

DOUBLY IONIZED RARE EARTHS IN  $\alpha^2$  CANUM VENATICORUM\*

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## ABSTRACT

The strongest lines of *Eu* III, *Gd* III, *Ce* III, *Sa* III, and *La* III in the region  $\lambda\lambda$  3070–3300 are identified in the spectrum of  $\alpha^2$  CVn. Their intensities and radial velocities undergo changes parallel to those of the lines of the corresponding singly ionized elements. Several unidentified lines in the blue-violet region are probably due to *Dy* III.

Several recent papers<sup>1</sup> have provided many new observational data regarding  $\alpha^2$  Canum Venaticorum, and attempts have been made to relate the spectroscopic anomalies of this star to those of a number of other peculiar A-type stars.<sup>2</sup> But a convincing interpretation of the spectroscopic variations and of the anomalous intensities of the rare-earth lines in  $\alpha^2$  CVn has not yet been found, although definite progress has been made. One of the difficulties lies in the fact that very few metals show lines of both the neutral and the ionized atom; and, moreover, all unblended arc lines are very weak and can hardly serve for a discussion of the ionization conditions and of their variations with phase. Yet it has been shown conclusively that the elementary theory of ionization fails to explain the observed variations in line intensities. As a consequence, an attempt has been made to attribute the abnormally high intensity of the *Eu* II lines as well as the abnormally low intensity of the *Ca* II line and other similar phenomena either to a reduced or to an enhanced ionization of the corresponding atoms in a field of radiation that is not of the black-body type. Within the spectrum of a specific atom there is no observed effect suggestive of a geometrical dilution of the exciting radiation. Hence a possible effect of the Lyman lines (in absorption or emission), of the Lyman continuum, and of other strong atomic lines around  $\lambda$  1000 was mentioned. For thermodynamic equilibrium the ionization of *Eu* II in  $\alpha^2$  CVn should be far advanced, and the *Eu* II lines should be weak, while those of *Eu* III should be strong. Moreover, at first thought one would be tempted to expect that a maximum intensity of *Eu* II lines should be associated with a minimum of *Eu* III and vice versa, regardless of the type of ionization equilibrium. Unfortunately, no spectrum of a doubly ionized rare earth (except *Ce* III) was available until recently; hence the various possibilities could not be discussed thoroughly, although it was felt that any progress in the understanding of  $\alpha^2$  CVn would have a direct application to the general problem of the peculiar A stars.

The only spectroscopic data on a doubly ionized rare earth previously published concern *Ce* III.<sup>3</sup> The published lines of *Ce* III lie in the region  $\lambda < 3550$  Å; and, although several of them were identified<sup>4</sup> in  $\alpha^2$  CVn with a fair degree of certainty, their behavior with

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<sup>1</sup> Struve and Swings, *Observatory*, **64**, 291, 1942, and *Ap. J.*, **98**, 361, 1943; O. Struve, *Proc. Amer. Phil. Soc.*, **85**, 349, 1942; W. S. Tai, *M.N.*, **100**, 94, 1939, and *Ap. J.*, **96**, 218, 1942; W. W. Morgan, *Pub. Yerkes Obs.*, **7**, Part III, 1935; Nikonov and Brodskaja, *Bull. Acad. Sci. Georgian S.S.R.*, **3**, No. 7, 657, 1942.

<sup>2</sup> The author has in view such A stars as were previously called "manganese stars" ( $\alpha$  And), "strontium stars" (73 Dra), etc., also the A stars which show abnormally weak lines of *Ca* II.

<sup>3</sup> A. S. and R. B. King, *Mt. W. Contr.*, No. 441; *Ap. J.*, **75**, 40, 1932; P. N. Kalia, *Indian J. Phys.*, **8**, 137, 1933; T. L. de Bruin, *Proc. Amsterdam Academy of Sciences*, **40**, 334, 1937; Russell, King, and Lang, *Phys. Rev.*, **52**, 456, 1937.

<sup>4</sup> Struve and Swings, *Ap. J.*, **98**, 361, 1943.

phase was unknown. Recently Dr. A. S. King has re-examined his spectrograms of the spark of rare earths with a view to detecting lines of doubly ionized elements; and he has generously put at my disposal unpublished lists of measured wave lengths of *Eu* III, *Gd* III, *Sa* III, *Nd* III, and *Pr* III in the ultraviolet region. The upper wave-length limits of Dr. King's tables are: for *Eu* III, 3194.3; *Gd* III, 3176.6; *Sa* III, 3398.4; *Nd* III, 3431.4; *Pr* III, 3568.4. It is in this ultraviolet region that the lines of these doubly ionized rare earths are most conspicuous, although other lines appear at longer wave lengths. No strong *Dy* III line appears in the *Dy* spark in the ultraviolet region around  $\lambda$  3200. We shall also include in the present study *La* III, which has the two strong  $6s^2S-6p^2P^\circ$  lines 3171.68 (lab. int. 300) and 3517.14 (lab. int. 200).<sup>5</sup> Lanthanum is a chemical analogue of scandium and yttrium and immediately precedes the group of the fourteen "rare earths." But the atom-building process accounting for the rare-earth elements is actually anticipated in the electron configurations of *La*; hence certain ionization properties of *La* are closely related to those of the rare earths, rendering logical the inclusion of *La* in the present study.

The previously published spectroscopic data on  $\alpha^2$  CVn in the region  $\lambda < 3400$  A are still insufficient for a discussion of the doubly ionized rare earths, since they were based on spectrograms of dispersion about 20 A/mm, which is definitely insufficient for  $\alpha^2$  CVn on account of the complexity of the spectrum. Three coude spectrograms taken by W. S. Adams with the 100-inch reflector were kindly placed at my disposal. These plates (dispersion 2.91 A/mm) are excellent, being well exposed as far toward the ultraviolet as  $\lambda$  3070. The dates and phases are 1944, April 10, phase 0<sup>d</sup>44 (0.08 per.); 1943, March 26, phase 1<sup>d</sup>91 (0.35 per.); and 1943, March 28, phase 3<sup>d</sup>28 (0.60 per.). The lines of the singly ionized rare earths are very strong on the first two plates and absent (or much weaker) on the third.

It would have been desirable to measure the spectrograms completely from  $\lambda$  3070 to  $\lambda$  3600, where adequate published data begin, but lack of time—due to the pressure of war research—prevented. Only those lines or groups of lines near the wave lengths of the strongest laboratory lines of the doubly ionized rare earths were measured. The identifications were based not only on wave-length coincidences but also, in blends, on the known intensity behavior with phase of the various singly ionized elements.

It was at once apparent that the absorption lines due to doubly ionized rare earths are definitely of class A, i.e., they reach their intensity maximum at the same time as *Eu* II. The lines of *Eu* III are absent at phase 3<sup>d</sup>28<sup>m</sup>, while the lines of *Gd* III behave similarly but have a slightly smaller range in intensity, and the lines of *Sa* III and *Ce* III have a much smaller range. The lines were measured for wave length and radial velocity for phases 0<sup>d</sup>44 and 1<sup>d</sup>91 only, with results summarized in Table 1. The lines which proved to be heavily blended are not included. The changes in radial velocity are given only for well-defined lines. On account of the uncertainty of the laboratory wave lengths<sup>6</sup> the changes in radial velocity have more meaning than the absolute values, except in the case of *Ce* III. There is no definite identification of *Nd* III or *Pr* III.

From Table 1 it is apparent that the identification of *Eu* III, *Gd* III, *Ce* III, *Sa* III, and *La* III is as reliable as can be expected in the present state of our laboratory knowledge of these spectra, although it would have been more satisfactory had the whole spectrograms been measured. Yet, even before any actual measurement, simple examination with a hand magnifier of the high-dispersion plates had definitely convinced the author that the doubly ionized elements are indeed present. This illustrates an obvious advantage of very high dispersion.

<sup>5</sup> A. S. King and Edna Carter, *Mt. W. Contr.*, No. 326; *A p. J.*, 65, 86, 1927; Russell and Meggers, *Bur. Standards J. Res.*, 9, 625, 1932.

<sup>6</sup> The lines of *Eu* III, *Gd* III, and *Sa* III are usually wide and diffuse in the heavy-current spark generally used by Dr. King; a weaker spark would narrow them, thus providing better wave lengths; but such laboratory work has to be postponed.

The mean ranges in radial velocity given in Table 1 are very similar to those of the corresponding singly ionized elements. A previous investigation<sup>4</sup> has shown that the changes in radial velocity from phase 0<sup>d</sup>44 to phase 1<sup>d</sup>91 have approximately the following values:

$$\begin{aligned} Eu \text{ II: } &+ 11 \text{ km/sec}; & Ce \text{ II: } &+ 9 \text{ km/sec (somewhat uncertain);} \\ Gd \text{ II: } &+ 4 \text{ km/sec}; & Sa \text{ II: } &+ 4 \text{ km/sec.} \end{aligned}$$

TABLE 1  
ESSENTIAL OBSERVATIONAL DATA ON LINES OF DOUBLY IONIZED RARE EARTHS

ELEMENT	LABORATORY		STELLAR INTENSITIES			STELLAR WAVE LENGTH		RADIAL VELOCITY		CHANGE IN RADIAL VELOCITY BETWEEN PHASES 0 <sup>d</sup> 44 AND 1 <sup>d</sup> 91		NOTES
	$\lambda$	Int.	Phase 1 <sup>d</sup> 91	Phase 3 <sup>d</sup> 28	Phase 0 <sup>d</sup> 44	Phase 0 <sup>d</sup> 44	Phase 1 <sup>d</sup> 91	Phase 0 <sup>d</sup> 44	Phase 1 <sup>d</sup> 91	Individual	Mean	
<i>Eu</i> III. . . . .	3170.97	150	3	Abs.	3	70.97	71.10	km/sec	km/sec	km/sec	km/sec	1 2
	3183.77	100	1	Abs.	1	83.7	83.9	+ 0.0	+12.3	+12.3	+12.3	
<i>Gd</i> III. . . . .	3118.01	1000	5	0	5	18.06	18.11	+ 4.8	+ 9.6	+ 4.8	+ 4.3	3 4
	3176.64	200	3	1	3	76.67	76.71	+ 2.8	+ 6.6	+ 3.8		
<i>Ce</i> III. . . . .	3106.97	200	4	2	4	06.93	07.05	- 3.9	+ 7.7	+11.6	+ 8.6	5 6 7 8
	3121.55	400	4	1	4	21.53	21.60	- 1.9	+ 4.8	+ 6.7		
	3141.25	250	6	2	6	41.25	41.37	.....	.....	.....		
	3143.96	200	6	1	6	43.93	44.01	- 2.9	+ 4.8	+ 7.7		
	3228.56	400	5	2	5	28.53	28.62	- 2.8	+ 5.6	+ 8.4		
<i>Sa</i> III. . . . .	3098.57	250	3	1	4	98.68	98.64	.....	.....	.....	Very small	9 10
	3100.64	200	1	0	1	00.8	00.8	.....	.....	.....		
	3269.39	400	2	Abs.	2	69.43	69.42	.....	.....	.....		
<i>La</i> III. . . . .	3171.68	.....	1	Abs.	1	71.46	71.54	-19.9	-12.3	+ 7.6	+ 7.6	.....

## NOTES TO TABLE 1

1. *Dy* II 70.75 (40), *Gd* II 71.09 (125), and *Eu* II 70.96 (10) have only minor effect.
2. Too faint for reliable radial velocity.
3. *Eu* II 17.99 (15) and *Gd* II 17.97 (40) have only minor effect.
4. *Eu* II 76.60 (8) has no effect.
5. *Gd* II 21.76 (80), *Ti* II 21.60 (20), and *Eu* II 21.78 (6) have only minor effect.
6. *Dy* II 41.13 (200) may have appreciable effect.
7. *Eu* II 44.21 (15), *Ti* II 43.76 (125), and *Dy* II 43.83 (50) may have a slight effect.
8. *Ti* II 28.60 (100) and *Gd* II 28.64 (15) may have slight effect.
9. *Gd* II 98.65 (800) has appreciable effect.
10. Too near strong *Gd* II 00.51 (10,000) for accurate measurement.

We may thus at least say that the changes in radial velocity for the doubly ionized rare earths are in the same direction and of very nearly the same amount as those of the singly ionized rare earths. In fact, if we consider the uncertainties of the laboratory and stellar wave lengths, the radial velocities of *Eu* III, *Gd* III, and *Ce* III at phases 0<sup>d</sup>44 and 1<sup>d</sup>91 agree very well indeed in absolute value with the radial velocities of the lines of the cor-

responding singly ionized elements. It seems logical to assume that the changes in radial velocity which are found to be the same for the singly and the doubly ionized rare earths between phases 0<sup>d</sup>44 and 1<sup>d</sup>91 will also be the same for other phases, but this point has not been checked.

The ranges in line intensity of the doubly ionized rare earths also parallel those of the singly ionized elements. Among the latter, *Eu* II has the largest intensity range; this is also true of *Eu* III among the doubly ionized elements. Similarly, *Ce* III has a much smaller intensity range, just as *Ce* II does.

Hence it appears justifiable to conclude that, in a general way, singly and doubly ionized rare earths behave alike both in intensity and in radial velocity.

The next step consists in examining whether or not some of the strong unidentified lines measured in  $\alpha^2$  CVn are also attributable to doubly ionized rare earths. In the blue-violet region there are about a dozen unidentified lines which reach an intensity of 3 or more at certain phases.<sup>4</sup> Dr. King kindly examined his spectrograms of sparks of rare earths with a view to deciding whether spark lines, absent in the arc (hence presumably due to doubly ionized elements), appeared near the  $\alpha^2$  CVn wave lengths. Three of the  $\alpha^2$  CVn lines— $\lambda$  4447.6,  $\lambda$  4621.2, and  $\lambda$  4621.6—cannot be examined because they are too near *N* II lines, which are very strong on Dr. King's spectrograms. No coincidence was found with the sparks of *Eu* and *Gd*; but a strong *Dy* spark<sup>7</sup> revealed two diffuse lines of fair strength not present in the arc—hence probably due to *Dy* III—at  $\lambda$  4410.0 and  $\lambda$  4572.9, which are strong (maximum intensity 5) unidentified lines in  $\alpha^2$  CVn. These two  $\alpha^2$  CVn lines have a similar intensity behavior with phase and are definitely of class A.

Next a list was prepared of all the unidentified lines of  $\alpha^2$  CVn which reach an intensity of at least 2 at a given phase, from  $\lambda$  3800 to  $\lambda$  4723. While very few coincidences with *Eu* III or *Gd* III lines can be observed,<sup>8</sup> approximately 60 of the 90 unidentified lines coincide reasonably well with spark lines of *Dy*. Considering that a number of identifications are simply impossible on account of the presence of lines of *O* I, *O* II, *N* II, *Dy* I, and *Dy* II in the spark, the percentage of coincidences—about 75 per cent—appears rather convincing. Practically all the corresponding  $\alpha^2$  CVn lines behave with phase more or less like  $\lambda$  4572.9; at any rate, very few intensity behaviors among the 60 coincidences indicate a different origin.

Because laboratory wave lengths are not very accurate, individual radial velocities have little if any meaning. But here again, as in the ultraviolet region, it is found that in a general way the radial velocities of the lines tentatively attributed to *Dy* III behave with phase exactly as the *Dy* II lines do. For lack of time, publication of the details of coincidences must be postponed.

Whether or not lines of doubly ionized rare earths appear in stellar spectra without the simultaneous presence of the singly ionized elements cannot be ascertained quite conclusively from the observational data available at present. The ultraviolet lines of *Eu* III, *Gd* III, *Ce* III, and *Sa* III are not found with certainty in the published lists of lines of  $\alpha$  Cygni<sup>9</sup> and of the B stars,<sup>10</sup> while an unidentified line measured in 55 Cygni at  $\lambda$  3517.15 is probably due to *La* III. On the other hand, many of the strongest unidentified lines of  $\alpha^2$  CVn in the violet-blue region coincide reasonably well with wholly or partly unidentified lines in the table of B-star lines published by H. Kühnborn.<sup>11</sup> This table is very com-

<sup>7</sup> The lines which appear to be due to *Dy* III are much stronger in the violet region than around  $\lambda$  3200.

<sup>8</sup> The two unidentified  $\alpha^2$  CVn lines  $\lambda$  4182.0 and  $\lambda$  4422.2 coincide with *Eu* III lines.

<sup>9</sup> J. H. Rush, *A p. J.*, **95**, 213, 1942; O. Struve, *A p. J.*, **90**, 699, 1939; A. B. Wyse, *Lick Obs. Bull.*, **18**, No. 492, 129, 1938.

<sup>10</sup> Adams and Dunham, *Mt. W. Contr.*, No. 583; *A p. J.*, **87**, 102, 1938; Struve, *loc. cit.*

<sup>11</sup> *Veröff. Univ.-Sternw. Berlin-Babelsberg*, **12**, 1, 1938.

plete, and, although the reality of some of the tabulated faint lines may be doubted, the very large percentage of excellent wave-length coincidences favors the conclusion that lines of doubly ionized rare earths are actually observed in the normal B-type stars, especially  $\gamma$  Pegasi.

The observations of  $\alpha^2$  CVn point thus to the following conclusions:

- a) *Eu* III, *Gd* III, *Ce* III, *Sa* III, and *La* III are observed in the ultraviolet region.
- b) The variations in intensity and radial velocity of these doubly ionized elements with phase are very similar to those of the singly ionized atoms.
- c) Several unidentified lines in the blue-violet region are very probably due to *Dy* III and are probably present in ordinary B-type stars.

We do not know the values of the third ionization potentials of the rare earths except cerium, for which it is probably 19.5 v. The ultraviolet region corresponding to approximately 20 v. ( $\lambda$  617 Å) does not contain lines or continua that can be thought of as capable of affecting strongly the ionization in a stellar atmosphere, although certain *Ne* I, *He* I, and metallic lines may possibly have some effect.

At any rate the new observational data indicate that a number of previous suggestions concerning the abnormal intensities of lines of *Eu* II, *Gd* II, etc., have to be revised, since singly and doubly ionized elements behave exactly alike. In a search for an explanation of the spectroscopic anomalies of  $\alpha^2$  CVn and related stars, we shall possibly have to return eventually to a modernized version of the stratification phenomena first suggested by A. Fowler in 1913,<sup>12</sup> possibly combined with considerations of nonblack-body exciting radiation.

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<sup>12</sup> *Observatory*, 36, 440, 1913.