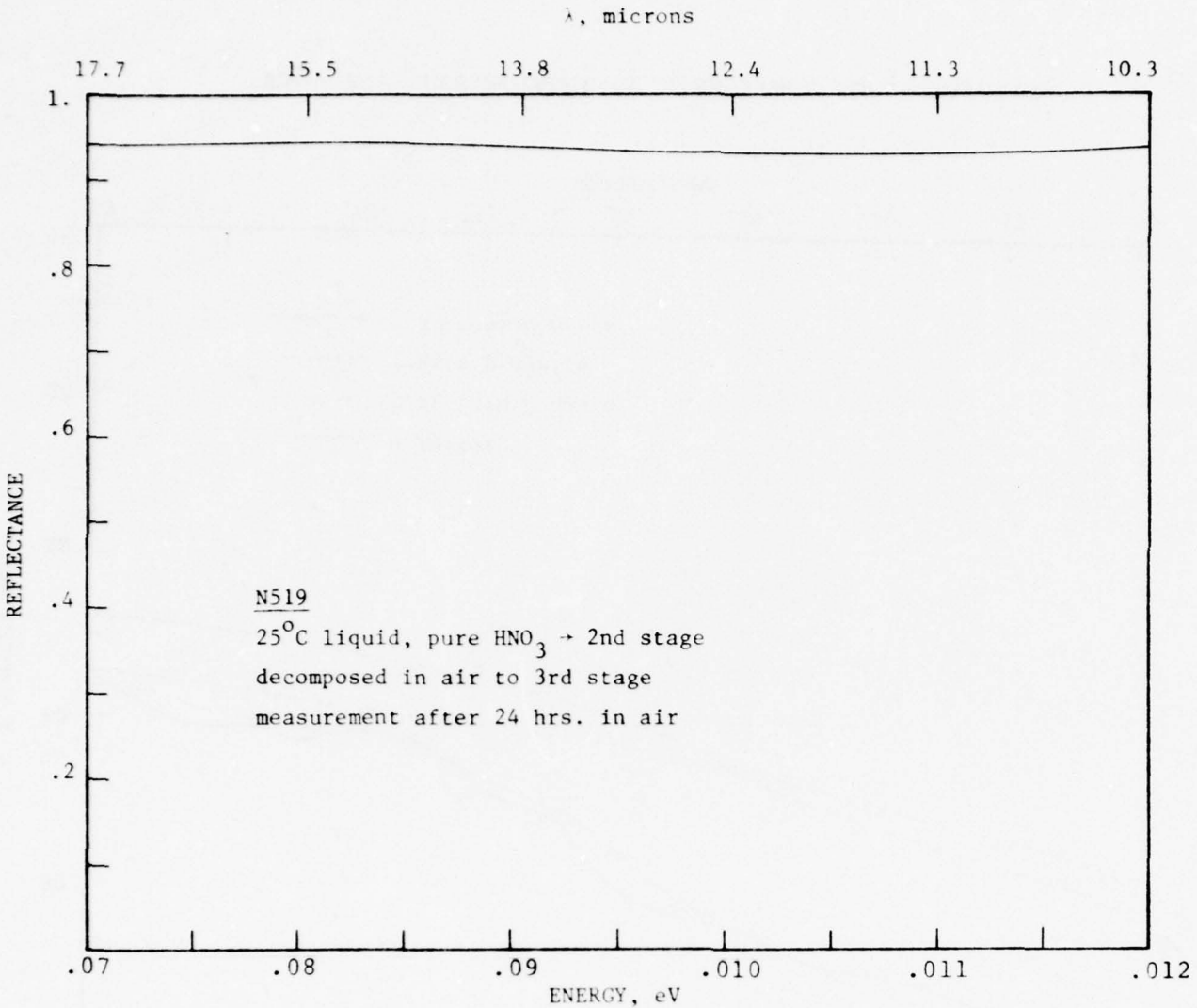


Fig. 19: IR REFLECTANCE OF HNO_3-GRAPHITE

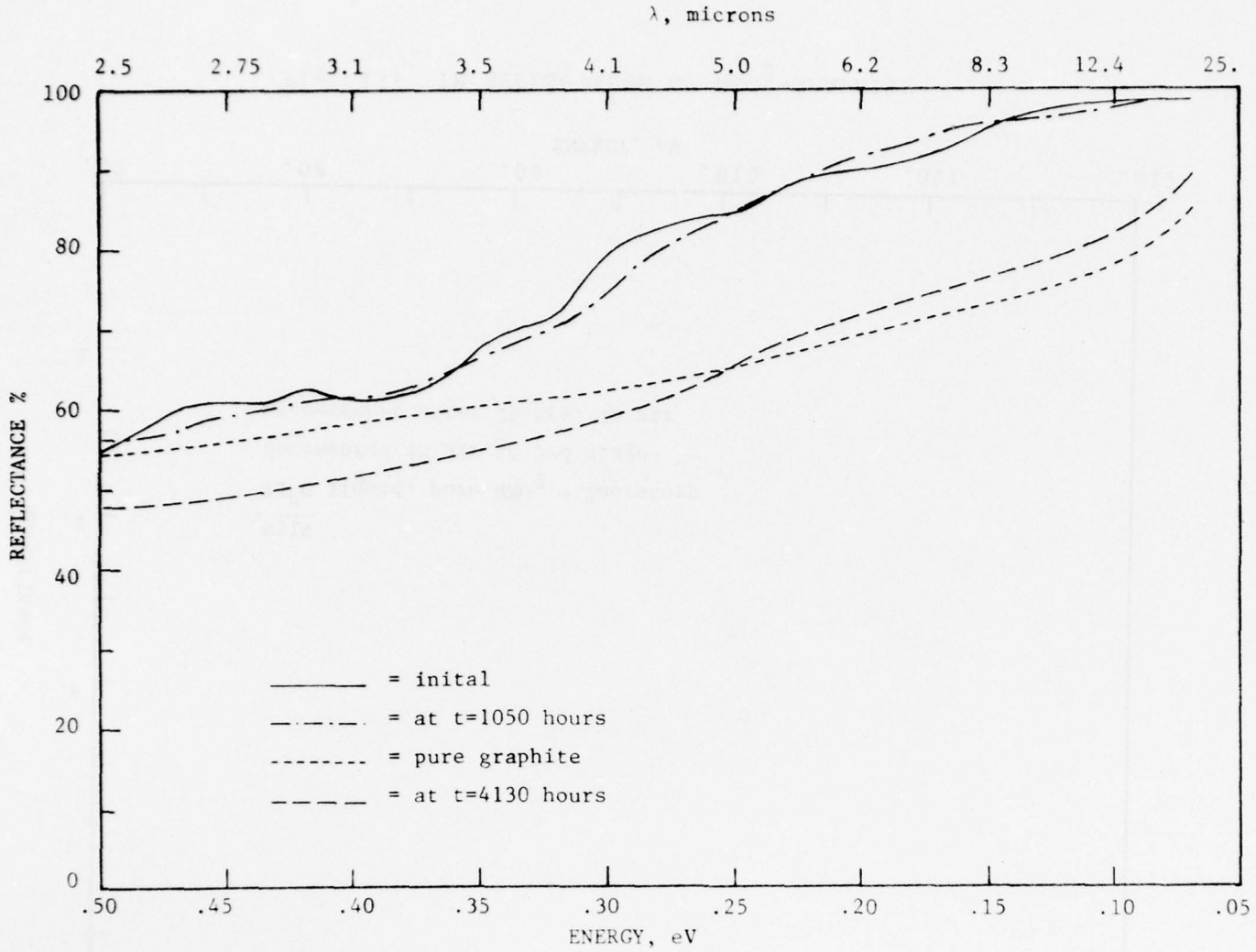


Fig. 20: REFLECTANCE OF HIGH-STAGE SbF_5-GRAPHITE

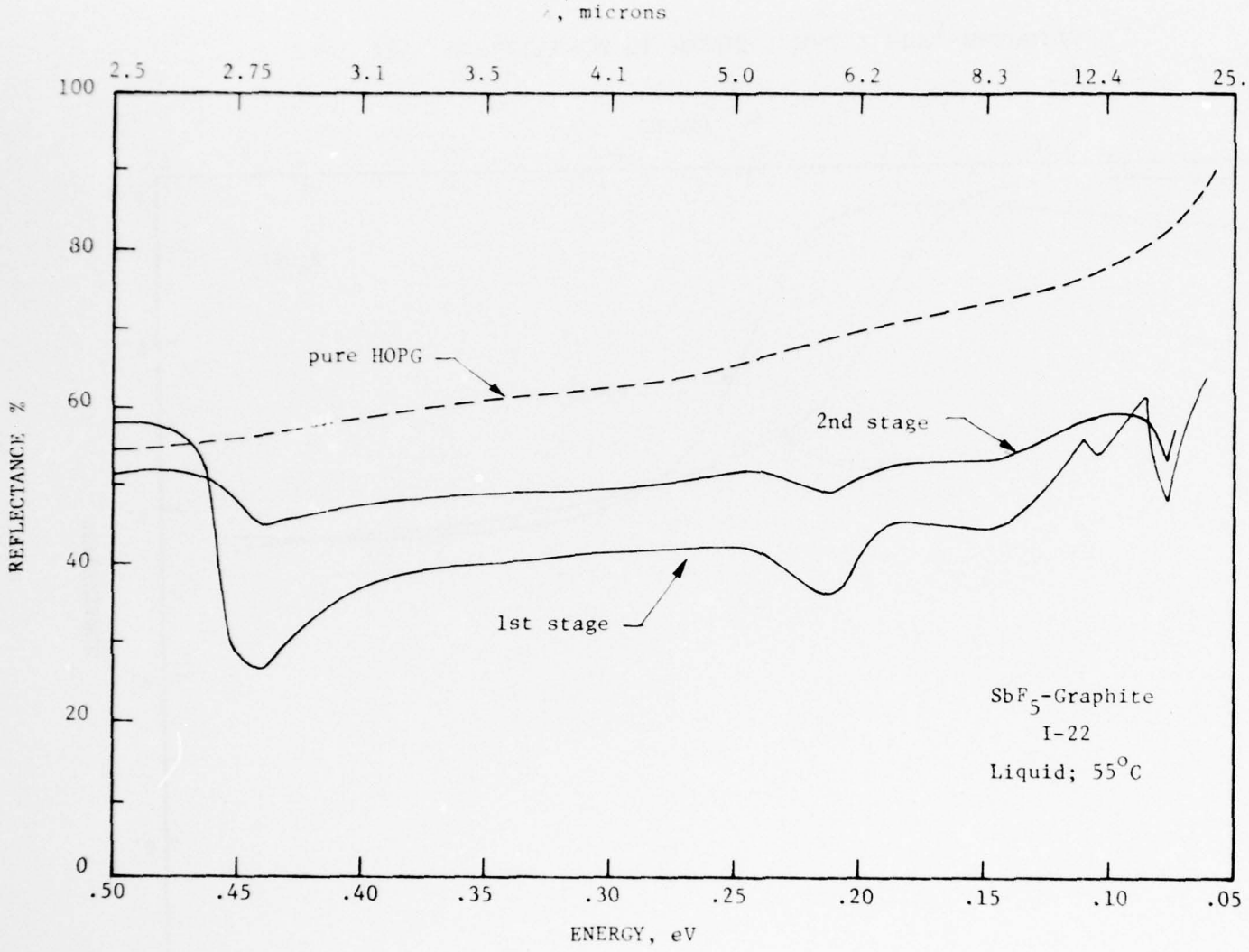


Fig. 21: REFLECTANCE OF LOW-STAGE SbF_5-GRAPHITE

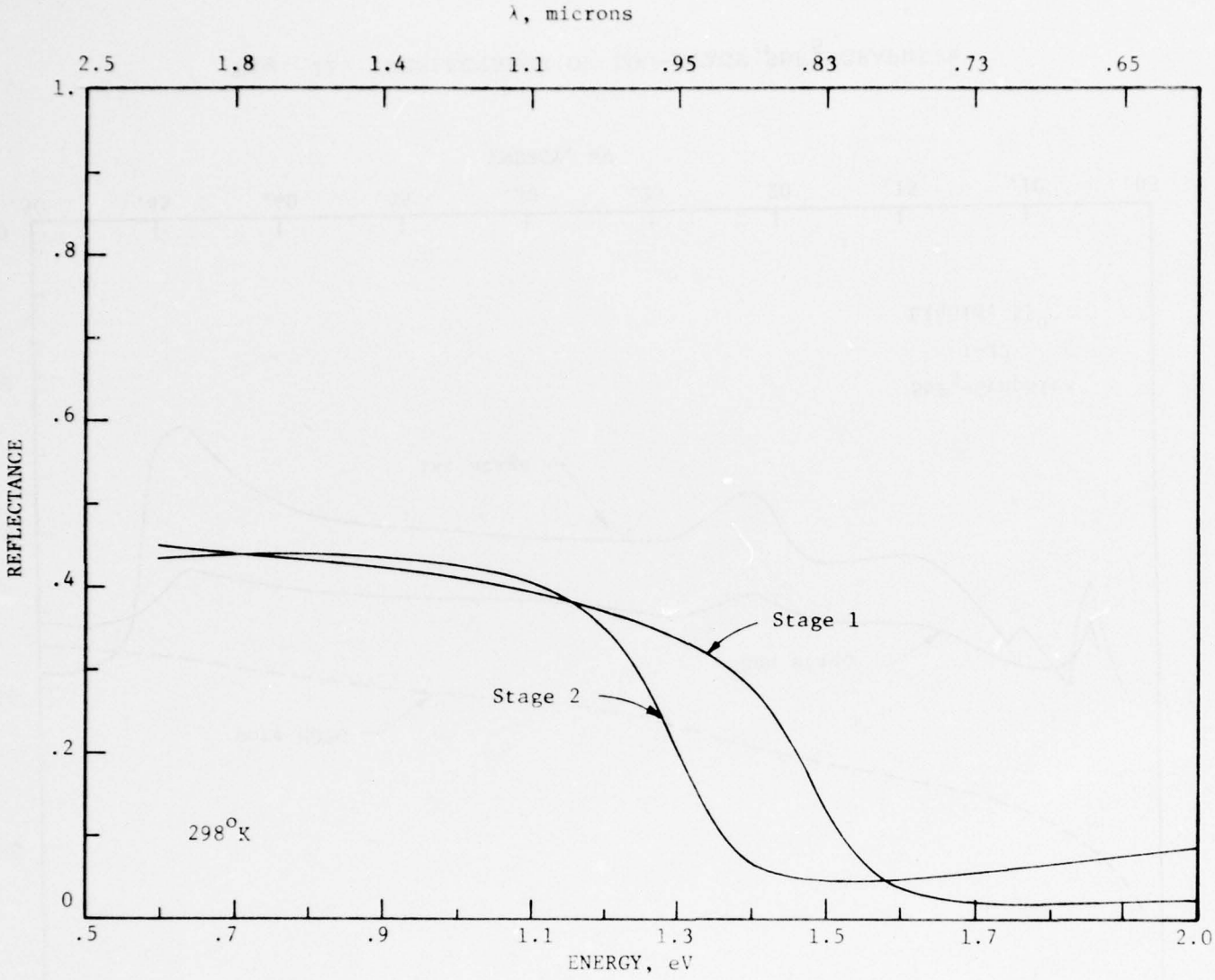


Fig. 22: REFLECTANCE OF STAGE 1 and 2 SbF_5-GRAPHITE

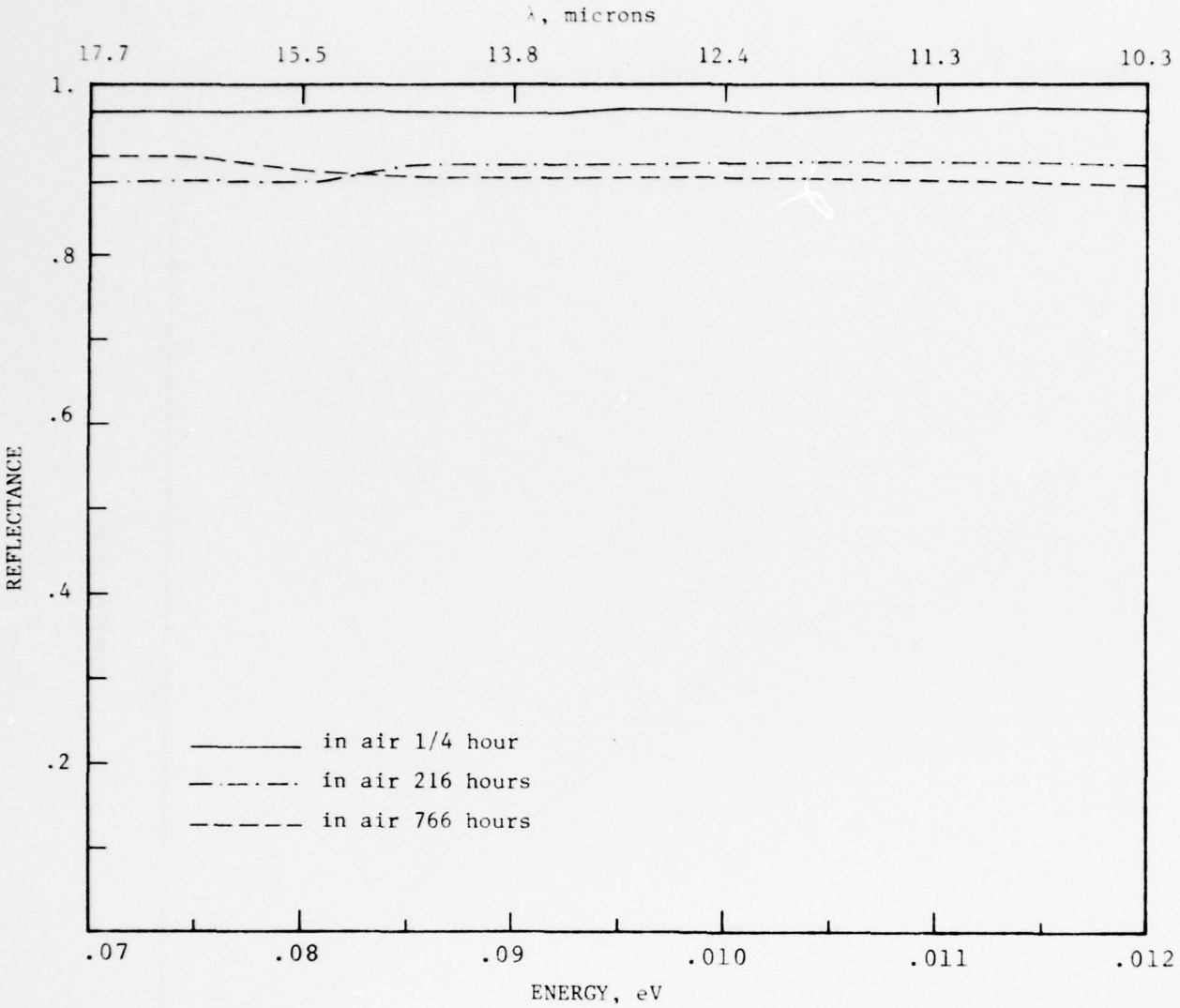


Fig. 23: IR REFLECTANCE OF 4th STAGE SbF_5-GRAPHITE

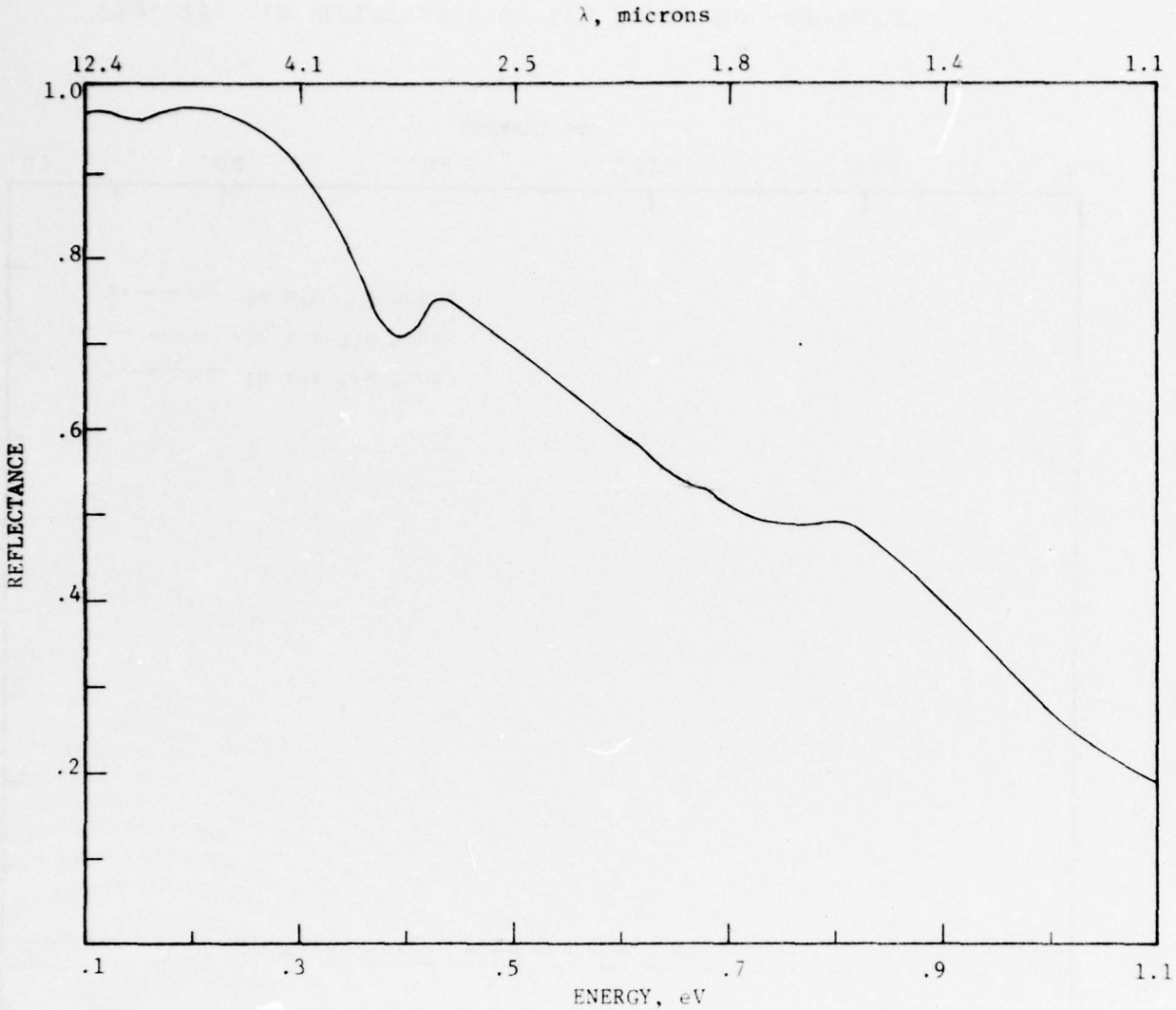


Fig. 24: REFLECTANCE OF 4th STAGE SbF_5-GRAPHITE

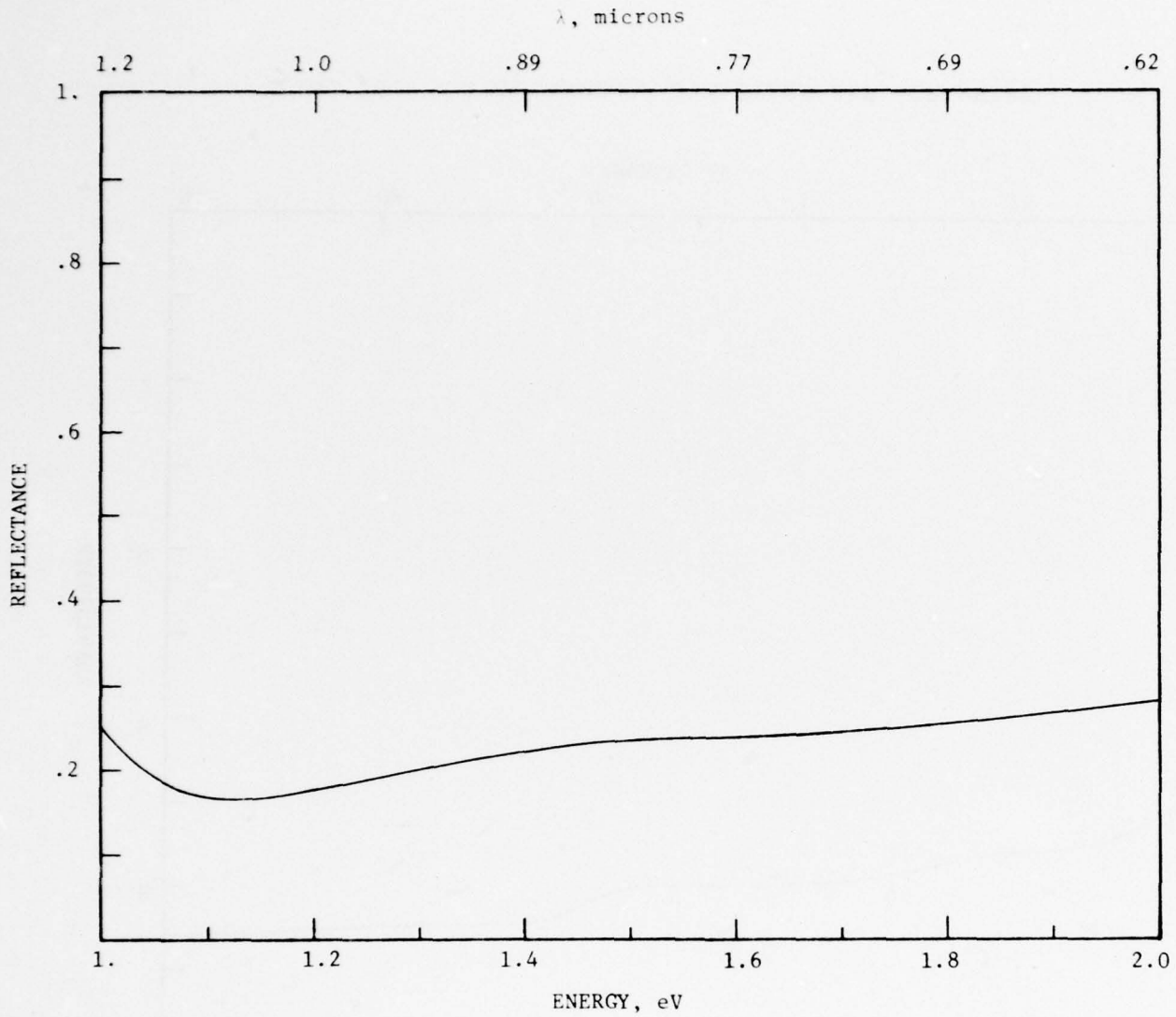


Fig. 25: REFLECTANCE OF 4th STAGE SbF_5-GRAPHITE

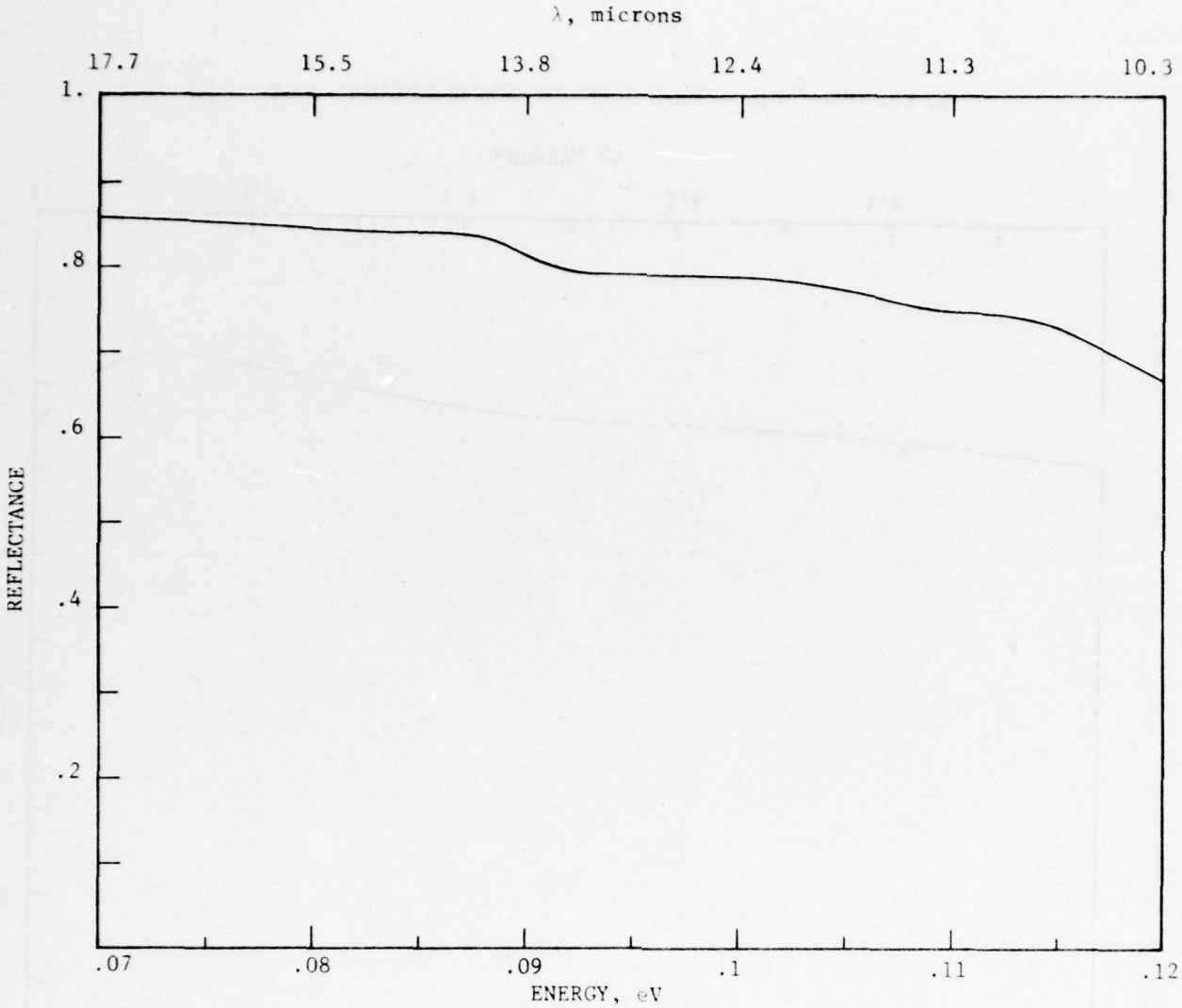


Fig. 26: REFLECTANCE OF 3rd STAGE SbF_5-GRAPHITE

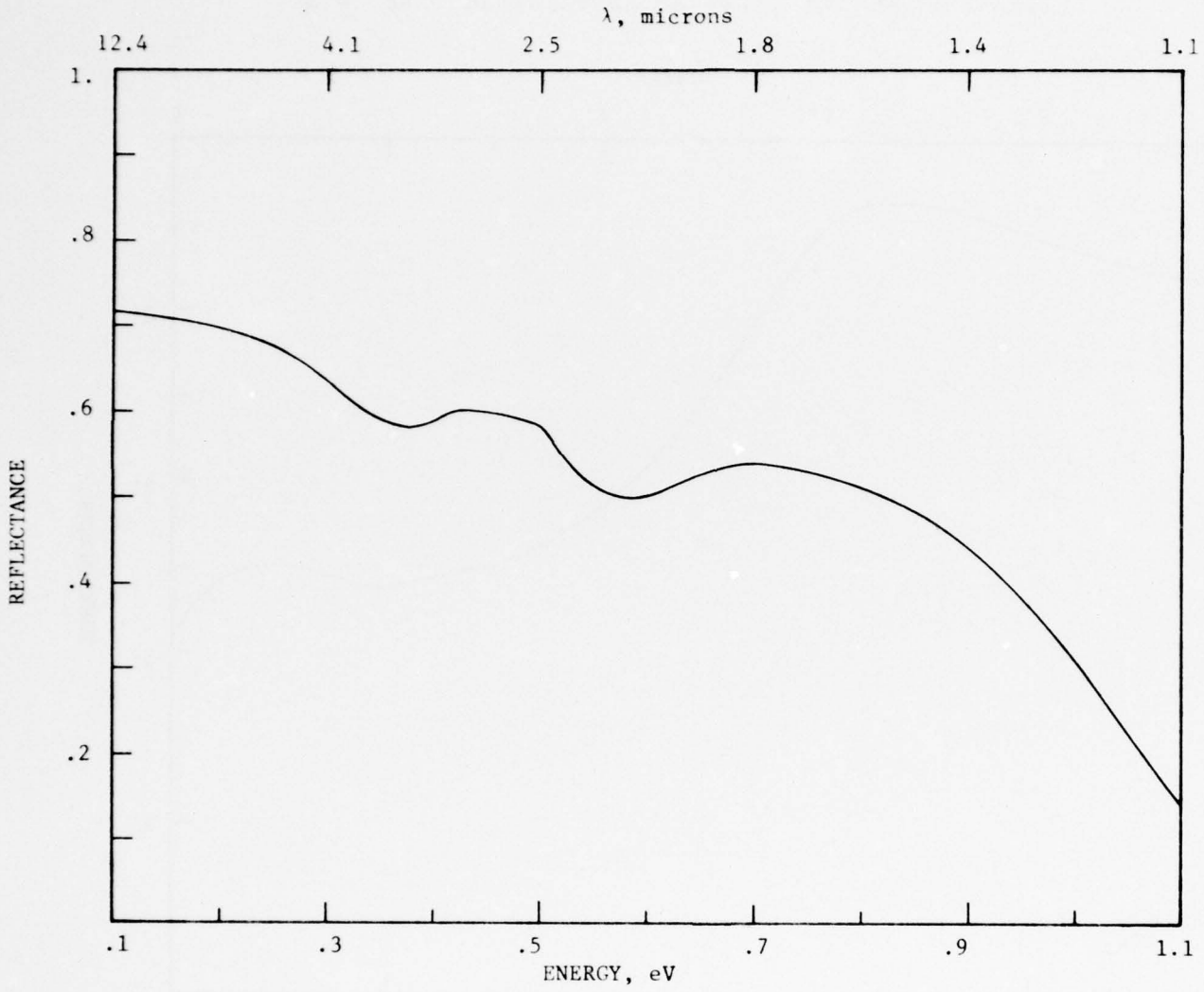


Fig. 27: REFLECTANCE OF 3rd STAGE SbF_5-GRAPHITE

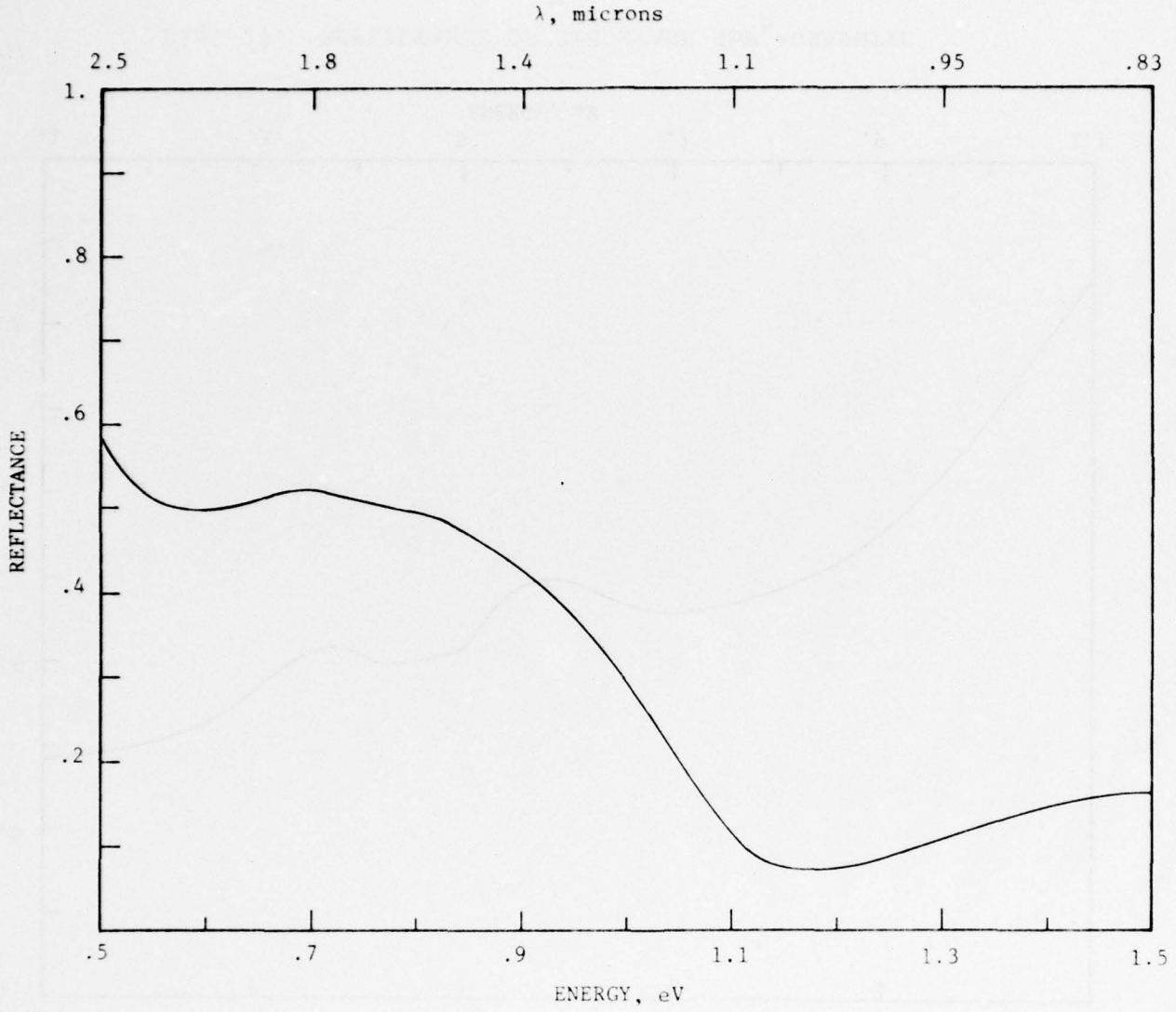


Fig. 28: REFLECTANCE OF 3rd STAGE SbF_5-GRAPHITE

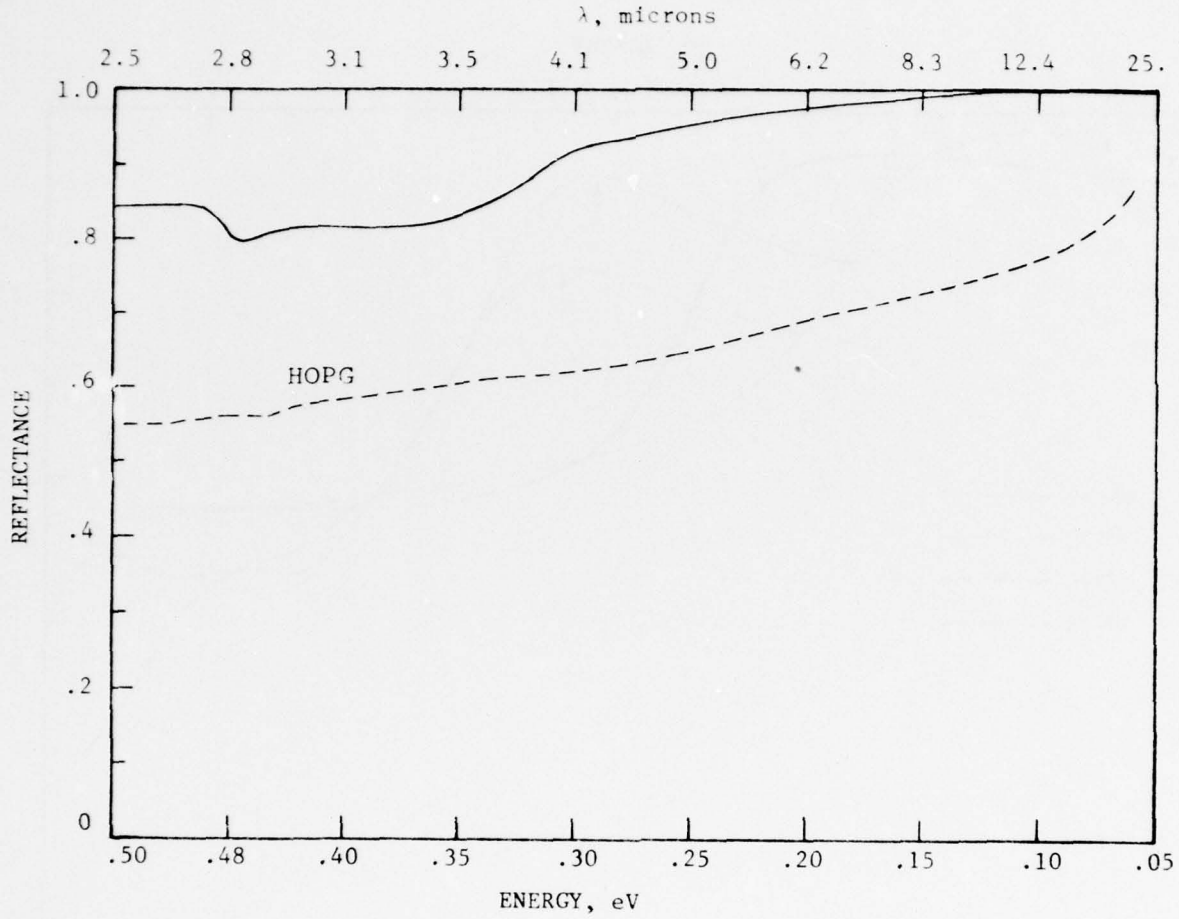


Fig. 29: REFLECTANCE OF SUPERACID-GRAPHITE

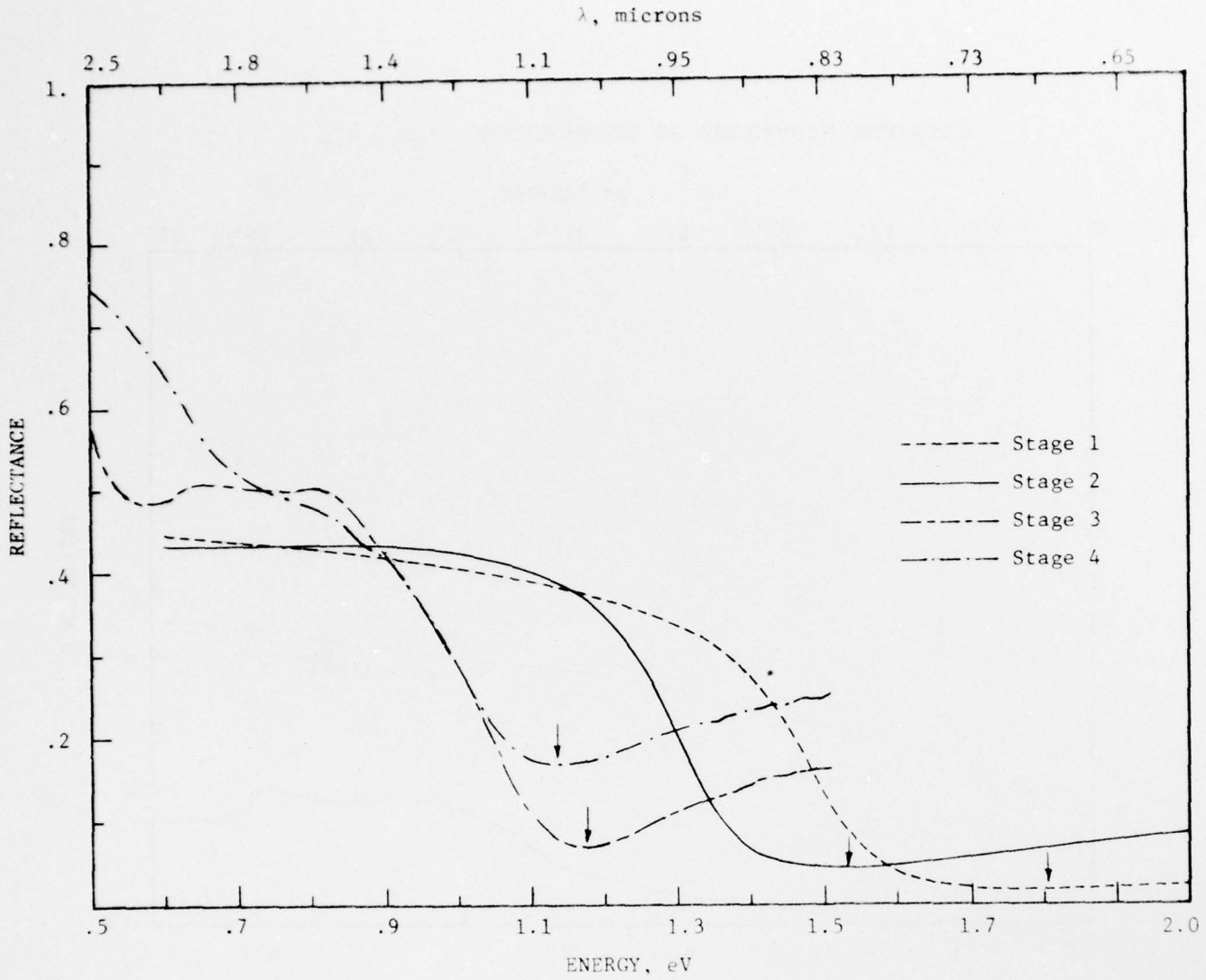


Fig. 30: REFLECTANCE EDGES OF SbF_5-GRAPHITE, STAGES 1-4

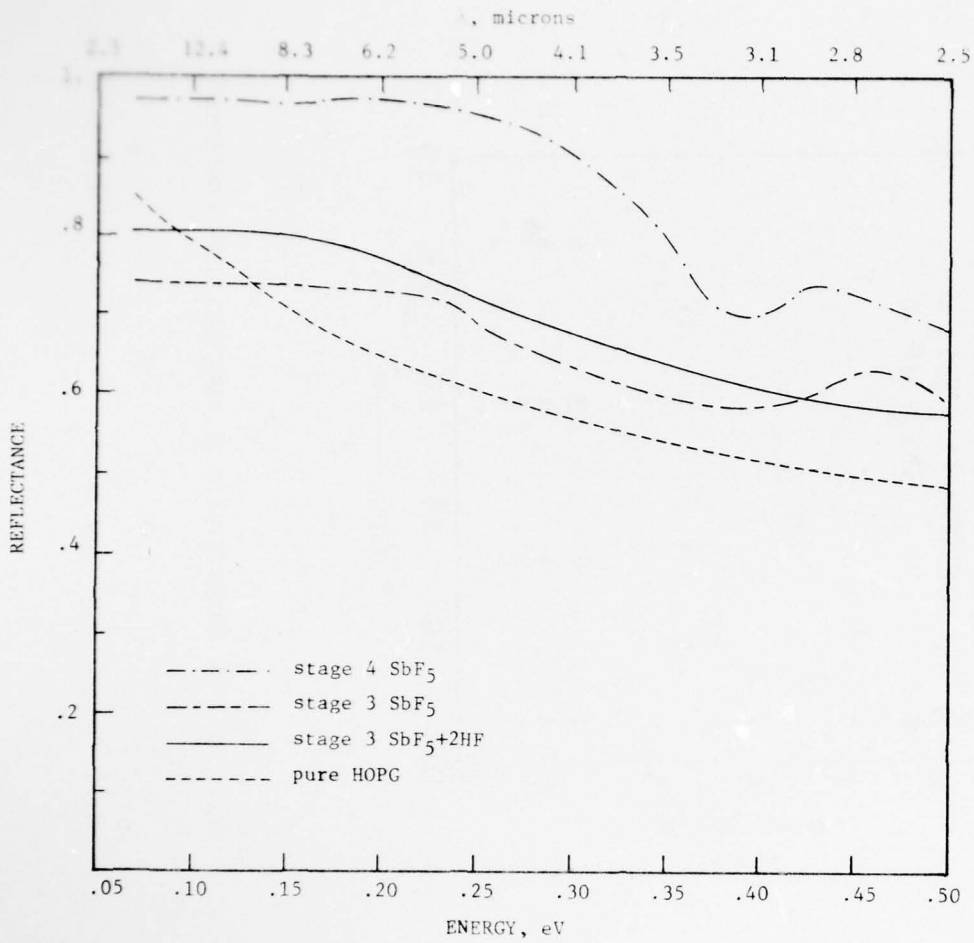


Fig. 31: REFLECTANCE OF SbF_5-GRAPHITE COMPOUNDS

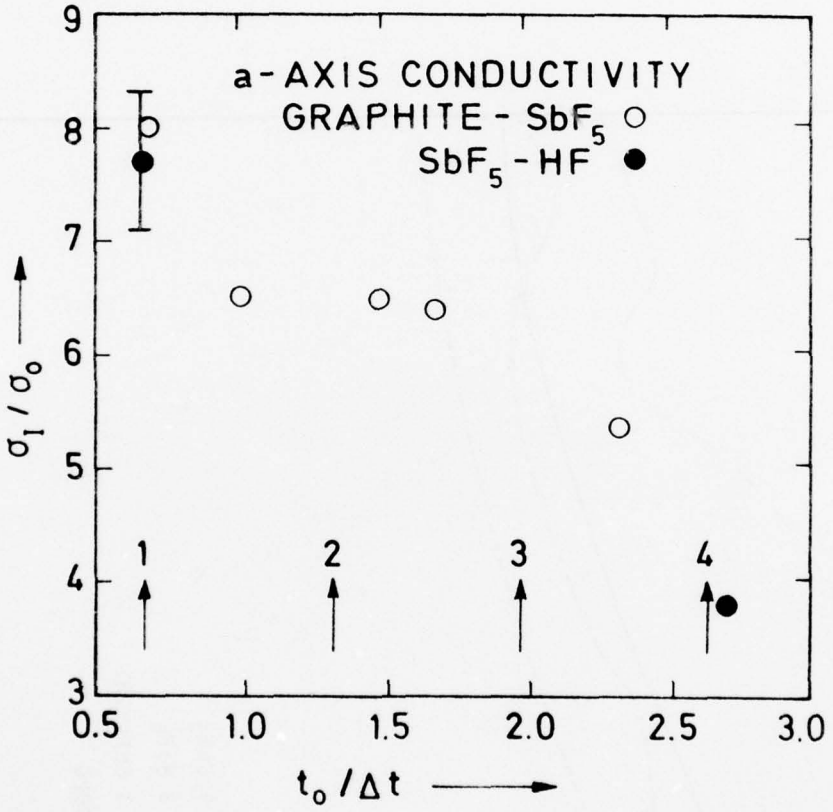


Fig. 32: DC CONDUCTIVITY OF SbF_5-GRAPHITE COMPOUNDS

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