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LINE REFLECTION SPECTRA OF SOLIDS

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Abstract

A new interpretation of reflection spectra in solids, particularly $SmCl_3 \cdot 6H_2O$, is offered. The appearance of new absorption lines and the strengthening of others in the spectrum of a conglomerate as compared with that of a single crystal is explained as being caused by an increased path length travelled by the light through the crystal rather than by surface atoms as heretofore considered. This increased path results from the high refractive index for the light of wave-length of the absorption lines, which makes it difficult for such a ray, once it has entered a small crystal fragment, to leave. A new phenomenon of reversal of lines from absorption in a single crystal to emission in a conglomerate is described for a multiplet of the $GdCl_3 \cdot 6H_2O$ spectrum.

THOUGH the absorption and reflection spectra of the rare earth solids have been studied by many investigators, except for a brief letter by one of us in collaboration with Dr. Freed,[3] no one to our knowledge has compared both types of spectrum from the same compound. In the letter mentioned it was stated that the reflection spectrum of $SmCl_3 \cdot 6H_20$, which was photographed by reflecting light from the surface of a conglomerate of small crystals, contained many more lines, particularly at low temperatures, than the absorption spectrum of the same salt obtained from light that had passed directly through a single crystal. It was also recorded that the lines arising from the electronic isomer which is stable at low temperatures are relatively more intense at room temperatures in the reflection spectrum than in the absorption spectrum. New photographs under high dispersion have confirmed these results, but additional experiments make it possible to offer an explanation with greater certainty.

The appearance of the new lines and the abnormal intensities of the others in the conglomerate appeared at the time of the preliminary note to be attributable to the different force fields present about the surface atoms of the crystal. These surface atoms would be of greater importance in a conglomerate because of the increased surface. This paper is a continuation of the above work and attempts to explain the anomalies of reflection spectra from a slightly different standpoint. In addition a peculiarity observed with $GdCl_3 \cdot 6H_2O$ is described.

Part I. $SmCl_3 \cdot 6H_2O$

Large single crystals of the chloride were grown, some being as large as two centimeters to an edge and eight millimeters in thickness. Photographs

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[3] Freed and Spedding, Phys. Rev. 35, 212 (1929).

of the absorption of these were obtained by the use of a three meter grating with a dispersion of about 5.6A per mm. Since the crystals are hygroscopic it was necessary to protect them at room temperatures by a glass cell, but at lower temperatures, those of liquid nitrogen and hydrogen, they could be immersed directly in the cooling liquid. The crystals were observed by means of windows in the Dewar.

The following experiments were performed and the results were as listed:

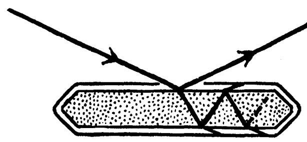

Fig. 1. Showing method used in shielding rare earth chloride crystal to eliminate all but direct reflections from a single crystal face.

1. A beam of parallel light was reflected from the surface of the crystal and the reflection observed by means of the grating at an angle equal to that of incidence. Only the continuous spectrum of the source was obtained, though various angles of incidence were tried.

2. A variation of the above with the angle of observed reflection *not* equal to the angle of incidence, i.e., scattered reflection, was tried. Though at first a faint spectrum was obtained, upon more careful shielding (see Fig. 1) the continuous spectrum of the source was again observed.

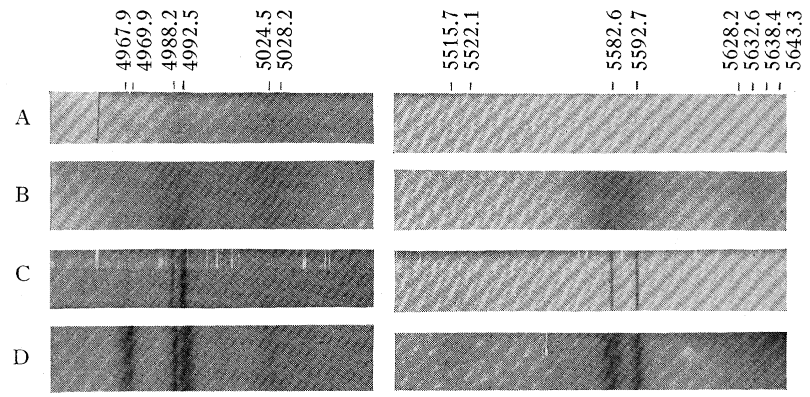

Fig. 2.

3. Light passed through or scattered from a conglomerate gave an absorption spectrum very rich in lines.

4. Photographs of light emerging from a very thick single crystal contained very faintly some of the lines that had previously been observed only with the conglomerates.

5. A large crystal was cut up into sections which were suitable for the passage of light through them in the three (monoclinic) axial directions.

Photographs of the spectra so obtained showed the same lines, though intensities varied, probably because of polarization effects. Especially noteworthy is the appearance of several new lines for the new path direction which had not been seen before in the pictures obtained with light that had traversed only the direction perpendicular to the large flat faces but had appeared in the reflection spectrum. This polarization explanation, however, can apply to only a few of the lines peculiar to the reflection spectrum.

The positions of the lines of the reflection spectrum seem to indicate slight shifts to the red as compared to the ordinary single-crystal spectrum, but this is not absolutely certain since the shifts are of the order of magnitude of our error in measurement. However, the positions of the sharpest lines measured on several plates taken at hydrogen temperatures of a single crystal and of a conglomerate gave an average displacement of 0.3 wave number to the red.

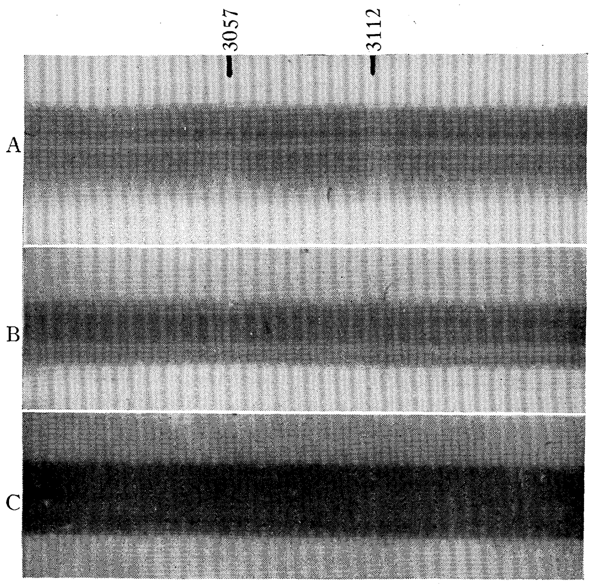

Fig. 3. A. Absorption by a single crystal of $GdCl_3 \cdot 6H_2O$. B. Absorption by a thin conglomerate of small crystals and fragments. C. Reflection from the cleavage face of a single crystal.

The observation of the greater number of lines obtained by use of thick crystals and the slight shift to the red led us to consider the following explanation as the most likely one for the increased number of lines found in the reflection spectrum, though other factors may be operating to a lesser degree. If one could examine the curve of the refractive index of the crystal plotted against the wave-length of the light, one would find in the neighborhood of the absorption lines a sudden increase in the index. After such light has entered the crystal fragment it is totally reflected many times before emerging (as with ordinary light in a diamond), resulting in a greatly increased path through what becomes effectively a very thick crystal and giving more opportunity for absorption. On the other hand the light of wave-length slightly different from the possible absorption lines has an ordinary index of refraction and travels only a relatively short distance through the crystal. This explanation indicates why the faint lines are the ones to appear or grow relatively intense in the reflection spectrum. They are the ones that offer the most possibility of intensification, whereas the strong lines are already practically completely absorbed.

The appearance of the satellites 160 cm^{-1} to the red of the "low temperature lines" in the conglomerate spectra at "higher temperatures", instead of being attributed to the different force fields at the surface of the crystal, should be attributed to the separation of the energy levels of the electronic isomers. Lines arising from the two basic levels and ending in a common upper level would give this common interval. The lines from the "high temperatures isomer" would be relatively faint at low temperatures as the relative abundance of that isomer would be small. In addition, the transition probabilities might be very low. However, due to the relatively greater distances travelled by light of those wave-lengths in the conglomerate enough would be absorbed to make the lines visible.

PART II. $GdCl_3 \cdot 6H_2O$

The study of the reflection spectrum of $GdCl_3 \cdot 6H_2O$ brought to light a very interesting phenomenon. The usual absorption spectrum of this salt consists of some ninety sharp lines which are chiefly in the ultraviolet.[4] They occur in groups or multiplets, one of which at about 3100A is composed of four very sharp lines that exhibit the following behavior. When a light from a hydrogen discharge is passed through a single crystal these lines appear strongly in absorption and are also polarized. If the same crystal is broken up into a conglomerate the four lines appear in emission in the reflection spectrum (Fig. 3).

Further description of this peculiarity will appear in the following account of the experiments performed.

1. A quartz wedge-shaped cell varying in thickness from about 0.5 mm to 2 mm was filled with a conglomerate of crystals formed by breaking up several large ones. Light from a hydrogen source was passed through the cell and photographed with a Hilger E2 instrument. All the intense lines except the four at 3100A appeared in absorption as usual. In the pictures of the absorption by the thinnest layer of conglomerate these four lines and four, possibly five, other fainter multiplets between 4000 and 3000A appeared as emission lines. As the thickness of the absorbing section increased the fainter emission multiplets faded out and at length became absorption lines again. The four stronger emission lines were the last to reverse, requiring the whole 2 mm of conglomerate to do so.

This change from emission to absorption seems to be caused by a shift in the balance between the natural tendency to absorption and a surface

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[4] Freed and Spedding, Phys. Rev. **34**, 945 (1929).

factor (see experiment 3) which causes emission or strong reflection of these lines.

2. Photographs taken with a larger E185 Hilger spectrograph with an arrangement of prisms that gave a dispersion of about 2A per mm in the region under consideration indicate that the four emission lines are shifted slightly to the red.

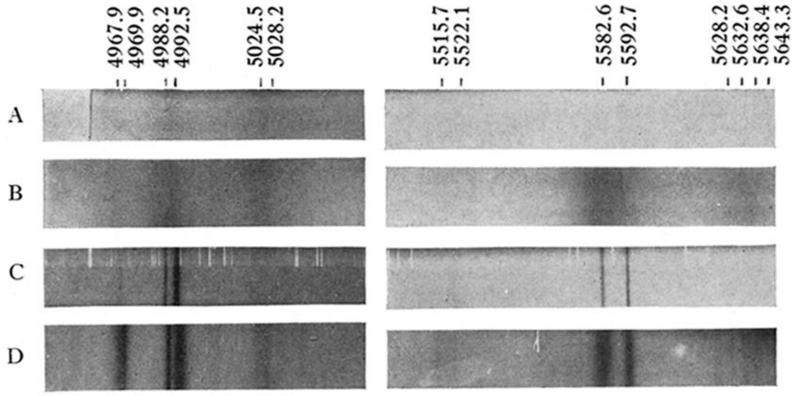
3. Large single crystals were prepared and a parallel beam of light was reflected from the faces of the crystal. While photographs (again with the small instrument) were made at different angles with the crystal, only those at which the angle of reflection was equal to the angle of incidence had intensity enough in the 3100A region to affect the plates. The four lines at 3100A could be observed faintly but clearly in emission against the continuous background. On the other hand the strong absorption lines at 3000 and 2700A were not even faintly visible on any of the plates examined. Careful shielding of the crystal prevented any but reflected light from being photographed.

4. Reflections from the (100) or cleavage faces of the crystals (monoclinic) seemed to be much more intense than those from the (010) or principal face. In the latter case the intensities were occasionally so faint as to be doubtful. Experiments also seemed to indicate that orientation of the crystal so that the longest axis was perpendicular to the plane of the incident and reflected rays caused the greatest intensity. However, the intensity differences were so small that it is difficult to be certain.

5. Photographs taken with a Nicol prism placed at several angles between the crystal and the spectrograph indicated that the emission lines were polarized, but because of general polarization of the background caused by the reflection further statements seem inadvisable. We hope with better experimental conditions to be able to say more about this.

It was concluded from these and other experiments that the emission lines arise from reflection from the surfaces of the crystals, particularly from the cleavage faces, and that they are not caused by fluorescence. They resemble very much the residual rays observed in the infrared with ionic crystals.

This phenomenon can not be caused by any impurity of the particular sample of $GdCl_3 \cdot 6H_2O$ used in these experiments, since with two lots having entirely different histories results agreed in every way. The conglomerate with which most of the work was done was from material of nearly atomic weight purity kindly furnished us by Professor Hopkins of the University of Illinois, and the other lot used was prepared from gadolinium salts obtained from the Wellsbach Company and containing as chief impurity about one percent of terbium.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4969.9
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4992.5
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5028.2
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A
B
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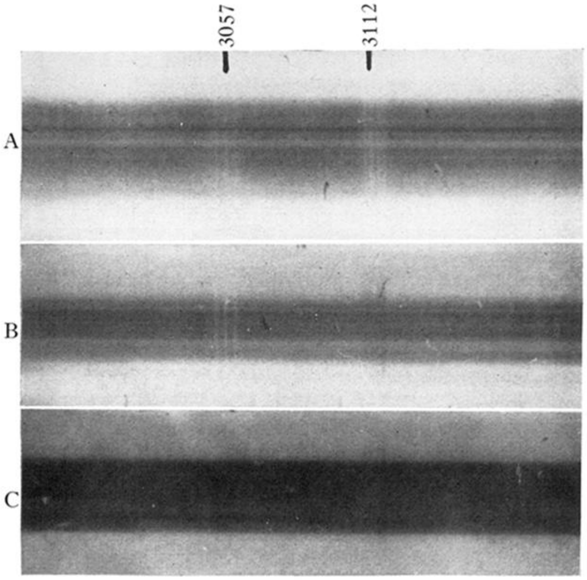
D

Fig. 2.



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