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SUBJECT: X-RAY EQUIPMENT FOR MAGNETIC RESEARCH

To: D. R. Brown

From: D. Tuomi and F. E. Vinal

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Abstract: After an examination of the manner in which x-ray techniques may be applied to a magnetic materials research program, the applications most meaningful to our particular interests have been selected. It is apparent that our program will achieve the most benefit from diffraction work of both service and research character. At present, x-ray fluorescent analysis does not seem to be well adapted to our needs. Equipment requirements are listed and commercially available equipment is examined both as to function and cost. For diffraction work the North American Phillips Co. equipment is preferred as it offers higher efficiency of use and lower cost when compared on an "equal performance basis" to the General Electric Co. diffraction equipment. In addition, through an integrated line of accessories, the accuracy and performance of the Norelco equipment may be raised to a standard not achievable with G.E. equipment.

In conclusion, a recommendation is made for the purchase of certain items, primarily manufactured by the North American Phillips Co., totaling approximately $18,000. A detailed comparison of the Norelco and G.E. equipment is included in Appendix I.

I. Introduction

It is the purpose of this memorandum to examine the possibilities for the application of x-ray techniques to a research program in magnetic materials and, in light of our particular interests, to select the most meaningful applications. Having defined the scope of a suitable x-ray program, equipment requirements are set forth and the commercially available equipment is examined for function and cost. As a result of this examination, a purchase recommendation is made.

II. Structural Chemistry Program

Application of x-ray techniques to a research program in magnetic materials divides naturally into service and research usages. The following applications outline has been made rather complete for such a program, bearing in mind that our emphasis is devoted primarily to solid state devices,

but phase identification, lattice parameter and crystal orientation work would apply equally well to either magnetic metals or ferrites.

1.0 Service Work

1.1 Phase Identification - Single crystal or polycrystalline

1.11 Verification of structural species present in a particular sample

1.12 Identification of foreign phases present in a particular sample

1.13 Lattice parameter determinations as an index of chemical constituency

1.14 Lattice parameter as a function of blended composition and heat treatment

1.2 Orientation - Single crystal or polycrystalline

1.21 Preparation of oriented, cut, ferrite crystals for specific applications, i.e. picture frame specimens for determination of physical constants in specimens whose magnetic domain configuration is known and elementary.

1.22 Mounting and orienting spheres, bars, etc., for specific investigations

1.3 Analytical Techniques

1.31 Qualitative identification of elements having atomic numbers greater than 22

1.32 Quantitative chemical analyses of metallic atoms in ferrites with a limiting precision of $\pm$ 0.05% for each major constituent

1.33 With the use of special attachments, qualitative and quantitative determinations with elements down to and including sodium, atomic number 11.

2.0 Research Work

2.1 Phase diagram studies in ferrite systems

2.11 Phase identification

2.12 Precision lattice constant determinations with analyzed specimens held at a constant temperature

2.13 Reaction kinetic studies on quenched samples

2.2 Polymorphic and Phase Transformations

2.21 Transformations occurring at high temperatures, up to about 1200° C

2.22 Transformations occurring at low temperatures, down to liquid air temperatures and possibly lower

2.23 Lattice constants as a function of temperature, i.e. shift of $MgO \cdot Fe_2O_3$ from normal to inverse might be studied as a function of temperature

2.3 Structural Chemistry

2.31 Structural determination of substances to aid fundamental studies of magnetic phenomena in ferrites, i.e., $ZnIn_2O_4$, $CdIn_2O_7$, $NiFe_2S_4$, $PdFe_2O_4$

2.32 Structural determination of perovskites

2.321 Ferromagnetic, i.e., $La_{(1-x)}Sr_xMnO_3$

2.322 Ferroelectric, i.e., $BaTiO_3$ $PbZrO_3$

2.33 Structural determinations of allied materials, i.e., oxides of manganese

3.0 Miscellaneous

3.1 Search for strain in specimens as shown by x-ray line broadening

3.2 Estimates of fine particle sizes and crystal grain sizes shown by x-ray line broadening

3.3 Attempts at radiographing crystals to detect internal flaws.

III. Limited Scope Program

From an examination of the possibilities for application of x-ray techniques to our ferrite program it is concluded that:

1. Our primary need lies in diffraction equipment for both routine and high-accuracy ferrite lattice-constant determinations

2. A second important use will be for crystal orientation, which is again, an application of diffraction equipment

3. A third need is phase identification, which is also an application of diffraction equipment

4. At present, we do not foresee production control problems in which x-ray fluorescent analysis is so useful and for which fluorescent analysis is applicable.

IV. Equipment Requirements

To implement the program outlined in Section III above, the following commercially available equipment would be required.

1. Basic x-ray diffraction unit with full current and voltage stabilization
2. Wide-angle, Geiger-counter diffractometer
3. Rate meter scaler circuit for the diffractometer
4. High accuracy, constant-counting-error scaler circuit
5. Suitable strip chart recorder for making a continuous record
6. X-ray diffraction tubes with targets of molybdenum, chromium, copper and possibly cobalt
7. Back-reflection crystal-orientation camera
8. Stroumanis film mount, powder diffraction-cameras
9. Miscellaneous accessories such as a film reader, illuminator, film punch, etc.
10. Film processing accessories

A need for various items, not usually commercially available is anticipated after such a program is underway. To cite several specific examples of this type, special sample holders for precision lattice constant measurements will probably be required, as well as special sample holders for high and low temperature studies.

V. Sources of Commercial X-Ray Equipment

There are five manufacturers who offer a fairly complete line of x-ray diffraction equipment in this country but for practical reasons consideration is limited to only two. The five manufacturers are:

1. The Ohio X-Ray Company - A post-war product which has not received sufficient reception in technical work to assure good serviceman and parts availability.
2. Hilger Company (Represented here by Jarrell-Ash Company) - An English manufacturer whose product is widely accepted in England and on the continent but, again, distribution in this country is not broad enough to assure good serviceman and parts availability. Hilger offers only a basic unit and does not manufacture a complete and integrated line of accessories and optional equipment.
3. Picker X-Ray Company - Well known in the field of medical x-ray equipment, this company offers a basic diffraction unit with a

limited line of accessories. It has not, however, achieved sufficient reception in technical work to assure good serviceman and parts availability.

4. The North American Phillips Company - The units offered by this company are widely known and used. They merit detailed consideration.

5. The General Electric Company - The units offered by this company are widely known and used. They merit detailed consideration.

VI. Relative Merits of Norelco and GE Equipment

A searching comparison has been made between the equipment manufactured by the North American Phillips Co. and that manufactured by the General Electric Co. The details of this comparison are to be found in Appendix I to this memorandum. Particular attention has been directed to the methods employed by the two manufacturers to achieve the various functions of a diffraction unit, as well as consideration of a few more general aspects such as physical form, safety, accuracy, flexibility and convenience. A comparative cost analysis is also included.

As a result of this examination it is concluded that the North American Phillips equipment is best suited to our needs because:

1. Their basic unit is intended for diffraction work only and it is accordingly a more efficient instrument for that purpose.

2. Their goniometer records are readily convertible to quantitative terms.

3. Their goniometer records may be obtained with higher accuracy by the addition of a constant-counting-error scaler circuit.

4. Their extensive and integrated line of accessories for higher accuracy, convenience and extended scope are indicative of a concerted and successful effort in the technical x-ray field.

5. Their fluorescent analysis unit may be added without alterations at any time the need for such equipment should become evident.

6. Their fluorescent analysis unit is completely independent of the diffraction unit and it is accordingly a more efficient unit for analytical procedures.

7. Their parts and service availability in this area are superior.

8. On an "equal performance basis" the costs for North American Phillips equipment are approximately $1500 less for diffraction work only and approximately $1000 less if both diffraction and fluorescent analysis equipment are obtained. The GE prices used in this comparison had already been reduced from list price by 10% for an "educational discount".

In selecting North American Phillips equipment, two useful features offered exclusively by the General Electric Co. have been lost. These features are:

1. The easy qualitative detection of minute amounts of a second phase and

2. The avoidance of reruns where improper range setting for the goniometer amplifier is made on the first trial.

It is felt that in the overall picture the balance swings heavily to favor the North American Phillips equipment. This conclusion is, in a way, corroborated by the approximate distribution of technical x-ray units in the New England area. North American Phillips Co. 80, General Electric Co. 3.

VII. Purchase Recommendation

It is recommended that a purchase order be placed for x-ray diffraction equipment and accessories and that this order be placed with Atlantic Precision Instrument Company, distributors for North American Phillips equipment, except as noted below.

Specifically, the following should be ordered:

From the Atlantic Precision Instrument Company

Capital Items

1	12045	Basic X-Ray Diffraction Apparatus	$ 3,475.00
1	42202	Diffractometer (geiger counter)	2,975.00
1	12049	Electronic Circuit Panel	2,790.00
1	52090	Brown Recording Instrument (with optional conversion to a Leeds and Northrup instrument within 6 mos. from delivery date and at no additional cost)	798.00
1	51152	Stabilizer, Voltage	598.00
1	51156	Stabilizer, Milliampere	350.00
1	42227	Step Scanning Device	2,500.00
1	52056	Large Powder Camera 114.59 mm. dia.	370.00
1	52057	Small Powder Camera 57.3 mm. dia.	330.00
1	100API	Back Reflection Flat Plate Camera with Screen	590.00
2	52019	Track and Bracket Assembly @ $275 each	550.00

Expendable Items

1	32112	Cu Target Tube	526.00
1	32113	Mo Target Tube	546.00
1	32116	Cr Target Tube	546.00
1	52027	Film Punch and Cutter	130.00
1	52184	Rotating Specimen Spinner	475.00
			$17,549.00

From the General Electric Company

1	A4929E	XRD Film Scale	$126.00	
1	Er026D	Illuminator, including E5026F Reflector Shield	32.62	
				158.62
			TOTAL COST	$17,707.62

Signed Donald Tuomi
Donald Tuomi

Signed F. E. Vinal
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Appendix I

A detailed comparison of North American Phillips Company and General Electric Company x-ray diffraction and fluorescent analysis equipment.

1. Physical Form

North American Phillips Co.

The "Basic Unit" contains all electric supply and metering circuits, goniometer amplifier but no water cooler unit for the x-ray tube, city water mains supply the required cooling water. The unit cabinet is severe, compact, upright and its top is the diffraction working surface. The tube is centered on the top, mounted vertically and has 4 ports available. It would be difficult to use more than 2 or 3 to good advantage coincidentally. Tracks and mountings for camera and goniometer are placed on the unit top but no extra space is available. The "Basic Unit" does not make any provision for fluorescent analysis other than to provide the electric supply and metering circuits. The "Basic Unit" does include one demountable goniometer, an electronic circuit panel and a suitable "Brown" strip chart recorder. The recorder and circuit panel are externally mounted. As quoted on June 11, the unit contains a Cu target tube.

General Electric Co.

The "Basic Unit" is a console type of pleasing appearance. Within are all electric supply and metering circuits, a self contained water cooling unit for x-ray tube cooling water, goniometer amplifier and associated circuitry. The extensive working surface, roughly the height and size of an executive desk, holds mountings for the x-ray tube goniometer and camera tracks. The tube is mounted horizontally and has 3 ports available although it would be difficult to use more than 2 to good advantage coincidentally. The ruggedness and scaling of the angle marker rotating head is excellent. To reset and check for a particular angle is both simple and quick and in this respect the GE unit is superior to the Norelco. The same "Basic Unit" is converted by certain modifications to perform fluorescent analysis. The conversion kit is an extra cost item and the goniometer, always used in the same position, is not demountable. A suitable Leeds and Northrup strip chart recorder for external mounting. As quoted on June 11, the unit contains a Cu target tube.

2. Ruggedness

The packaging of the "Basic Unit" in an upright cabinet of fairly small cross-section makes it rather simple to achieve a firm support for tubes, goniometer and camera mounts.

The large flat surface of the GE unit has led in the past to reports of some instability to camera and goniometer mounts but the presently available unit is crossbraced below the surface and seems to provide adequate stability. There seems to be no basis at the present time to consider either unit more stable than the other.

North American Phillips Co.	General Electric Co.
3. Cooling System	
The reliance on city water supply for cooling water has, in some instances of low summer pressure, led to inadequate cooling. Also the line filters are a source of some maintenance, variable of course with the particular water supply. The uncertainties introduced may be overcome with an independent readily-available self-contained cooling unit.	The built-in self contained cooling system is an asset to this unit.
4. Safety	
Both instruments are potentially dangerous and can inflict serious injury to a careless operator. Assuming no careless oversight, both instruments are designed to be adequately shielded for stray radiation. If operated properly there is some favor for Norelco unit as it is not possible to manipulate a sample under test.	With the GE unit, the arrangement of the goniometer is such that insertion of a hand in the x-ray beam is possible when the machine is operating. Both machines should be surrounded with extra shielding in the form of portable lead-glass panes. Also it is essential with either instrument to have available a portable radiation counter to check for stray radiation.
5. X-Ray Diffraction	
From any tube, the possibilities for generating x-rays off the target are two high intensity beams of a somewhat "point source" character off opposite sides of the target and two broad beams of lesser intensity per unit area from the remaining sides. These latter might be called "line-source". The vertical mounting of the tube in the Norelco unit permits all four of these beams to be available simultaneously although practical considerations make it doubtful that more than two or three could be used to good advantage at any one time. As a separate unit is offered for fluorescent analysis, the diffraction unit is designed for maximum efficiency, permitting use at all times of the high-intensity narrow beams for camera work with the shortest exposure times (operating time).	The GE unit mounts the tube horizontally. One beam is lost outright in the mounting, two more are available in the horizontal plane while the fourth is in the vertical plane over the instrument. The two which are available in the horizontal plane are the broad, low-intensity beams while the purchaser is left to his own devices as to how to utilize the high-intensity vertical beam. It might well be considered bad practice to mount any equipment over the tube where a slip would result in a broken tube (at $675) aside from the necessary design and construction of suitable mounting tracks for equipment. This arrangement is the result of the GE design which utilizes a large heavy (150 lbs) goniometer which, once located, is never moved, and is used in that position for both diffraction and fluorescent analysis. Since the

North American Phillips Co.	General Electric Co.
	correct diffraction film exposure for a particular substance is a time-intensity product, exposures on the GE machine would be several times longer than on the Norelco because the camera tracks and mounts provided operate in the horizontal beam of lower intensity. There would be no material difference in operating times using the Geiger-counter. It would appear that attempting a single unit for diffraction and fluorescent analysis causes serious disadvantage to occur to the GE unit in terms of convenience.
6. Fluorescent Analysis	
This method, once set up, is an extremely valuable one for control analyses such as used in a steel plant for control checks of minor alloying additions. The setting up of such a method is not simple. Much effort must be made in the preparation of standards, by comparison to which, the unknown is evaluated. These standards must be checked out by wet chemical methods. For research problems where very few samples would be analogous in character there is considerable doubt about the usefulness of this method. By the time suitable standards are prepared and analyzed, the samples could have been determined by wet chemical methods. Further the method provides information only in terms of atomic weight percent for elements above 22 in atomic number, no information about valence states is obtainable nor about the balance (such as oxygen or elements less than 22 in atomic number) for which the method cannot analyze. Norelco provides, as an optional item, an attachment which permits a helium atmosphere for the x-ray beam. By reducing scatter, this atmosphere effectively increases beam intensity, permitting the method to be employed, with limitations, down to atomic	The GE basic unit is designed to be employed for both diffraction and fluorescent analysis with as little change as possible. For example the goniometer is fixed in position and by a kit of conversiton parts and changing the x-ray tube the diffraction set up is modified for fluorescent analysis. Since the GE unit is a two-purpose unit it becomes more critical to evaluate the possible applications of the fluorescent analysis technique to our own contemplated program than is the case with Norelco equipment where the separate diffraction and analysis units permit a more clearent separation in consideration of applicability of the two techniques. The elements of immediate and predominant interest to us are Mg(12), Al(13), V(23), Cr(24), Mn(25), Fe(26), Co(27), Ni(28), Cu(29), and Zn(30). In the spinel lattice all of the above are combined with oxygen so that the oxygen is always predominant. The scatter from the oxygen atoms and the "dilution" by oxygen combine to make detection more difficult and less precise. We would also be working with atomic numbers near the lower limit of the scope of the method, requiring thereby more exacting technique. Mg and Al would

North American Phillips Co.

number 11. From the above discussion of limitations of the method and that given in the adjoining column, combined with an absence of routine production control analyses it is recommended that no fluorescent analysis provision be purchased until more need for it has been demonstrated. This conclusion indicates the purchase of Norelco equipment where the two units are completely separable, and with which the goniometer is interchangeable.

General Electric Co.

be barely detectable only with the use of helium atmosphere. It is concluded that fluorescent analysis of ferrites would require study time which is hard to justify without more requirements of a production control analysis type than we now foresee.

7. Electronic Circuitry and Circuit Panels

Discussion of circuitry ties in with other items below but it should be pointed out that the amplifier of the Norelco unit is a single ended linear amplifier which provides a linear signal to the recorder from the plate circuit of the final amplifier. Users of this equipment report little or no maintenance other than occasional vacuum tube replacement. No difficulty has been reported in calibrating the strip chart record. The record obtained from the Norelco unit is a linear plot of intensity of the reflected beam vs. the 2 θ angle. Such a record is immediately translateable into quantitative terms by simple integration of the area under the record peaks, either graphically or by planimeter. The Norelco linear amplifier may, from time to time, require re-runs on samples in which the relative amounts of phases present varies over a wide range, in order to obtain the best records for both low and high intensity peaks. The range switch on this amplifier provides scale factors of 1 to 256 in steps of 2. The probable counting errors vary from 0.4% for scale 256 to 1.2% for scale 32. For work of the highest accuracy a counting rate computer may be purchased as optional equipment which will advance the recorder accordingly after a fixed number of

The GE unit records a logarithmic plot of line intensities and therefore requires an amplifier whose output varies in a logarithmic manner. To achieve this, three tubes are coupled in the output stage and among them a certain balance must be maintained. Users have reported calibration difficulties resulting from unbalance in this circuit. The GE organization apparently has under development a linear amplifier to be used interchangeably with the logarithmic amplifier. The use of a logarithmic amplifier in the GE circuitry offers a convenient approach to qualitative work where phase identification, particularly those in minor amounts, is desired. The relatively large size peaks on chart records for the minor constituents makes them stand-out clearly against the background and permit easy identification of the 2 θ angle for each. The high intensity peaks are, conversely, not as well defined as would be found with a linear chart record. Although not impossible, the conversion of the logarithmic chart record to quantitative terms is mathematically difficult and decidedly inconvenient when compared to the easily obtained quantitative data available from a linear chart record. It is anticipated that our needs will be more

North American Phillips Co.	General Electric Co.
counts. Such records contain a constant counting error over the entire intensity range.	quantitative than qualitative and we should therefore consider the lack of ease in obtaining quantitative data as a significant disadvantage for the GE equipment
8. Strip Chart Recorder	
Norelco supplies, as standard equipment, a Brown Strip Chart Recorder. Assuming the purchase of Norelco equipment, a provision for a suitable Leeds and Northrup instrument should be required of the supplier, if we so desire.	GE supplies as standard equipment a Leeds and Northrup Strip Chart Recorder. The writer has experienced much smoother mechanical operation and less maintenance with L & N equipment than with Brown. A better field engineering service and repair service has also been obtained from L & N than from Brown.
9. The Counter Tube	
The use of a linear amplifier in Norelco circuitry permits, through its range switch, the use of a low counting rate geiger counter tube. Such a tube, using a halogen quench gas has a satisfactory recovery time and offers advantages of long life and low cost.	The GE counter must accept high counting rates to give proper signal to the logarithmic amplier. The tube (several units in parallel) is quenched with an organic substance and parallel sections are provided to lessen the likelihood of insufficient recovery speed. Users report less life and 4 times the cost of the Norelco tube.

10. Costs

Quotations have been submitted by the General Electric Co. through their local representative Mr. Fletcher, and by the Atlantic Precision Instrument Co., the local distributor and service organization for North American Phillips equipment. Both of these quotations are under the date of June 11, 1954 and are in such 'grouped form' as to make a basis for price comparison. Following the comparison, a breakdown is shown of the Atlantic Precision Instrument quotation as submitted July 12, 1954. This detailed price list enables us to identify and order such individual items as present considerations warrant. It should be noted that the GE prices have <u>already</u> been reduced by 10% for "educational discount".

North American Phillips Co.

"Basic" Unit

Generator, control, goniometer, Cu target tube, amplifier, recorder, voltage stabilizer, camera mount, city water cooling provision	$11,787

Required Diffraction Accessories

Large Powder Camera	370
Crystal Orientation Camera No. AP1-100	590
Mo Target Tube	540
Cr Target Tube	540
Film Scale est.	100
Illuminator est.	25
	$13,952

Fluorescent Analysis Equipment

X-ray spectrographic attachment, including sodium chloride crystal, liquid sample holder, solid specimen holder and Machlett AEG50T tube with tungsten target, mounted in the spectrograph attachment	1,995
	$15,927

Optional Equipment

Additional goniometer to facilitate change over from diffraction to fluorescent work	2,600
	$18,527

General Electric Co.

"Basic" Unit

Generator, control, goniometer, Cu target tube, amplifier, recorder, voltage stabilizer, camera mount, and self-contained cooling unit	$13,095

Required Diffraction Accessories

Large Powder Camera	648
Crystal Orientation Camera	540
Mo Target Tube	675
Cr Target Tube	675
Film Scale	126
Illuminator	33
	$15,592

Fluorescent Analysis Equipment

Fluorescent x-ray spectrometer assembly including mica crystal analyzer for automatic focusing of diffracted beams, sample mounting fixtures and mica crystals	945
Machlett AEG50T tube with tungsten target and adapter kit for the XRD-3 unit	540
	$17,077

Optional Equipment

(No way to facilitate change over from diffraction to fluorescent work)	
	$17,077

Step scanner or computer to provide a constant counting error and increase chart accuracy for exacting work	2,500	(No way to control counting error or increase chart accuracy)	
	$21,027		$17,077
Helium path attachment for fluorescent analysis of elements whose atomic number lie from 11 to 21 inclusive	250	(No provision for fluorescent analysis of elements whose atomic numbers lie below 22)	
	$21,277		$17,077
Flat Specimen Spinner	350	Flat Sample Spinner	360
	$21,627		$17,437
Additional Circuit Panel and recorder for second goniometer	3,588	(Circuit panel not available because a second goniometer cannot be employed with the GE XRD-3 set up)	
	$25,215		$17,437
Miscellaneous attachments, accessories, etc., estimated	2,000	Miscellaneous attachments, accessories, etc., estimated	2,000
	$27,215		$19,437

A detailed, item by item, quotation has been supplied by the Atlantic Precision Instrument Company as follows

Capital Items

No.	Norelco Cat. No.	Item	Cost
1	12045	Basic X-Ray Diffraction Apparatus	$3475
1	42202	Diffractometer (geiger counter)	2975
1	12049	Electronic Circuit Panel	2790
1	52090	Recording Instrument	798
1	51152	Stabilizer, Voltage	598
1	51156	Stabilizer, Milliampere	350
1	42227	Step Scanning Device	2500
1	52056	Large Powder Camera 114.59 mm. dia.	370
1	52057	Small Powder Camera 57.3 mm. dia.	330
1	100API	Back Reflection Flat Plate Camera with Screen	590
2	52019	Track and Bracket Assembly @ $275 ea.	550

Expendable Items

1	32112	Cu Target Tube	526
1	32113	Mo Target Tube	546
1	32116	Cr Target Tube	546
1	32114	Fe Target Tube	546
1	52027	Film Punch and Cutter	130
1	52184	Rotating Specimen Spinner	475

North American Phillips Co.	General Electric Co.
11. Delivery Date	
Both GE and Norelco offer 30 to 60 day delivery	
12. Parts and Service Availability	
The Atlantic Precision Instrument Co. of Boston is a distributor for the North American Phillips Co. and also acts as a parts and service company for this equipment. By past performance this company has set a superior standard for Norelco parts and service availability.	The General Electric Company's X-Ray Division maintains local offices in Boston and associated with the offices is a company operated parts and service shop. This local GE organization is by relative sales volume in New England almost exclusively a medical x-ray sales and service organization. There is considerable doubt that satisfactory service could be obtained as there is no one associated with the local organization who operates x-ray diffraction and fluorescent analysis equipment.