

# Hyperfine Structure in the Spectra of Sb, Sm, Hg, and Cd†

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Using two samples that were enriched in  $Sb^{121}$  and  $Sb^{123}$ , respectively, the hyperfine structure (hfs) of the spectrum of  $Sb\ II$  was studied, and the quadrupole moments were determined to be  $Q(Sb^{121}) = (-0.52 \pm 0.10) \times 10^{-24} \text{ cm}^2$ ,  $Q(Sb^{123}) = (-0.67 \pm 0.10) \times 10^{-24} \text{ cm}^2$ . Study of the hfs of the spectra of  $Sm\ I$  and  $Sm\ II$ , using two samples enriched in  $Sm^{147}$  and  $Sm^{149}$ , respectively, yielded the result that the nuclear spins of  $Sm^{147}$  and  $Sm^{149}$  are  $7/2$  and their nuclear magnetic moments are  $\mu(Sm^{147}) = -0.76 \pm 0.08 \text{ nm}$  and  $\mu(Sm^{149}) = -0.64 \pm 0.06 \text{ nm}$  with  $\mu(Sm^{147})/\mu(Sm^{149}) = 1.198 \pm 0.015$ . Using a sample containing 1.5 percent of  $Hg^{196}$ , the hfs of the line  $Hg\ II\ \lambda 6150$  was studied, and the existence of the  $Hg^{196}$  component was just observed. Shifts of the even isotopes in the lines  $Hg\ I\ \lambda 5461$ ,  $Hg\ I\ \lambda 6123$ , and  $Hg\ III\ \lambda 4797$  were measured, and it was found that they follow the regularity mentioned earlier. Using natural cadmium, the hfs of the line  $Cd\ II\ \lambda 4415$  was studied, and the shift  $Cd^{114} - Cd^{116}$  was found to be anomalously small compared with the shift  $Cd^{112} - Cd^{114}$ .

## I. HFS OF THE SPECTRUM OF $Sb\ II$

EACH of the antimony isotopes contains only one proton outside closed proton shells, so that their quadrupole moments would be especially suited for comparison with theory. In a previous work by Suwa and the author,<sup>1</sup> the quadrupole moment  $Q$  of  $Sb^{121}$  was deduced from the hyperfine structure (hfs) of the line  $Sb\ II\ \lambda 5640$  ( $5p6s\ ^3P_2 - 5p6p\ ^3S_1$ ),<sup>2</sup> and  $Q(Sb^{123})$  was deduced from the hfs of the line  $Sb\ II\ \lambda 5895$  ( $5p6s\ ^3P_1 - 5p6p\ ^3P_0$ ) measured by Tombouliau and Bacher.<sup>3</sup> A simple calculation shows that the quadrupole effect is far larger in the term  $5p6s\ ^3P_2$  than in the term  $5p6s\ ^3P_1$ , so that it is desirable to measure the hfs of  $5p6s\ ^3P_2$  for  $Sb^{123}$ , but this was almost impossible owing to the complexity of the hfs of the line  $\lambda 5640$ , if natural antimony only was used.

The separated isotopes  $Sb^{121}$  and  $Sb^{123}$  were available to the author in 1951. Using a hollow cathode discharge tube<sup>4</sup> and a Fabry-Pérot etalon the hfs of  $\lambda 5640$  was examined. All the important components could be measured, but some weak components could not owing to the ghosts of the strong helium line  $\lambda 5876$ . The hfs diagram of  $\lambda 5640$  for the natural antimony could now be completely constructed and is shown in Fig. 1. A number in parentheses was calculated, because the

expected component was disturbed by the ghost and could not be measured accurately. The components  $b, c, e, \bar{b}, \bar{c}, \bar{e}, \bar{g}$ , and  $\bar{i}$  were measured on plates that were taken using separated isotopes. The other components were measured on plates that were taken using natural antimony.

From Fig. 1 we get

$$A^{121} = 73.8 \times 10^{-3} \text{ cm}^{-1}, \quad B^{121} = -0.159 \times 10^{-3} \text{ cm}^{-1};$$

$$A^{123} = 40.0 \times 10^{-3} \text{ cm}^{-1}, \quad B^{123} = -0.098 \times 10^{-3} \text{ cm}^{-1}$$

for the term  $5p6s\ ^3P_2$ . From the ratio of  $B^{121}$  and  $B^{123}$ , we get the ratio of the quadrupole moments of  $Sb^{121}$  and  $Sb^{123}$ :

$$Q^{123}/Q^{121} = 21B^{123}/10B^{121} = 1.29 \pm 0.10.$$

This value is in agreement with that published by Loomis and Strandberg<sup>5</sup> (1.263) and that published by Dehmelt and Krüger<sup>6</sup> (1.2689). Putting the values

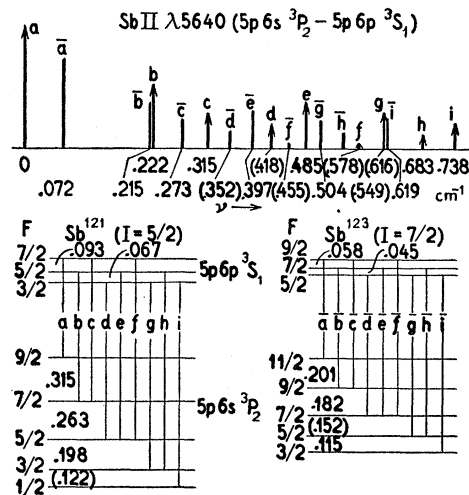


FIG. 1. Hfs of the line  $Sb\ II\ \lambda 5640$ .

† The work with enriched isotopes was performed at the University of Wisconsin in 1950-1951 and was supported by the U. S. Office of Naval Research. The work with natural samples was performed in Tokyo. The enriched isotopes were produced by the Y-12 plant, Carbide and Chemicals Division, Oak Ridge, and were obtained by allocation from the U. S. Atomic Energy Commission.

<sup>1</sup> K. Murakawa and S. Suwa, *Phys. Rev.* **76**, 433 (1949).

<sup>2</sup> The  $Sb\ II$  spectrum was classified by J. S. Badami, *Z. Physik* **79**, 224 (1932) and extensively by R. J. Lang and E. H. Vestine, *Phys. Rev.* **42**, 233 (1932). In the course of the study of the hfs of  $Sb\ II$  it was found that the classifications of a considerable number of lines given by Lang and Vestine should be modified, and the modified and extended classification was published by K. Murakawa and S. Suwa, *Rept. Inst. Sci. Tech. Univ. Tokyo* **I**, 90 (1947) in Japanese.

<sup>3</sup> D. H. Tombouliau and R. F. Bacher, *Phys. Rev.* **58**, 52 (1940).

<sup>4</sup> O. H. Arroe and J. E. Mack, *J. Opt. Soc. Am.* **40**, 386 (1950).

<sup>5</sup> C. C. Loomis and M. W. P. Strandberg, *Phys. Rev.* **81**, 798 (1951).

<sup>6</sup> H. G. Dehmelt and H. Krüger, *Z. Physik* **130**, 385 (1951).

of  $B$  in Casimir's formula (quoted in reference 1) we get

$$Q^{121} = (-0.52 \pm 0.10) \times 10^{-24} \text{ cm}^2,$$

$$Q^{123} = (-0.67 \pm 0.10) \times 10^{-24} \text{ cm}^2.$$

These values are more accurate than those given in the previous work.<sup>1</sup> Loomis and Strandberg set the upper limit of  $Q^{121}$  and  $Q^{123}$  at  $-0.50$  and  $-0.62$  (in unit of  $10^{-24} \text{ cm}^2$ ), respectively and the lower limit of  $Q^{121}$  and  $Q^{123}$  at  $-0.35$  and  $-0.45$ , respectively. Their estimates are in essential agreement with the values deduced here. Quite recently Sprague and Tomboulia<sup>7</sup> have deduced the values  $Q^{121} = -1.3 \times 10^{-24} \text{ cm}^2$  and  $Q^{123} = -1.7 \times 10^{-24} \text{ cm}^2$ . From their short description it is not possible to find source of the discrepancy.

### II. HFS OF THE SPECTRA OF Sm I AND Sm II

In a previous work by Ross and the author<sup>8</sup> the hfs of the spectra of Sm I and Sm II was examined, using two samples that were enriched in Sm<sup>147</sup> and Sm<sup>149</sup> (see Table I and reference 9), respectively; and it was concluded Sm<sup>147</sup> and Sm<sup>149</sup> have the same spins equal to  $5/2$ , that because the maximum number of hyperfine components of any Sm line with a flag pattern was observed to be six. This conclusion was based unfortunately on the

TABLE I. Isotopic constitution (percent) of the samples of samarium.

Sample label	144	147	148	Isotope 149	150	152	154
149	0.55	5.09	11.88	71.53	3.98	4.85	2.13
147	1.10	81.63	6.96	3.94	1.20	3.41	1.77
Natural	3.16	15.07	11.27	13.84	7.47	26.63	22.53

assumption that the contribution of the complex  $4f^6$  to the hfs splitting of the configuration  $4f^66s$  or  $4f^66p$  was negligible, so that the hfs of the transition  $4f^66s-4f^66p$  represented directly the approximate hfs of  $4f^66s$ . The contribution of  $4f^6$  is small only when the  $J$  value of the term is small, for example, equal to 1 or  $1/2$ . However, in order to determine the nuclear spin, just those lines<sup>10</sup> that involve sufficiently high  $J$  values should be chosen. In this case the aforementioned finding leads to the conclusion that the spin is probably equal to  $5/2$  or larger, because the hfs of any line attributed to the transition  $4f^66s-4f^66p$  does not represent the splitting of the term  $4f^66s$  directly, it being possible that both the upper and the lower term have the same order of magnitude of hfs splitting. It is, therefore, necessary to determine the nuclear spins and magnetic moments, keeping these points in mind.

<sup>7</sup> G. Sprague and D. H. Tomboulia, Phys. Rev. **91**, 476 (1953).

<sup>8</sup> K. Murakawa and J. S. Ross, Phys. Rev. **82**, 967 (1951).

<sup>9</sup> The isotopic constitution of natural samarium was taken from Inghram, Hayden, and Hess, Phys. Rev. **73**, 180 (1948).

<sup>10</sup> The classification of the spectra of Sm I and Sm II was published by W. Albertson, Phys. Rev. **47**, 370 (1935); **52**, 644 (1937) and Astrophys. J. **84**, 26 (1936), respectively. That of Sm I was extended by P. Brix, Z. Physik **126**, 431 (1949). The literature concerning the shift of even isotopes was summarized by D. D. Smith and J. R. McNally, J. Opt. Soc. Am. **40**, 878 (1950).

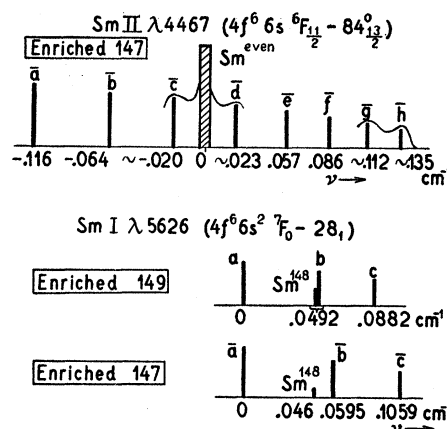


FIG. 2. Hfs of the lines Sm II  $\lambda 4467$  and Sm I  $\lambda 5626$ .

After measurement of the hfs splittings of numerous terms of Sm II, it was found that the term  $4f^66s \ ^6F_{11/2}$  has a small splitting, and finally the line Sm II  $\lambda 4467$  ( $4f^66s \ ^6F_{11/2} - 84^{\circ}_{13/2}$ ) was chosen for determining the spin. This line is so weak that it was overlooked in the previous work.<sup>8</sup> The measured hfs for the sample 147 is given in Fig. 2. The two tail components were not so well resolved, but they could still be recognized as two. From Fig. 2 we can conclude that the term  $84^{\circ}_{13/2}$  of Sm<sup>147</sup> is inverted (hfs level with the largest  $F$  lies deepest) and splits into eight hfs levels, so that the spin of Sm<sup>147</sup> is  $7/2$ . The hfs of  $\lambda 4467$  of the sample 149 is quite similar to that of the sample 147; however, the scale is somewhat smaller. The spin of Sm<sup>149</sup> is, therefore, also  $7/2$ . The hfs of the line Sm I  $\lambda 5626$  ( $4f^66s^2 \ ^7F_0 - 28_1$ ) shown in Fig. 2 also supports qualitatively this spin value. This conclusion is in agreement with that of Bogle and Scovil,<sup>11</sup> who found the spins from para-

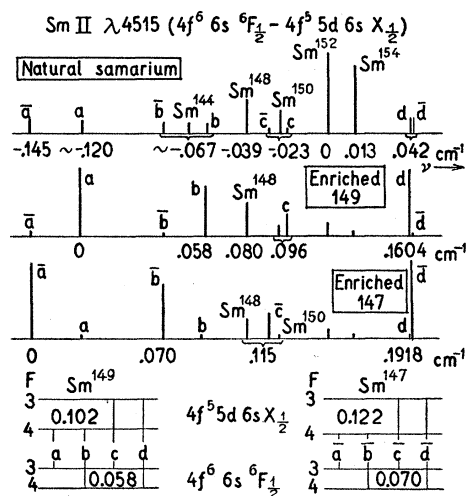


FIG. 3. Hfs of the line Sm II  $\lambda 4515$ .

<sup>11</sup> G. S. Bogle and H. E. D. Scovil, Proc. Phys. Soc. (London) **65**, 368 (1952).

magnetic resonance measurements of samarium ethyl sulfate.

The ratio of the nuclear magnetic moments ( $\mu^{147}/\mu^{149}$ ) can be determined from the line Sm II  $\lambda 4515$ , which was classified in the previous work<sup>8</sup> as due to a transition  $J=\frac{1}{2}\rightarrow J'=\frac{1}{2}$ . In the mean time this line has been classified as  $4f^6 6s^2 6F_{3/2}-4f^5 5d 6s X_{3/2}$  ( $X_{3/2}=23660.03$ ). The hfs of this line is given in Fig. 3, from which we get

$$\mu^{147}/\mu^{149} = (\bar{d}-\bar{a})/(d-a) = 1.198 \pm 0.015.$$

This value is more accurate than that of the previous work,<sup>8</sup> because the hfs was now measured more carefully and on more plates. Bogle and Scovil<sup>11</sup> got the value  $1.222 \pm 0.008$  for the ratio. This is probably in essential agreement with the value obtained here.

From Fig. 3 we get  $A^{147}(4f^6 6s^2 6F_{3/2}) = -0.0175 \text{ cm}^{-1}$ . In the previous work<sup>8</sup> it was found that the splitting of the term  $4f^6 6s^2 8F_{3/2}$  of Sm<sup>147</sup> is  $-0.120 \text{ cm}^{-1}$ . We, therefore, get  $A^{147}(4f^6 6s^2 8F_{3/2}) = -0.0300 \text{ cm}^{-1}$ .  $A(8F_{3/2}) + A(6F_{3/2})$  should be independent of coupling, and is equal to  $\frac{2}{3}a(6s)$ , where the contribution of the complex  $4f^6$  is neglected. We get, therefore,  $a^{147}(6s) = -0.0712 \text{ cm}^{-1}$ . Putting this value and  $n^{*3}/(dn^*/dn) = 9.85$  in the Fermi-Segrè-Goudsmit formula, we get finally

$$\mu^{147} = -0.76 \pm 0.08 \text{ nm}.$$

Using the above-mentioned value of  $\mu^{147}/\mu^{149}$ , we get

$$\mu^{149} = -0.64 \pm 0.06 \text{ nm}.$$

Elliott and Stevens<sup>12</sup> obtained  $|\mu^{147}| = 0.68 \pm 0.1 \text{ nm}$  and  $|\mu^{149}| = 0.55 \pm 0.1 \text{ nm}$  from the data of Bogle and Scovil.<sup>11</sup>

From the hfs of the line Sm I  $\lambda 5626$  ( $4f^6 6s^2 7F_0-28_1$ ) shown in Fig. 2, the following constants for the term  $28_1$  are obtained:

$$A^{147} = -13.33 \times 10^{-3} \text{ cm}^{-1},$$

$$B^{147} = (-0.021 \pm 0.08) \times 10^{-3} \text{ cm}^{-1}.$$

This  $A^{147}$ , when combined with the above-mentioned value of  $\mu^{147}/\mu^{149}$ , gives the value of  $A^{149}$ , and then we get from the distance  $ac$  the value of  $B^{149}$ :

$$A^{149} = -13.20 \times 10^{-3} \text{ cm}^{-1},$$

$$B^{149} = (-0.00 \pm 0.08) \times 10^{-3} \text{ cm}^{-1},$$

where the uncertainty in the values of  $B$  comes mainly from the disturbance due to the existence of minor quantities of Sm<sup>150</sup>, Sm<sup>152</sup>, and Sm<sup>154</sup> in the enriched isotope samples. In the same way the constants  $B$  in some terms with  $J=1$  were measured, but no definite quadrupole effect could be detected. On the other hand it is possible that the upper terms with  $J=1$  perturb each other, and it is difficult to calculate accurate wave functions for these terms. The limit for  $Q$  was roughly estimated, and it is possible at the present time

<sup>12</sup> R. J. Elliott and K. W. H. Stevens, Proc. Phys. Soc. (London) **65**, 370 (1952).

TABLE II. Isotopic constitution (percent) of the samples of mercury.

Sample label	Isotope						
	196	198	199	200	201	202	204
196	1.46	7.48	9.03	13.15	7.87	25.24	35.78
Natural	0.15	10.1	17.0	23.3	13.2	29.6	6.7

to give the estimates only:

$$|Q^{147}|, |Q^{149}| < 1 \times 10^{-24} \text{ cm}^2.$$

Elliott and Stevens<sup>12</sup> got the limit  $|Q^{147}|, |Q^{149}| \leq 0.72 \times 10^{-24} \text{ cm}^2$ .

In order to get more accurate values of  $Q$ , it would be necessary to get the sample in an isotopically pure state. Especially Sm<sup>147</sup> would deserve further study in view of the discussion by Hill and Wheeler<sup>13</sup> about the nuclear deformation in connection with the alpha activity<sup>14</sup> of Sm<sup>147</sup>.

### III. ISOTOPE SHIFT IN THE SPECTRA OF Hg I, Hg II, AND Hg III

In order to study the isotope shift of Hg<sup>196</sup>, the enriched 196 sample (see Table II) was placed in an iron hollow cathode discharge tube and, using helium as the carrier gas, the line Hg II  $\lambda 6150$  ( $7s^2 S_{1/2}-7p^2 P_{3/2}$ ) was obtained with strong intensity. The hfs of  $\lambda 6150$  is shown in Fig. 4, in which the calculated relative intensity (in percent) is given under the notation of each component. If the shift 198-196 were of the same order of magnitude as 204-202, the 196 component should lie about midway between 198 and  $a$ , but this is not the case. The 198 component is somewhat diffuse to the smaller-frequency side, and this was interpreted as due to the unresolved 196 component, whose position was estimated to be about  $-0.110 \text{ cm}^{-1}$ . The shift 198-196 is then about  $0.019 \text{ cm}^{-1}$ .

Since the 196 sample contains larger percentage of Hg<sup>204</sup> than natural mercury, shift of even isotopes in

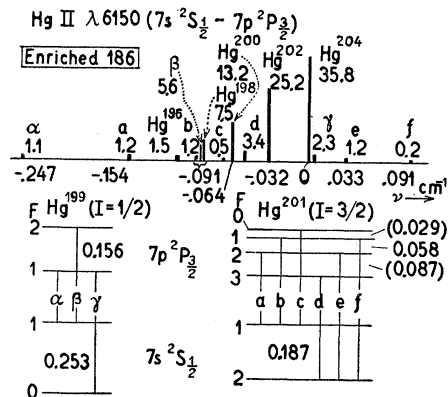


FIG. 4. Hfs of the line Hg II  $\lambda 6150$ .

<sup>13</sup> D. L. Hill and J. A. Wheeler, Phys. Rev. **89**, 1102 (1953).

<sup>14</sup> Rasmussen, Reynolds, Thompson, and Ghiorso, Phys. Rev. **80**, 475 (1950).

the line Hg I  $\lambda 5461$  ( $6s6p\ ^3P_2-6s7s\ ^3S_1$ ) was also measured. The shift 204–202 was measured to be  $0.0306\text{ cm}^{-1}$ . Since the 202 component (intensity 25.2) is expected to have superimposed on it a partial component (intensity 5.4) of Hg<sup>199</sup> lying  $0.0299\text{ cm}^{-1}$  to the smaller-frequency side of the 204 component, the corrected shift 204–202 is  $0.0309\text{ cm}^{-1}$ . The shift of the even isotopes is given in Table III, together with the measurement of Sterner<sup>15</sup> for the same line. The position of Hg<sup>198</sup> given by Sterner deviates somewhat from that of the present author, but the source of the discrepancy is difficult to find at present.

In the measurement using natural mercury, a high-frequency electrodeless discharge tube was used. This light source was found to give sharper lines than a hollow cathode tube. Hg I  $\lambda 6123$  ( $7s\ ^3S_1-5d^96s^26p\ ^1D_2$ ) and Hg III  $\lambda 4797$  ( $5d^86s^2\ 12_4-5d^96p\ 2_3^0$ )<sup>16</sup> were especially strong, and the result of the measurement is given in Table III. The present measurement for  $\lambda 6123$  is

TABLE III. Isotopic shift of the even isotopes of mercury<sup>a</sup> ( $\Delta\nu$  in  $\text{cm}^{-1}$ ).

Line	Isotope			
	198	200	202	204
Hg I $\lambda 5461$	$\Delta\nu$ (J.S.) <sup>b</sup>	0.0240	0.0326	0.0298
	$\Delta\nu$ (K.M.) <sup>c</sup>	0.0276	0.0311	0.0309
	Ratio(K.M.) <sup>c</sup>	0.89 : $\pm 0.03$	1.01 : $\pm 0.03$	1
Hg I $\lambda 6123$	$\Delta\nu$	0.1886	0.2131	0.2090
	Ratio	0.902 : $\pm 0.012$	1.020 : $\pm 0.012$	1
Hg III $\lambda 4797$	$\Delta\nu$	0.552	0.604	0.599
	Ratio	0.922 : $\pm 0.006$	1.009 : $\pm 0.006$	1

<sup>a</sup> In all three lines listed the 204 component lies on the highest-frequency side.

<sup>b</sup> J. Sterner (see reference 15).

<sup>c</sup> Our results.

more accurate than the previous one.<sup>17,18</sup> From Table III we see that the ratio  $\Delta\nu(198-200) : \Delta\nu(200-202) : \Delta\nu(202-204)$  is constant at least as a first approximation, as was inferred in references 17 and 18. If the

<sup>15</sup> J. Sterner, Phys. Rev. **86**, 139 (1952). All the data of previous workers concerning  $\lambda 5461$  are listed in his article. See also K. Burns and K. B. Adams, J. Opt. Soc. Am. **42**, 56, 716 (1952).

<sup>16</sup> The hfs of the line Hg III  $\lambda 4797$  was interpreted by S. Mrozowski, Phys. Rev. **57**, 207 (1940), and later the classification was published by E. W. Foster, Proc. Roy. Soc. (London) **A200**, 429 (1950). E. W. Foster [Proc. Roy. Soc. (London) **A208**, 367 (1951)] also measured the hfs of  $\lambda 4797$ , but, since he employed a small resolving power, he could resolve the structure only incompletely. In the present work the hfs of  $\lambda 4797$  could be resolved completely, and the result of the measurement is:  $-1.1560$  (198),  $-1.0746$  (199),  $-0.6043$  (200),  $-0.4293$  (201),  $0$  (202),  $0.5994$  (204)  $\text{cm}^{-1}$ , the accuracy being  $\pm 0.0012\text{ cm}^{-1}$ . Contrary to the calculation of Foster, the 199 and 201 components are sharp and each of them has a splitting smaller than about  $0.010\text{ cm}^{-1}$ .

<sup>17</sup> K. Murakawa, Phys. Rev. **78**, 480 (1950).

<sup>18</sup> K. Murakawa and S. Suwa, J. Phys. Soc. Japan **5**, 429 (1950).

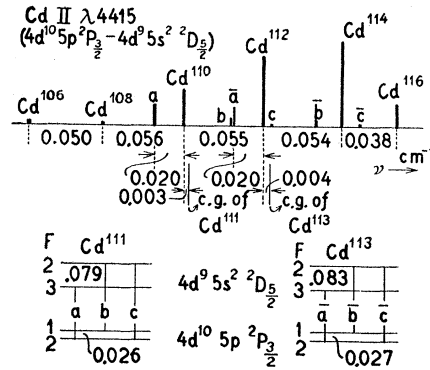


FIG. 5. Hfs of the line Cd II  $\lambda 4415$  (c.g. means center of gravity).

result of Sterner<sup>15</sup> were accepted,  $\Delta\nu(198-200)/\Delta\nu(202-204)$  for  $\lambda 5461$  would have the anomalous value 0.805. Such an anomalous value for  $\lambda 5461$  only is very improbable, however.

#### IV. ISOTOPE SHIFT IN THE SPECTRUM OF Cd II

Koch and Rasmussen<sup>19</sup> and Ross and the author<sup>20</sup> found an anomalous shift of the even isotopes in the spectra of Xe I and of Te II, respectively. The neutron numbers of the Cd isotopes are fairly near to those of the Te isotopes, and the isotope shift in the spectrum of Cd deserves investigation. This was studied by previous workers,<sup>21</sup> but they detected components due to Cd<sup>110</sup>, Cd<sup>112</sup>, and Cd<sup>114</sup> only.

In the present work the hfs of the line Cd II  $\lambda 4415$  ( $4d^{10}5p\ ^2P_{3/2}-4d^95s^2\ ^2D_{3/2}$ )<sup>22</sup> was studied, using natural cadmium and a liquid-air-cooled hollow-cathode discharge tube. The result of measurement is shown in Fig. 5. The hfs splittings of the odd isotopes were calculated, using the magnetic moments given in the literature.<sup>23</sup> The distance 114–116 is anomalously small, and

$$\Delta\nu(114-116)/\Delta\nu(112-114)=0.70\pm 0.02.$$

This kind of anomaly would be probably interpreted according to the idea recently proposed by Wilets, Hill, and Ford.<sup>24</sup>

The author would like to express his appreciation for the kind cooperation of Dr. J. S. Ross in the work with enriched isotopes. It was a great pleasure to be able to talk about interesting related subjects with Professor J. E. Mack, Dr. J. G. Hirschberg, and Dr. J. S. Ross during my stay in Madison, Wisconsin.

<sup>19</sup> J. Koch and E. Rasmussen, Phys. Rev. **77**, 722 (1950).

<sup>20</sup> J. S. Ross and K. Murakawa, Phys. Rev. **85**, 559 (1952).

<sup>21</sup> H. Schüler and H. Westmeyer, Z. Physik **82**, 685 (1933); P. Brix and A. Steudel, Z. Physik **128**, 260 (1950).

<sup>22</sup> This and other lines of Cd II were classified by Y. Takahashi, Ann. Physik **3**, 27 (1929).

<sup>23</sup> J. E. Mack, Revs. Modern Phys. **22**, 64 (1950); P. F. A. Linkenberg, Revs. Modern Phys. **24**, 63 (1952).

<sup>24</sup> Wilets, Hill, and Ford, Phys. Rev. **91**, 1488 (1953).