Hyperfine Structure of Boron, Yttrium, Rhodium, and Palladium

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The spectra of boron, yttrium, rhodium, and palladium, excited in an uncooled Schuler lamp, were investigated in the region λλ2500–4000 with a 20-cm quartz Lummer-Gehrcke plate, in an attempt to find hyperfine structure. None was discovered that could be interpreted either as isotope shift, or as structure due to a nuclear magnetic moment.

INTRODUCTION

HYPERFINE structure may be due to nuclear magnetic moments or to the presence of isotopes. Structure from the former theoretically might be observed with any nucleus of nonvanishing spin and magnetic moment, and would be expected in elements whose nuclei are composed of an odd number of primary particles. That due to the isotope effect should from elementary considerations, be more apparent in the lighter elements. Experimentally, hyperfine structure is most easily observed in the heavier elements, because the lines are sharper, and because the separations are found to be fairly large. Spectral lines of the very light elements are so broad, because of the Doppler effect, that small h.f.s. is concealed; on the other hand, the elements in the middle of the periodic table have been found as a group to possess extremely small structure of any type.

The elements on which we report include boron, a very light element, and yttrium, rhodium, and palladium, in the central portion of the periodic table.

BORON

Boron consists of two isotopes, B^{10} and B^{11}, which occur in relative concentrations of 1 to 4. According to elementary theory, the spectral terms of the two isotopes should be separated by an energy difference proportional in the first approximation to the product of the term value for an infinitely heavy nucleus, and the difference of the reduced electron masses for the two nuclei. Similarly every spectral line will have two components of wave number separation approximately proportional to the product of the average wave number of the two, and the difference of the reduced electron masses. Thus each fine structure component of the boron resonance doublet at λ2496.73 and λ2497.93 should, under high dispersion and if sufficiently sharp, be doubled with separations of about 0.2 cm^{-1}.

A spin and nuclear moment have been predicted for the boron isotopes by Bethe and Rose;[1] these predictions suggest rather small magnetic splittings, so that each isotope should have a hyperfine structure pattern of about 0.02 cm^{-1} over-all breadth. The total pattern of each of the resonance lines would theoretically be a doublet of separation about 0.2 cm^{-1}, each component of which would be complex with breadth of about 0.02 cm^{-1}.

The boron resonance lines were excited in a Paschen-Schuler tube with an uncooled cathode. Attempts to excite the lines in water cooled and dry-ice cooled tubes were unsuccessful. Although for the estimated temperatures in the source the Doppler breadth is computed to be so large that the isotope doublets would probably not be resolved, we considered it quite possible that an asymmetry in the lines would be observable.

The lines were therefore photographed by use of the uncooled source. The spectrograph was a large Hilger 185 instrument, used with a 20-cm quartz Lummer plate, thickness 3.518 mm, in series with a Rochon prism and a quartz-fluorite achromat in front of the slit. The high dispersion apparatus was mounted on a lathe bed to reduce vibration, and enclosed in a box the temperature of which was controlled in the customary manner with a mercury thermostat and heater.

Exposures of 24 hours were sufficient to photograph the lines; the lines were not observ-

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[1] Bethe and Rose, Phys. Rev. **51**, 205 (1937); **51**, 993 (1937).

TABLE I.

Wave-Length	Transition	Structure
Lines reported in yttrium II spectrum		
3982.59	$a^3D_2 - z^1D_2'$	Single
3788.70	$a^3D_1 - z^3F_2$	"
3776.56	$a^3D_2 - z^1P_1$	"
3774.33	$a^3D_2 - z^3F_3$	"
3747.55	$a^3D_1 - z^1P_1$	"
3710.30	$a^3D_3 - z^3F_4$	"
3664.62	$a^3D_3 - z^3D_2'$	"
3633.13	$a^1S_0 - z^1P_1$	"
3611.06	$a^3D_2 - z^3D_2'$	"
3601.93	$a^3D_1 - z^3D_1'$	"
3600.74	$a^3D_3 - z^3D_3'$	Two components, intensities, 1 : 4
3549.02	$a^3D_2 - z^3D_3'$	Single
3496.08	$a^1S_0 - z^3D_1'$	"
3327.89	$a^1D_2 - z^1F_3$	"
3242.30	$a^3D_3 - y^3P_2$	"
3216.70	$a^3D_2 - y^3P_1$	"
3195.62	$a^3D_1 - y^3P_1$	Two components, one broad. 5 : 4
3173.07	$z^3F_4 - a^3G_5$	Two components, one broad. 10 : 11
Lines reported in yttrium III spectrum		
2945.92	$5^2S_1 - 5^2P_1$	Single
2817.03	$5^2S_1 - 5^2P_2$	"

ably asymmetrical. Rough measurement on λ2497.73 gave a half-breadth of 0.4 cm⁻¹.

YTTRIUM

Yttrium is an odd element consisting of a single isotope. Its visible spectrum has been found free of h.f.s. by Schuler and Schmidt[2] and by Kruger.[3]

In the ultraviolet, between λ3000 and λ4000, the stronger lines of the first spark spectrum are found. These were photographed by use of the same type of source and the same dispersing apparatus as in the investigation on boron. Although 17 of the 18 lines observed involve transitions of an s electron, no significant structure appeared. Table I is a list of the lines reported; they were examined and identified simultaneously with a comparator. The lines

[2] Schuler and Schmidt, Naturwiss. 22, 839 (1934).
[3] Kruger, Phys. Rev. 47, 509 (1935).

TABLE II. *Lines reported in the rhodium I spectrum.*

Wave-length	Transition	Structure	Wave-length	Transition	Structure
3975.32	$^2\bar{D}_3' - 2^7_2$	Single	3498.74	$^4F_2 - ^2D_3$	Single
3958.86	$^2F_3 - ^2G_4$	"	3478.91	$^2\bar{D}_3 - ^2D_3$	"
3942.71	$^4P_2 - ^4\bar{P}_1$	"	3474.79	$^4F_2 - ^4G_3$	"
3934.23	$^2F_4 - ^4G_4$	"	3462.04	$^4F_3 - ^4\bar{F}_3$	"
3856.51	$^2F_4 - ^2G_5$	"	3440.68	Unclassified	2 comp., 3 : 2; heavier broadened
3833.87	$^2F_3 - ^2D_2$	"			
3822.25	$^2F_3 - ^2\bar{F}_3$	"	3434.90	$^4F_5 - ^4G_6$	2 components, equal
3806.77	$^4F_3 - ^4D_3$	"	3424.39	$^2F_3 - ^4D_3'$	2 components, 3 : 2
3805.92	$^2\bar{D}_3' - ^2D_3^3$	"	3399.68	$^4F_3 - ^2\bar{F}_4$	Single
3799.32	$^2F_4 - ^2\bar{F}_4$	2 components, 20 : 1	3396.82	$^4F_5 - ^4\bar{F}_5$	2 components, equal
3793.22	$^2F_4 - ^2D_3$	Single	3385.78	$^2D_3' - ^2\bar{F}_4^2$	Single
3788.58	$^2\bar{D}_2 - ^2D_3$	"	3380.64	$^4F_4 - ^4G_4$	2 components, 10 : 2, dim.
3778.13	$^2\bar{D}_3' - 34_3$	"	3372.24	$^4F_3 - ^4G_3$	Single
3769.98	$^2\bar{D}_2' - 40_2$	"	3369.68	$^2P_2 - 34_3$	"
3765.08	$^2F_4 - ^4G_3$	"	3368.38	$^4F_3 - ^4\bar{F}_2$	"
3748.23	$^4P_2 - ^4D_3^1$	"	3360.81	$^2\bar{D}_2 - ^4P_2$	"
3713.01	$^4F_2 - ^4D_2$	2 components, 3 : 1	3359.90	$^2P_1 - 44\frac{1}{2}_1$	"
3700.90	$^4F_2 - ^4G_5$	Single	3344.20	$^4P_1 - 40_3$	"
3698.61	$^2\bar{G}_5 - (^2\bar{F}_4^2)$	2 components, 3 : 1	3342.90	$^4P_3 - 30_3$	"
3692.36	$^4F_5 - ^4D_4$	2 components, equal	3338.53	$^4F_4 - ^4\bar{F}_3$	"
3690.72	$^2\bar{D}_3 - ^4D_2$	Single	3323.09	$^4F_4 - ^2G_5$	"
3681.06	$^2P_2 - 30_3$	"	3300.46	$^4P_2 - 38_2$	"
3658.00	$^4F_4 - ^4D_3$	"	3294.26	$^4D_2 - \eta_3$	"
3626.61	$^4P_3 - ^4D_4'$	"	3289.13	$^4F_2 - ^2\bar{D}_2$	"
3612.47	$^4F_2 - ^4D_1$	"	3286.38	$^2F_3 - ^2\bar{P}_2$	"
3597.15	$^2\bar{D}_3 - ^4G_4$	"	3283.57	$^4F_3 - ^2G_4$	"
3596.19	$^4F_3 - ^4D_2$	"	3280.54	$^4F_4 - ^2\bar{F}_4$	2 components, 4 : 3
3583.09	$^4P_2 - ^2\bar{P}_2$	"	3271.61	$^2\bar{D}_3 - ^2D_2$	Single
3549.53	$^2\bar{D}_3 - ^4\bar{F}_3$	"	3263.14	$^2\bar{D}_3 - ^2\bar{F}_3$	"
3543.97	$^2\bar{D}_2 - ^2D_2$	"	3254.96	$^4\bar{F}_4 - ^4G_3$	"
3570.18	$^4F_2 - ^4\bar{F}_3$	3 components, 2 of them barely resolved	3214.31	$^4F_4 - ^4G_4$	2 components, 5 : 4
			3211.37	$^4P_2 - 40\frac{1}{2}$	2 components, 1 : 4
3538.26	$^4F_4' - 42\frac{1}{2}$	Single	3197.13	$^4F_3 - ^2D_2$	Single
3538.12	$^2F_4 - ^2\bar{F}_3$	"	3193.83	$^4G_3 - \nu$	2 components, 3 : 2
3528.03	$^4F_4 - ^4\bar{F}_4$	"	3194.54	$^2F_4 - ^4D_3^1$	Single
3507.32	$^4F_3 - ^4G_4$	"	3191.31	$^2\bar{D}_2 - ^4D_3^1$	"
3502.54	$^4F_5 - ^4G_5$	2 components, equal	3189.16	$^4F_3 - ^2F_3$	"

λλ3600.74 and 3195.62, each of which was observed to be a doublet, are transitions between levels which are proven to be single by the presence of single lines ending on them. The line λ3173.07, which also appears doubled, is a transition not involving an s electron. It is impossible in this case, to be certain the doublet is true h.f.s. because no other transitions to the levels involved were photographed. We conclude the structure is not genuine in any case, but due to some impurity in the source.

In addition to the lines in the first spark spectrum, a pair in the second spark spectrum were barely visible on the plates. No complexity was observed.

Rhodium

Like yttrium, rhodium is an element of odd charge and mass number; it consists of the single isotope, number 103, except for a spectroscopically negligible concentration of rhodium 101. Its visible spectrum was observed by Schuler[2] who failed to find hyperfine structure. The ultraviolet region has been recently investigated by L. Sibaiya[4] who reports a spin of $\frac{1}{2}$ on the basis of h.f.s. doublets, of separation equal to 0.058 cm^{-1} in the two resonance lines λλ3434.90, and 3692.36. He rules out the possibility of absorption in the source as the origin of the structure on the basis of the following argument: The copper resonance lines appear unreversed under identical conditions of excitation; copper has a lower melting and boiling point than has rhodium.

Our investigation, first undertaken with the uncooled Schuler lamp in the ultraviolet region of the spectrum, revealed no significant structure in the lines listed in Table II. Doublet structure in the four resonance lines was proven to originate in absorption in the source. The resonance lines referred to are those ending on the level $^4F_5$, namely λλ3692.36, 3502.54, 3434.90, and 3396.82. The apparent complexity in the other lines cannot be considered evidence of true

TABLE III. *Half-breadths in cm^{-1} of rhodium resonance lines photographed by use of water-cooled source.*

Current through Source	λ3434.90	λ3692.36
0.15 ampere	0.089 cm^{-1}	0.062 cm^{-1}
0.60 "	0.16 "	0.12 "

[4] L. Sibaiya, Proc. Ind. Acad. Sci. **6A**, 229 (1937).

h.f.s., for the same reason as applied to the apparent structure in the yttrium spectrum.

In order to verify Sibaiya's results, if possible, we set up a Schuler tube with an aluminum water-cooled cathode, and photographed the spectrum again. No significant structure appeared; in particular, the lines reported as complex by Sibaiya, which we had previously found reversed, showed, in this case, a single component only.

Half-breadths for λλ3434.90 and 3692.36 were measured on two plates, the first plate taken with a current of 0.15 ampere and the second with 0.6 ampere through the source. The results appear in Table III. It can be seen that when the current was small, the half-breadths were just a little larger than the doublet separation reported by Sibaiya. Under these circumstances one would expect the two components, if they exist, to be more or less completely resolved. As a matter of fact, one should apparently expect such doublets to show up even on the plates taken with the larger current; for although in that case the half-breadths are large, they appear no larger than the half-breadth of the unresolved pattern whose microphotometer trace Sibaiya shows in his article.

We conclude that the rhodium arc spectrum has no hyperfine structure. We judge Sibaiya's results to have been the result of reversal due to absorption.

Palladium

The element palladium is composed of six isotopes: 102, 104, 105, 106, 108, 110. Its spectrum has been investigated in the ultraviolet by L. Sibaiya,[5] who found no significant hyperfine structure.

The lines photographed and reported by us lie in the region λλ2700–4000, so that the anomalous term observed by Shenstone[6] was not involved in any transition. All the lines reported in Table IV are due to transitions of an s electron; no hyperfine structure was found. The slight broadening of the three lines which end on the resonance level, $^3D_3$, as well as of the line λ3718.91, is not considered by us to be of significance.

In the course of the research, we found that

[5] L. Sibaiya, Proc. Ind. Acad. Sci. **2A**, 313 (1935).
[6] Shenstone, Phys. Rev. **36**, 669 (1930).

TABLE IV. *Lines reported in the palladium I spectrum.*

WAVE-LENGTH	TRANSITION	STRUCTURE	WAVE-LENGTH	TRANSITION	STRUCTURE
3894.18	$5s^1D_2-5p^3D_3^0$	Single	3433.44	$5s^1D_2-5p^1P_1^0$	Single
3799.16	$5s^3D_2-5p^3P_2^0$	"	3421.24	$5s^3D_2-5p^3D_2^0$	"
3718.91	$5s^3D_1-5p^3P_2^0$	Broadened	3404.60	$5s^3D_3-5p^3F_4^0$	Broadened
3690.34	$5s^1D_2-5p^3F_2^0$	Single	3373.02	$5s^3D_2-5p^3D_3^0$	Single
3634.70	$5s^3D_3-5p^3P_2^0$	Broadened	3302.15	$5s^3D_1-5p^3D_1^0$	"
3609.56 −	$5s^3D_2-5p^3F_3^0$	Single	3287.26	$5s^3D_3-5p^3D_2^0$	"
3571.16	$5s^3D_1-5p^3P_0^0$	"	3258.78	$5s^3D_1-5p^1D_2^0$	"
3553.10	$5s^1D_2-5p^1F_3^0$	"	3251.64	$5s^3D_1-5p^1P_1^0$	"
3516.95	$5s^3D_2-5p^3P_1^0$	"	3242.71	$5s^3D_3-5p^3D_3^0$	Broadened
3489.79	$5s^1D_2-5p^3D_1^0$	"	3114.05	$5s^3D_2-5p^1F_3^0$	Single
3481.17	$5s^3D_1-5p^3F_2^0$	"	3065.31	$5s^3D_2-5p^3D_1^0$	"
3460.76	$5s^3D_3-5p^3F_3^0$	"	3027.92	$5s^3D_2-5p^1D_2^0$	"
3441.40	$5s^1D_2-5p^1D_2^0$	"	2763.08	$a^1S_0-5p^3P_1^0$	"

the iron lines were excited when the current was large. One might expect that such lines would be sharper when excited in the Schuler tube than when excited in the ordinary arc. We photographed and examined about 190 of them, but found no structure. The half-breadth of two of the stronger unreversed lines was about 0.11 cm^{-1}, which, if the broadening is due to the Doppler effect, would correspond to a temperature of about 1200°C.

Ultraviolet Band Spectra of HgCl, CdCl, and ZnCl*

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The spectra of the chlorides of mercury, cadmium, and zinc, excited in a high frequency discharge, are examined at high dispersion in the region 3200–2000A. Vibrational analyses of several systems are presented. Included is a discussion of the electronic configurations involved in the systems analyzed.

INTRODUCTION

THE most extensive spectroscopic work on the halides of mercury, cadmium, and zinc appears to be that of Wieland[1, 2] in which he explored the wave-length region between 7000A and 2200A. This work was done in emission, a Geissler tube discharge serving as source, and at a relatively low dispersion, 10A per millimeter at best. A number of band systems were found; those of interest to the present discussion are as follows: for mercury chloride, a system between 2650A and 2400A, degraded to the violet, ascribed to HgCl, and a system from 2900A to 2700A, likewise degraded to the violet, but ascribed to $HgCl_2$; for cadmium chloride, nothing in the region of the present investigation; for zinc chloride, a system between 3100A and 2900A, degraded to the violet, and tentatively ascribed to ZnCl, although the author expresses some doubt concerning its true origin.

Of these systems, only the shorter wave-length one of HgCl appears well developed and for this system Wieland presents an extensive vibrational analysis. Detailed analyses are made for none of the other systems, although in a later paper[3] Wieland mentions the "poorly established" fundamental frequency of 290 cm^{-1} for the 2900A–2700A system.

Walter and Barratt,[4] working in absorption, at very low dispersion, list ten heads between 3000A

[1] K. Wieland, Helv. Phys. Acta 2, 46 (1929).
[2] K. Wieland, Helv. Phys. Acta 2, 77 (1929).
[3] K. Wieland, Zeits. f. Physik 77, 157 (1932).
[4] J. M. Walter and S. Barratt, Proc. Roy. Soc. 122, 201 (1929).