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# THE ABSORPTION SPECTRA OF SOLIDS

by

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# I. INTRODUCTION

Absorption spectroscopy has found increasingly wide applications in both theoretical and applied chemistry with the advent of improved equipment and technique. The more theoretical applications have been made in the determination of energy levels, interatomic distances, forces between atoms in the molecule, heats of dissociation, specific heats, and magnetic susceptibilities. Empirical applications of absorption spectra data have contributed to some of the advances made in studies on complex molecules by making possible predictions of structure and proof of synthesis with comparatively small amounts of material or with compounds which are too unstable for conventional chemical methods. Rapid and accurate quantitative analyses by spectrophotometric methods have now become standard procedures.

The absorption of radiation is accompanied by changes in the absorbing molecule which depend on the frequency of the radiation involved. In general, absorption in the far infrared produces molecular rotation; the near infrared corresponds to atomic oscillations and absorption in the visible and ultraviolet regions results in electronic activation of the molecule. These changes are quantitized and involve definite quantities of energy which are of the order of from one thousand to several hundred thousand calories per mole.

The appearance of the spectra depends upon the nature of the transition; if both the lower and the excited energy levels are sharp, the transition will give rise to a sharp absorption band. If the light has enough energy to expel an electron, a broad continuum results from the unquantitized transition. Combinations of electronic, vibrational, and rotational transitions produce close-lying bands which appear as continuous absorption except with instruments of the highest dispersion. Broad states are usually produced when the valence electron is excited except in the cases of a double bond or a resonating bond where sharp states may exist.

In some cases a reduction in thermal vibration by cooling results in a sharpening of diffuse bands. The strength of the electrical field produced by surrounding atoms determines the degree of splitting of the degenerate energy levels and this Stark effect varies as the interatomic distances fluctuate. The diffuse bands observed at room temperature are a summation of many sharp transitions of slightly different magnitude. The changes in band intensities accompanying the reduction in temperature are an aid in interpreting the spectra observed. The bands arising from low-lying levels gain in intensity as the temperature is lowered while those from higher levels vanish with the disappearance of the population of these levels.

The presence of a solvent increases the diffuseness of the bands since it allows greater interatomic movement. Correlations between the spectra and the absorbing molecule are frequently obscured by chemical combinations between the solute and the polar solvent molecules. It is necessary to add only one or two drops of alcohol to a chloroform-iodine solution to change the color from purple to brown; the complicating effects of the solvent may be minimized to some extent by the use of non-polar solvents.

Among the sharpest bands observed in solids have been those of the rare earth compounds which resemble the line spectra of gases. The origin of the bands with the metal atom is shown by a comparison of different salts having the same metal ion; the intense bands are found in approximately the same place in crystals of similar symmetry. The reason for the unusual sharpness of the bands of the rare earths originates in their electronic configuration: $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$, $4s^2$, $4p^6$, $4d^{10}$, $4f^X$, $5s^2$, $5p^6$. The sharp spectra arise from electronic transitions within the incomplete 4f shell and the completed 5s and 5p shells reduce the influence of neighboring atoms on the energy levels. The incomplete layer is not similarly shielded in the case of other transition elements such as iron and cobalt and their bands are more diffuse than those of the rare earths at higher temperatures.

The action of the crystalline forces on the degenerate levels of the free ion changes the appearance of the spectra from that of the gaseous ion which is influenced only by the symmetrical fields of the atom itself to one having a greater number of components. In addition to the decrease in degeneracy, vibrational and oscillational frequencies have been found superimposed on the electronic frequencies. These lines usually are weak and are not found repeated from salt to salt. They occur on the short-wave-length side of the main lines at distances in accord with the Raman frequencies for the anion; fundamental frequencies of the crystal lattice are also found repeated in a similar manner.

This research was undertaken to study further some of the forces existent in the solid state and to provide experimental data for the checking of theoretical work such as the prediction of magnetic susceptibilities and specific heats from the energy states of the molecule.

It is hoped to develop a more accurate and rapid method of determining the absorption spectra of solids to replace the inordinately slow and limited photographic techniques.

## II. PREVIOUS INVESTIGATIONS

### A. Methods

Recent developments in the field of electronics and optics have made possible the development of high-precision spectrophotometers which will automatically plot an absorption spectra curve in as little as a few minutes with an error of less than 1% in the absolute values of absorption coefficients; this is in marked contrast to the earlier practice of reporting the approximate position of the band edges.

The introduction of the echelette type of ruled grating along with the development of high quality replica gratings has led to a more extensive use of gratings in spectrophotometers. Harrison[1] has pointed out that the advantages of a grating lie in the greater dispersive power available for a given investment; this is particularly true for replica gratings which are relatively inexpensive. One grating is sufficient to cover the entire spectrum that can be photographed in air, whereas a prism instrument must have interchangeable glass and quartz optics in order to provide a satisfactory dispersion over a wide range. The low intensities commonly associated with gratings have been raised to a level comparable with prisms by the use of an echelette type of ruling which throws most of the energy reflected from the face of the grating into one first order and by replacing the speculum metal ordinarily used with an aluminum-on-glass surface of high reflectivity. One of R. W. Woods echelette type gratings tested by Harrison had 80% of its reflected light in one first order. The scattered light level for many grating instruments was estimated by Harrison to be less than a hundredth of that found in a prism instrument and the spectral purity obtained might be favorably compared with that from a double monochromator.

Cary and Beckman[2] compared eight different gratings including both originals and replicas, with prisms in five different types of monochromators. They measured the light leaving the exit slit with and without the addition of a secondary filter which completely absorbed the monochromatic light but transmitted most of the scattered light; the difference in the readings after the absorption of scattered light by the filter had been corrected for was taken as a measure of the scattered light. The data obtained indicated that the quartz prism has a marked advantage over the grating with respect to scattered light. The complete lack of agreement between this conclusion and that reached by Harrison probably arose from the use of different quality gratings or different mountings.

Dieke[3] has made a comparison of the properties of various mountings now in use; of these, the properties of the Eagle and the Wadsworth mounts lend themselves to the requirements of a monochromator. Both mountings possess a compactness which favors a high mechanical rigidity and reduces thermostating difficulties. The Eagle mount is the more compact and a grating so mounted has twice as much dispersion as with the Wadsworth mount; however, the latter produces a stigmatic image with four times as great an intensity.

The methods used to determine the transmission of a sample may be divided into general types: (1) a visual matching of intensities with some device such as a polarizing prism to reduce the intensity of one beam; (2) a comparison of a series of photographs of two beams in juxtaposition, one of which passed through the absorbing substance while the other passed through the solvent and an adjustable sector; (3) a measuring of the relative intensities of a beam passing through the solvent and one passing through the sample with some photosensitive device such as a photocell or thermopile. The visual method is limited to the visible region and is not of high precision, particularly at high intensities; and while the photographic method has an extended range it is generally regarded as slow and of insufficient precision. With few exceptions, the spectrophotometers introduced in the past five years have depended upon some type of photosensitive surface to measure the light intensities, and the electrical current produced is frequently employed to actuate an automatic recorder.

Hogness[4] described one of the first precision photoelectric spectrophotometers along with a critical analysis of the errors of absorption measurements. A single beam of monochromatic radiation from a constant deviation monochromator is alternately passed through the solvent and the solution by shifting the absorption cells in and out of the beam. The photoelectric current produced by the light reaching the photocell is amplified 400,000 times by a Pliotron tube and is measured by a galvanometer. The range of the instrument extends from 2200 to 7800 angstroms and wave-lengths settings may be made with an accuracy of ±2 angstroms; the spectral region isolated is 10 angstroms or less. This arrangement is capable of producing very accurate results since the use of but a single light beam avoids such errors as differences in paired photocells and in twin optical paths which are common to split-beam instruments but the large amount of time required for the focussing of two collimating lenses, the rotation of the prism, and the shifting of the cells reduces its value.

Data obtained on benzene by Hogness[4] illustrate the necessity of securing sufficient sensitivity and dispersion to isolate a narrow spectral region. The spectral region isolated is defined as the width of the second slit of the monochromator plus the width of the image of slit one on the plane of slit two in terms of angstrom units; some confusion exists regarding this term since many instrument makers calculate this value by using a second slit of zero width. The molecular absorption coefficient of benzene at 2540 angstroms decreased to 35 per cent of its maximum value and the coefficient at 2525 angstroms increased to 160 per cent of its minimum value when the spectral region isolated was changed from 6 to 160 angstroms. This variation of absorption coefficient with spectral region isolated is most serious with sharp or complicated spectra and is minimized by broad bands.

A high-speed-recording spectrophotometer described by Harrison[5] is capable of plotting an absorption curve over the region 9800 to 3400 angstroms in 70 seconds and from 3400 to 2200 angstroms in a few minutes. A concave grating is used for the dispersive system and a narrow vibrating mirror which acts as an exit slit alternately sends the isolated beam through the sample and through the comparison cell to an electron multiplier. These tubes have a lower signal to noise ratio than is obtainable at comparable amplifications with conventional direct current amplifying tubes. The action of the electron multiplier depends upon the secondary electrons emitted when primary electrons fall through a potential drop and strike the caesiated surfaces at each successive stage; the cumulative effect is an amplification in geometrical proportion to the number of stages. Zworykin[6] eliminated the disturbing effects caused by electron multiplier dark currents and direct current amplifier drift by interrupting the light 150 times a second with a sector disc; the 150 cycle component from the multiplier is then amplified with an alternating current signal amplifier.

A photocell and a vibration galvanometer were employed by Jacobsohn, Bent, and Harrison[7] to indicate the point of balance of the two beams in a Martens polarizing photometer. The results obtained on a Bureau of Standards filter indicated a high degree of accuracy was possible with their instrument but since the filter was of a neutral tint, the test showed only the accuracy of the photometer system. Cary and Beckman[2] employed interchangeable photocells to obtain greater sensitivity throughout the spectrum; in addition, the effect of the scattered light is reduced by the selective response of the photosensitive surface. Transmission readings are made with a direct-reading potentiometer with an electronic amplifier and a balance-indicating meter. Some investigators[8] have used barrier layer cells in conjunction with galvanometers of high sensitivity to eliminate complicated electrical circuits and to avoid dark currents.

## B. Materials

The polymorphic sesquioxides of the rare earth elements were first systematically investigated by Goldschmidt, Ulrich, and Barth[9]. They reported the existence of three crystal modifications which they designated as types A, B, and C. On the basis of x-ray powder diagrams, the A-type oxide was interpreted as being hexagonal with one molecule to the unit prism; no atomic arrangements nor lattice dimensions were given. The B-modification has a much lower symmetry and was described as pseudotrigonal and biaxial; two forms of the B-modification were observed but in only a few cases were they able to prepare them in the pure state. The C-modification is cubic and the abundance of lines in its Debye-Scherrer diagram corresponds to the large unit cell which contains 16 molecules of $R_2O_3$. The unit cell for the cubic sesquioxides was found to be approximately 10 angstroms on an edge.

The temperature stability of the various crystal modifications followed a general pattern: the hexagonal form is stable at the highest temperature; the pseudotrigonal type is stable at intermediate temperatures; and the cubic modification is stable at the lowest temperatures. The polymorphic relations of the sesquioxides were shown by plotting the atomic numbers of the cations against the temperatures at which the corresponding crystal modifications were prepared. The diagram showed that the stability of the individual lattice depends upon the atomic number and the temperature; and that a given crystal modification of the rare earth sesquioxides is stable at increasingly lower temperatures, the smaller the atomic number of the cation. The diagram predicts but two oxide forms for individual rare earths; those with the lower atomic numbers can exist in the hexagonal or the pseudotrigonal modifications and the others are stable in the pseudotrigonal and cubic forms. The oxides were prepared by heating the nitrate or the hydroxide, and the sulfate may also be employed at temperatures of 1100° C. and over. For very high temperatures, a small pill was made in a hydraulic press and held in an oxy-acetylene flame with a pair of metal pincers.

The hexagonal modification of lanthanum sesquioxide was obtained by Goldschmidt[9] at 550°, 1100°, 1300° C., and at its melting point; no other crystal form was observed, although the heating time at 550° C. was varied from $2\frac{1}{2}$ to 74 hours. Zintl and Croats[10] prepared hexagonal lanthanum sesquioxide by igniting lanthanum nitrate in a platinum dish for 20 hours at 1275° C.; they observed that shorter heating times or the application of lower temperatures gave oxide preparations with diffuse lines. Löhberg[11] was able to prepare a cubic modification of lanthanum oxide although the scheme presented by Goldschmidt does not predict a stable cubic form for lanthanum; in addition to the cubic and B modifications, two other unidentifiable powder patterns were observed. Ignition of the nitrate for 3 hours at 500° C. gave a powder pattern that was neither that of the cubic nor the hexagonal; a further ignition at 450° C for 20 hours produced the cubic modification. The addition of 1 per cent sodium nitrate to the lanthanum nitrate resulted in the formation of another unknown modification. Lines of the A-type oxide first appeared in the powder patterns on samples ignited at 650° C.

A length of 11.4 angstroms was found by Löhberg[11] for the unit cell of the cubic modification of lanthanum sesquioxide.

Zachariasen[12] reported the A-type oxide is hexagonal and has one molecule in the unit prism with $a = 3.93$ angstroms and $c = 6.12$ angstroms. Pauling[13] suggested an atomic arrangement that is considered more probable than the one originally suggested by Zachariasen; the cation is surrounded by seven equally distant oxygen atoms and some degree of polarization is indicated by the shortening of the interatomic distances from those calculated on the basis of the ionic radii.

Goldschmidt[9] prepared europium oxide in the cubic form by heating at 735° C. and at 750° C.; ignition at 1100° C. produced the pseudotrigonal modification. No data on the crystal structure of the B-modification are available. The crystal structure of the cubic form of the rare earth oxides has been described by Zachariasen[14,15,16,17]. The elementary cube contains 16 molecules of $R_2O_3$ and in the case of europium is 10.84 angstroms on an edge. On the basis of the similarity of the x-ray powder patterns of the cubic sesquioxides and the mineral bixbyite, Zachariasen concluded that they have the same structure; and determined an atomic arrangement for the bixbyite from Laue patterns of the large crystals which are available. The interatomic distances for the sesquioxides of the rare earths were calculated from the length of the cube edge with the bixbyite parameters; the value obtained for the europium to oxygen distance was 2.42 angstroms. Pauling and Shappell[18] used Zachariasen's experimental data on bixbyite to calculate a new atomic arrangement which is more in agreement with known ionic radii. The ions are nearly in cubic close-packing and each cation is surrounded by six oxygen ions placed at the corners of a highly distorted octahedron; each oxygen is common to four octahedra. The europium to oxygen distance calculated by Pauling is 2.33 angstroms and he states that possible changes in the oxygen parameters with changes in the size of the unit cell might introduce errors up to 0.1 angstroms.

## C. Absorption Spectra and Magnetic Susceptibility

The praseodymium ion affords the best opportunity for the checking of theoretical calculations with experimental values obtained from absorption spectra and has been studied extensively. Rearrangements within the incomplete 4f shell of the rare earth ion result in absorption bands of unusual sharpness because of the shielding effect of the outer shells. The first rare earth, cerium, contains but one 4f electron and its absorption spectra beyond the one band falling in the infrared consists of diffuse bands in the ultraviolet which arise from transitions to levels outside the 4f shell. The $f^2$ configuration of the praseodymium ion is the next simplest case and its absorption spectra consist of seven groups of sharp bands; three are in the infrared, one in the red, and three in the blue region.

Spedding, Howe, and Keller[19] measured the absorption bands of hydrated praseodymium sulfate at 20°, 105°, 169°, 200°, and 300° K. Gobrecht [20] extended his investigations to the infrared and has reported the absorption spectra of some praseodymium compounds from 5000 to 20,000 cm.$^{-1}$. Merz[21] investigated the absorption spectra of the following series of praseodymium salts of varying crystal symmetry: Hexagonal $Pr_2Mg_3(NO_3)_{12} \cdot 24H_2O$, $Pr(C_2H_5SO_4)_3 \cdot 9H_2O$, $Pr(BrO_3)_3 \cdot 9H_2O$; Tetragonal $Pr_2(MoO_4)_3$; Rhombic $Pr(C_6H_3Br_2SO_3)_3 \cdot 9H_2O$; Monoclinic $Pr_2(SO_4)_3 \cdot 8H_2O$. Hellwege[22] studied a similar series of salts and resolved some of the diffuse bands into sharp close-lying lines with the use of light polarized parallel or perpendicular to the optic axis; Lehman[23] and Lange[24] contributed similar data on praseodymium.

The allowable states of $^1S$, $^1D$, $^1G$, $^1I$, $^3P$, $^3F$, and $^3H$ were calculated by Gibbs, Wilber, and White[25] for the two equivalent 4f electrons of Pr IV. It is generally accepted[20,21,22,26,27] that the three bands observed in the blue region arise from transitions from the ground state of $^3H_4$ to levels of $^3P_0$, $^3P_1$, and $^3P_2$. However, the red band has been variously designated as a transition from the ground state to a $^1D_2$ level by Ellis[26], to a $^1I_6$ by Spedding[27], and to a $^1G_4$ by Lange[24]. Spedding[27] has objected to the levels calculated by Lange[24] on the grounds that the Russell-Saunders coupling assumed by Lange for all levels is far from being obeyed for the upper levels and that the perturbations which he neglected amount to as much as 1,000 cm.$^{-1}$. Spedding[27] calculated the levels for Pr IV taking the effect of the perturbations into account and secured excellent agreement with the observed values. All of the theoretically predicted bands have been found except one for a $^3H_4 - ^3H_5$ transition which falls in a region of the infrared not yet observed and no band was observed where none was predicted. His interpretation is consistent with similar calculations accounting for the spectrum for Tm IV which is the companion rare earth to Pr IV.

The complexity of the spectra is increased by a Stark effect produced by the crystal fields. The magnitude of the splitting of a level is governed by the intensity of the electrical field and the number of components is determined by the field symmetry as well as the J value of the term. Bethe[28] has calculated from group theory the number of levels produced by the splitting of a term of given J value in fields of various symmetry; the lower the symmetry about the absorbing ion, the greater the number of components, and the maximum number possible is equal to 2J + 1.

A variety of methods have been used to provide information as to the separation of the lower states and ultimately to deduce the energy diagram for the absorbing ion. The method used by Spedding[19] involves a comparison of the spectra at different temperatures and depends upon the fact that the absorption corresponding to a given transition is proportional to the number of atoms in the state from which the line originated. As the sample is cooled, those lines arising from upper states will decrease in intensity while those from the lower states become stronger; the population distribution ratio between a given level and the basic state may be calculated from the Boltzman relationahip if the temperature and the separation between levels are known. If transitions from the lower states terminate in a common upper state, the separations of these bands correspond to the separation of the lower states and these intervals will be repeated at each common transition.

Ewald[29] observed the shifts in the spectra produced by replacing the water of crystallization with deuterium oxide and by exchanging zinc for magnesium in double salts. The lines which were markedly shifted to the red in accordance with the greater mass were interpreted as being associated with a lattice vibration. Hellwege[22] observed the spectra with light polarized perpendicular to the crystal axis and found that many of the lines had disappeared; the combined spectra of the perpendicular and parallel radiation were the same as those observed for non-polarized radiation. Fluorescence affords information for spectral interpretations which is complementary to that of absorption; emission lines are produced by transitions from a higher-lying term to the ground term. Unfortunately, no pure praseodymium compounds have been observed to fluoresce[20,24].

The types of lines observed have been divided into three groups. The lines corresponding to pure electronic transitions are characterized by their intensity and sharpness; some of them show a hyperfine structure when photographed at a dispersion high enough to resolve lines approximately 0.5 $cm.^{-1}$ apart. Electronic transitions coupled with crystal lattice vibrations produce moderately strong lines 60 to 300 $cm.^{-1}$ on the short-wave-length side of the electronic line; they are particularly sensitive to changes of the crystal lattice constituents. Electronic transitions coupled with characteristic vibrations of the anion give rise to weak diffuse lines situated at a distance of 500 to 1800 $cm.^{-1}$ on the short-wave-length side of the electronic line.

Hellwege[22] has assigned transitions to some of the absorption lines observed for a series of four praseodymium salts and has shown the $^3P_0$ term of three of the salts as being split into two components. According to theory the $^3P_0$ term should not split regardless of the field symmetry since $J = 0$; non-equivalent praseodymium atoms were postulated by Hellwege[22] to explain the extra components. The unit cell of the hydrated sulfate contains eight praseodymium atoms; four of these occupy different places in the crystal lattice and it was suggested by Hellwege that part of these may be subjected to crystal fields of sufficiently different intensity and symmetry to account for the extra lines. He estimated the transitions from a lower to a higher level would differ from 10 to 50 $cm.^{-1}$ for the assumed ion types and points out that many of the intense lines may be shown by polarization effects to consist of several intense lines 3 to 5 cm.$^{-1}$ apart. It was assumed that some transitions were forbidden when the number of components found was less than that calculated by Bethe[28] for the symmetry of the crystal field. The energy levels of some praseodymium salts are given in Table 1.

If the extent of the separation and the nature of the lower levels are known, the magnetic susceptibility and specific heat may be calculated and these quantities checked with experimental values. The theory of paramagnetic susceptibilities developed for gases has been applied with considerable success to similar calculations for the paramagnetic rare earth ions; the metallic ion has been regarded as field free because of the shielding effects of the 5s and 5p shells on the 4f electrons responsible for the paramagnetism. Many substances follow the Weiss law over a considerable temperature range in preference to the Curie law. Van Vleck[30] pointed out that only the lowest energy level need be considered in the calculation of magnetic susceptibility if the energy difference between the two lowest states is large compared to kT since ions with higher J values will be present in inappreciable quantities. However, at ordinary temperatures kT is of the same order as the energy separations produced by the crystal field and Penney and Schlapp[31] consider the failure of both the Curie and the Weiss laws at very low temperatures to result from the splitting of the levels produced by the electric fields of the surrounding ions.

## Table 1

### Energy Levels of Praseodymium Salts

| | $Pr_2(SO_4)_3\cdot 8H_2O$ | | | | | | $Pr(C_2H_5SO_4)_3\cdot 9H_2O$ | | $Pr_2Mg_3(NO_3)_{12}\cdot 24H_2O$ |
|---|---|---|---|---|---|---|---|---|---|
| | Ellis[26] | | Spedding[19] | | Hellwege[22] | | Ellis[26] | | Hellwege[22] |
| | 0 | | 0 | | 0 | | 0 | | 0 |
| | 50 | | | | 52 | | 12 | | 96 |
| | 110 | | 110 | | | | | | |
| $^3H_4$ | 180 | $^3H_4$ | | $^3H_4$ | | $^3H_4$ | | $^3H_4$ | |
| | 230 | | 235 | | | | | | |
| | 500 | | 500 | | | | | | |
| | | | | | 16,686 | | 16,708 | | 16,873 |
| | | | | $^1G_4$ | 16,798 | $^1D_2$ | 16,858 | $^1G_4$ | 16,897 |
| | | | | | 17,184 | | 16,955 | | 16,922 |
| | | | | | | | | | 16,936 |
| $^3P_0$ | 20,720 | | | | | $^3P_0$ | 20,685 | $^3P_0$ | 20,800 |
| | | | | | | | | | 20,842 |
| | 21,158 | | | | | | 21,275 | | 21,422 |
| $^3P_1$ | 21,238 | | | | | $^3P_1$ | 21,289 | $^3P_1$ | 21,461 |
| | 21,359 | | | | | | | | |
| | | | | | | | 22,410 | | 22,621 |
| | | | | | | $^3P_2$ | 22,480 | $^3P_2$ | 22,654 |
| | | | | | | | | | 22,687 |
| | | | | | | | | | 22,713 |

## III. EXPERIMENTAL

### A. Design of Apparatus

A grating spectrophotometer embodying a satisfactory compromise between high dispersion and speed was constructed for use in the determination of the absorption spectra of solids. The instrument may be converted into a stigmatic grating spectrograph covering the range from 1850 to 12000 angstroms with an almost normal dispersion of 11 angstroms per millimeter; the range of the spectrophotometer is limited to from 3000 to 10000 angstroms by the spectral sensitivity of the photoelectric surface.

The schematic arrangement of the instrument may be seen in Figure 1. Light from a single filament incandescent lamp or a hydrogen arc[32] is focused on the slit $S_1$ by the quartz condensing lens $L_1$ which is at the focal length of the concave mirror M and fills the grating G with parallel light. The spectra are brought to focus without appreciable astigmatism at the slit $S_2$ and the collimating lens $L_2$ collects the narrow spectral region isolated. A practically parallel beam of radiation passes through one of the cells and onto the cathode of the photo-multiplier. The amplified photoelectric current is measured by observing the galvanometer deflection with a telescope and an illuminated scale.

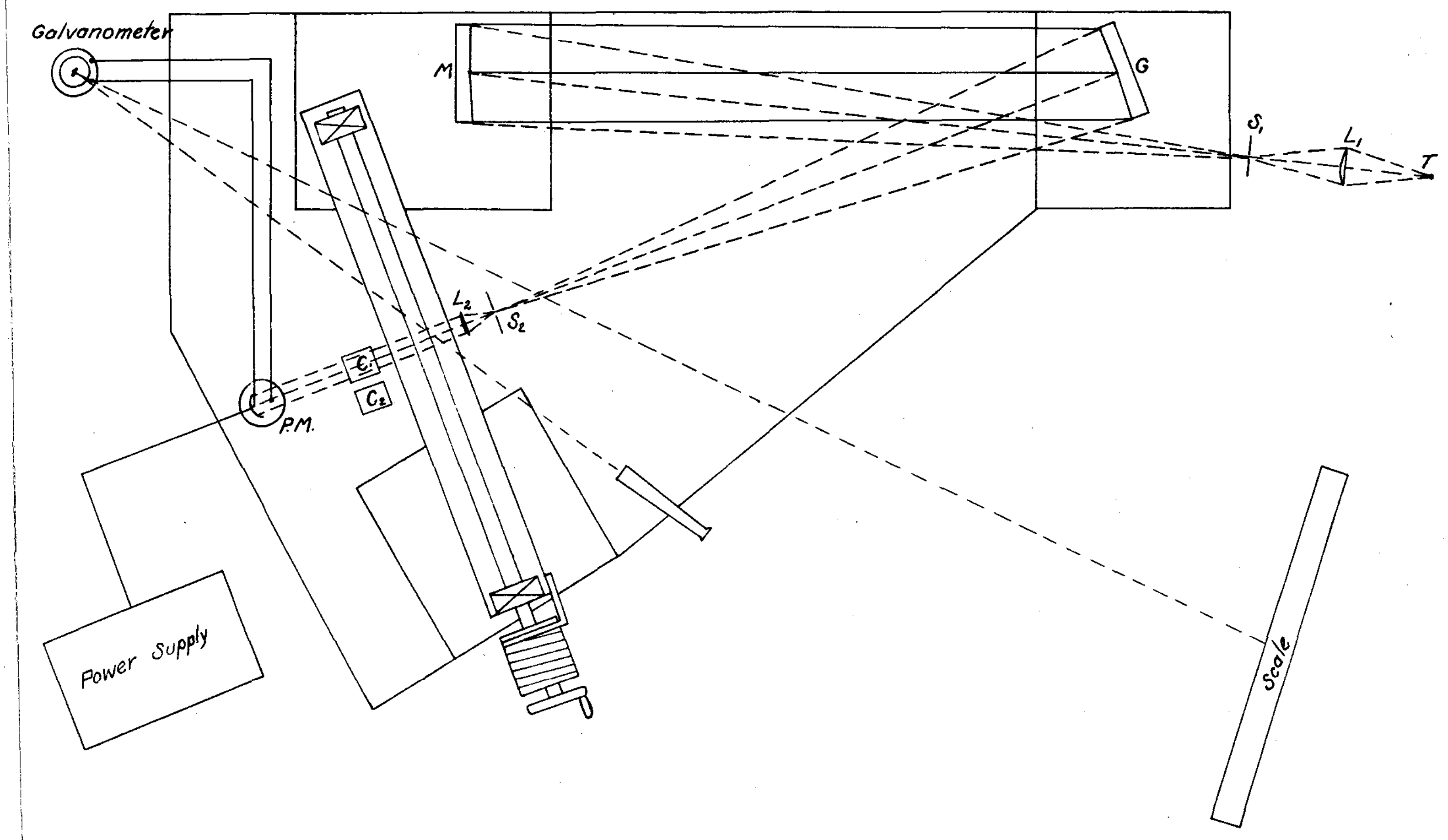

Fig. 1. Diagram of spectrophotometer

The arrangement of the Wadsworth mounting employed is similar to that described by Meggers and Burns[33] for a stigmatic grating spectrograph. The wave length, L, passing through the second slit at a given position is determined from the relationship:

$$L = \frac{b \sin i}{n}$$

where b is the grating space, i is the angle between incident and diffracted beams, and n is the order of the spectrum. This wave length is in focus at a distance d from the grating where:

$$d = \frac{R}{1 - \cos i}$$

and R is the radius of curvature of the grating. The focal curve is not a circle and a gradual increase in dispersion accompanies the increasing grating to slit distance.

The six-inch concave grating of aluminum-on-glass has a ten-foot radius of curvature and was ruled with 14,448 lines to the inch by R. W. Wood. The first surface mirror of aluminum-on-glass has a focal length of 6 feet and was supplied by the Chicago Optical Company. The reflectivity of aluminum surfaces on glass is high throughout the infrared and the visible but becomes very low below 2500 angstroms.

The grating, second slit, collimating lens, cell holder, and photo-cell multiplier are mounted on a steel beam which is pivoted on a vertical axis passing through the middle of the grating and the spectrum is traversed by turning the screw which swings the beam. The wave length at the second slit or the center of the photographic plate is indicated on the drum by a spiral scale and a fractional disc which may be read to the nearest 0.01 angstrom. The reduction for the spiral scale is accomplished with a gear train and the fractional reading is taken from a disc keyed directly to the shaft to avoid backlash errors. A single adjustment is sufficient to bring the desired region into focus since the follower on the slit cart is pushed against a cam by a spring and keeps the slit in the focal plane as it is moved across the spectrum. The collimating lens behind the second slit is rendered an effective achromat by another cam which keeps the lens placed at its focal length from the slit.

The instrument may be converted to a spectrograph by replacing the slit and lens with a rack for the plate holder; two bolts and a pair of alignment pins keep the plate or the slit in the same position, and the cam used for the slit serves to keep the photographic plate in focus. Flat plates 2 x 5 inches are used with an adapter and are in satisfactory focus the length of the plate; considerable bending of the glass plate is required if 4 x 10 inch plates are used. The motor on the plate holder permits the dark slide to be opened or closed without darkening the room.

Three concrete piers covered with steel bedplates furnish a support of high rigidity for the optical parts. The cabinet is of sheet metal bolted to a welded angle iron framework. Access to the plateholder and the cells is had through a sliding panel above the wave length drum; another panel on the side of the instrument was provided to make any part of the interior accessible. The grating compartment is covered with a removable hatch to check the illumination of the grating; a protective celluloid hood is used to cover the grating when it is not in use. The interior of the instrument has been painted a flat black with an optical paint and numerous light baffles have been added to reduce the scattered light level.

By placing the cell holder (Figure 2) behind the second slit, the absorption sample is exposed to radiation of only the wave length being measured and the amount of photochemical decomposition is reduced. The small motor on the cell holder is controlled by a reversing switch close to the wave-length drum and rotates the samples in and out of the light path; reproducible stops hold the sample in the center of the optical path during a measurement. A disassembled absorption cell is shown in front of the cell holder in Figure 2. The cells are similar to those described by Hogness[4] and consist of a glass spreader of the desired length between crystal quartz windows which are held together by brass caps screwed to a brass spreader. The solutions are not exposed to possible contamination from washers and sealing compounds, since the rubber washers used to protect the windows from breakage are between the windows and the caps; the ends of the spreaders

Fig. 2. View of cell holder showing a disassembled absorption cell

must be ground sufficiently flat to prevent leakage. Different spreaders are used to give cells of 0.5, 1, 2, 4, and 8 cm. length; these lengths are accurate to 0.1 per cent. The windows are 4 cm. in diameter, 3 mm. thick, and were cut perpendicular to the optic axis from the same quartz crystal.

The electrical connections for the photocell multiplier may be seen in Figure 4. The eleven-stage photocell multiplier tube, manufactured by Farnsworth Television and Radio Corporation, is a type B tube wherein the dark current and noise are reduced. The tube has a special quartz window to extend its range below the transmission cutoff for pyrex glass. The caesium-coated cathode has a sensitivity of 20 microamperes lumen and the over-all sensitivity of the tube is 0.182 amperes lumen at 100 volts/stage; the dark current at this operating voltage is equivalent to 4 microlumens.

The tube may be operated from 30 to 140 volts/stage; it is necessary to apply twice the voltage per stage between the cathode and the first stage to insure that all electrons from the photo-cathode enter the multiplier. The voltage between the last stage and the positive pole of the voltage divider is 50 volts greater than the voltage per stage to compensate for any voltage drop across the galvanometer at peak output. The sensitivity of the tube is greater at higher voltages, but the fluctuations in the dark current also increase; the optimum voltage per stage was found to be 100 volts by setting the fluctuation equal to 1 millimeter with a galvanometer shunt

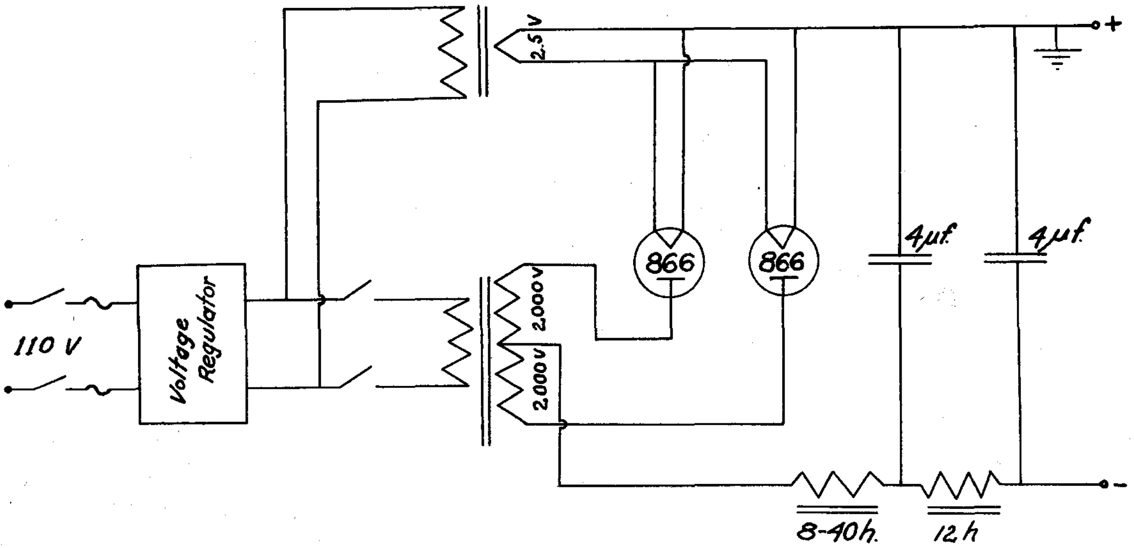

Fig. 3. Diagram of power supply for photo-multiplier

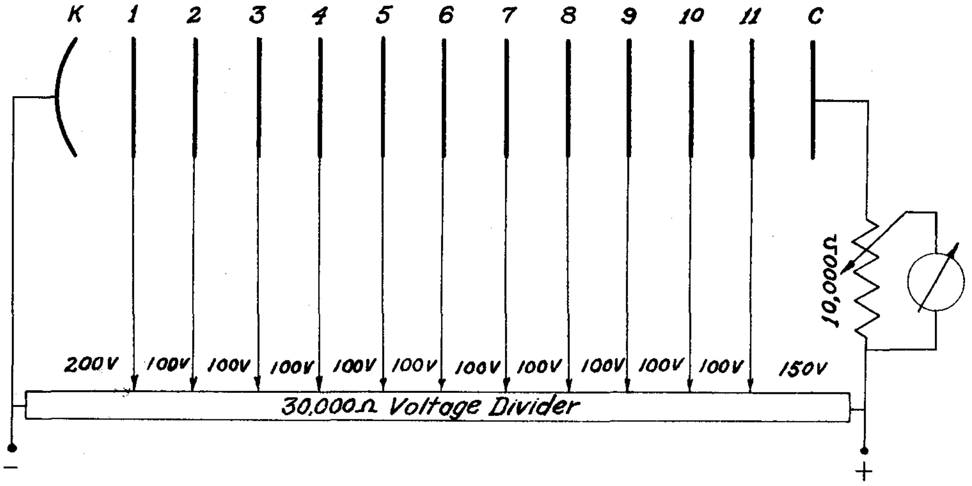

Fig. 4. Diagram of photo-multiplier connections

and measuring the response to a standard intensity source at a given wave length. A variation in the voltage from stage to stage of more than 5 per cent will markedly reduce the sensitivity of the tube by destroying the electrostatic focusing. Approximately 35 minutes of operation is required for the tube to come to equilibrium. The tube is mounted in a sheet iron box on the end of the rotating I-beam and the leads are brought to the tube in flexible shielded cables. Anhydrone is kept in the box to reduce insulation leakage difficulties, and leakage between the collector and stage terminals was prevented by grounded metal guard rings.

The full-wave rectifier circuit shown in Figure 3 provides a 2000-volt potential across the 30,000-ohm voltage divider; the bleeder current of 60 milliamperes is sufficiently large to prevent noticeable fluctuations in input voltage with load variations. A two-stage filter is necessary to reduce the ripple in the rectified voltage to prevent a corresponding fluctuation in the output. The electromagnetic voltage regulator reduces the disturbances caused by ambient fluctuations in the line voltage. The power supply and the galvanometer shunt are mounted on a relay rack with adequate shielding to protect against accidental contact with high voltages. The effect of stray currents has been minimized by shielding and grounding all leads to a common ground.

The amplified photoelectric current is registered by a Leeds and Northrup moving coil galvanometer having a current sensitivity of $1.67 \times 10^{-9}$ amperes/millimeter at the scale distance of 5 meters. The galvanometer shunt is used to maintain the scale deflection at 1 meter as the spectral sensitivity of the tube and the energy of the source vary with changing wave length. The galvanometer is mounted on a heavy concrete block suspended by coiled steel springs to reduce the magnitude of vibrations which at the scale distance employed are ordinarily troublesome. The illuminated scale is graduated in centimeters and may be read to the nearest millimeter with a telescope mounted on the instrument. The dark current is compensated for by zeroing the galvanometer when the voltage has been applied to the tube; the final zeroing is accomplished by adjusting the sliding scale rather than the galvanometer mirror.

## B. Test of Apparatus

The wave-length drum of the monochromator was calibrated with standard lines from a mercury arc, a neon tube, and a helium tube. Radiation from the standard source was focused on the first slit and a series of readings were made as the slit was moved across the spectral line by rotating the drum. The drum readings at the point of maximum deflection were plotted against the wave lengths of the corresponding lines and a smooth curve drawn through the points; the slight deviation from a straight line is produced by the gradual increase in dispersion that occurs as the slit is moved away from the grating. The intensities of the lines were regulated with a diaphragm to obtain a galvanometer deflection of one meter at the maximum; both slits were of equal width and the spectral region isolated was two angstroms. One turn of the screw corresponds to 19 angstroms and a wave length setting may be reproduced to within 0.1 angstrom if it is approached from the same side each time. When the slit is replaced by the plateholder and subsequently returned in the conversion from a spectrograph to a spectrophotometer, the shift in the calibration curve amounts to less than 3 angstroms. The shape and position of the cam used to keep the slit and plateholder in the focal plane were adjusted by tightening or loosening the forming bolts until satisfactory focus plates were obtained; this adjustment is sufficient for both slit and plateholder since their distances from the cam are the same.

The spectral regions isolated in the testing of the spectrophotometer varied from one to ten angstroms but the lower limits of the spectral band widths have not been reached. The minimum band width occurs at 8000 angstroms near the peak of the tube sensitivity; the band width required at a given wave length is determined by the spectral distribution of the energy of the source and the spectral sensitivity of the cathode. The over-all sensitivity and accuracy of the spectrophotometer are determined by the stability of the photo-multiplier and of the light source which in turn are governed by the constancy of the alternating current voltage supply. The random fluctuations in line voltage were so great at certain periods of the day that the electromagnetic voltage regulator would not reduce them to a satisfactory level.

The over-all linearity of response of the spectrophotometer has been tested by determining the transmission at various wave lengths of two calibrated filters furnished by the Bureau of Standards. An indication of the amount of scattered light was obtained by determining the transmission with and without supplementary filters using both a line source and an incandescent lamp. The values obtained are given in Tables 2 and 3. Transmission is defined as the ratio of the radiant energy emerging from the filter to that incident upon the filter, the directions of both the incident and emergent beams being effectively at right angles to the surface of the filter. The wave lengths given are in angstrom units.

The values given are an average of five determinations and the reproducibility varies with the magnitude of the fluctuations in the supply voltage. The line source with a supplementary filter produced monochromatic radiation and the results obtained check the Bureau of Standards values within the limits of error. The results obtained with the line source without a filter are much better than the corresponding values with the incandescent lamp since the scattered light is appreciably less. The high red sensitivity of the cathode

## Table 2

### Transmission of Bureau of Standards Filter G55A 16

| Wave length | Bureau of Standards | Line Source | Line Source - Filter | Incandescent Source | Incandescent Source - Filter |
|---|---|---|---|---|---|
| 7500 | 0.902 ±.005 | | | 0.890 | 0.890 |
| 7200 | 0.847 ±.01 | | | 0.848 | 0.830 |
| 7065 | 0.72 ±.02 | 0.742 | 0.747 | 0.733 | 0.719 |
| 6900 | 0.38 ±.01 | | | 0.381 | 0.379 |
| 6800 | 0.16 ±.01 | | | 0.1673 | 0.1724 |
| 6678 | 0.047 ±.002 | $0.046^{8}$ | $0.47^{0}$ | $0.047^{1}$ | $0.46^{0}$ |
| 6600 | 0.024 ±.001 | | | 0.0303 | 0.0249 |
| 6400 | 0.0121 ±.0003 | | | 0.0158 | 0.0118 |
| 5876 | 0.0138 ±.0002 | 0.0142 | | 0.01714 | 0.0168 |
| 5460.7 | 0.0477 ±.0003 | 0.0490 | | 0.0565 | 0.0539 |
| 4358 | 0.819 ±.003 | 0.818 | 0.821 | 0.840 | |
| 4047 | 0.885 ±.005 | 0.891 | 0.887 | | 0.900 |

## Table 3

### Transmission of Bureau of Standards Filter OG-3

| Wave length | Bureau of Standards | Line Source | Line Source - Filter | Incandescent Source | Incandescent Source - Filter |
|---|---|---|---|---|---|
| 7500 | 0.912 ±.005 | | | 0.894 | 0.895 |
| 7200 | 0.912 ±.005 | | | 0.898 | 0.896 |
| 6900 | 0.912 ±.005 | | | 0.892 | 0.866 |
| 6600 | 0.911 ±.005 | | | 0.915 | 0.916 |
| 6400 | 0.908 ±.005 | | | 0.910 | 0.899 |
| 5876 | 0.172 ±.005 | 0.1506 | | 0.1630 | 0.1579 |
| 5460 | 0.0000 ±.0000 | 0.0000 | 0.0000 | 0.0088 | 0.0000 |
| 4358 | 0.0000 ±.0000 | 0.0000 | 0.0000 | 0.292 | 0.0000 |

amplifies the effect of the scattered light in the blue region and a supplementary filter must be used to absorb the red radiation. A filter to absorb the second order is not required below 10,000 angstroms because of the low intensity of the second order and the selective response of the photomultiplier cathode. The scattered light may produce high or low results depending upon whether the average transmission of the scattered light is greater or smaller than the transmission of the wave length isolated.

## C. Preparations

The praseodymium, europium, and lanthanum salts used in this investigation were obtained from a personal supply of Dr. F. H. Spedding; they were of unusual purity and no indications of the presence of other rare earths in detectable quantities were observed. The praseodymium was molecularly mixed with other rare earths to permit the preparation of a number of crystal modifications.

The ignitions which required a controlled temperature were carried out in a quartz tube-furnace heated by resistance coils; the desired temperature was obtained by adjusting the heating current with an auto-transformer. A voltage regulator was used to supply the auto-transformer with a constant voltage to reduce the heating current fluctuations. Temperature measurements in the furnace were made with an iron-constantan thermocouple and were considered accurate to within 5° C. Some of the ignitions were carried out over a Meker burner and estimates of the temperatures were obtained with a Leeds and Northrup optical pyrometer. Because of the highly refractory nature of the rare earth oxides, it was found advantageous to interrupt the heating occasionally to powder and mix the sample in order to secure a homogeneous oxide without resorting to inordinately long heating periods. The rate and period of heating as well as the maximum temperature attained are the factors that determine which crystal modification of the oxide is formed. Platinum crucibles were used throughout after alundum crucibles proved to be unsatisfactory by reacting with praseodymium oxide at higher temperatures.

Praseodymium is easily oxidized to the tetravalent state by atmospheric oxygen at elevated temperatures and a hydrogen atmosphere was used with all preparations containing praseodymium. A nitrogen atmosphere was found inadequate to prevent the formation of the tetravalent oxide; small quantities of the dioxide would cause considerable trouble because of its strong general absorption of light. A supply of europium oxalate was used as the starting point for the preparation of europium compounds. The tetragonal crystal modification of europium oxide was prepared by the ignition of the hydroxide starting with a cold-resistance furnace and heating for 24 hours at 600° C. If the ignition temperature was raised rapidly, a mixture of tetragonal and cubic forms was obtained; an amorphous oxide appeared at ignition temperatures below 600° C. Only a small amount of the tetragonal form was converted to the cubic modification by 187 hours of heating at 750° C. and an additional 68 hours at 930° C. was required to complete the transformation. If the furnace is rapidly brought to a temperature of 740° C., a few hours ignition of the hydroxide is sufficient to prepare a pure cubic oxide. A mixture of the B and C forms was obtained by igniting the hydroxide over a Meker burner for 11 hours; further ignition at the full heat of a Meker burner produced no change in the relative amounts of the two forms. The influence of crystal structure on the blue multiplet of europium oxide shown in Figure 5 afforded a rapid and easy method of identifying the crystal modifications.

Lanthanum sesquioxide was obtained in the hexagonal form by igniting the oxalate over a Meker burner for 77 hours at 950° C.; the sample was removed at intervals and pulverized to insure an even heating. A Debye-Scherrer diagram made on this sample after 11 hours of heating showed some X form to be present. A sample prepared by igniting the hydroxide in the electric furnace for 165 hours at 975° C. still showed traces of the X form.

The X modification of lanthanum sesquioxide was prepared by igniting the hydroxide over a Meker burner at 950° C. for 3 hours; this sample contained 3 per cent praseodymium

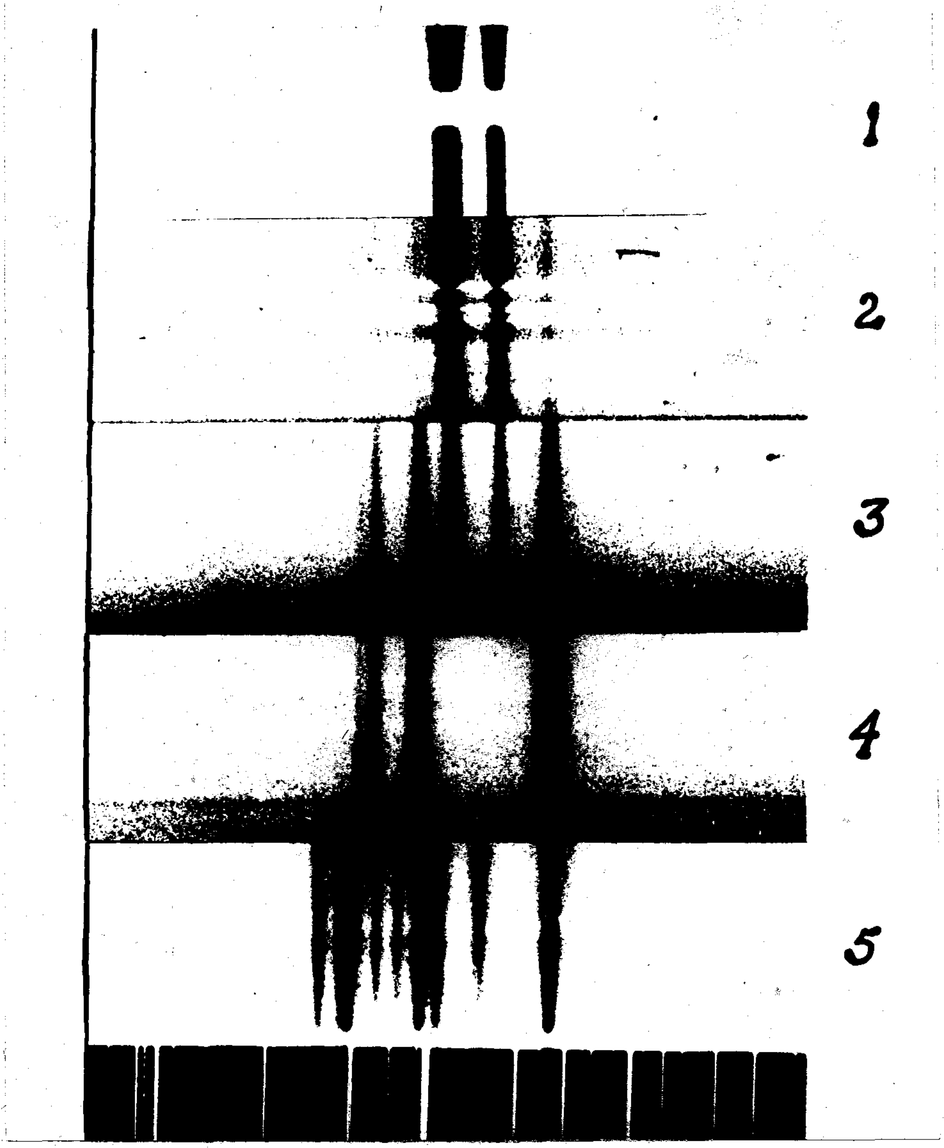

Fig. 5. Influence of Crystal Structure on Blue Multiplet of Europium Oxide. (1) Tetragonal modification; (2) tetragonal plus small amount of cubic form; (3) approximately equal amounts of tetragonal and cubic forms; (4) cubic modification; (5) mixture of cubic and pseudo-trigonal modification.

sesquioxide. Prolonged heating converted the X to the hexagonal form. A mixture of a more complicated form and the hexagonal modification was prepared by igniting the hydroxide over a Meker burner at 950° C. for 10 hours; this sample contained 10 per cent praseodymium sesquioxide.

## D. Methods of Procedure

Samples of the desired thickness were made by squeezing the oxide paste between two pyrex plates and sealing the cell with Plycene cement. The paste was made by grinding the oxide together with a drop of mineral oil for a binder to a stiff paste in an agate mortar; the thicknesses of the samples varied from 0.02 to 0.001 inch. The glass cell was attached to a piece of cardboard having a hole cut for the light beam and the assembled sample was mounted on a wooden dowel stick.

The low temperature spectra at 78° K. were made by immersing the samples in liquid nitrogen contained in a large Dewar flask similar to those described by Spedding and Bear[34]. It is necessary that the liquid nitrogen be comparatively free from liquid oxygen to avoid the wide absorption bands of the oxygen that occur in the red region. The Dewar was placed between the light source and the slit of the spectrograph and the light passed through by means of two windows left unsilvered in the sides of the flask. The most satisfactory light source for the regions covered was a single filament incandescent lamp operated with 7.5 amperes at 50 volts; radiation from the lamp was concentrated on the sample with a large condensing lens. An additional quartz lens was used to focus a sharp image of the sample on the slit of the spectrograph. The three-meter grating spectrograph used had an almost normal dispersion of 11 angstroms per mm. The exposure time for the oxide samples varied from a few minutes in the visible region to two days in the infrared region. Although four more optical surfaces are introduced in the optical path when the Dewar is used, the exposure times for the low temperature plates remained about the same as those made at room temperature because of the decrease in the scattering power of the sample produced by the solidification of the mineral oil. A reference spectrum was photographed in juxtaposition to the oxide spectra with the aid of a Hartmann diaphragm; a standard iron arc was used in all regions except from 5750 to 8000 angstroms where the neon spectrum is more suitable.

The class of sensitization of the spectrographic plate used for a given region was that recommended by Eastman Kodak Company[35]. A 103 type emulsion was used to explore a region and when the lines had been located the plates to be measured were made on the slower but more contrasty type 111 emulsion. The plates were examined on a viewing box with the aid of a jeweler's lens and the emulsion was pricked at the edges of the lines which were too faint to observe with the high-power microscope on the measuring engine. The plate was then clamped on the stage of the comparator and readings were made at the edges and center of each line; appropriate lines from the reference spectrum were also included. The wave lengths of the absorption lines were then calculated by interpolating between two standard lines of the reference spectrum; the deviations between other standard lines and their calculated values were plotted against the comparator readings and slight corrections taken from this plot were added to the calculated wave lengths. A minumum of two values from different spectrograms were used to establish the wave length of the lines. The intensities of the lines were more satisfactorily established on the arbitrary scale by comparing a group of plates than by assigning a value to each isolated line.

The wave lengths of the lines were converted from angstrom units in air to reciprocal centimeters in vacuo and their positions were plotted on a large graph to facilitate the interpretation of the spectra.

The samples for the x-ray powder patterns were taken from the cells used for the absorption spectra to avoid any errors arising from non-homogeneous preparations.

# IV. RESULTS

## A. Crystal Structure of Europium and Lanthanum Oxides

Europium oxide was prepared in three crystal modifications, a low temperature form which has been satisfactorily indexed on the tetragonal system and the cubic and pseudotrigonal forms which have been previously reported by other investigators. The x-ray data for the tetragonal crystal are given in Table 4. The dimensions for the unit cell are similar to those observed for the hexagonal modification of the rare earth oxides but the density has been decreased from approximately 7 to 5.4 by the more loosely packed arrangement. The crystal data from the Debye-Scherrer diagram of the cubic modification are given in Table 5; the value obtained for the unit cube edge is slightly smaller than that reported by Zachariasen[14]. The pseudotrignal modification was not obtained in the pure form and no attempt was made to index the crystal since it appears to be of low symmetry. No single crystals were obtainable for these highly refractory oxides and powder data alone is inadequate to definitely establish the correct cell and space group for crystals of a symmetry much lower than cubic.

The slow rate of conversion from one crystal form to another makes the temperature at which the oxide is formed

## Table 4

### X-Ray Data for Tetragonal Modification of $Eu_2O_3$

| Ring Diameter in mm. | Intensity | Bragg Angle in degrees | $\sin^2 \theta$ experimental | $\sin^2 \theta$ calculated | Indices |
|---|---|---|---|---|---|
| 22.74 | 3 | 6.51 | 0.01281 | 0.0129 | 001 |
| 44.83 | 8 | 12.84 | 0.04908 | 0.0497 | 011 |
| 54.83 | 6 | 15.70 | 0.07323 | 0.0736 | 110 |
| 60.33 | 7 | 17.27 | 0.0881 | 0.0884 | 012 |
| 69.77 | 1 | 19.98 | 0.11679 | 0.1161 | 003 |
| 72.42 | 2 | 20.84 | 0.1265 | 0.1252 | 112 |
| 77.69 | 3 | 22.25 | 0.1436 | 0.1472 | 020 |
| 82.25 | 1 | 23.55 | 0.1596 | 0.1601 | 021 |
| 90.18 | 1 | 25.833 | 0.1899 | 0.1897 | 113 |
| 91.95 | 2 | 26.34 | 0.1968 | 0.1969 | 121 |
| 101.39 | 3 | 29.05 | 0.2358 | 0.2356 | 122 |
| 103.36 | 1 | 29.60 | 0.2440 | 0.2432 | 014 |
| 107.86 | 1 | 30.88 | 0.2635 | 0.2633 | 023 |
| 111.68 | 1 | 31.97 | 0.2803 | 0.2800 | 114 |
| 114.78 | 1 | 32.89 | 0.2950 | 0.2944 | 220 |
| 125.69 | 1 | 35.99 | 0.3455 | 0.3441 | 031 |
| 130.47 | 1 | 37.37 | 0.3697 | 0.3693 | 015 |
| 133.40 | 1 | 38.21 | 0.3824 | 0.3828 | 032 |
| 134.94 | 1 | 38.61 | 0.3892 | 0.3904 | 124 |
| 138.95 | 1 | 39.81 | 0.4100 | 0.4105 | 223 |
| 140.94 | 1 | 40.38 | 0.4198 | 0.4196 | 132 |

Dimensions of unit cell: $a_o = 4.04$ A. U.
$c_o = 6.78$ A. U.

Axial ratio $C = 1.67$
Experimental Density $D = 5.4$ g./cc.
Calculated Density (one molecule per unit cell) $D = 5.3$ g./cc.

Cu $K_a$ radiation; Camera radius = 5 cm.

### Table 5

### X-Ray Data for Cubic Modification of Europium Oxide

| Ring Diameter in mm. | Intensity | Bragg Angle | $\mathrm{Sin}^2\ \theta$ | Indices | Unit Cube Edge |
|---|---|---|---|---|---|
| 35.27 | 1 | 10°-6' | 0.03075 | 211 | 10.77 |
| 50.33 | 8 | 14°-25' | 0.06199 | 222 | 10.76 |
| 58.27 | 3 | 16°-41' | 0.08242 | 400 | 10.75 |
| 61.74 | 1 | 17°-41' | 0.09227 | 114,330 | 10.76 |
| 68.60 | 1 | 19°-39' | 0.1131 | 233 | 10.74 |
| 75.06 | 1 | 21°-30' | 0.1343 | 150,134 | 10.73 |
| 83.44 | 3 | 23°-54' | 0.1641 | 440 | 10.77 |
| 91.68 | 1 | 26°-16' | 0.1958 | 116,235 | 10.73 |
| 99.08 | 1 | 28°-23' | 0.2260 | 226 | 10.75 |
| 101.03 | 1 | 28°-57' | 0.2343 | 136 | 10.79 |
| 103.86 | 1 | 29°-45' | 0.2462 | 444 | 10.75 |

| | Zachariasen[14] | Experimental |
|---|---|---|
| Unit Cube Edge | 10.84 A.U. | 10.75 A.U. |

Cu $K_a$ radiation; Camera radius = 5 cm.

the most important factor in the preparation of a given crystal modification rather than the final temperature to which it is heated. If the preparation is carried out by starting the ignition in a cold electric resistance furnace and heating to the desired temperature, the tetragonal form is always obtained and prolonged heating is required to convert it to the cubic form. However, if the oxide is produced by rapidly igniting the hydroxide for a short time at temperatures over 750° C., a mixture of the cubic and pseudotrigonal forms is obtained whose relative amounts remain unchanged upon further heating. The transition temperature between the tetragonal and the cubic modifications lies below 600° C.; no tetragonal form was produced by the ignition of the oxalate which decomposes at a higher temperature than the nitrate or the hydroxide. The cubic form was heated for 68½ hours at 1000° C. without undergoing any transition to the pseudotrigonal modification. A 48-hour ignition of the hydroxide at 500° C. produced an amorphous oxide. The absorption spectra of this oxide consisted of extremely diffuse bands and the Debye-Scherrer diagram possessed no definite pattern; further heating at 600° C. gave a mixture of the cubic and tetragonal forms.

Lanthanum sesquioxide was prepared in the hexagonal form and in two unidentifiable crystal modifications which have been designated by X and B. The x-ray data for the hexagonal form are given in Table 6; the dimensions calculated for the

## Table 6

### X-Ray Data for Hexagonal Modification of $La_2O_3$

| Ring Diameter in mm. | Intensity | Bragg Angle in degrees | $Sin^2 \theta$ experimental | $Sin^2 \theta$ calculated | Indices |
|---|---|---|---|---|---|
| 45.52 | 7 | 13.03 | 0.0508 | 0.0508 | 100 |
| 50.79 | 4 | 14.55 | 0.0631 | 0.0628 | 002 |
| 52.24 | 10 | 14.96 | 0.0667 | 0.0665 | 101 |
| 68.86 | 6 | 19.73 | 0.1140 | 0.1136 | 102 |
| 80.36 | 8 | 23.02 | 0.1528 | 0.1533 | 110 |
| 90.90 | 7 | 26.04 | 0.1926 | 0.1921 | 103 |
| 93.74 | 1 | 26.85 | 0.2040 | 0.2032 | 200 |
| 96.67 | 7 | 27.69 | 0.2161 | 0.2161 | 112 |
| 97.57 | 6 | 27.95 | 0.2197 | 0.2189 | 201 |
| 105.24 | 1 | 30.15 | 0.2500 | 0.2512 | 004 |
| 108.49 | 2 | 31.08 | 0.2665 | 0.2660 | 202 |
| 116.63 | 1 | 33.42 | 0.3014 | 0.3020 | 104 |
| 125.59 | 5 | 35.98 | 0.3452 | 0.3445 | 203 |
| 127.85 | 1 | 36.62 | 0.3557 | 0.3057 | 210 |
| 131.28 | 6 | 37.60 | 0.3723 | 0.3214 | 211 |
| 137.85 | 3 | 39.50 | 0.4046 | 0.4045 | 114 |
| 140.73 | 2 | 40.29 | 0.4130 | 0.3685 | 212 |
| 145.81 | 2 | 41.77 | 0.4437 | 0.4433 | 105 |
| 148.51 | 2 | 42.54 | 0.4570 | 0.4572 | 300 |
| 156.44 | 5 | 44.81 | 0.4965 | 0.4470 | 213 |
| 161.21 | 2 | 46.18 | 0.5206 | 0.5200 | 302 |

| Dimensions of Unit Cell: | Experimental | Zachariasen[12] |
|---|---|---|
| | $c_o$ = 6.15 | 6.12 |
| | $a_o$ = 3.95 | 3.93 |
| | $c$ = 1.555 | 1.558 |

Cu $K_a$ radiation; Camera radius = 5 cm.

unit cell are in close agreement with those obtained by Zachariasen[6]. Attempts to index the X modification from the x-ray data given in Table 7 were unsuccessful on the hexagonal and tetragonal systems. It is not certain whether the X form is the pseudotrigonal form predicted by Goldschmidt's table[1] since another modification was observed to be present in some of the mixtures obtained. The appearance of the absorption spectra of the praseodymium oxide contained in solid solution with the lanthanum oxide suggests the X form possesses a symmetry comparable to that of the hexagonal form and much higher than that of the B form. Considerable trouble was experienced in preparing a given crystal modification in a pure state; the X form may be converted into the hexagonal modification by prolonged heating. Methods for the preparation of the various crystal modifications are discussed under the heading EXPERIMENTAL.

## B. Spectra

The absorption lines of praseodymium sesquioxide in different types of crystal lattices are given in the following three tables. The values given are an average of at least two measurements from different spectrograms. The accuracy of the wave lengths listed depends upon the character of the line; in general, the center of the more intense lines can be depended on to two wave numbers while some of the weak diffuse lines may be in error from 5 to 10 cm.$^{-1}$ The width of the

## Table 7

## X-Ray Data for "X" Modification of $La_2O_3$

| Ring Diameter in mm. | Intensity | Bragg Angle in degrees | $\mathrm{Sin}^2\ \theta$ experimental | d/n |
|---|---|---|---|---|
| 27.01 | 5 | 7° 45' | 0.01819 | 5.71 |
| 47.05 | 4 | 13° 29' | 0.05437 | 3.30 |
| 48.25 | 4 | 13° 50' | 0.05717 | 3.22 |
| 54.76 | 1 | 15° 41' | 0.07307 | 2.85 |
| 62.46 | 1 | 17° 54' | 0.09447 | 2.51 |
| 68.23 | 3 | 19° 33' | 0.1120 | 2.30 |
| 73.14 | 1 | 20° 55' | 0.1274 | 2.16 |
| 81.45 | 1 | 23° 20' | 0.1569 | 1.94 |
| 84.02 | 3 | 24° 5' | 0.1665 | 1.89 |
| 86.42 | 1 | 24° 46' | 0.1755 | 1.84 |
| 95.62 | 1 | 27° 23' | 0.2115 | 1.67 |
| 97.39 | 1 | 27° 54' | 0.2190 | 1.65 |
| 110.85 | 1 | 31° 44' | 0.2766 | 1.46 |
| 120.53 | 1 | 34° 32' | 0.3214 | 1.36 |

Cu $K_a$ radiation; Camera radius = 5 cm.

lines depends upon the thickness of the sample and the optical density of the spectrogram.

Lines designated by L are low temperature lines and are believed to have originated from the lowest lying level; the high temperature lines are denoted by H and are definitely increased in intensity at higher temperatures. The character of the line is given under the heading I; the letter s was used to designate lines having sharp edges and d indicates a diffuse line. The intensities of the lines are from visual comparisons with adjacent lines on a scale extending from 0 to 10. Lines marked 0 were so weak they were barely discernible and those marked 10 were completely absorbed in the thin samples. The edges of the weaker lines were pin pricked in the gelatine of the plate and comparator measurements were made to these points.

Table 11 gives evidence for the existence of a level lying 99 wave numbers above the lowest level. Theory[28] predicts that the basic state of Pr IV which is a $^3H_4$ level will be split into 4 components by a field of cubic symmetry and into a maximum of 9 components by fields of much lower symmetry. The small number of lines occurring in the oxide spectra militated against the finding of all levels and it is possible that additional low-lying levels exist. The two low-lying states were established by the repetition of their spacing in several multiplets and by the temperature dependence of these lines. Lines arising from the two states and terminating in common upper levels should be separated by an interval equal to that separating the two lower levels. Those transitions arising from the lowest level should show a marked increase in intensity as the temperature is lowered because of the increase in the population of this level, and those arising from the higher level should increase in intensity as the population of the level increases with increasing temperatures. The intensity cannot be relied upon with certainty to indicate the lines of electronic origin since it is possible for a coupled electronic and vibrational line to be very intense under favorable conditions.

A value of 108 wave numbers was obtained for the mean separation of the two levels at a temperature of 300° K; this shift from 99 cm.$^{-1}$ at 78° K was produced by the change in the effective fields on the electrons as the crystal expanded on warming. In general, the lines at room temperature are shifted about ten wave numbers to the blue from the corresponding lines at the temperature of liquid nitrogen; the magnitude of this temperature shift varies with the relative amounts the levels of origin and terminus are influenced by the change in fields. In addition to the shift in the positions of the lines, some of them were observed to become more diffuse at higher temperatures; the thermal vibrations produce fields of varying intensity and the diffuse lines observed are a summation of many sharp transitions to a fluctuating level. Close-lying sharp lines may appear at room temperatures as a single diffuse line because of this thermal broadening. The number of lines observed increased with increasing sample thickness as the weaker lines were brought out with the increased path length of the light.

In general, intense lines may be traced from salt to salt and lines appear in approximately the same place with salts of similar crystal symmetry. However, the spectra for the three crystal modifications of praseodymium sesquioxide observed are shifted several hundred wave numbers to the red from comparable multiplets of other praseodymium compounds; this is possibly a result of the more intense crystal fields. The spectra of the oxide consist of a red multiplet at 6000 angstroms corresponding to the transition $^3H_4$ to $^1I_6$; this multiplet is moderately weak at room temperatures and strong at low temperatures. The three very strong multiplets occurring in the blue region arise from transitions from a $^3H_4$ to a $^3P_0$, $^3P_1$, and $^3P_2$. The strong lines observed overlie a general absorption which becomes increasingly strong with shorter wave lengths.

An indication of the relative symmetry of the electrical fields about the rare earth ion in the various crystal modifications was obtained from a comparison of their spectra. It has been observed that the spectra become increasingly complex as the symmetry about the ion decreases. In general, the symmetry about the ion will not be the same as the crystal symmetry but will be closely related to it. The praseodymium multiplets in the tetragonal modification of europium oxide are somewhat shifted in position from those in the hexagonal and the X forms of lanthanum oxide but are comparable in simplicity to those of the hexagonal modification. The spectrum of the X form is very similar to that of the hexagonal crystal but contains an additional number of lines.

The influence of crystal structure on a particular multiplet of the absorption spectra of europium oxide may be seen in Figure 5; the Debye-Scherrer diagrams for these forms have been given in Figure 6 for comparison. The origin of the large number of sharp lines observed in the spectra of the B oxide is not clear; both the complex x-ray powder pattern and the spectra indicate a crystal of low symmetry. It is possible that the crystal contains non-equivalent europium ions in fields of sufficiently different intensity and symmetry to account for the extra lines. A decrease in the degeneracy of the lattice vibrations in crystals of lower symmetry with a resultant increase in the number of coupled vibrational and electronic lines is an alternate possibility to the postulate of non-equivalent rare earth ions. If the multiplets containing an extra number of sharp lines are established by further work as electronic in origin, the close-lying lines probably arise from non-equivalent europium ions; and if they are not electronic, the probability favors the postulate of the increased number of allowed vibrations with a lower crystal symmetry.

## Table 8

## Absorption Spectra of $Pr_2O_3$ in an Hexagonal Lattice of $La_2O_3$

| Liquid $N_2$ Temp. | | | | Room Temp. | | | |
|---|---|---|---|---|---|---|---|
| A° | cm.$^{-1}$ | I | T | A° | cm.$^{-1}$ | I | T |
| 6115.6 | 16347 | 8d | L | 6120.8 | 16337 | 0d | |
| 6113.0 | 16354 | | | 6111.5 | 16358 | | |
| 6110.4 | 16361 | | | 6103.6 | 16379 | | |
| 6107.4 | 16369 | 8d | L | | | | |
| 6104.4 | 16377 | | | | | | |
| 6101.8 | 16384 | | | | | | |
| 5984.5 | 16705 | 0d | | 5980.2 | 16717 | 0d | |
| 5978.4 | 16722 | | | 5973.1 | 16737 | | |
| 5972.7 | 16738 | | | 5966.3 | 16756 | | |
| 5947.9 | 16808 | 10d | L | 5947.5 | 16809 | 2d | |
| 5941.5 | 16826 | | | 5937.3 | 16838 | | |
| 5935.1 | 16844 | | | 5920.0 | 16867 | | |
| 5911.3 | 16912 | 5d | L | 5908.1 | 16921 | 0d | |
| 5906.7 | 16925 | | | 5900.8 | 16942 | | |
| 5902.2 | 16938 | | | 5893.5 | 16963 | | |
| | | | | 5123.8 | 19511 | 0d | |
| | | | | 5117.5 | 19535 | | |
| | | | | 5111.5 | 19558 | | |
| 4964.1 | 20139 | 6s | | 4964.8 | 20136 | 6d | |
| 4959.4 | 20158 | | | 4959.1 | 20159 | | |
| 4955.0 | 20176 | | | 4953.7 | 20181 | | |
| 4937.8 | 20246 | 10s | L | 4934.7 | 20259 | 4d | |
| 4933.0 | 20266 | | | 4930.8 | 20275 | | |
| 4928.1 | 20286 | | | 4926.6 | 20292 | | |
| 4828.8 | 20703 | 0d | | | | | |
| 4825.1 | 20719 | | | | | | |
| 4821.4 | 20735 | | | | | | |
| 4811.2 | 20779 | 0d | | | | | |
| 4807.5 | 20795 | | | | | | |
| 4804.0 | 20810 | | | | | | |

## Table 8

(Continued)

| Liquid $N_2$ Temp. | | | | Room Temp. | | | |
|---|---|---|---|---|---|---|---|
| A° | cm.$^{-1}$ | I | T | A° | cm.$^{-1}$ | I | T |
| 4792.2 | 20861 | | | 4789.0 | 20875 | | |
| 4780.1 | 20892 | 10d | L | 4781.2 | 20909 | 2d | |
| 4778.3 | 20922 | | | 4773.7 | 20942 | | |
| | | | | 4604.2 | 21713 | | |
| | | | | 4592.8 | 21767 | 0d | |
| | | | | 4581.8 | 21819 | | |
| 4516.4 | 22135 | | | 4506.0 | 22166 | | |
| 4507.7 | 22178 | 6d | L | 4491.3 | 22259 | 1d | |
| 4498.9 | 22221 | | | 4471.8 | 22356 | | |
| 4493.1 | 22250 | | | | | | |
| 4489.8 | 22266 | 1d | | | | | |
| 4486.6 | 22282 | | | | | | |

## Table 9

## Absorption Spectra of $Pr_2O_3$ in the "X" Lattice of $La_2O_3$

| Liquid $N_2$ Temp. | | | | Room Temp. | | | |
|---|---|---|---|---|---|---|---|
| A° | cm.$^{-1}$ | I | T | A° | cm.$^{-1}$ | I | T |
| 6112.6 | 16355 | 0d | | 6119.7 | 16336 | 0d | |
| 6107.4 | 16369 | | | 6111.1 | 16359 | | |
| 6102.2 | 16383 | | | 6103.3 | 16380 | | |
| 6042.4 | 16545 | 5s | L | 6040.7 | 16525 | 0d | |
| 6040.9 | 16549 | | | 6042.8 | 16544 | | |
| 6039.1 | 16554 | | | 6036.2 | 16562 | | |
| 6036.9 | 16560 | 5s | L | | | | |
| 6035.5 | 16564 | | | | | | |
| 6033.7 | 16569 | | | | | | |
| 6000.7 | 16660 | 0d | | | | | |
| 5998.9 | 16665 | | | | | | |
| 5997.1 | 16670 | | | | | | |
| 5946.8 | 16811 | 10d | L | 5941.8 | 16825 | 3d | |
| 5938.3 | 16835 | | | 5935.8 | 16842 | | |
| 5929.9 | 16859 | | | 5929.9 | 16859 | | |
| 5907.4 | 16923 | 0d | | | | | |
| 5905.0 | 16930 | | | | | | |
| 5902.2 | 16938 | | | | | | |
| 5822.8 | 17169 | 0s | | | | | |
| 5821.8 | 17172 | | | | | | |
| 5820.8 | 17175 | | | | | | |
| 5785.7 | 17279 | 3s | L | 5793.4 | 17256 | 0d | |
| 5784.0 | 17284 | | | 5786.7 | 17276 | | |
| 5783.7 | 17289 | | | 5780.0 | 17296 | | |
| 5775.7 | 17309 | 2s | | | | | |
| 5774.7 | 17312 | | | | | | |
| 5774.0 | 17314 | | | | | | |
| 5748.1 | 17392 | 0d | | | | | |
| 5747.5 | 17394 | | | | | | |
| 5746.5 | 17397 | | | | | | |

Table 9

(Continued)

| Liquid $N_2$ Temp. | | | | Room Temp. | | | |
|---|---|---|---|---|---|---|---|
| A° | cm.$^{-1}$ | I | T | A° | cm.$^{-1}$ | I | T |
| | | | | 5121.0 | 19522 | | |
| | | | | 5114.1 | 19548 | 0d | |
| | | | | 5107.3 | 19574 | | |
| 4960.6 | 20153 | | | 4962.6 | 20145 | | |
| 4958.6 | 20161 | 2s | | 4957.9 | 20164 | 5d | H |
| 4956.9 | 20168 | | | 4953.5 | 20182 | | |
| 4934.7 | 20259 | | | 4934.2 | 20261 | | |
| 4933.0 | 20266 | 4s | | 4931.0 | 20274 | 2d | |
| 4931.2 | 20273 | | | 4927.8 | 20287 | | |
| 4902.7 | 20391 | | | | | | |
| 4901.3 | 20397 | 1s | | | | | |
| 4899.6 | 20404 | | | | | | |
| 4875.9 | 20503 | | | 4878.1 | 20494 | | |
| 4871.4 | 20522 | 10s | L | 4873.1 | 20515 | 5d | |
| 4866.9 | 20541 | | | 4867.9 | 20531 | | |
| 4849.2 | 20616 | | | 4852.5 | 20602 | | |
| 4845.4 | 20632 | 0d | | 4847.1 | 20625 | 0d | |
| 4841.2 | 20650 | | | 4841.5 | 20649 | | |
| 4827.7 | 20708 | | | | | | |
| 4824.6 | 20721 | 0d | | | | | |
| 4821.4 | 20735 | | | | | | |
| 4810.9 | 20780 | | | | | | |
| 4806.8 | 20798 | 0d | | | | | |
| 4802.6 | 20816 | | | | | | |
| 4790.1 | 20840 | | | | | | |
| 4795.0 | 20849 | 0d | | | | | |
| 4793.2 | 20857 | | | | | | |
| 4789.7 | 20872 | | | 4785.1 | 20892 | | |
| 4784.7 | 20894 | 8d | | 4782.4 | 20904 | 3d | |
| 4779.9 | 20915 | | | 4779.6 | 20916 | | |
| 4773.7 | 20942 | | | | | | |
| 4771.2 | 20953 | 0d | | | | | |
| 4768.5 | 20965 | | | | | | |

## Table 9

(Continued)

| Liquid $N_2$ Temp. | | | | Room Temp. | | | |
|---|---|---|---|---|---|---|---|
| A° | $cm.^{-1}$ | I | T | A° | $cm.^{-1}$ | I | T |
| 4747.4 | 21058 | | | 4746.3 | 21063 | | |
| 4740.9 | 21087 | 10d | L | 4741.6 | 21084 | 5d | |
| 4734.4 | 21116 | | | 4737.1 | 21104 | | |
| 4730.1 | 21135 | | | | | | |
| 4729.2 | 21139 | 0d | | | | | |
| 4728.1 | 21144 | | | | | | |
| 4721.4 | 21174 | | | 4720.5 | 21178 | | |
| 4718.5 | 21187 | 5d | L | 4717.2 | 21193 | 1d | |
| 4715.2 | 21202 | | | 4713.8 | 21208 | | |
| 4703.6 | 21254 | | | | | | |
| 4699.2 | 21274 | 0d | | | | | |
| 4695.0 | 21293 | | | | | | |
| 4672.6 | 21395 | | | | | | |
| 4666.1 | 21425 | 0d | | | | | |
| 4659.1 | 21457 | | | | | | |
| 4516.2 | 22136 | | | | | | |
| 4513.0 | 22152 | 0d | | | | | |
| 4509.7 | 22168 | | | | | | |
| 4503.2 | 22200 | | | | | | |
| 4492.9 | 22251 | 10d | | | | | |
| 4482.6 | 22302 | | | | | | |
| 4478.6 | 22322 | | | | | | |
| 4473.2 | 22349 | 5d | | | | | |
| 4467.8 | 22376 | | | | | | |

## Table 10

### Absorption Spectra of $Pr_2O_3$ in a Tetragonal Lattice of $Eu_2O_3$

| Liquid $N_2$ Temp. | | | | | | | |
|---|---|---|---|---|---|---|---|
| A° | cm.$^{-1}$ | I | T | A° | cm.$^{-1}$ | I | T |
| | | | | 6248.6 | 15999 | | |
| | | | | 6243.5 | 16012 | 0d | |
| | | | | 6238.9 | 16024 | | |
| | | | | 6196.3 | 16134 | | |
| | | | | 6192.1 | 16145 | 0d | |
| | | | | 6187.9 | 16156 | | |
| 6151.0 | 16253 | | | 6146.8 | 16264 | | |
| 6145.7 | 16267 | 5d | L | 6143.0 | 16274 | 1d | |
| 6150.5 | 16281 | | | 6139.3 | 16284 | | |
| 6056.3 | 16507 | | | | | | |
| 6053.0 | 16416 | 2d | | | | | |
| 6049.7 | 16525 | | | | | | |
| 6035.8 | 16563 | | | 6024.6 | 16524 | | |
| 6026.0 | 16590 | 5d | | 6018.8 | 16610 | 5d | |
| 6016.2 | 16617 | | | 6013.0 | 16626 | | |
| 5937.8 | 16668 | | | | | | |
| 5991.3 | 16686 | 2d | | | | | |
| 5984.9 | 16704 | | | | | | |
| 5016.9 | 19927 | | | 5023.7 | 19900 | | |
| 5012.8 | 19943 | 0d | | 5012.8 | 19943 | 6d | H |
| 5008.8 | 19959 | | | 5001.8 | 19987 | | |
| 4962.8 | 20144 | | | 4959.4 | 20158 | | |
| 4955.9 | 20172 | 10s | L | 4952.0 | 20188 | 6d | |
| 4949.6 | 20198 | | | 4944.9 | 20217 | | |
| | | | | 4924.9 | 20299 | | |
| | | | | 4917.7 | 20329 | 0d | |
| | | | | 4910.4 | 20259 | | |
| | | | | 4895.7 | 20420 | | |
| | | | | 4882.8 | 20474 | 0d | |
| | | | | 4870.2 | 20527 | | |

## Table 10

(Continued)

| Liquid $N_2$ Temp. | | | | | | | |
|---|---|---|---|---|---|---|---|
| A° | cm.$^{-1}$ | I | T | A° | cm.$^{-1}$ | I | T |
| 4839.8 | 20656 | | | 4839.6 | 20657 | | |
| 4834.4 | 20679 | 10s | | 4832.3 | 20688 | 8d | |
| 4829.5 | 20700 | | | 4825.3 | 20718 | | |
| 4810.5 | 20782 | | | 4809.1 | 20805 | | |
| 4802.1 | 20818 | 10s | | 4798.1 | 20836 | 8d | |
| 4794.3 | 20852 | | | 4791.1 | 20866 | | |
| 4747.0 | 21060 | | | | | | |
| 4743.8 | 21074 | 0d | | | | | |
| 4740.9 | 21088 | | | | | | |
| 4725.6 | 21155 | | | 4640.7 | 21542 | | |
| 4720.7 | 21177 | 0d | | 4634.7 | 21570 | 1d | |
| 4715.8 | 21199 | | | 4629.1 | 21596 | | |
| 4587.3 | 21793 | | | 4587.1 | 21794 | | |
| 4582.9 | 21814 | 8s | L | 4576.4 | 21845 | 2d | |
| 4578.7 | 21834 | | | 4565.5 | 21897 | | |
| 4574.1 | 21856 | | | | | | |
| 4570.9 | 21871 | 7s | | | | | |
| 4567.4 | 21888 | | | | | | |
| 4547.0 | 21986 | | | 4540.8 | 22016 | | |
| 4538.6 | 22027 | 10s | L | 4532.8 | 22055 | 3d | |
| 4530.3 | 22067 | | | 4524.8 | 22094 | | |

## Table 11

### Evidence for 99 cm.$^{-1}$ Level for Praseodymium Sesquioxide

| "X" Form | Hexagonal | Tetragonal |
|---|---|---|
| 16931 - 16835 = 96 | 16925 - 16826 = 99 | 16686 - 16590 = 96 |
| 20266 - 20161 = 105 | 16942 - 16838 = 104* | 21177 - 21074 = 103 |
| 20275 - 20164 = 111* | 20892 - 20795 = 97 | |
| 20894 - 20798 = 96 | | |
| 21187 - 21087 = 100 | | |
| 21193 - 21084 = 109* | | |
| 22349 - 22251 = 98 | | |

Mean value at 78° K = 99 cm.$^{-1}$
Mean value at 300° K = 108 cm.$^{-1}$

*Separation at 300° Kelvin

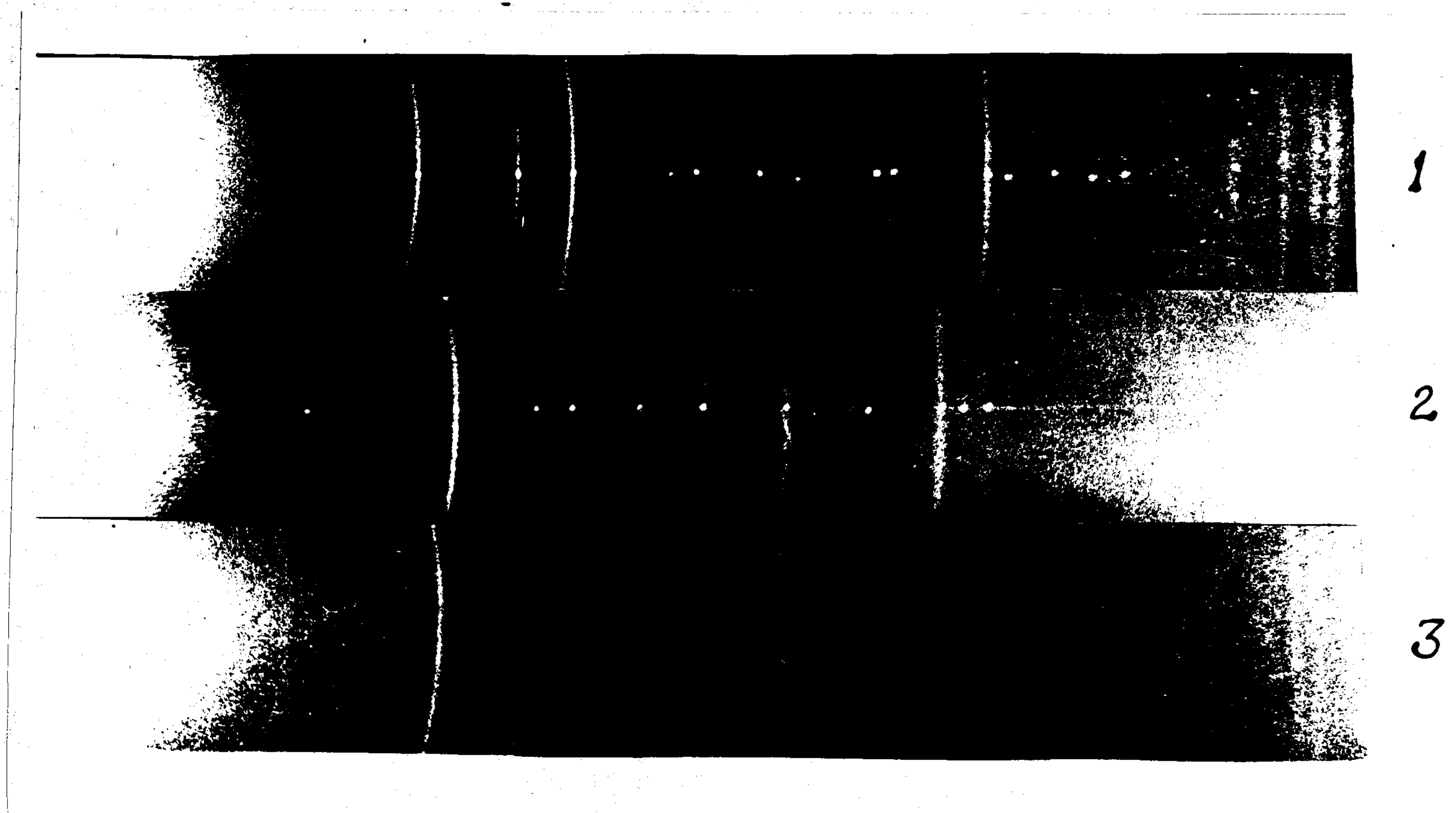

Fig. 6. Debye-Scherrer Diagrams of the Crystalline Forms of Europium Oxide: (1) Tetragonal; (2) Cubic; (3) Pseudo-trigonal plus cubic.

## V. DISCUSSION OF RESULTS

The instrument constructed for the determination of the absorption spectra of solids produced the most satisfactory results when used as a spectrograph since the electromagnetic method of voltage control used proved inadequate for the operation of the spectrophotometer at the level of sensitivity required by the high optical density of the samples. If a constant voltage supply is obtained for the source and the photomultiplier, the spectrophotometer would provide more accurate information on the relative intensities of the lines. It would be desirable to convert the spectrophotometer to an automatic recording instrument to reduce the overall time required for the determination of the absorption spectra.

Although theory predicts that the basic $^3H_4$ level of praseodymium will be split into four components by crystal fields of cubic symmetry and into nine components with fields of low symmetry, definite evidence was obtained for the existence of only two low-lying levels. It is probable that the other levels are higher since the fields are stronger and the splitting of the levels is greater. The population in these higher levels would be negligible at the temperatures of the measurements and no transitions arising from these levels would be expected. The use of fluorescent spectra data would provide information as to the existence of these higher levels. If the absence of transitions from these levels resulted from selection rules, it is possible that they might be observed in the fluorescent spectra since the selection rules are not the same as those for absorption spectra.

After a more thorough understanding has been gained of the relationship between the spectra and the solid state, precise quantitative information will be available on the strength of crystal fields and the positions of the units of the crystal lattice. Absorption spectra data would be complementary to x-ray data and since the spectrum observed is particularly sensitive to the symmetry about the metal ion, it should prove more satisfactory in the selection of a space group than the indirect method provided by x-ray data. This application should be of especial value when no large crystals suitable for Laue patterns are obtainable and powder data alone are available. Once the absorption spectrum has been established for a particular crystal structure, it may be used as a rapid and convenient method of determining the crystal modifications present; the relative ease of identification by means of absorption spectra and by powder pattern may be seen by comparing figures 5 and 6.

The position and nature of these low-lying levels influence optical properties such as index of refraction and optical rotation; theoretical calculations of specific heats and magnetic susceptibilities may also be made with a knowledge of these levels. Penney and Kynch[36] concluded that some of the data are wrong or that they have been incorrectly interpreted after they unsuccessfully attempted to develop a theory capable of quantitatively correlating all of the results on magnetic susceptibilities and absorption spectra of rare earth crystals. It is probable that many of the discrepancies that have arisen are due to variations in the samples used. Selwood[37] has shown that concentration changes in solutions of neodymium salts are accompanied by changes in absorption spectra and magnetic susceptibility. His values for the gram ion magnetic susceptibility of neodymium oxide in solid solution with lanthanum sesquioxide showed a large decrease as the magnetic dilution was increased. He suggested the change in susceptibility was due to a decrease in the interaction of the neodymium atoms as the lanthanum content was increased; such a variation could also be explained by assuming that two crystal modifications were present and that the magnetic susceptibility changed with the relative amounts of the two forms.

The difficulties encountered in the preparation of pure forms of the various crystal modifications of the rare earth oxides suggest that Goldschmidt's[9] methods for the preparation of the various polymorphic forms are not reliable and samples should be checked with an x-ray analysis.

## VI. SUMMARY AND CONCLUSIONS

The absorption spectrum of praseodymium sesquioxide contained in the tetragonal lattice of europium oxide as well as in the hexagonal and X forms of lanthanum oxide was obtained at 78° and 300° Kelvin. Electronic levels at 0 and 99 wave numbers were found for the praseodymium oxide in these three types of crystal structure.

Methods of preparation and x-ray data are given for the following crystal modifications of the rare earth sesquioxides: a tetragonal and a cubic form of europium oxide, a hexagonal and an X form of lanthanum oxide.

The design and performance are given for a high dispersion grating spectrophotometer constructed in the course of this investigation.

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