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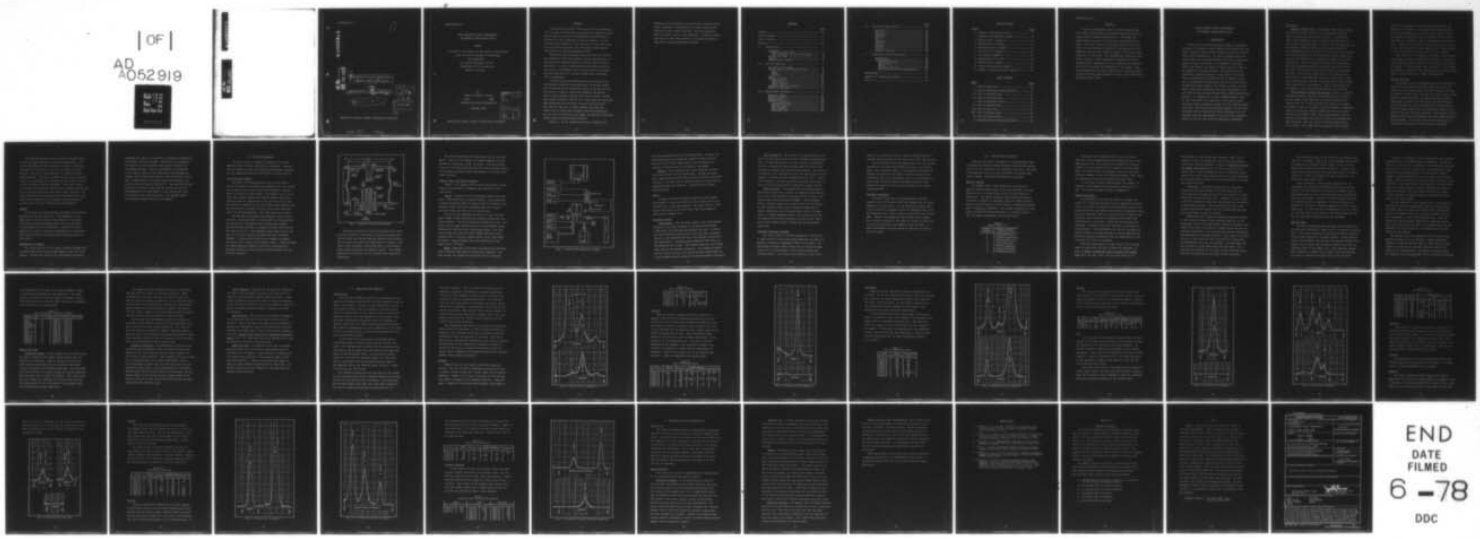

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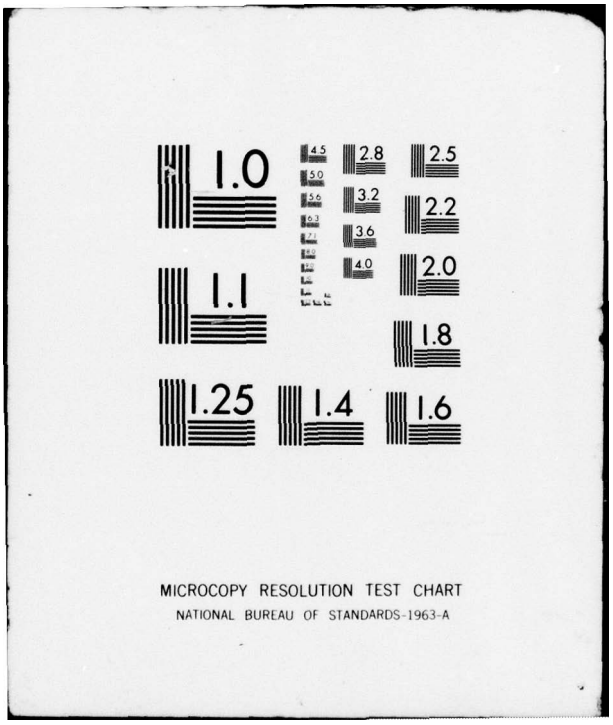
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(6) GLOW DISCHARGE OPTICAL SPECTROSCOPY OF MAGNETIC BUBBLE GARNET FILMS.

THESIS

(14) AFIT/GE/EE/77-12 | (10) Larry D. Crocker
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GLOW DISCHARGE OPTICAL SPECTROSCOPY OF MAGNETIC BUBBLE GARNET FILMS

THESIS

Presented to the Faculty of the School of Engineering
of the Air Force Institute of Technology
Air University
in Partial Fulfillment of the
Requirements for the Degree of
Master of Science

by

Larry D. Crocker, B.S.E.E.
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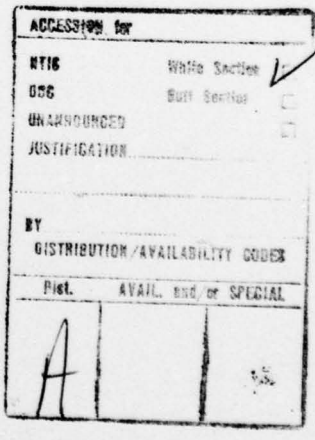
December 1977



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Preface

The project described in this report in the application of a new form of spectroscopy for analysis of magnetic bubble garnet material has been a challenging and educational experience for this fledgling electrical engineer. It was different from anything I ever expected to be involved with as an electrical engineer, and was certainly far removed from anything I anticipated doing at AFIT.

The project was the result of an idea from the fertile and imaginative mind of my sponsor, Doctor Millard Mier, of the Electronics Research Branch of the Air Force Avionics Laboratory. I want to thank him for the concept itself as well as his encouragement and his intervention on my behalf when red tape had to be cut and strings had to be pulled to get things done.

I could never have accomplished the work required for this project without the help and advice of several people. Two technicians at the laboratory deserve a special mention. They are Mr. Donald E. Johnson who prepared the samples and did some excellent machine work for me, and Mr. Jim Ray whose glass work was a work of art. Both these fine gentlemen gave generously and cheerfully of their time and talent. Very special thanks go to Senior Airman Jack Roddy who worked with me frequently throughout the whole experience. His help with the detection and repair of numerous frustrating vacuum leaks was particularly valuable.

Finally, I owe an inexpressible debt of gratitude to

Professor Jerzy Lubelfeld, my advisor and venerable mentor, whose confidence in my ability and eventual success far exceeded my own on many occasions. His retirement from AFIT is a great loss to future students. I consider myself very lucky to have been exposed to his wisdom and philosophy and his unique educational methods.

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Abstract

A basic spectrographic study of seven different magnetic bubble garnet films was conducted using the Glow Discharge Optical Spectroscopy technique. Both argon and krypton gas were used in the discharge for sputtering the films. The lines of most of the major elements within the films were successfully identified in the spectra, but the apparatus used was not sensitive enough to detect any trace impurities in the films. The equipment and techniques used, and the methods of data analysis are explained in detail. Suggestions for improvement of the equipment and techniques are given to increase the usefulness of the system. This study demonstrates the basic feasibility of using the GDOS technique for the characterization of rare earth substituted, epitaxial garnet films.

GLOW DISCHARGE OPTICAL SPECTROSCOPY OF MAGNETIC BUBBLE GARNET FILMS

I. Introduction

The Air Force Avionics Laboratory (AFAL) is presently involved in a program of basic research and advanced development of magnetic bubble digital memory devices for a variety of Air Force applications. The basic building blocks for these devices use epitaxially grown, rare earth substituted, magnetic garnet films grown on a nonmagnetic substrate. These films support the magnetic bubbles which are used as the digital bit storage elements. The quantitative and qualitative characterization of these films, as received from the manufacturers by AFAL for their research, could aid in choosing the best material for use by the Air Force. Of particular value would be the ability to detect the presence of any trace impurities that were incorporated into the films during the Liquid Phase Epitaxy (LPE) manufacturing process. No capability to do this characterization exist at this time within the laboratory. This report covers work done toward providing a method for this material characterization using presently available equipment and the Glow Discharge Optical Spectroscopy (GDOS) technique. The work was done under the sponsorship of the Electronics Research Branch of the Air Force Avionics Laboratory (AFAL/DHR).

Background

Magnetic Bubble Film. The magnetic films used in bubble devices are epitaxially grown on a nonmagnetic substrate wafer of gadolinium gallium garnet (GGG). The growth is from a high temperature melt of yttrium and rare earth trioxides plus Ga_2O_3 and Fe_2O_3 in a flux of PbO and B_2O_3 (Ref. 6). The resulting epitaxial films have the basic formula of $(YRe)_3(FeGa)_5O_{12}$, where Re is any of a variety of rare earths. The relative proportions of the yttrium and rare earths, and the iron and gallium can be adjusted by changes in the melt composition. Among the impurities that can be included in the films during the growth process are lead or boron from the flux or platinum from the crucible used in the process. The exact structure and composition of the films grown by this method is very dependent upon the various growth conditions and parameters, and has a profound effect upon the magnetic properties of the material. This in turn affects the performance of the devices constructed with the material.

Glow Discharge Optical Spectroscopy. GDOS is a recently developed technique used for depth profiling the concentration of dopant atoms implanted into gallium arsenide substrates (Ref. 2). In this process the surface of a sample is sputter etched in an atomic collision process by impinging ions of an inert gas (usually argon) that have been accelerated in an electric field. The atoms sputtered from the surface of the sample are excited in the glow discharge and upon relaxation they emit photons of light characteristic of the atoms. This light can be analyzed by spectroscopic

methods to characterize the excited atoms and hence the surface of the sample. In the depth profiling technique one of the spectral lines produced by the dopant atoms in the plasma is monitored, and the intensity of the line is recorded over a period of time as the surface is sputtered away. This recorded intensity versus time plot is related to the sputtering rate of the sample to give a depth profile of the concentration of dopant atoms in the substrate.

The extension of the process to multiple element detection using a scanning spectroscope to produce an intensity versus wavelength plot similar to conventional spectroscopy is obvious. In this process only the surface of the sample is examined as opposed to the bulk material characterization done in conventional arc or spark spectrography.

Purpose and Scope

The purpose of this investigation was to determine the feasibility of extending the GDOS system for use in the detection of both desired and undesired component elements in magnetic bubble films. An exhaustive search of the literature on sputtering, GDOS, and magnetic bubble material technology, produced no evidence that the GDOS technique has previously been tried for analysis of bubble material. The most common method used for composition studies of the material has been microprobe analysis. This method involves magnetic field mass spectroscopy, and uses costly, specialized equipment. It is also very time consuming, and is relatively insensitive to trace amounts of material.

The GDOS process was tried on several LPE grown films of various types supplied by several manufacturers. The spectra obtained were then analyzed in detail to determine the amount of information that could be obtained by this process. The area of investigation was between 2000 and 6000 Angstroms. This area included the most active spectral lines of the elements in the garnet and was within the range of the available detection equipment. Only small regions of interest throughout the spectrum were recorded and analyzed due to the slow scan rate used to give best resolution. No exact quantitative measurements were attempted at this time. Only the development of the equipment and procedures and an evaluation of their usefulness were accomplished.

Results

The project was only partially successful when measured against the original objectives. The capability of the GDOS system to detect many of the elements in the bubble films was successfully demonstrated, but the sensitivity of the apparatus was not sufficient to detect any trace impurities as hoped. Ideas for modifications to the system that could provide the necessary sensitivity are given in this report.

Organization of Report

The second section of this report contains diagrams and a detailed description of the GDOS apparatus used for these studies. Section III outlines the experimental procedures

developed and used for the studies, including an explanation of the data reduction methods. Section IV is a summary of the results of the analysis of the spectra obtained with the bubble material. The data presentation is primarily in the form of tables of the identified lines arranged by element, and includes some copies of the actual data recordings. Explanations of the data tables and recordings are included with each part of Section IV. The last main section gives the conclusions drawn from the project as well as recommendations for improvements to the system that could be included in any future projects. The appendix gives the cleaning procedure used for the samples.

II. The GDOS Apparatus

In this section, a detailed description of all the apparatus used in these experiments is provided. Included are the details of both the commercially available equipment and the apparatus specially constructed for these studies.

The Sputtering Chamber

The heart of the GDOS system is the vacuum chamber where the elements of interest are sputtered from the surface of the sample and excited in the glow discharge. Figure 1 shows the details of the chamber. The chamber is a 1/4 inch thick pyrex glass cylinder with quartz windows built into opposite sides for observation of the spectrum of the glow. The chamber is sealed with 1/4 inch thick rubber gaskets that are countersunk in grooves in the 1/2 inch thick stainless steel top and bottom plates. All other seals are O-rings.

The top and bottom plates are grounded, and the bottom electrode, insulated from the bottom plate by teflon gaskets, is connected to the negative high voltage power supply. The bottom plate includes a cylindrical shield that encloses the lower electrode. This grounded shield helps confine the glow to the region between the upper and lower electrode surfaces. During actual operation the chamber is wrapped in aluminum foil except for the quartz windows. This increases the light gathering capability as well as providing more grounded shielding to help confine the glow between the two electrode surfaces.

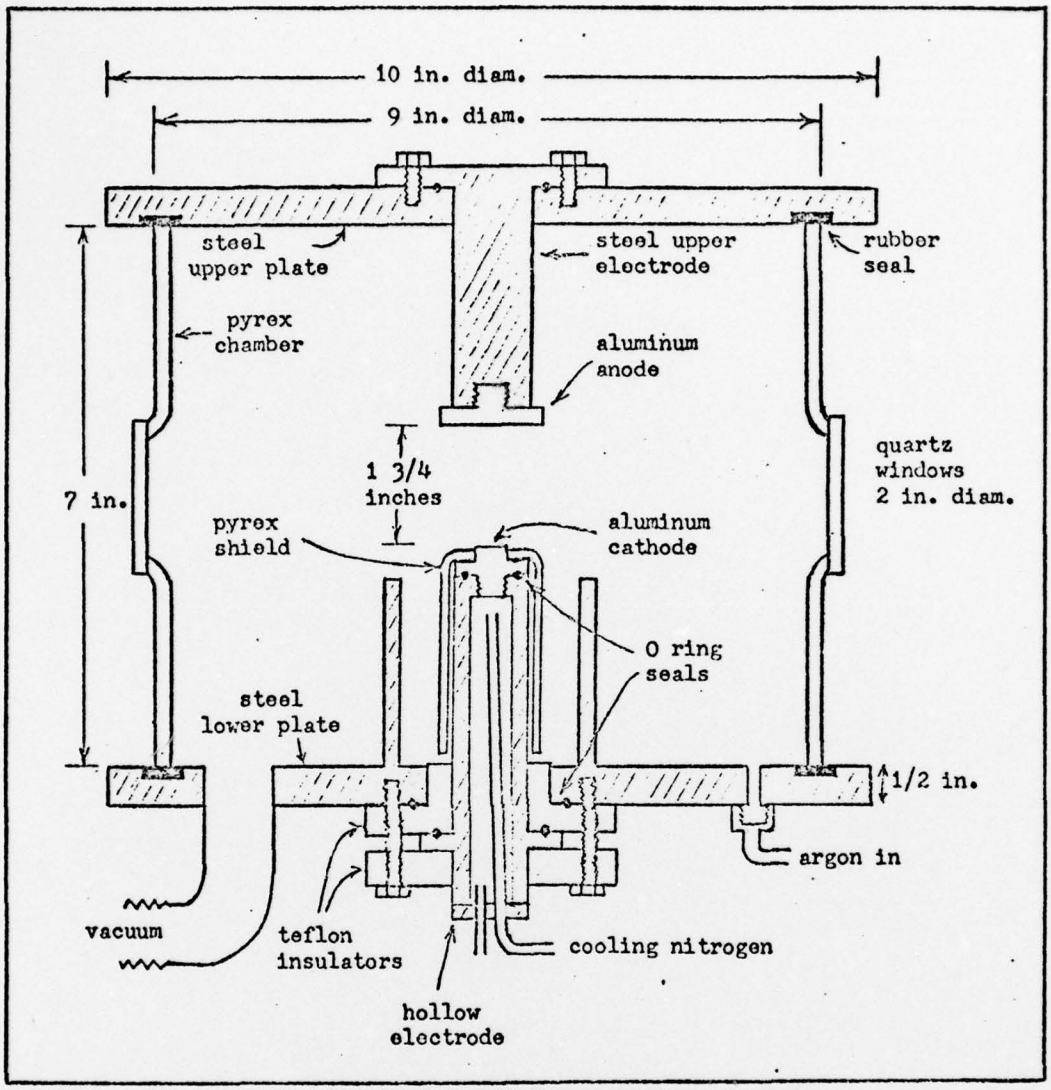

Fig. 1. Diagram of Sputtering Chamber

The lower electrode is hollow and provided with inlet and outlet tubes for circulation of cooling nitrogen gas. Both the anode and cathode caps are machined from aluminum and are easily removable for replacement or cleaning. The entire lower electrode is protected with a close-fitting pyrex shield except for the cathode surface. This shield protects the lower part of the electrode from extraneous sputtering.

The vacuum attachment and argon inlet are on the lower plate. Access to the cathode for sample changing is accomplished by lifting the entire top plate. This also allows removal of the main pyrex tube and the lower electrode shield for frequent cleaning without disassembly of the lower electrode structure.

Vacuum, Argon, and Cooling Systems

Figure 2 is a diagram of the entire GDOS system including the instrumentation, plumbing, and electrical interconnections.

Vacuum. Evacuation of the sputtering chamber was done with a Varian Model PS-10 Pumping Station. This system has a single mechanical pump for roughing and for backing of the diffusion pump, and an oil diffusion pump with a liquid nitrogen cooled cold trap for the high vacuum.

The vacuum was measured directly in the one inch diameter copper tubing connecting the pumping station with the vacuum chamber. Two vacuum measuring systems were used. The medium vacuum range was measured with a Consolidated Vacuum Corporation, Type GIC-110B, thermocouple gauge. The high vacuum range was monitored with a VEECO Instruments Incorporated, RGS-6, Ionization Gauge Control with a Type RG75P ion gauge. Vacuum obtained with this system was of the order of 5×10^{-5} Torr.

Argon. Argon gas of 99.99 per cent purity was provided from a standard high pressure bottle with regulator. Gas flow through the system was controlled with a calibrated

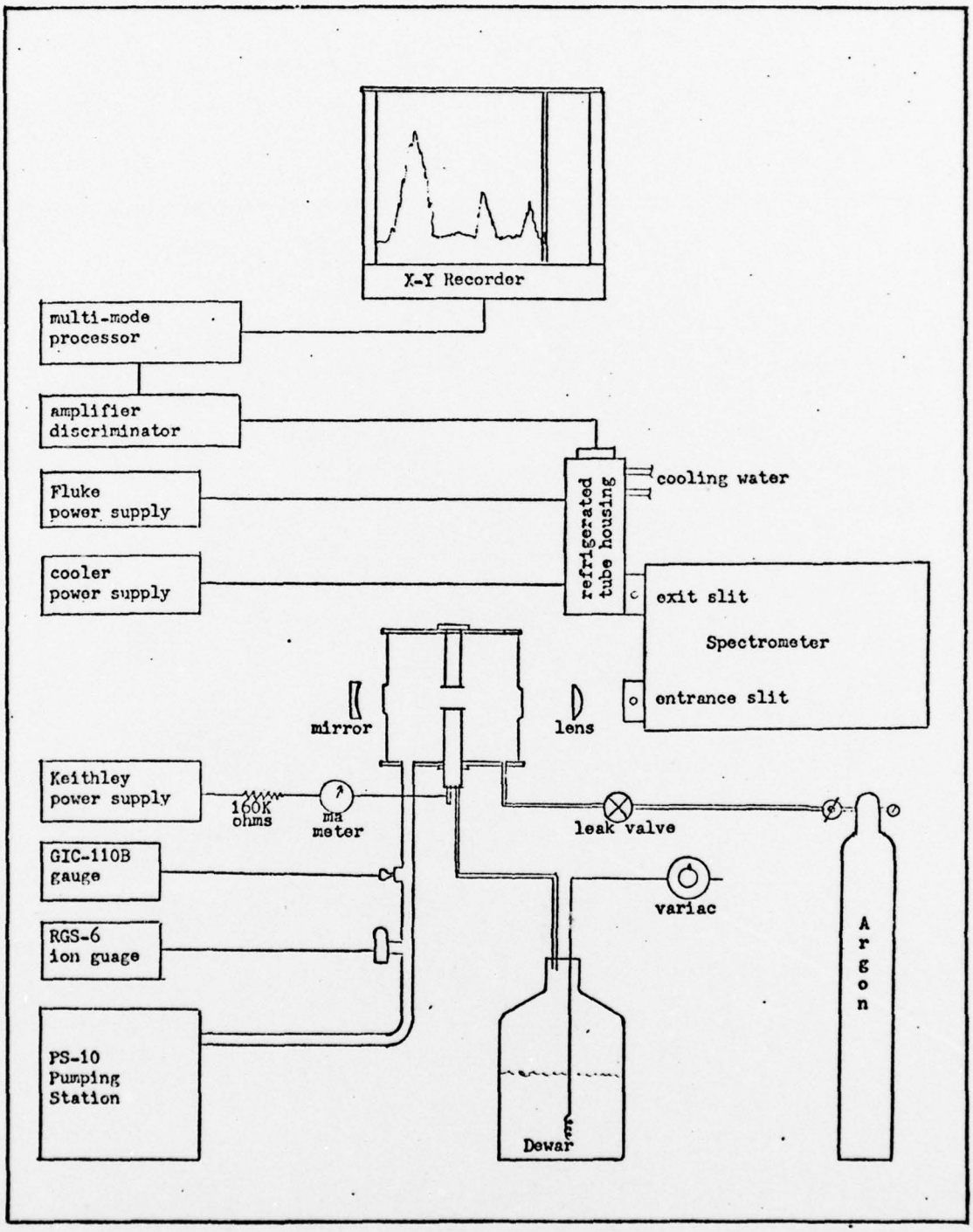

Fig. 2. Complete GDOS Apparatus Diagram

leak valve manufactured by Granville-Phillips. Pressure for these experiments was maintained normally at 25 microns as measured by the thermocouple gauge, and no fluctuations could be observed within the accuracy of the gauge.

Cooling. The cooling for the lower electrode was provided with a flow of cold nitrogen gas. The gas was piped from a large Dewar through teflon tubing to provide electrical isolation. The gas flow was adjusted using a heating element suspended within the Dewar and controlled with a Variac autotransformer.

Optics

A spherical mirror was placed behind the rear window and adjusted to focus the center of the cathode glow on the entrance slit of the spectrometer. The light from the front window was focused on the slit with a two inch diameter, plano-convex, quartz lens.

Detection System

Spectrometer. For the first stage in the spectrographic analysis of the glow discharge in the sputtering chamber, a SPEX Model 1704 scanning spectrometer was used. A Bausch and Lomb diffraction grating with 1200 lines per millimeter blazed at 3000 Angstroms was the active element installed in the spectrometer. Scanning speeds available were from 2 to 1000 Angstroms per minute. The slowest speed was used during these studies for maximum resolution. The variable entrance and exit slits were set at 30 and 60 microns respectively for a good tradeoff between signal level and wavelength resolution.

Light Detection. The output of the spectrometer at the exit slit was detected using an RCA C31034A02 photomultiplier tube. The photomultiplier tube was housed in a thermoelectrically refrigerated tube housing, Model TE-104-RF, manufactured by Products for Research Incorporated. The housing was provided with flowing water for heat dissipation, and was capable of maintaining the temperature below -20° C. With this equipment, the dark count was maintained below three or four counts per second after a sufficient cooling period.

Photon Counter. The signals from the photomultiplier tube were counted using a Model 1120 Amplifier-Discriminator and a Model 1108 Multi-Mode Processor Photon Counter, both manufactured by SSR Instrument Company. This equipment allows variable signal count times of from one microsecond to 1000 seconds, with a pulse resolution capability of twelve nanoseconds, and a maximum signal rate of 85 megahertz. A signal sampling interval of 1/2 second with the two Angstroms per minute scanning rate gave a good compromise between usable signal strength and good wavelength resolution.

Graphical Spectrum Recording

The final output of the GDOS apparatus in the form of a light intensity versus wavelength graph was recorded on a Houston Instruments, Omnigraphic 3000, X-Y recorder. The Multi-Mode Processor Photon Counter has an analog voltage output that is proportional to the counts recorded per counting period. This output was connected to the Y axis

input of the recorder to give a vertical representation of detected light intensity at the exit slit of the spectrometer.

The X-Y recorder moves the graph paper under the recording pen at a constant speed during the scan of the spectrometer. The horizontal scale of the graph was calibrated by placing tick marks on the graph at certain integral wavelengths as read on the wavelength scale of the spectrometer. These light intensity versus wavelength plots were then analysed for spectral lines of the elements in the sample being sputtered.

Additional Equipment

The high voltage for the photomultiplier tube was supplied from a Fluke Model 412B Power Supply with an output capability of 2100 volts. For the sputtering chamber electrodes a Keithley Instruments Model 242 Regulated High Voltage Supply was used, with a range of ±3500 volts at 25 milliamps. Between this supply and the cathode of the chamber was a resistor network of 160 Kohms at 20 watts to limit the ion current and protect the supply in case of shorts. A small milliammeter was also placed in this line to monitor the ion current.

III. Experimental Procedures

This section gives a description of the procedures used to gather data from the bubble material using the GDOS system, as well as the method used for analysis of the data. This was a developmental process as the procedures and methods were tried, changed, and improved throughout the studies.

Material Samples

The samples used in this study were cut from seven magnetic bubble garnet wafers of one inch diameter that were obtained from Dr. Millard Mier of the Air Force Avionics Laboratory. The wafers, produced under several government contracts, consisted of epitaxial layers of bubble material grown by the LPE process on both sides of a gadolinium gallium garnet ($Gd_3Ga_5O_{12}$) substrate. The nominal composition of the films, as given by the manufacturers, is listed in Table I with the sample designation used in this report.

Table I
Garnet Films Used

Sample Designation	Nominal Content of Epitaxial Film
A	$(YLaTm)_3(FeGa)_5O_{12}$
B	$(YEuTmCa)_3(FeGe)_5O_{12}$
C	$(YGdTm)_3(FeGa)_5O_{12}$
D	$(YEu)_3(FeGa)_5O_{12}$
E	$(YEuTm)_3(FeGa)_5O_{12}$
F	$(YSmLu)_3(FeGa)_5O_{12}$
G	$(YSmTm)_3(FeGa)_5O_{12}$

The wafers were originally halved, and one half of each was cut into square pieces four millimeters on a side. These pieces were to be used for all studies for standardization, but they proved to be too small to produce useful data. The final series of successful runs were done with 1/4 wafer samples cut from the remaining halves. This larger size sample proved better for producing useful data.

To avoid any erroneous spectral data from sample contamination, all samples were thoroughly cleaned prior to use. The cleaning method is given in Appendix A.

System Calibration

The preliminary runs with the system to examine the nature of the spectrum obtained from the apparatus indicated a need for closer calibration of the wavelength scale of the monochrometer for successful identification of spectral lines. This was found when some of the strong lines of argon in the glow were found as much as 1.5 Angstroms from where they were expected on the scale. Before any more analysis was attempted, a comprehensive error chart was constructed for the instrument. This calibration was done by recording the spectral peaks in an argon lamp and a mercury lamp and comparing the plotted wavelengths with the values given in the literature for these two elements.

Using the argon lamp as a light source, the 40 strong lines of argon from 3319.3346 to 5650.7054 Angstroms, as given in Tables of Spectral Lines of Neutral and Ionized Atoms (Ref. 5), were found, and the scale error of the

spectrometer at these points was recorded. Next, the 10 analytical lines of mercury from the mercury lamp between 2536.52 and 5769.59 Angstroms, as given in Coincidence Tables for Atomic Spectroscopy (Ref. 4), were recorded and the errors noted. These readings, as well as subsequent sample spectra were taken while scanning from low to high wavelength at two Angstroms per minute with the monochrometer to assure best reproducibility.

Originally, a calibration graph for the instrument using these data was planned, but it was found that the error was very irregular and did not lend itself to a correction graph of any reasonable size. Instead, the error chart of the 50 calibration points was used directly for correction of wavelengths plotted. The corrections were made using linear interpolation between the two closest known spectral line wavelengths of argon or mercury.

During operation, integral wavelength marks were placed on the horizontal scale of the recording manually. As the wavelength scale on the spectrometer reached an integral wavelength point (each 30 seconds at 2 Angstroms per minute) the vertical attenuation of the recorder was switched momentarily from Calibrated to Variable and back. This caused the recording pen to drop below the zero line about 1/8 inch giving an identifiable tick mark on the graph. The wavelength was then written in on the chart under the tick mark. This procedure was repeated at the start of each recording and as often as necessary across the range of each recording.

The horizontal scale of the recording (in Angstroms per inch) is a function of the speed of the scanning spectrometer (in Angstroms per minute) and the speed of the recording paper under the pen (in inches per minute). Using the manually inserted tick marks, this scale was found to be approximately 0.7 inches per Angstrom (7 small divisions on the particular graph paper used).

During analysis of the recorded spectral data, the wavelength of a peak was determined by measuring from the closest tick mark using the 0.7 inches per Angstrom factor. This measurement was then corrected using error information from the error chart. Accuracy using this method was found to be within about 0.2 Angstroms. A better accuracy was obtained if the line of interest happened to be near a known argon line. In this case direct measurement from the center of the argon peak to the center of the unknown peak was used and the error chart correction was not necessary.

Baseline Data

The final preliminary work necessary before analysis of any GDOS data from garnet samples was the recording of baseline data. These data consisted of recordings of spectra obtained from the GDOS system with no sample present. These baseline spectra were compared directly with the spectra obtained from sample runs to verify that the peaks observed were from the sputtered atoms of the sample film. These baseline spectra were expected to contain lines of argon from the discharge and lines of aluminum from sputtering of the electrode.

During the recording of these baseline data one important characteristic of the GDOS system was observed. During the first 20 to 30 minutes of operation of the system the spectrum was very rich in lines, and the glow itself appeared cloudy. During this preliminary period, the ion current steadily dropped to approximately half of its initial value and stabilized. After this period the glow was stable, distinct, and contained in the area between the electrodes, but more importantly the spectrum became clean and contained only lines of argon and aluminum, and a few lines identified as carbon, a common impurity in systems using an oil diffusion vacuum pump in the vacuum system.

For all operations of the system after the discovery of this initial period of instability, both for baseline data and sample data, the system was cleaned with a preliminary period of discharge until the ion current dropped, and the glow stabilized to insure valid spectral data. This procedure was found necessary whenever the system was opened even for a brief period of time. The stabilization time was minimized by careful attention to cleanliness of the electrodes and the samples.

The baseline data were gathered over all areas of the spectrum expected to be of interest. Table II gives the elements of interest and the number of lines used for identification of each of the elements to give an idea of the extent of the data gathered. The amount of baseline data was augmented as work progressed, and the resulting recordings

were assembled into a loose leaf volume arranged in order of increasing wavelength for easy reference. The final volume contained more than 100 pages of reference spectra. This volume and the correction chart represent an important tool for future use of the system.

Table II
List of Elements and Lines Searched

Elements	No. of Lines	Range Covered (in Angstroms)
Boron	3	2496.77 - 3451.41
Calcium	10	2398.56 - 4454.78
Europium	8	3819.66 - 4627.23
Gadolinium	10	3350.48 - 4346.46
Gallium	3	2943.64 - 4172.06
Iron	9	3465.86 - 4078.36
Lanthanum	7	3171.67 - 6249.93
Lead	7	2169.99 - 4057.82
Lutetium	10	2615.42 - 6221.87
Platinum	7	2659.45 - 5301.02
Samarium	10	3609.49 - 4467.34
Thulium	9	3131.26 - 4359.93
Yttrium	5	4077.37 - 4674.85

Bubble Film Data

Preliminary Steps. During operation of the GDOS system the inner surfaces of the chamber become coated with the products of sputtering. Prior to any series of runs the pyrex chamber and windows and the electrode shield were cleaned thoroughly with potassium hydroxide. The electrodes were also polished to a smooth surface and cleaned using the same procedure used to clean the samples. After this cleaning, the chamber was evacuated for several hours and then run under plasma for 20 to 30 minutes to thoroughly clean the electrodes and outgas impurities.

The chamber was then vented with argon and the sample was placed at the center of the lower electrode. After reevacuation, the argon flow was set with the leak valve and the system was again operated for 20 to 30 minutes until the glow and current stabilized. During this stabilization period some arcing occured around the edges of the sample, but this arcing stopped as the sharp edges causing localized concentration of electric field were sputtered away.

Also during this stabilization period the surface of the sample became slowly covered with a characteristic glow quite distinct from the overall argon glow. The color of this glow varied from sample to sample, typically having a greenish tint. With prolonged sputtering the epitaxial film was completely sputtered away, and the glow from the sputtering of the GGG substrate had an orange color.

Standard Conditions. The standardized conditions used throughout these experiments were with the electrode power supply set at -3500 volts and the leak valve adjusted for 25 microns of argon pressure. This resulted in an ion current of 2.5 milliamps after the initial stabilization period. The spectrometer entrance and exit slits were set at 30 and 60 microns respectively. The counting period of the Multi-Mode Processor Photon Counter was set at 1/2 second, and the analog output of the counter and the vertical input of the recorder were set so that the vertical scale of the recorder represented 100 counts per inch.

Data Recording. The areas of the spectrum containing the lines of the elements of interest were recorded in a series of runs using the standard conditions given. These areas included both those with lines of the known elements in the film and those with lines of the suspected impurities. These recordings produced hundreds of pages of raw data for analysis.

Data Analysis. The spectral recordings were compared to the baseline data and to each other to find lines of interest. These lines were then measured as accurately as possible and identified using the two previously mentioned spectral line tables (Ref. 4 and 5) and the more comprehensive work, Massachusetts Institute of Technology Wavelength Tables, (Ref. 3). These data were then tabulated by element and sample to facilitate cross reference.

Additional Data. In addition to the many recordings made with argon gas, one was made using krypton gas for sputtering of the sample. A small cylinder of krypton gas was obtained and connected to the system in place of the argon gas cylinder. A short run was made with sample C using the same standard conditions as the other runs. The spectrum obtained was then compared to the same spectrum obtained using argon gas.

IV. Results of Data Analysis

Introduction

This section contains a summary of the analysis of the spectral recordings obtained with the GDOS apparatus using the garnet film samples. Because of time constraints, not all the possible lines of all the elements in all the samples could be searched for, but the number of data recorded and analyzed represents a large sampling of the stronger lines. The data, representing identified lines, are arranged in tabular format with the tables listed according to element. Each table is accompanied by a brief explanation of the data, as well as figures of some of the actual recorded data that are of particular interest.

In the tables, the entries give the maximum values of detected peaks in units of counts per 1/2 second. An entry of ND indicates that no peak could be detected at the given point, and an empty entry indicates that no data were taken at that particular point. In the figures showing copies of the actual X-Y recorder output, the horizontal scale is wavelength with seven small divisions equal to one Angstrom, and on the vertical scale, one inch is equal to 100 counts per 1/2 second.

The intensity figure given for the lines in the tables is the spark spectrum relative intensity figure for the line as given in the spectral table literature. This intensity and the GDOS signal level show only very rough correlation, as would be expected considering the difference in the

excitation methods. For this reason and because of some additional equipment limitations, no useful quantitative information about relative concentrations of elements can be derived using the present GDOS system. The same data from the same sample taken on different runs show a marked difference in amplitude. The adjustment of the optics (the mirror and lens) is very critical, and a slight movement of either causes a large variation in signal level. Also, as sputtering proceeds the windows become obscured, and the signal level slowly decreases.

Any significant improvement in quantitative information would require modifications to insure standard sputtering, detection, and recording conditions for adequate intensity calibration across the spectrum of interest. With these improvements, quantitative information could then be obtained by comparison of line strengths of elements of known concentration and those of unknown concentration within the sample, and by comparison with spectra obtained from standard samples under standard conditions.

Calcium

Sample B was the only sample tested that contained calcium. The line at 4226.73 Angstroms was strong and easy to measure because it was near a known argon line at 4228.16 Angstroms. Figure 3 is a copy of this area of the spectrum from sample B compared to the baseline spectrum. Table III gives a summary of the calcium data obtained using sample B.

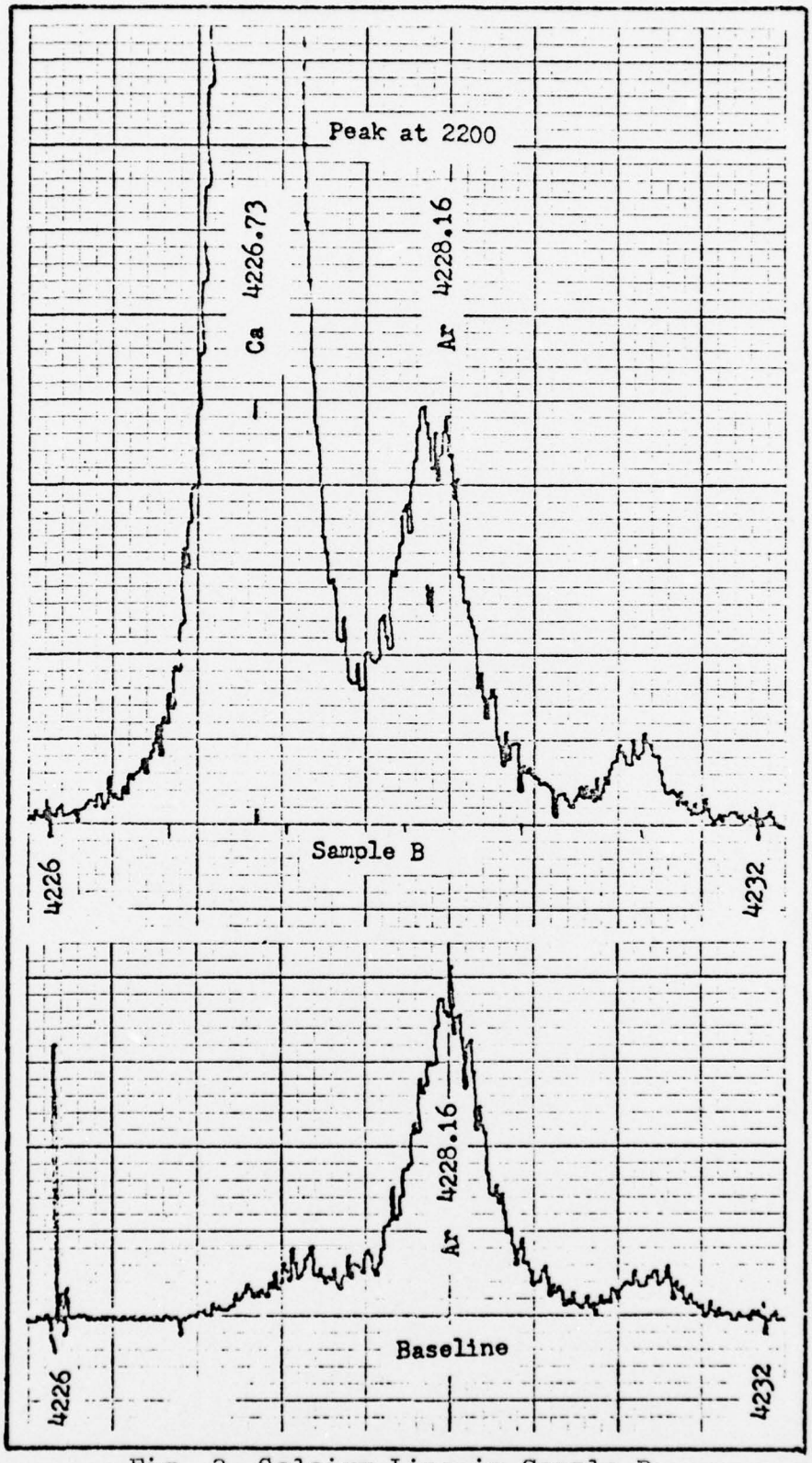

Fig. 3. Calcium Line in Sample B

Table III
List of Calcium Lines

Line Wavelength	Spark Intensity	GDOS Counts Sample B
3933.67	600	400
4226.73	50	2200
4425.44	20	line obscured
4434.36	25	line obscured
4454.78	5	50

Europium

When the lines of europium were first analyzed it appeared that the line at 3819.66 Angstroms was the most useful line, but the spectrum obtained with sample A, which was known to contain no europium, also contained this line. It was concluded that the peak was more likely caused by the 3820.73 Angstrom line of iron. This misidentification points up the need for a more accurate spectrometer if the system is to be of practical use. The line at 4205.06 Angstroms did not appear in the spectrum of sample A and therefore it should be a useful line for measurement of europium. Figure 4 is a copy of one of the spectra with this line. Table IV summarizes the europium data.

Table IV
List of Europium Lines

Line Wavelength	Spark Intensity	GDOS Counts			
		Sample B	Sample D	Sample E	Sample A
3819.66	500	390	180	70	370
3907.11	500	60	40	ND	-
3971.99	-	ND	-	-	-
4129.74	50	line obscured by Y line at 4128.30			
4205.06	50	200	450	-	ND
4435.60	100	ND	-	-	-
4494.02	200	55	ND	100	-
4627.23	15	ND	-	-	-

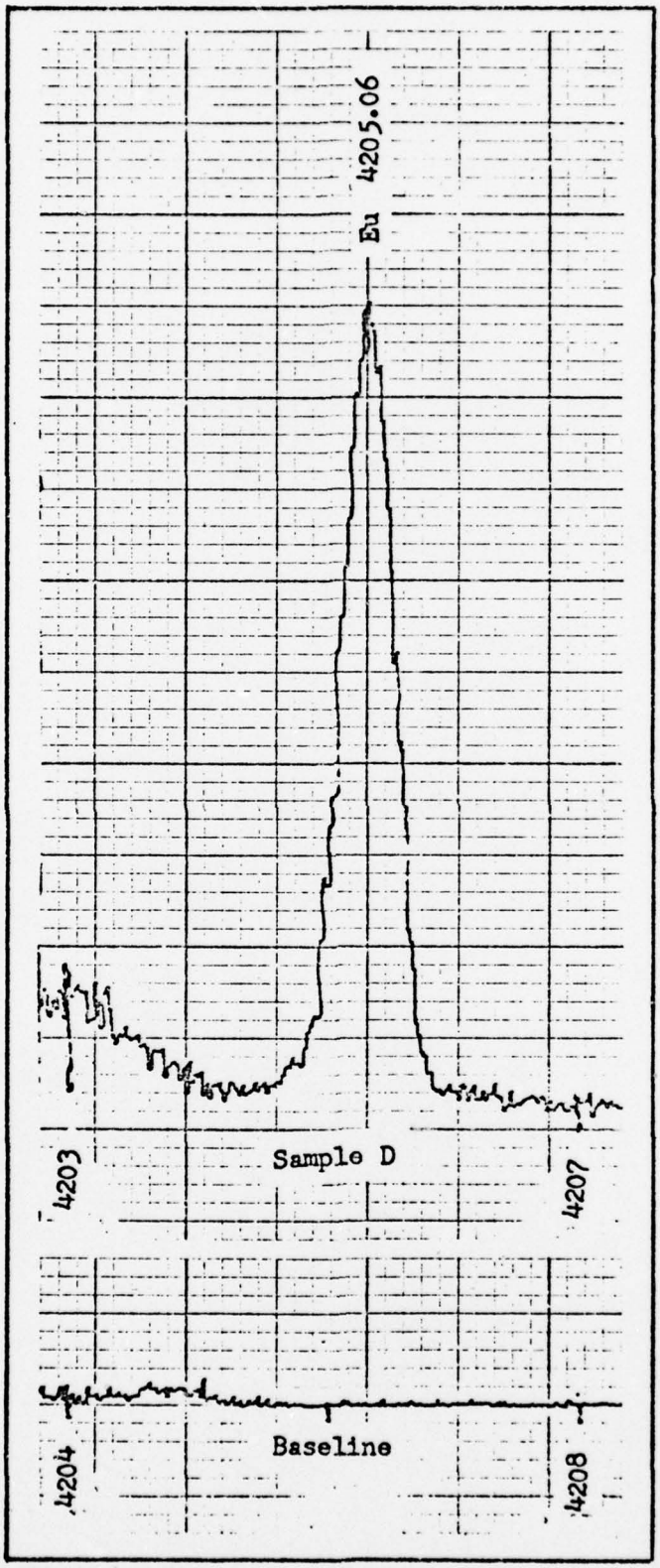

Fig. 4. Europium Line in Sample D

Gadolinium

Sample C was the only wafer obtained with gadolinium in the film. Of the ten lines of this element that were searched for, only the two lines indicated in Table V were detected. Both these lines were weak, but the 4346.46 Angstrom line was conveniently located between two known argon lines allowing very accurate wavelength measurement.

It was observed that after long periods of sputtering (about two hours) of some of the samples, the epitaxial film layer would be completely sputtered away. This was indicated by a change in color of the glow over the surface of the sample. At this point the gadolinium in the substrate could be detected with the two lines given. Figure 5 shows the weak gadolinium line at 4346.46 Angstroms recorded with sample C.

Table V
List of Gadolinium Lines

Line Wavelength	Spark Intensity	GDOS Counts Sample C
3350.48	180	ND
3422.47	200	ND
3584.96	100	ND
3646.20	150	ND
4098.61	100	ND
4184.26	150	ND
4225.85	50	40
4251.74	10	Obscured
4262.10	10	ND
4346.46	60	40

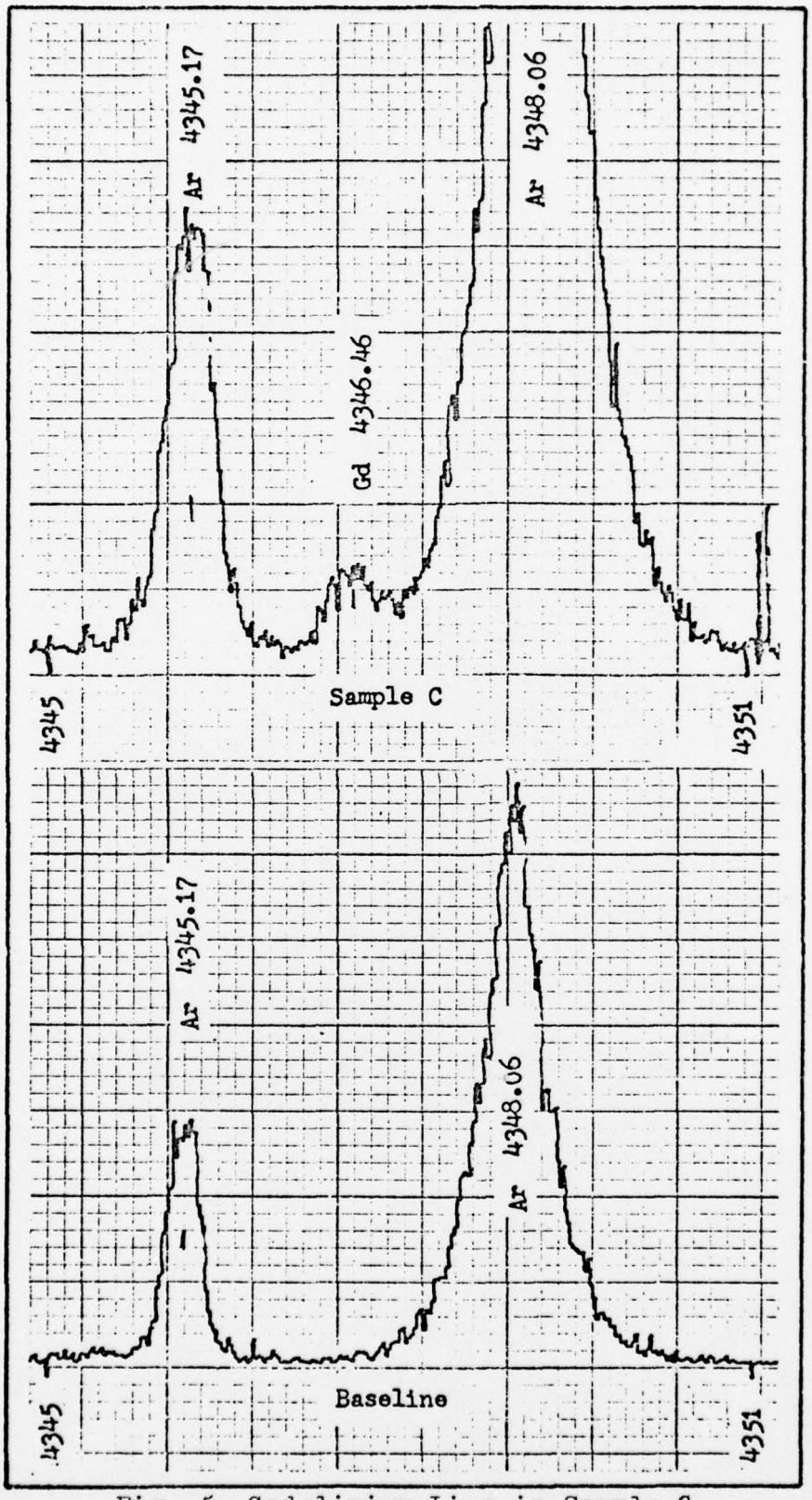

Fig. 5. Gadolinium Line in Sample C

Gallium

The strong line of gallium at 4172.06 Angstroms was easily found in the spectrum of all samples listed. Figure 6 shows this peak from one of the runs with sample D compared to the clean baseline recording in this area of the spectrum. Table VI gives the gallium line data.

Table VI
List of Gallium Lines

Line Wavelength	Spark Intensity	GDOS Counts			
		Sample D	Sample E	Sample F	Sample G
2943.64	20	obscured by argon background			
4032.98	500	300	-	-	-
4172.06	1000	450	470	350	1200

Iron

Iron lines were not searched for specifically in these studies, but several were discovered in the course of doing the analysis of the spectra for the other elements. On several occasions, before cross checking or more careful measurement, iron lines were misidentified as lines of other elements. Figure 7 shows two of the iron lines identified in the spectrum of sample A, and Table VII lists all the iron lines that were found.

Iron lines would occur in the spectrum of all magnetic bubble garnet films, and they could provide good reference peaks for location of other elements if they were cataloged and their positions indicated on the baseline data.

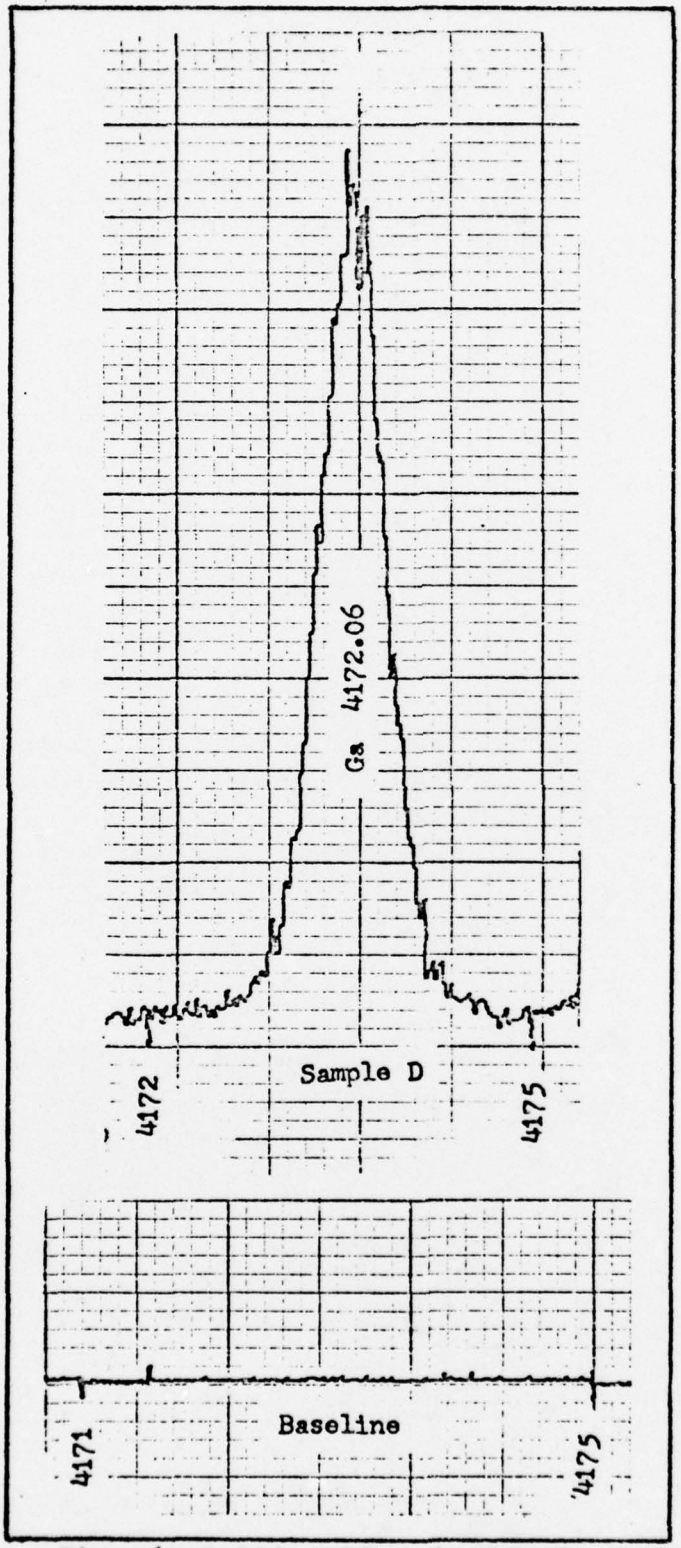

Fig. 6. Gallium Line in Sample D

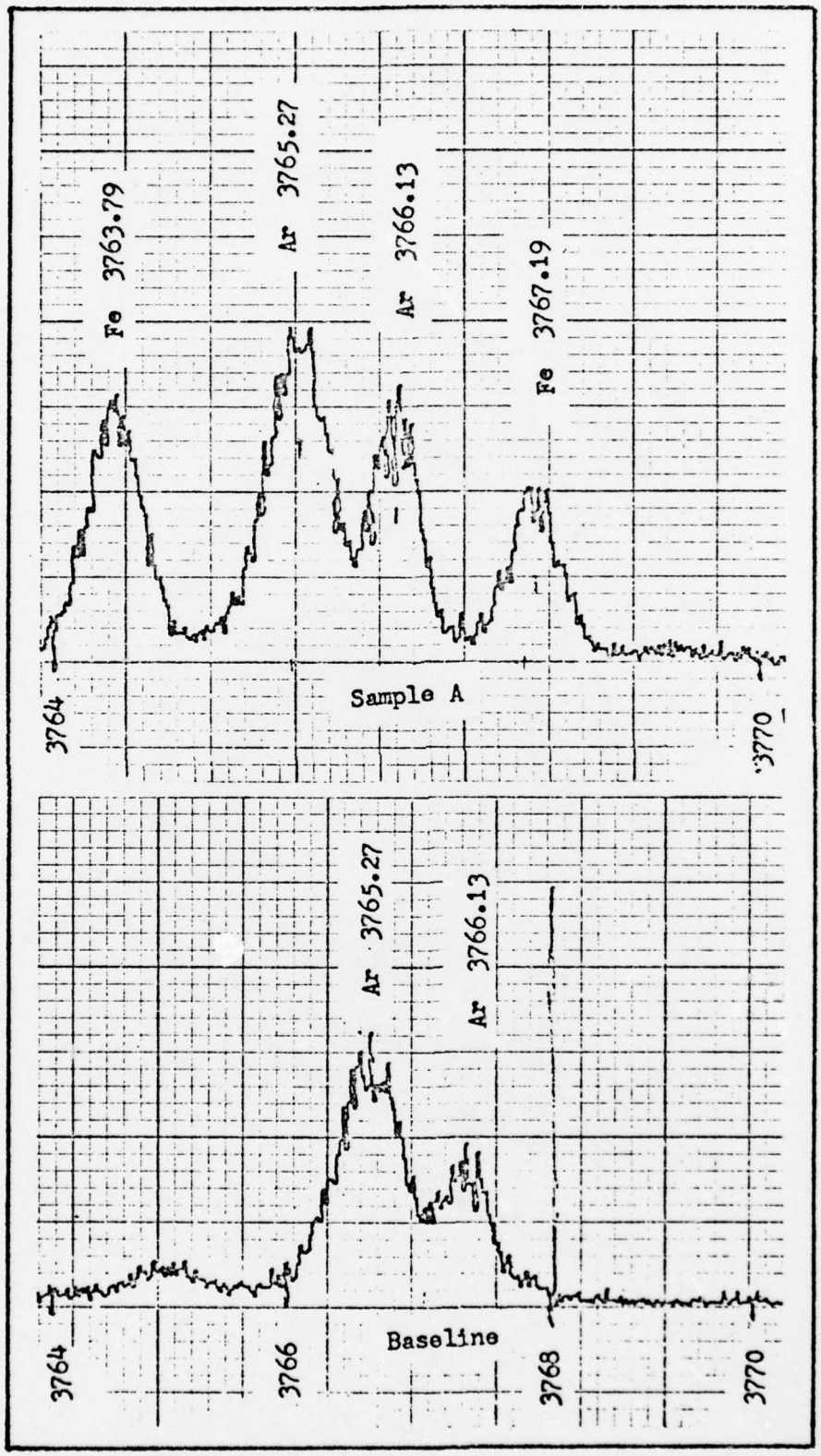

Fig. 7. Iron Lines in Sample A

Table VII
List of Iron Lines

Line Wavelength	Spark Intensity	GDOS Counts Sample A	C	D	E	F	G
3465.86	400	460	-	-	-	-	-
3570.097	300	-	-	380	130	240	-
3581.20	600	-	350	-	-	540	-
3608.86	400	-	-	-	100	80	100
3719.93	700	-	-	-	-	3100	-
3763.79	400	150	-	-	-	-	-
3767.19	400	100	130	-	-	-	-
3820.43	600	370	-	180	-	-	-
4078.36	40	390	-	-	-	-	-

Lanthanum

Seven areas of the spectrum known to contain lines of lanthanum between 3171.67 Angstroms and 6249.93 Angstroms were recorded using sample A. A line near 4077.34 Angstroms was first thought to be a lanthanum line but after more careful measurement and crosscheck it was attributed to the 4078.36 Angstrom iron line. No satisfactory peak for the identification of lanthanum could be found.

Lutetium

Ten analytical lines of lutetium between 2615.42 and 6221.87 Angstroms were searched for in sample F. No peaks could be found attributable to this element.

Samarium

Ten lines of samarium between 3609.49 and 4467.34 Angstroms were searched for using sample F and sample G with no success. One line near 3609.49 was found, but as a cross check the same area was recorded using sample E which was

known to contain no samarium, and the line was present in this spectrum also. The peak was then attributed to the 3608.86 Angstrom line of iron. Figure 8 illustrates this misidentified peak.

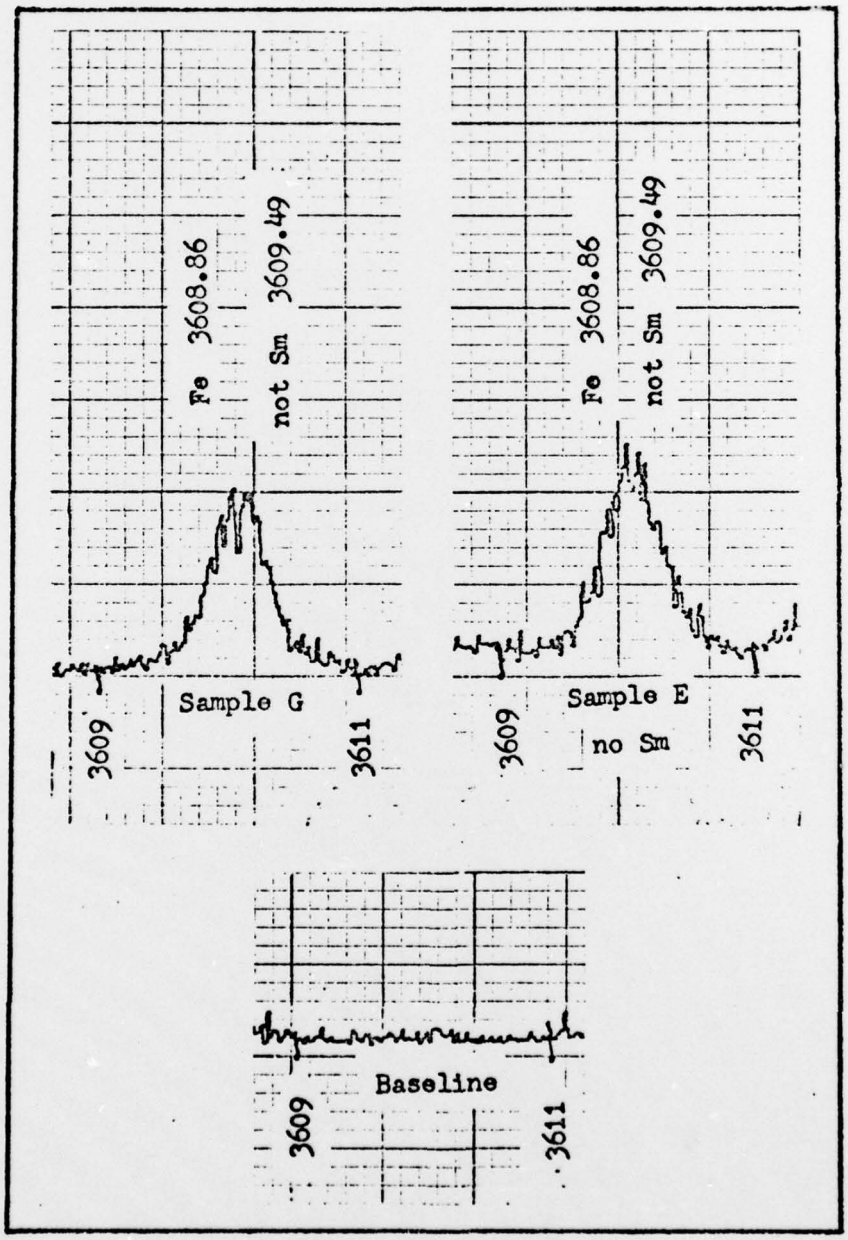

Fig. 8. Misidentified Iron Line

Thulium

The thulium lines were among the more thoroughly investigated lines because thulium was present in four of the seven samples tested. The 4187.62 Angstrom line was a good strong line that had a nearby argon line at 4191.07 Angstroms for accurate wavelength measurement. Figure 9 shows a copy of this peak.

The thulium line at 4105.84 Angstroms was another interesting line that occured as part of an yttrium, argon, thulium triplet that was found in several samples. Figure 10 shows this area of the spectrum as recorded using sample B. The data gathered on thulium are shown in Table VIII.

Table VIII
List of Thulium Lines

Line Wavelength	Spark Intensity	GDOS Counts		
		Sample A	Sample B	Sample C
3131.26	500	ND	ND	ND
3462.20	200	ND	ND	40
3761.33	120	-	50	-
3761.92	150	-	ND	-
4094.18	30	280	120	300
4105.84	30	500	190	550
4187.62	30	380	170	440
4242.15	100	-	ND	ND
4359.93	30	-	100	280

Yttrium

Lines of yttrium were identified in several samples. Of particular interest was the 4102.38 Angstrom peak that was part of the yttrium, argon, thulium triplet mentioned earlier and shown in Figure 10. This area of the spectrum was also recorded using krypton as the sputtering gas. In

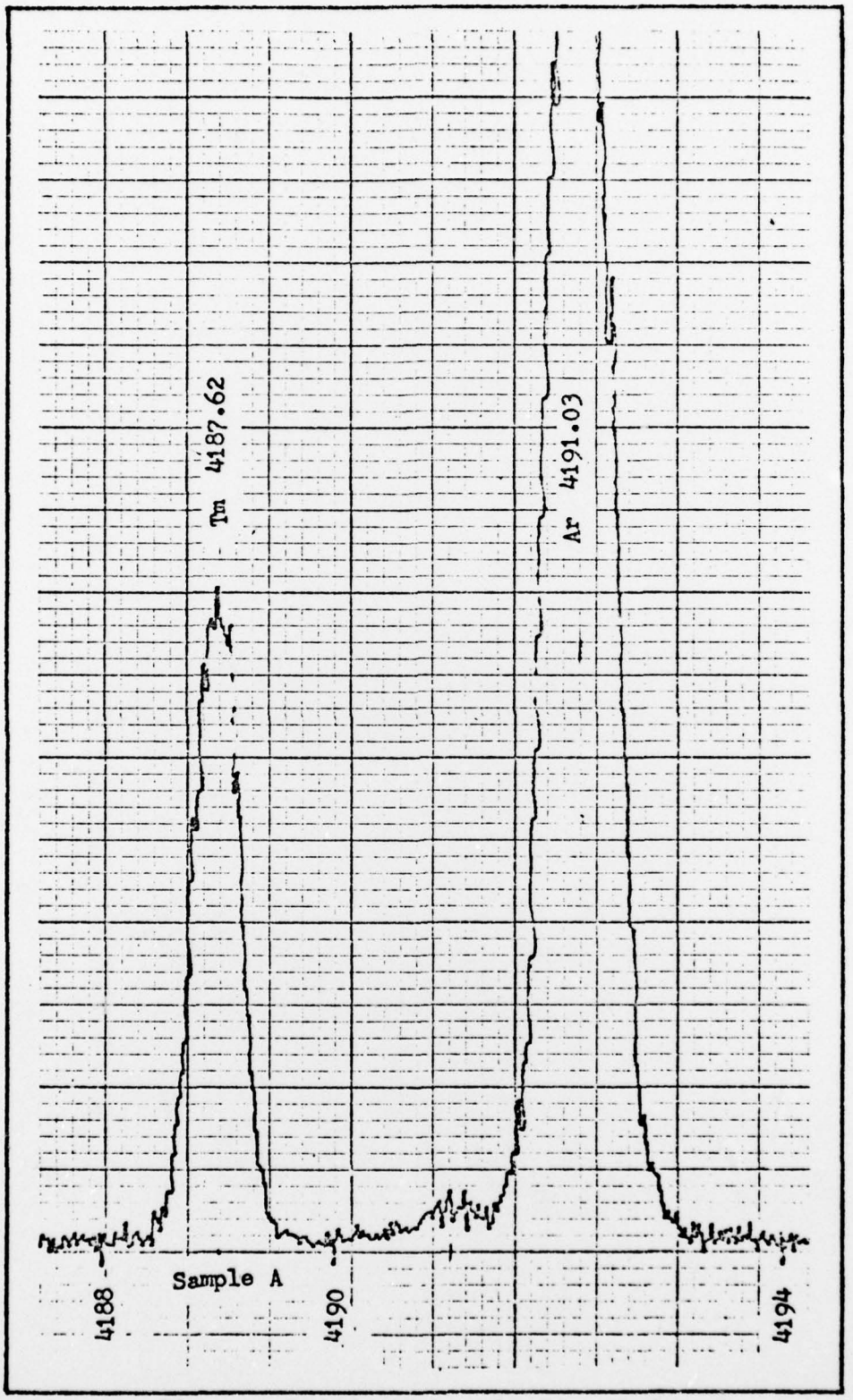

Fig. 9. Thulium Line in Sample A

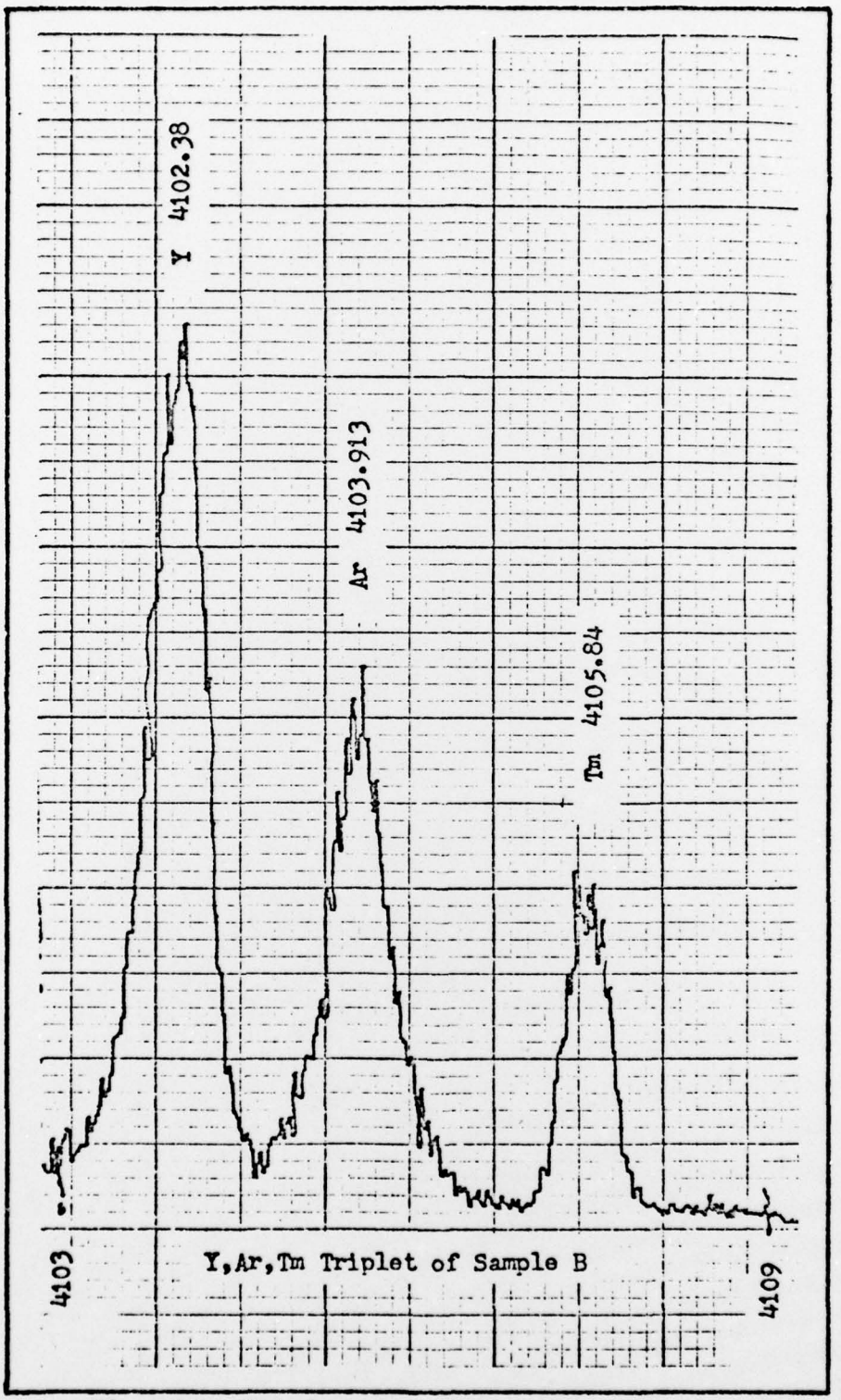

Fig. 10. Yttrium and Thulium in Sample B

this spectrum the argon line was missing, of course, but the yttrium and thulium peaks were still present. Figure 11 shows this part of the spectrum produced using krypton gas compared to the argon gas baseline. Table IX is a list of the yttrium data.

Table IX
List of Yttrium Lines

Line Wavelength	Spark Intensity	GDOS Counts			
		Sample A	Sample B	Sample C	Sample G
4077.37	40	-	-	-	500
4102.38	30	520	530	290	-
4128.30	30	-	450	-	-
4643.70	100	110	-	180	-
4674.85	100	270	250	150	-

Impurity Elements

A large amount of time during these studies was spent trying to detect impurities in the bubble films. The impurities looked for were boron, lead, and platinum. Table X lists the spectral lines sought for indication of these elements. These areas of the spectrum were recorded with all seven sample wafers, but no peaks could be found to indicate the presence of any of these elements.

Table X
Spectral Lines of Impurity Elements

Boron		Lead		Platinum	
Wavelength	Intensity	Wavelength	Intensity	Wavelength	Intensity
2496.77	300	2169.99	1000	2659.45	500
2497.73	400	2203.50	5000	2830.29	600
3451.41	100	2614.18	80	2929.79	200
		2833.07	80	2997.97	200
		3639.58	50	3064.71	300
		3683.47	50	4442.55	25
		4057.82	300	5301.02	10

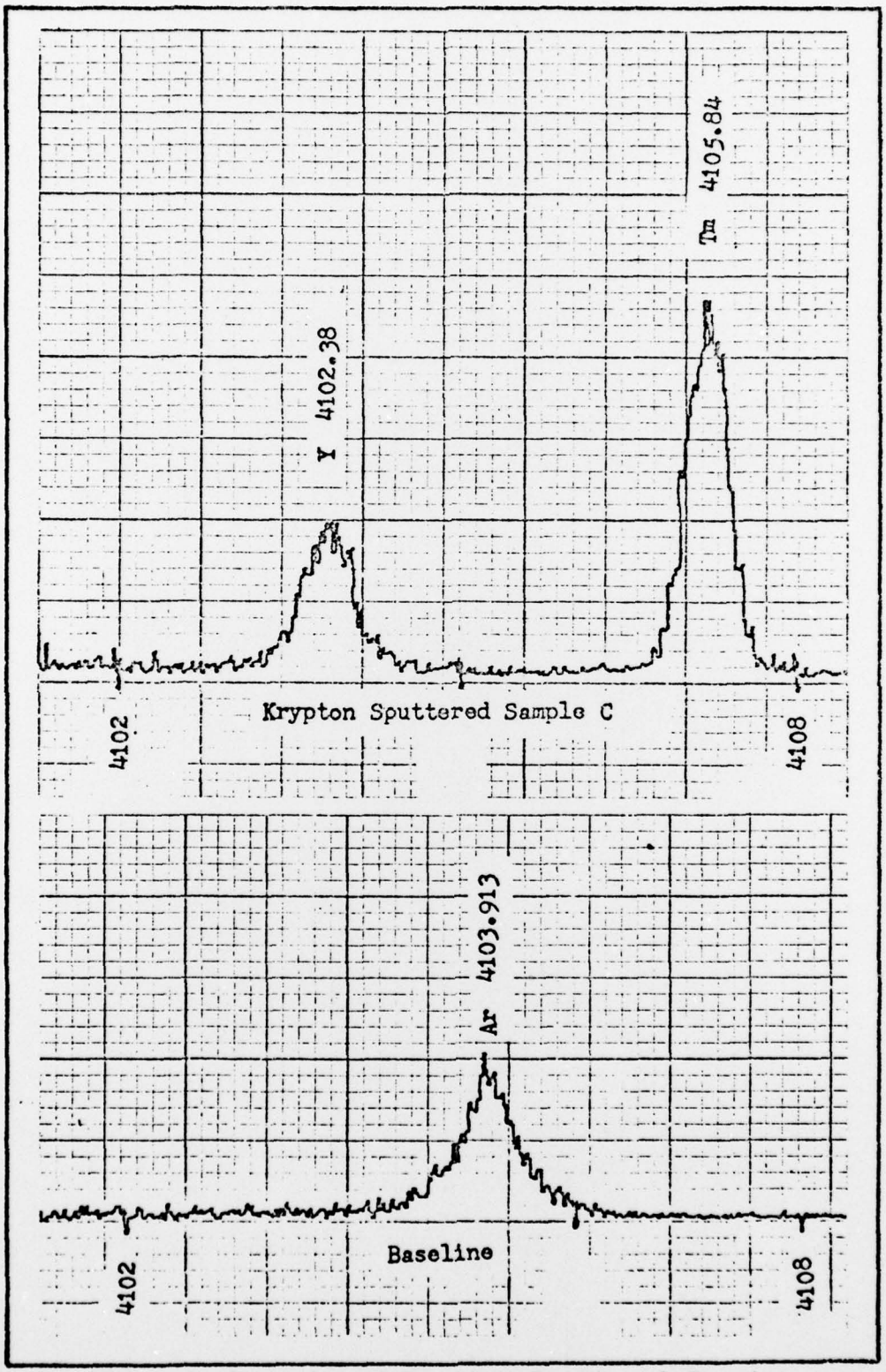

Fig. 11. Example of Krypton Sputtered Spectrum

V. Conclusions and Recommendations

Conclusions

This study has demonstrated the feasibility of applying the GDOS technique to the analysis of magnetic bubble garnet films. The sensitivity of the apparatus used was insufficient for detection of trace impurities in the film in its present configuration, but many of the basic elements in the films, including the substituted rare earths, were successfully identified in the spectra obtained. The system could be made more useful and practical by an increase in accuracy and sensitivity, and by modifications to improve the convenience of operation.

Recommendations

Given here are a number of suggestions for improvements to the system and areas for further studies.

Sputtering Chamber. An RF sputtering unit would be more suitable for sputtering the garnet material, and would increase the sputter yield by avoiding charge build up on the surface of the sample (Ref. 1). A commercially available RF sputtering unit could be converted for use with the GDOS system. This would include a better vacuum system that would reduce pump down time and contamination. The quartz viewing windows should be made removable for cleaning between runs to avoid the problem of having to disassemble the whole chamber for cleaning. Ideally, the chamber would include internal manipulation devices to allow running several samples before opening the chamber.

Spectrometer. A better spectrometer with more dispersion and an accurate wavelength scale should be used. This would give narrower peaks on the recordings for better discrimination, and would greatly aid in the identification and verification of the spectral lines. The spectrometer should also include a system for automatically placing the calibration tick marks on the horizontal scale of the X-Y recorder.

Optics. The glow over the sample and the electrode is oriented in a horizontal direction, while the entrance slit of the spectrometer is vertical. Because of this, the light entering the spectrometer is only a small portion of the useful glow above the sample. The system could be improved by either orienting the spectrometer to align the slit with the sample, by orienting the chamber or sample holder to align the sample vertically with the slit, or by adding a prism between the sputtering chamber and the spectrometer that would rotate the image of the glow 90 degrees for alignment with the slit. This would increase the sensitivity of the system considerably by utilizing much more of the light from the excited sputtered species, giving a much higher signal level without increasing the noise level.

Reference Spectrum. A complete, well calibrated baseline reference spectrum should be recorded and put in a convenient form for use. This spectrum should have all the argon, aluminum, and carbon peaks identified, and the location of iron and oxygen lines marked. This would allow rapid and accurate identification of unknown peaks.

Additional Areas for Investigation. More studies should be done using other gases for sputtering to determine their possible advantages and disadvantages. Optimum conditions of gas pressure, voltage, and electrode spacing should be explored for detection of some of the more important lines, and sputtering rates should be checked for various materials and sputtering conditions. A large amount of work could be done toward developing the quantitative capability of the system.

With improvements to the system and further refinements in operating procedures, the GDOS system could become a valuable analytical tool for use in the Air Force Avionics Laboratory.

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Appendix A

Cleaning Procedure

The Avionics Laboratory has developed a standard cleaning procedure for cleaning gallium arsenide wafers and chips prior to all processing steps that require maximum surface perfection. This procedure has been found to be very successful for removing all common forms of contamination, and leaves no residue from the cleaning process itself. This process was used throughout these studies to clean the samples used as well as for cleaning the surface of the sputtering chamber electrodes.

The sample chips were held with a vacuum chuck during the cleaning operation, and the chemicals were applied in a fine stream from the nozzle of a plastic squeeze bottle. The following steps outline this cleaning procedure.

1. Five minutes of ultrasonic agitation in a solution of 10% aquasol and deionized water.
2. 30 seconds rinse in deionized water.
3. 20 seconds wash in trichloroethylene.
4. 20 seconds wash in acetone.
5. 20 seconds wash in methonol.
6. Blow dry with nitrogen gas.

Vita

Larry D. Crocker was born on December 5, 1939, in Picayune, Mississippi. Upon graduation from Picayune Memorial High School in 1957, he enlisted in the Air Force, and after seven years of enlisted service he entered the University of Wyoming under the Airman Education and Commissioning Program. After graduating in 1966 with a Bachelor of Science degree in Electrical Engineering, he entered Officers Training School and was commissioned in November of that year. He then attended Pilot Training at Laredo Air Force Base, Texas, and subsequently served as an aircraft commander and instructor pilot in the F-100 and F-111 type aircraft. This aviation service included three combat tours in Southeast Asia. His decorations include the Silver Star, the Distinquished Flying Cross with one oak leaf cluster, the Air Medal with twenty-one oak leaf clusters, and the Air Force Commendation Medal. He was assigned to the Air Force Institute of Technology in June of 1976. He is a member of Sigma Tau, Phi Kappa Phi, and Eta Kappa Nu.

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A spectrographic study of several magnetic bubble garnet films was done using the Glow Discharge Optical Spectroscopy technique. Argon and krypton were used to sputter the samples for analysis. Lines of most of the elements in the films were successfully identified, but the apparatus used was not sensitive enough to detect trace impurities. Equipment and techniques used and the methods of data reduction are explained in detail. Suggestions for improvements to the system are also included. The study demonstrates the feasibility of using the GDOS method for characterization of rare earth substituted garnet films.

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