

combinations of a^2G and a^2H (§4); but, since the faint components of the multiplets have not been found, they cannot be classified.

This spectrum may now be regarded as pretty well analyzed. Between $\lambda 11,900$ and $\lambda 2500$ there are 90 unclassified lines out of 2388; between $\lambda 2500$ and $\lambda 2200$, 52 out of 279; and between $\lambda 2200$ and $\lambda 1810$, 140 out of 340.

The classification is therefore fairly complete except in the remoter ultraviolet. Here many of the lines we list may belong to Co II, a spectrum still very incompletely analyzed. Some of these

are noted by "Co II?" following the intensity in Table VIII.

It is a pleasure to express our gratitude to Dr. M. T. Antunes for making the important work of Catalan and himself accessible to us; to Dr. Keivin Burns for the communication of his extensive and accurate measures,—especially with the interferometer—; to Dr. A. S. King for the loan of a set of plates of the spectrum, and for Zeeman data; and to Dr. A. G. Shenstone for taking the spectrogram which permitted the extension of our work beyond $\lambda 2230$.

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The Effect of an Activator on the Absorption Spectrum of Zinc Sulphide Powders

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The absorption of zinc sulphide powders, both pure and with various concentrations of activator, was measured in the region 3200–4800A by the diffuse reflection method. It was found that the long wave-length limit of the absorption band for a pure ZnS powder was at 3800A and that this limit moved to longer wave-lengths with increasing concentration of Ag activator. No evidence could be found of a secondary absorption peak characteristic of the activator.

IF pure zinc sulphide is to luminesce under ultraviolet light, it must be activated. This is usually done by heating the powder with a trace of the salt of a foreign atom, such as silver or copper. In order to get a clearer picture of the nature of this activating process, it seems desirable to find out what effect the heat treatment and the presence of foreign atoms have on the absorption spectrum of the pure powder. Gisolf,¹ studying the transmission of thin layers of ZnS powder, has reported that, within an accuracy of 10 angstrom units, no difference is found between the wave-lengths of the absorption edge for both pure ZnS and for ZnS activated with traces of Cu or Ag. He also claims to have found a secondary absorption peak, characteristic of the impurity, on the long wave-length side of the principal absorption edge.² These results were not confirmed, however, in the experiments about to be described.

¹ J. H. Gisolf, *Physica* **6**, 87 (1939).

² See reference 1, Fig. 2 on page 87, and remarks on page 88.

The absorption spectra of the ZnS powders were obtained by the diffuse reflection method. The source of radiation was a 120-watt tungsten lamp with a quartz window.³ The ZnS powder⁴ was sprinkled in a thin layer over the corrugated end of a black wooden rod, held at an angle of approximately 45° in front of the slit of a small Littrow quartz spectrograph. During preliminary experiments a quartz mercury arc was used as a source of radiation. The appearance on the photographic plate, with small but uniformly diminished intensity, of the mercury lines in the region 3342 to 2537A was interpreted as indicating that a little light enters the spectrograph after one surface reflection from the crystals. Most of the reflected light, however, is apparently totally reflected internally, perhaps several times, so that it arrives at the slit of the

³ Kindly loaned by Professor George Winchester of Rutgers University.

⁴ Thanks are due to Dr. G. R. Shaw, Dr. L. B. Headrick and Mr. H. W. Leverenz of the RCA Manufacturing Company, for supplying the samples of ZnS used in these experiments.

spectrograph after having passed through an unknown thickness of ZnS.

The spectrum of the light reflected from ZnS was photographed on an Eastman Spectroscopic Plate, Type IV-O; exposure times were around 20 minutes. On the same plate was photographed the spectrum of the source as reflected from an aluminum mirror which is known⁵ to have a uniform reflectivity of approximately 90 percent over the range 3000–5000Å. The exposure time was adjusted so as to duplicate the blackening of the ZnS spectrum in the region 4500–5000Å; usually this required an exposure of about one second.

The density of blackening of the plate was determined by using a crude densitometer.⁶ The absorption spectrum of ZnS was obtained by plotting the difference between the densitometer readings in the spectrum of the light reflected from ZnS and the densitometer readings in the spectrum of the light reflected from the aluminum mirror. Curves obtained in this way for a sample of pure ZnS, precipitated and dried, and for another sample of ZnS containing 0.128 percent Ag, which had been fired with NaCl flux at

940°C for two hours, are shown in Fig. 1. Measurements are less reliable at high absorption but for all the samples which were studied, absorption was complete for wave-lengths less than 3500Å. There is no evidence, either in the curves of Fig. 1, or in similar curves obtained with different concentrations of Ag activator, of a secondary absorption peak on the long wave-length side of the main absorption edge—at least as far as 4800Å. These curves are in fair

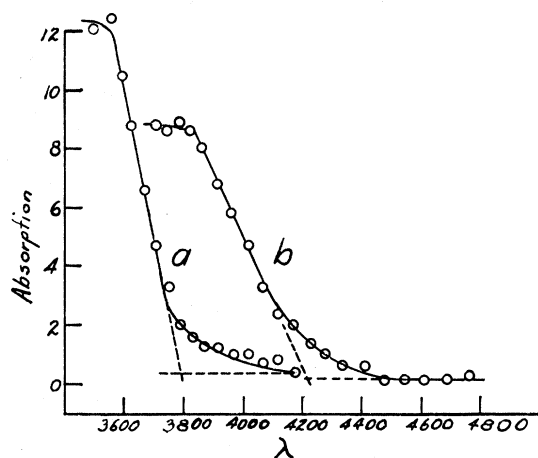


FIG. 1. Absorption spectrum of (a) pure ZnS, precipitated and dried; (b) ZnS containing 0.128 percent Ag which had been fired with NaCl flux at 940°C for two hours.

TABLE I. Absorption limits under various conditions.

SAMPLE	LONG WAVE-LENGTH LIMIT OF ABSORPTION
1. Pure ZnS, precipitated and dried	3800Å
2. Pure ZnS, heated at 940°C; no flux	4220Å
3. Pure ZnS, heated at 940°C for 2 hours with NaCl	3980Å
4. ZnS+0.005% Ag, heated at 940°C for 2 hours with NaCl	4120Å
5. ZnS+0.032% Ag, heated at 940°C for 2 hours with NaCl	4180Å
6. ZnS+0.128% Ag, heated at 940°C for 2 hours with NaCl	4220Å
7. ZnS+0.512% Ag, heated at 940°C for 2 hours with NaCl	4280Å
8. ZnS+0.001% Cu, heated at 1200°C with 2% NaCl	4120Å

⁵ See for example M. Auwarter, J. App. Phys. **10**, 706 (1939). The mirror was kindly supplied by Dr. A. B. Focke of Brown University.

⁶ The densitometer was constructed by focusing the filament of a straight-filament incandescent lamp, suitably masked, on the spectroscopic plate. The plate was clamped to the carriage of an old Michelson interferometer, and could thus be moved across the beam of light. Behind the plate was mounted a Weston Photronic Cell connected to a L. & N. model 2420-C galvanometer (sensitivity 0.02 microampere per mm) whose deflection was a measure of the quantity of light transmitted by the spectroscopic plate.

agreement with similar curves obtained by Kitchener⁷ and by Kroger,⁸ but, as previously mentioned, differ from the curve shown by Gisolf.²

The long wave-length limit of the absorption edge was determined, as indicated in Fig. 1, by extrapolating the steep portion of the curve. Values for this long wave-length limit for various samples of ZnS are shown in Table I. For the first and third samples, values should be accurate within 20Å; for the other samples, within 50Å. It is apparent from this table that, contrary to Gisolf's findings, previously mentioned, the long wave-length limit of the absorption band of a ZnS powder in general moves toward longer wave-lengths with increasing activation. Moreover, the long wave-length limit even for pure powdered ZnS is considerably greater than re-

⁷ Kitchener, Trans. Faraday Soc. **35**, 98 (1939).

⁸ F. A. Kroger, Physica **7**, 1 (1940). Note, however, that Kroger defines the long wave limit of absorption as the longest wave-length at which absorption is complete.

ported by Gisolf¹ (*viz.* 3350Å); Kroger's curve,⁸ on the other hand, indicates an "extrapolated" long wave-length limit around 3800Å, in good agreement with the value in Table I. Dr. Headrick has suggested that since sample No. 2 oxidized considerably on firing, the unusually high value for its long wave-length limit may be characteristic of ZnO rather than ZnS. The long wave-length limit for sample No. 8 is not very different from a value of 4250Å found for a ZnS single crystal containing about 0.004 percent Cu.⁹

The emission spectrum of samples 3, 4, 5 and 6 is of appreciable intensity over the range 4200 to 5000Å, with a peak around 4600Å.¹⁰ Since a tungsten filament emits little ultraviolet light, the intensity of the fluorescent light from the ZnS powders was small; however, some of the

blackening of the plates was undoubtedly due to fluorescent light. To correct for this, densitometer readings for wave-lengths greater than 4200Å should be increased. This would mean that, in curves similar to those of Fig. 1, all points on the long wave-length side of 4200Å might be raised as high as, but no higher than, the point at 4200Å. If this correction is made, it turns out that the long wave-length limit of the absorption edge for samples 3, 4, 5 and 6 would be shifted an average of 20Å toward shorter wave-lengths; this correction is within the limit of error (50Å) claimed for these measurements.

In conclusion, it has been found that the long wave-length limit of the absorption band for a pure ZnS powder was at 3800Å and that this limit moved to longer wave-lengths with increasing concentration of Ag activator. No evidence could be found of a secondary absorption peak characteristic of the activator. An interpretation of these results cannot be given at this time.

⁹ C. J. Brasefield, Phys. Rev. **57**, 162 (1940).

¹⁰ See H. W. Leverenz and F. Seitz, J. App. Phys. **10**, 487 (1939). Samples 1, 3, 5, 6 and 7 described in Fig. 15 of this article are identical with samples 3, 4, 5, 6 and 7 of Table I.

On the Radiofrequency Spectra of Sodium, Rubidium and Caesium*

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The hyperfine structures of the ground state of Na²³, Rb⁸⁵, Rb⁸⁷ and Cs¹³³ were measured by observing radiofrequency spectra of these atoms. In each case the particular lines chosen for study and the magnetic fields at which they were observed were such as to yield the greatest precision for the hyperfine structure measurements, consistent with frequencies conveniently obtainable in our laboratory (up to 700 megacycles). The measured h.f.s. separations are given both in absolute frequency units and in wave numbers.

	sec. ⁻¹ × 10 ⁻⁶	cm ⁻¹
Na ²³	1771.75	0.059103
Rb ⁸⁵	3035.7	0.10127
Rb ⁸⁷	6834.1	0.22797
Cs ¹³³	9191.4	0.30661

INTRODUCTION

IN a previous paper¹ methods were described for the study of the radiofrequency spectra of

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¹ P. Kusch, S. Millman and I. I. Rabi, Phys. Rev. **57**, 765 (1940).

atoms and in particular for the accurate determination of the hyperfine structure of the ground states of atoms. These methods were applied to the measurement of the h.f.s. separation of the normal states of Li⁶, Li⁷, K³⁹ and K⁴¹. In the present paper we present the results of the