

this Laboratory common to both samarium and neodymium and stronger in intermediate fractions. These consist of 130 lines in the red and infra red, and five lines toward the violet.

2. The presence in our intermediate fractions of absorption bands which become stronger as the characteristic bands of neodymium and samarium become weaker. The bands at 5816 Å. and 5123 Å. are especially prominent and their positions confirm the belief that there is a systematic drift in the absorption bands of the rare earth group.

3. The presence of lines in the X-ray emission spectrum corresponding closely to the theoretical positions for  $L\alpha_1$  and  $L\beta_1$  of Element 61. The mean value obtained for  $L\alpha_1$  agrees within 0.0004 Å. of the value calculated from Siegbahn's precision values. The single reading obtained for  $L\beta_1$  varies by 0.0040 Å. from the calculated value.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

## OBSERVATIONS ON THE RARE EARTHS. XXIV. A THEORY OF COLOR

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Rare earth ions are characterized in most cases by extremely sharp absorption bands in the visible spectrum and in the small portion of the ultraviolet that has been explored. The striking similarity in chemical properties exhibited by members of this group is due to a similarity in arrangement of the outer, or valence electrons. Differences in physical properties, such as colors of compounds, must be due to differences in the arrangement in inner levels or shells. According to Bohr<sup>1</sup> the addition of an electron takes place in the fourth level. Thus lanthanum (57) is assigned the arrangement 2-44-666-666-441-(2) and lutecium (71) the arrangement 2-44-666-8888-441-(2). In both instances the number of electrons in the fourth shell is such that it may be considered complete. Neither element has absorption bands, as far as is known. However, most of the elements of atomic number between 57 and 71 do have absorption bands.

The accompanying chart shows the frequency/mm. of the absorption bands of the rare earths for most of the region for which data are available.<sup>2</sup>

The length of each line is made equal to 4-log of the equivalent thickness of the last appearance. This arbitrary method of plotting affords a means of showing the most persistent bands as the longest lines.

<sup>1</sup> Bohr, *Nature*, **112**, 29 (1923).

<sup>2</sup> THIS JOURNAL, **45**, 907 (1923).

As the number of electrons in the fourth shell increases from the 666 of lanthanum to the 6666 of europium, there is a successive increase and decrease in the number of bands, europium having very few. The positions of only the most prominent bands of illinium have been given; there are a number of others that are probably due to this element.<sup>3</sup> Likewise, an increase from the 6666 of europium to the 8888 of lutecium is accompanied by an increase and then a decrease in the number of bands, holmium, with a possible arrangement of 7777, and dysprosium and erbium on either side having the most.

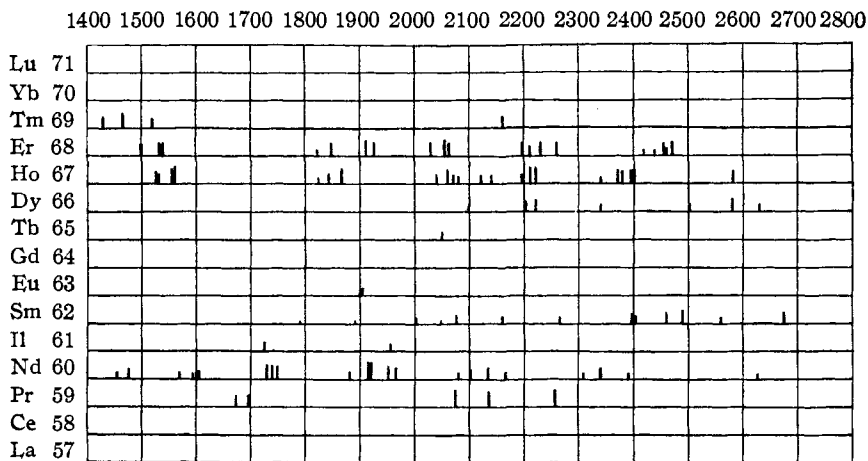


Fig. 1.

These facts would seem to indicate that the origin of the characteristic lines for each element is in the fourth level. When the shell is incomplete, there is a shift of electrons from orbit to orbit within the unfilled shell and each shift is accompanied by giving off or absorption of energy, equal to  $h\nu$ . In the latter case  $\nu$  represents the frequency of the resulting band. The striking similarity between the spectra of holmium and erbium may be noted from the chart.

The phosphorescence spectra also of the colored earths may be due to the presence of an unfilled shell.

This explanation of the presence of absorption bands may be extended likewise to the more common elements having colored ions. It is pointed out by Lewis<sup>4</sup> that a "great majority of the compounds of elements of variable kernel, which appear in the transition regions of the long periods of the Mendéleeff table are colored." Two instances may be cited. Copper may have a complete kernel 2-44-666 or, more simply, 2-8-18, and it is

<sup>3</sup> Harris with Hopkins, *THIS JOURNAL*, 48, 1585 (1926).

<sup>4</sup> Lewis, "Valence and the Structure of Atoms and Molecules," *The Chemical Catalog Co.*, 1923, p. 161.

monovalent and colorless. When the third level or shell is incomplete, 2-8-17, it is bivalent and colored. Iron may have the kernel 2-8-13, or the kernel 2-8-14; both states are incomplete and the ions are colored. Possibly, the non-existence of color in elements with incomplete kernels is due to the fact that absorption bands lie outside the visible spectrum. This is known to be true for the rare earth gadolinium which has a number of bands in the extreme ultraviolet. The explanation of the source of color given by Stieglitz<sup>5</sup> accounts for the color of ions having a variable valence as "by the proximity of a strong reducing atom to a strong oxidizing atom," but makes no mention of the color of the rare earth ions which have, in most cases, a fixed valence.

Another interesting feature of the chart is that a fairly uniform curve may be drawn through the following bands: Nd 1606, Il 1719, Sm 1788, Eu 1902, Tb 2049, Dy 2103 and Ho 2198. Europium has only two bands, very close together, and terbium only one in the region covered by the chart. The most prominent band of illinium also lies close to the curve. The fact that these bands occur in such regularity and are of increasing frequency with increasing atomic numbers, as may be expected from analogy with X-ray and spark spectra, would indicate a basic similarity in the electron shift causing the band.

It is probably accidental that so many absorption bands do fall within the narrow limits of the explored spectrum. An extension of the study to the ultraviolet and the infra-red should, in many cases, reveal the presence of many more bands and aid in the study of atomic structure.

### Summary

1. The presence of color in the rare earths and some common elements seems to be due to an incomplete kernel.
2. A relationship among the spectra of some of the rare earths is pointed out.

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### NOTES

**The Diffusion of Helium and Hydrogen through Quartz Glass at Room Temperature.**<sup>1</sup>—The permeability of silica glass to helium and other gases at high temperatures has long been known<sup>2</sup> and its permeability to helium and hydrogen at room temperatures has been suspected, various observers<sup>3</sup> having reported the apparent loss of these gases from quartz glass bulbs

<sup>5</sup> Stieglitz, "A Theory of Color Production," The Franklin Institute, 1924.

<sup>1</sup> Presented at the New Haven Meeting of the American Chemical Society, April, 1922.

<sup>2</sup> Jacquerod and Perrot, *Compt. rend.*, **139**, 789 (1904). Williams and Ferguson, *THIS JOURNAL*, **44**, 2160 (1922).

<sup>3</sup> Keyes and others, *J. Math. Phys.*, **1**, 289 (1922). Henning, *Z. Physik*, **5**, 264 (1921).