many fruitful discussions and continual encouragement. I am also indebted to Mr. Howard Schultz for the design and construction of the amplifier.

*Note.* As this paper was being submitted, May and Vaidyanathan[13] published the results of new measurements on the ranges of disintegration protons from fluorine, from which they deduce for the *first* excited level in the product neon nucleus the value 1.5 Mev. This coincides exactly with our value for the energy of the hard $\gamma$-ray and indicates quite definitely that it is emitted by the neon nucleus. Since they give no term differences in the neon level scheme of less than 1.1 Mev, the soft $\gamma$-ray which we find ($\sim$0.5 Mev) is most probably to be ascribed to the fluorine nucleus itself, or possibly to the sodium nucleus formed after the neutron disintegration.

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[13] A. N. May and R. Vaidyanathan, Proc. Roy. Soc. **A155**, 519 (1936).

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OCTOBER 15, 1936 PHYSICAL REVIEW VOLUME 50

# Effects of Chemical Combination on the $K$ Beta Lines of 26 Fe–30 Zn

JOHN C. MCDONALD,* *University of Minnesota*

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The $K\beta$ lines of 26 Fe–30 Zn from the sulfides of those metals have been studied in fluorescence with a focusing crystal spectrograph of the Johansson type. The only lines showing a shift from their position in the spectra of the pure metals are the $K\beta_5$ lines of Fe and Ni. Calculation of the second ionization potential of Cu by application of Pauling's theory gave a value much too high The term values of the levels in which the $K\beta_5$ has its origin, for Fe, Co and Ni in the sulfides, were somewhat larger than in the pure metal, whereas for Cu and Zn they were about the same.

## I. INTRODUCTION

VARIOUS workers in the past fifteen years have investigated the effects of chemical combination on x-ray absorption edges and line spectra. In the study of the line spectra it was soon found that consistent results, independent of target material, could be obtained best by the secondary radiation method, except in the case of refractory materials which suffered no chemical change under electron bombardment. Different apparatus, all using the principle that the substance studied must be kept cool and shielded from the direct electron beam, have been constructed and used by Alexander and Faessler,[1] Lundquist,[2] Valasek,[3] and Privault.[4] Yoshida[5] and Tanaka and Okuno[6, 7] used essentially the method of Alexander and Faessler. All these workers except Privault used a plane crystal spectrograph and photographic plate. Privault used a focusing crystal spectrograph of the Cauchois[8] type.

Valasek[3] studied the $K\alpha$ and $K\beta$ lines of S in the sulfides of 26 Fe–30 Zn and found a considerable effect due to chemical combination. Since the $K\beta$ lines might originate in crystal levels common to both ions, in which levels certain lines in the metallic spectra could possibly arise also, it was thought desirable to make a study of the $K\beta$ lines of the metals in those sulfides, particularly of the $K\beta_5$, which has its origin in the outermost levels of the atom. Since it is a quadrupole line and therefore of low intensity,[9, 10] it would be difficult to photograph it in fluorescence with a plane crystal spectrograph. For this reason a focusing crystal vacuum spectrograph constructed much like that of Johansson,[11] which gives theoretically the perfect focusing first suggested by DuMond and Kirkpatrick,[12] was built. Use of such a spectrograph in x-ray spectroscopy

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* Now with The Dow Chemical Co., Midland, Michigan.

[1] Alexander and Faessler, Zeits. f. Physik **68**, 260 (1931).

[2] Lundquist, Zeits. f. Physik **77**, 778 (1932); **83**, 85 (1933).

[3] Valasek, Phys. Rev. **43**, 612 (1933); **47**, 896 (1935).

[4] Privault, Ann. de physique **5**, 280 (1936).

[5] Yoshida, Inst. Phys. Chem. Res. Tokyo **20**, 298 (1933).

[6] Tanaka and Okuno, Jap. J. Phys. **9**, 75 (1934); **10**, 1 (1935); **10**, 45 (1935).

[7] Tanaka and Okuno, Proc. Phys. Math. Soc. Jap. **17**, 540 (1935).

[8] Cauchois, J. de phys. et rad. (7) **3**, 320 (1932).

[9] Meyer, quoted in Siegbahn, *Spektroskopie der Röntgenstrahlen*, second edition (Springer, Berlin, 1931), p. 355.

[10] Williams, Phys. Rev. **44**, 146 (1933).

[11] Johansson, Zeits. f. Physik **82**, 507 (1933).

[12] DuMond and Kirkpatrick, Phys. Rev. **35**, 136 (1930).

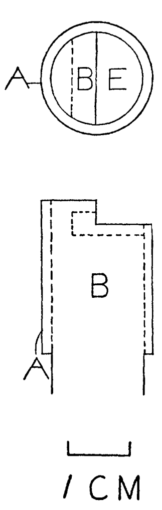

FIG. 1. Target for secondary radiation.

has not yet been reported, although Johansson did make some spectrographs with it which are reproduced in his article.

This spectrograph employs a crystal which is ground cylindrically to a radius twice that of the cylinder to which it is bent after grinding. Source of radiation, crystal and film are all placed symmetrically on a circle formed by cutting the cylinder normally with a plane. The gain in intensity over the plane crystal spectrograph is large, and it was found in practice that the focusing attainable was sufficient for accurate determination of wave-lengths of not too asymmetrical lines, so that the advantages of such an instrument for the type of work outlined above is manifest. The chief disadvantage is the lack of high resolution due to the comparatively small radius of the instrument, and the departures from perfect focusing. Another disadvantage is the greater susceptibility to breakage of the crystal, in comparison with the bent crystal of the Johann[13] type spectrograph, which may account for the lack of reports of its use in research up to this date.

## II. Apparatus

The tube was of the usual metal type, sweated into the side of the camera so that the source of radiation would lie on the focal circle, along with the crystal and film. The high voltage was applied to the filament, hence a glass insulator was used in the filament assembly. In this assembly was also incorporated a piece of sylphon tubing so as to permit easy change of the location of the electron focus on the target. The construction of the target is illustrated in Fig. 1. The water-cooled portion, *B*, was surrounded by a cylinder, *A*, cut so that the primary rays caused by electrons striking at *E* could not reach the diffracting crystal. The primary rays and some scattered electrons struck the substance being studied, which was placed in the recess in *B*, and there produced secondary rays which emerged through a horizontal window covered with aluminum foil into the camera. This foil, 0.0003 in. in thickness, served to separate the high vacuum of the tube from the low vacuum of the camera, and also prevented filament light from fogging the film. It was cemented to the tube with clear glyptal lacquer.

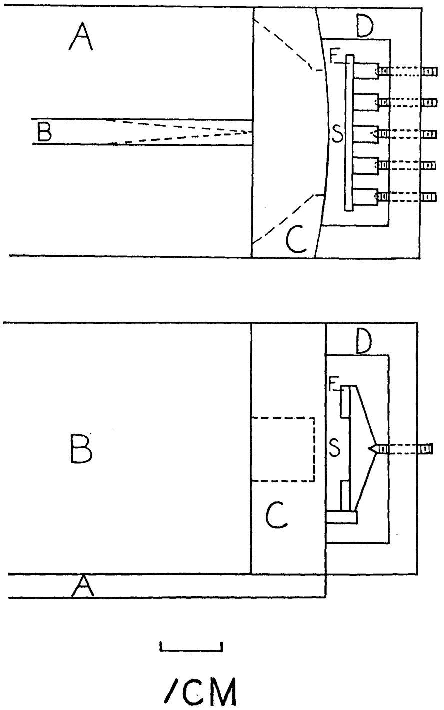

FIG. 2. Crystal holder: plan, above; elevation, below.

The high vacuum was produced by a diffusion pump using Apiezon *B* oil. Apiezon grease was used on the filament and target cones; the camera cover was sealed with Lubriseal.

The crystal was of quartz, about 0.4 mm thick, ground by Bausch and Lomb to a radius of 14 in.,

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[13] Johann, Zeits. f. Physik **69**, 185 (1931).

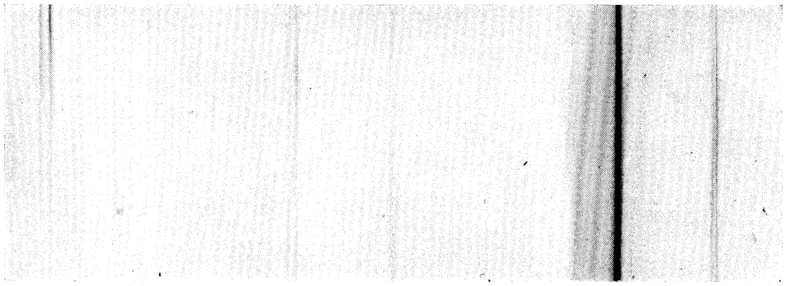

FIG. 3. Typical spectrogram. From left to right, Cu $K\alpha$, Zn $K\alpha$, Cu $K\beta_1$, Zn $K\beta_1$, and Va $K\alpha$ in the first order. Enlargement about $3X$. Ghost structure on long wave-length side of Zn $K\beta_1$. Zn $K\beta_{2,5}$ was visible on the original negative. Obtained from ZnS.

the radius of the focal circle being 7 in. The type of crystal holder constructed first would not give an even distribution of pressure, which resulted in the eventual destruction of the first crystal. A holder was then built along the lines of Johansson's, and is sketched in Fig. 2. *A* is the crystal arm, extending out from the inner central cone of the camera; *B* is a screen to prevent direct radiation from reaching the film, beveled in the center to make the opening to the crystal a maximum; *C* is the steel piece, cut to a 7 in. radius, against which the crystal is pressed by the screws passing through *D* and bearing against the phosphor bronze strips *F*. The opening in *C* for the radiation to strike and leave the crystal is shown with dotted lines. The crystal itself is placed in the space *S*. The four parts *A*, *B*, *C*, and *D* are fastened rigidly together with screws before the bending is begun. This apparently produced no large deformation of the cylindrical surface, as good focusing has been obtained, marred to a certain extent by the existence of easily recognizable "ghosts." The crystal was etched in 48 percent HF for 24 hours at 20°C before being bent. Both the first and second crystals purchased had corners crack off during or immediately after this operation. The second crystal cracked once after having been in place three months, the larger of the two pieces then remaining was bent and has now been in place a year without breaking. Its original dimensions were 2×3 cm, while the opening in *C* is 1×2 cm.

The film holder is provided with a plate drawn up against the film by springs; the film is thus also pressed to a cylindrical surface of 7 in. radius. This type of construction was used by Sandstrom.[14] The opening in the film holder is about 1×6 cm, permitting more than the wave-length spread allowed by the range in angle subtended at the crystal by the extended source to be photographed.

## III. OPERATION

The substance to be studied was placed in the recess in the target and left there until well pumped out, before turning the power on. Most of the work was done at 25–30 kv and 5–10 milliamperes. Exposures ranged from 10 to 30 hours for the faintest lines. The crystal was set so that the central angle between its center and the center of the target was twice the Bragg angle in the second order for the $K\beta_1$ line, and the film holder was then set so that its center was as far from the crystal center as the crystal was from the target. Eastman Process film, developed in solution D–19, was used to give good contrast.

Determination of wave-lengths was carried out by the same interpolation process used by Sandstrom,[14] positions of the apparent centers of the lines being measured with a Gaertner comparator. The reference lines were nearly all $K\alpha$ lines, fairly narrow and symmetrical, so that the dis-

TABLE I. *Wave-lengths of the $K\beta_5$ line in the metals in X.U.*

| | Present work | Siegbahn |
|---|---|---|
| 26 Fe | 1740.80±5 | 1740.80 |
| 27 Co | 1605.65±5 | 1605.62 |
| 28 Ni | 1485.58±5 | 1485.61 |
| 29 Cu | 1378.0±2 | 1378.24 |
| 30 Zn | 1281.7±1 | 1281.07<br>1281.2 |

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[14] Sandstrom, Nova Acta Reg. Soc. Sci. Upsaliensis (4) **9** (1935).

persion could be measured accurately, but many of the lines studied were wide and asymmetrical, so that the wave-lengths obtained are not those of the peak intensity. The dispersion varied somewhat from film to film, of course, due to varying shrinkage of the film, but wave-lengths of "good" lines were reproducible consistently to the accepted values. The limit of error in any determination was estimated from the spread in values obtained in measuring, and from the consistency of results from different spectrograms. All results were checked on at least two spectrograms.

An enlargement of a typical spectrogram, obtained with ZnS, is shown in Fig. 3.

As a check on the method, wave-lengths of the $K\beta_5$ were first obtained from the metals. Good results were secured except for Cu and Zn. In Cu the $K\beta_5$ line is highly asymmetrical; in Zn the $K\beta_2$ and $K\beta_5$ could not be visually resolved, because of the low resolution of the spectrograph and the closeness and high natural widths of the lines. The wave-lengths of other lines are often somewhat different from the peak values given by Bearden and Shaw,[15] but check well with the photographically determined values given by Siegbahn. When studying Ni and Zn, a Mo filament was used to eliminate the W lines which would otherwise have obscured lines being studied.

These results with the metals are listed in Table I, along with Siegbahn's values for comparison. The two values for Zn are those of the $K\beta_2$ and $K\beta_5$ peaks as determined by Bearden and Shaw.

## IV. RESULTS

The compounds studied were: $FeS_2$, CoS, NiS, $Cu_2S$, and ZnS. Pyrites and marcasite, cubic and orthorhombic crystals respectively, were the source of $FeS_2$. Results from both were the same. $Cu_2S$ was studied in the form of chalcocite; ZnS, wurtzite. These minerals were ground into shape to fit into the recess in the target.

NiS and CoS were obtained by precipitation with $H_2S$ from ammoniacal $NiCl_2$ and $CoCl_2$ solutions; they were dried in vacuo and then pressed into semi-cylindrical pills which fit into the recess. With these last two compounds it was necessary to hold the current and voltage down to 5 mills and 25 kv, otherwise they would disintegrate leaving a magnetic residue in the recess. Spectrograms obtained under that condition gave the same results as the metal.

FIG. 4. Microphotometer trace showing the Ni $K\beta_5$ (designated as 2).

With the sulfides of Fe, Co, Cu and Zn no difficulty was experienced in determining wave-lengths to within the same limit of error as in the metal. With NiS, however, five spectrograms gave a mean wave-length of 1485.5±2, the error thus being much larger than in the metal. Three of these films were therefore microphotometered, two traces, each at a different point, being made of each film. Four of these traces showed a definite peak for the $K\beta_5$; one of the traces is shown in Fig. 4. The Zn $K\alpha_1$ is marked 1, the Ni $K\beta_5$, 2, and the Cu $K\alpha_1$, 3. Wave-lengths of the point of inflection on the short wave-length side of 2 and of the two peaks of 2 were determined by measuring the trace in a two way Société Genêvoise measuring engine and then applying the same interpolation process used on the originals. The point of inflection appeared on two traces as a peak, and the long wave-length component appeared on one trace as a point of inflection. The values found checked within ±0.1 X.U., but because of possible systematic errors in the microphotometer the limit of error was set at ±0.2 X.U.

A microphotometer trace of a spectrogram taken with $Cu_2S$ is reproduced in Fig. 5. The lines marked 1 and 3 are the comparison lines Ti $K\alpha_1$ in the first order, and Zn $K\alpha_1$ in the second order; 2 is the Cu $K\beta_5$. The mean peak wave-length from several traces was 1378.2±2, checking with the known peak wave-length in the metal.

A line believed to be the same as the $K\beta_5'$ of Yoshida[5] was observed with $Cu_2S$ at 1381.0±2; the $K\beta''$ was obtained with CoS at 1610.1±2. The rest of the results are contained in Table II,

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[15] Bearden and Shaw, Phys. Rev. **48**, 18 (1935).

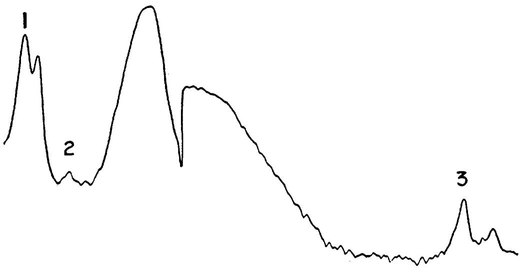

FIG. 5. Microphotometer trace showing the Cu $K\beta_5$ (designated as 2).

the corresponding values given by Siegbahn for the metals being listed for comparison.

## V. DISCUSSION

Previous work on the effects of chemical combination on emission spectra has been done chiefly on elements of lower atomic number.

Karlsson,[16] using a concave mica crystal in the Johann manner, with direct bombardment, studied the $K\alpha$ and $K\beta$ lines of the metals in refractory compounds of 12 Mg, 13 Al, and 14 Si. A considerable effect of chemical combination was evident.

The $K\alpha$ lines of sulfur have been studied by Faessler,[17] Lundquist,[2, 18] Valasek,[3] and Parratt.[19] The general effect noticed was a shift to longer wave-length in the sulfides and to shorter wave-length in the sulfates. Parratt followed the disintegration of compounds under direct bombardment by noting the change in the $K\alpha$ pattern.

Lundquist[2] found a shift to shorter wave-length of the $K\alpha$ lines of 17 Cl when in chemical combination.

Valasek[3] studied the $K\beta$ pattern of 16 S in the sulfides of this research and in the sulfides of the alkali earths; he also measured the shifts of the $K\beta_1$ of 19 K and 17 Cl in the potassium halides and alkali chlorides. Lundquist,[20] however, with primary radiation, found no shift in the $K\beta_1$ and $K\beta''$ of 19 K, possibly due to the change of each compound to the oxide, similarly to what Wetterblad[21] found with 20 Ca.

Shifts in the $K\beta_5$ have been reported by Wetterblad[21] in 20 Ca and 25 Mn, and by Yoshida[5] in 22 Ti, 24 Cr, and 25 Mn. Yoshida also reported no shift in the $K\beta_5$ of Co in $Co_3O_4$, and no shift in the $K\beta_1$ of Ti, Cr, Mn, and Co within a limit of error of ±0.3 X.U. Privault,[4] on the other hand, reported no shift in either the $K\beta_1$ or the $K\beta_5$ in Cr and Mn.

Within a limit of error of ±0.2 X.U., Tanaka and Okuno[6, 7] found shifts in both the $K\beta_1$ and $K\beta'$ of Cr, Mn and Fe in various compounds, which shifts had a total range of 0.7 X.U. In particular, in $FeS_2$, where a direct comparison with the results of the present research may be made, they found a wave-length of 1753.43 for the $K\beta_1$, and reported the $K\beta'$ as a band. While the present results did not show the $K\beta'$ as a sharp line, nevertheless it was distinct from the $K\beta_1$ and measurable with, for this research, a rather large limit of error. That the cause of the discrepancy does not lie in a possible reduction of the $FeS_2$ to Fe is shown by the fact that the $K\beta_5$ has shifted. Possibly either their compounds or those of the author were sufficiently impure to account for the difference in the results.

Shearer,[22] with primary radiation and the same spectrograph Karlsson used, found no shift or change in the $L\alpha$ and $L\beta$ of Ni from the oxide and sulfide of nickel. His limit of error was of about the same order as the effects reported here for the $K\beta_5$ of Ni, which may account for his results. However, since NiS decomposes so easily, as was demonstrated in the present work, it would seem more probable that his NiS decomposed as soon as the power was turned on, thus giving him the spectrum of the pure metal.

Roseberry and Bearden,[23] using primary radiation with a double crystal spectrometer, found no

TABLE II. *Wave-lengths in X.U. of the $K\beta$ lines of 26 Fe–30 Zn in their sulfides.* The first column under each heading gives the results of the present work in the sulfides, the second column gives Siegbahn's values for the metal.

| | $K\beta'$ | | $K\beta_1$ | | $K\beta_5$ | |
|---|---|---|---|---|---|---|
| 26 Fe | 1756.6±2 | 1756.46 | 1752.99±5 | 1753.01 | 1741.3±1 | 1740.80 |
| 27 Co | 1620.1±1 | 1620.11 | 1617.42±5 | 1617.44 | 1605.7±1 | 1605.62 |
| 28 Ni | | 1499.10 | 1497.01±5 | 1497.05 | 1485.4±2<br>1485.9±2<br>1486.6±2 | 1485.61 |
| 29 Cu | | | | 1389.35 | 1377.9±2 | |
| 30 Zn | | | 1292.52±5 | 1292.55 | 1281.7±1 | |

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[16] Karlsson (Flemberg), Zeits. f. Physik **88**, 76 (1934); **96**, 172 (1935).
[17] Faessler, Zeits. f. Physik **72**, 374 (1931).
[18] Lundquist, Zeits. f. Physik **89**, 274 (1934).
[19] Parratt, Phys. Rev. **49**, 14 (1936).
[20] Lundquist, Zeits. f. Physik **33**, 901 (1925).
[21] Wetterblad, Zeits. f. Physik **42**, 603 (1927).
[22] Shearer, Phil. Mag. **20**, 133 (1935).
[23] Roseberry and Bearden, Phys. Rev. **50**, 204 (1936).

effect on the width, intensity or asymmetry of the $K\beta_5$ lines of the metals in the oxides of Ti, Cr, Mn, Fe, and Zn. Unfortunately they made no wave-length determinations, so no attempt at a comparison between their work and this is possible.

Attempts to explain theoretically these effects have been made by Wentzel,[24] Stelling,[25] Aoyama, Kimura and Nishina[26] and Pauling.[27] The theory of Pauling was applied with considerable success by Valasek[3] to a calculation of the second ionization potential of K, and the electron affinity of the Cl ion, but with no success to a calculation of the electron affinity of the S ion. A similar attempt can be made to calculate the second ionization potential of Cu from the present results.

According to Pauling, the term value $h\nu$ of an electron in an ion of an ionic lattice bears the following relationship to the term value $h\nu_0$ in the free ion:

$$h\nu_0 = h\nu - (\pm e\varphi - E_c)$$

where $\varphi$ is the lattice potential as determined from Madelung's formula or the Born cycle, $+\varphi$ being used for negative ions and $-\varphi$ for positive ions; $E_c = -0.8 \times 6.43 \times 10^6 \kappa$ volts, where $\kappa$ is the volume specific diamagnetic susceptibility. Of the compounds studied, the only one given by Wyckoff[28] as forming an ionic crystal is $Cu_2S$. It has the same structure as $CaF_2$. The constants of the Madelung formula, $\varphi = Ae/r$, as given by Sherman[29] and Wyckoff are:

$$A = 11.64 \qquad r = 5.59.$$

The value of the mass susceptibility is taken from the International Critical Tables and is $-0.18 \times 10^{-6}$ c.g.s. units. The density of $Cu_2S$ is 5.6 g/cc. Using these constants we find $(-e\varphi - E_c) = (-29.6 - 5.2)$ volts. The term value of the levels in which the $K\beta_5$ line has its origin may be obtained from the wave-length of the $K\beta_5$ and the $K$ edge as measured by Lindh[30] for CuS. Presumably the edge would be in about the same position as in $Cu_2S$, within a difference not significant to this problem at least. This edge is at 1376.8 X.U., giving $h\nu$, the term value of the outermost electrons of the Cu ion in $Cu_2S$, as 7.9 volts, so that the second ionization potential of Cu would be $7.9 - (-34.8)$ volts, or 42.7 volts. Sherman [29] lists it at 20 volts, so the theory is seen to break down completely in this application. Evidently some term, not important in the potassium halides or the alkali chlorides but important in $Cu_2S$, is missing from the formula. This ought not be a term to take care of polarization, however, for the lattice potentials as determined by the Madelung formula and by the Born cycle differ by but 11 percent, whereas the $e\varphi$ term of our formula would have to be decreased to a fourth of its present value to bring about agreement.

TABLE III. *Term values of the outermost electrons of 26 Fe–30 Zn in their sulfides.*

| | $K_\infty$ | $K\beta_5$ | $\nu/R$-compounds | $\nu/R$-pure metal |
|---|---|---|---|---|
| 26 Fe | 1738.9 | 1741.3 | 0.73 | 0.4 |
| 27 Co | 1602.9 | 1605.7 | 1.01 | 0.5 |
| 28 Ni | 1483.1 | 1485.4 | 0.95 | 0.7 |
| | | 1485.9 | 1.15 | |
| | | 1486.6 | 1.44 | |
| 29 Cu | 1376.8 | 1377.9 | 0.58 | 0.4 |
| 30 Zn | 1280.1 | 1281.7 | 0.90 | 0.9 |

The $\nu/R$ values in Rydberg units of the outermost terms of the metals in the sulfides are listed in Table III, together with the corresponding term values for the pure metals, taken from Siegbahn. Again it is true that the edges in the actual compounds studied have not been measured, but since the edge does not change much for all compounds in which the metal has the same valence, the average of De Boer's[31] values for $Co^{2+}$ have been taken, and those of Lindh[30] for $Ni^{2+}$ and $Zn^{2+}$. For lack of anything better, Lindh's[30, 32] data for FeS and CuS have been used in the case of iron, and copper.

Table III shows that the average binding of the outermost electrons in Cu and Zn in their sulfides is about the same as in the pure metal, whereas in the other three elements it is somewhat greater. The average bindings of the corresponding electrons in S in the sulfides, when calculated from the data of Valasek[3] and Lindh,[32]

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[24] Wentzel, Naturwiss. **104**, 64 (1922).

[25] Stelling, Diss. Lund (1927).

[26] Aoyama, Kimura and Nishina, Zeits. f. Physik **44**, 810 (1927).

[27] Pauling, Phys. Rev. **34**, 954 (1929).

[28] Wyckoff, *Structure of Crystals* (Chemical Catalog Co., New York, 1931).

[29] Sherman, Chem. Rev. **11**, 93 (1932).

[30] Lindh, Zeits. f. Physik **63**, 106 (1930).

[31] De Boer, Arch. Neerl. Sc. (3A) 10, 101 (1927).

[32] Lindh, *Handbuch der Exptl. Physik* XXIV, 2. Teil, p. 291. (Ak. Verlagsg. M. B. H., Leipzig, 1930).

are much less, showing that the $K\beta_5$ of the metals and the $K\beta_1$ of S do not have their origin in levels in the lattice common to both atoms. In addition, in the cases of Co, Cu and Zn, the multiplicity observed by Valasek in the S lines does not have its counterpart in the corresponding line of the metals.

ACKNOWLEDGMENTS

The writer wishes to acknowledge his indebtedness to Dr. Joseph Valasek, who suggested the problem, and whose advice and criticism have been invaluable in the carrying out of the research; and to Mr. Christian Dane, machinist, for his careful construction of the apparatus.

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OCTOBER 15, 1936 PHYSICAL REVIEW VOLUME 50

# The Ultraviolet Absorption Spectrum of Ammonia

## III. The Absorption Spectra of the Deuteroammonias. A Note on Rydberg Series in Ammonia

A. B. F. DUNCAN, *Department of Chemistry, Brown University*

(Received June 22, 1936)

The absorption spectrum of mixtures of $ND_3$, $ND_2H$, and $NDH_2$ has been obtained from 2200 to 800A in a normal incidence vacuum spectrograph with a dispersion of about 8.5A/mm. The spectrum above 1675A (the end of the first electronic transition) is made up of very diffuse bands. Below 1675 all the bands are sharp. Two electronic transitions are found between 1675 and 1220A. Each electronic transition is accompanied by many vibrational transitions. Relatively long $v'$ progressions are found for each of the molecules. Evidence for a fourth electronic state below 1220A was found, but no analysis of the bands could be made. Only one excited state frequency appears for each molecule. This is most probably the parallel deformation frequency, which is also the only frequency found for ammonia in the ultraviolet. The numerical values of the frequencies were calculated from ammonia frequencies in corresponding excited states considering changes in mass alone, and agreed with experiment. The electronic terms for the excited states were also calculated. A discussion is given of a possible Rydberg series in ammonia.

THE absorption spectrum of ammonia has been photographed[1] in the region between 2300 and 850A, with a dispersion of 8.5A/mm. Part of the spectrum between 1620 and 1450A was recently studied[2] with much higher dispersion (1.3A/mm) and the rotational structure resolved and analyzed.

The present experiments were made with a sample of $ND_3$ gas given us by Professor H. S. Taylor of Princeton University and prepared in his laboratory. A preliminary report has been made on this work.[3] The sample, received in a glass bulb provided with an inner seal, was connected to the vacuum spectrograph through two small volumes separated by stopcocks. By use of these calibrated volumes the pressure of heavy ammonia was varied from 0.014 to 0.70 mm in the spectrograph, which was cut off from the pumps during exposures. At lower pressures no absorption could be observed, and no additional bands appeared between 0.28 and 0.70 mm pressure. The light source was the Lyman continuum operated as described previously.[4] The exposure times were ten seconds to two minutes on Hilger Schumann plates. These plates do not give as good contrast in our experience as Eastman III–O oiled with Nujol, but they were about twenty times as fast, and we wished to avoid as far as possible exchange reactions of $ND_3$ in the spectrograph. Several photographs of pure $NH_3$ were made on each plate at corresponding pressures for visual comparisons of intensity, and as a general check on the accuracy of measurement.

The measurement of ammonia bands on these plates agreed within experimental error with previous work. All bands reported here have been measured on at least two photographs, some on as many as twelve. The accuracy of measurement is considered to be 5–15 $cm^{-1}$ for

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[1] A. B. F. Duncan, Phys. Rev. **47**, 822 (1935).

[2] A. B. F. Duncan and G. R. Harrison, Phys. Rev. **49**, 211 (1936).

[3] A. B. F. Duncan, Phys. Rev. **47**, 886 (1935).

[4] Noyes, Duncan and Manning, J. Chem. Phys. **2**, 717 (1934).

FIG. 3. Typical spectrogram. From left to right, Cu $K\alpha$, Zn $K\alpha$, Cu $K\beta_1$, Zn $K\beta_1$, and Va $K\alpha$ in the first order. Enlargement about $3X$. Ghost structure on long wave-length side of Zn $K\beta_1$. Zn $K\beta_{2,5}$ was visible on the original negative. Obtained from ZnS.