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Physics. - "Researches on the Spectra of Tin, Lead, Antimony, and Bismuth in the Magnetic Field." By Dr. P. A. van der Harst. (Communicated by Prof. P. Zeeman).
(Communicated in the meeting of June 28, 1919).

To carry out the observations of which the description will follow here, I have made use of the grating apparatus of the Physical Laboratory at Amsterdam, which had been placed at my disposal by Prof. P. Zeeman.

The experiments will be described more at length in my thesis for the doctorate, which will be published under the above title.

1. The spectra of tin, lead, antimony, and bismuth have been little, if at all, studied as to their Zeeman effect. The only scientist that made systematic observations on these elements in this respect, is Purvis ${ }^{1}$ ). As is known, his results often present, bowever, great deviations from those of others, which is chiefly owing to an error in the measurement of the intensity of the field. Besides, Purvis measures but few lines of these elements, viz. only those for which no longer time of exposure was required than half an hour to get them distinclly enough on the photographic plate to be measured. It seemed, therefore, desirable to me to subject the magnetic resolution for these elements to a closer examination.
2. The grating apparatus has been described by Mrs. H. B. Bilderbeek-van Meurs ${ }^{2}$ ). The grating is a concave one of Rowland; radius 3 m ., width 8 cm ., 14438 lines per inch. Slit and grating are rigid with respect to each other, and with respect to an iron circular arch, on which the photographic plates are clasped, so that the exposure can be simultaneous in all orders.

The width of the slit generally amounted to about $20 \mu$, i.e. 8

[^0]times the normal width of the slit ${ }^{1}$ ) for the arrangement used. As lens I used a double lens of quartz-calcium fluorite, transparent to ultraviolet rays, and moreover achromatic. The image of the source of light always fell at the same place of the slit.

It was generally necessary to separate the vertical and horizontal components with a calcspar rhombohedron, placed between the source of light and the lens. One of the two images formed in this - way, was projected on the slit.

The magnet was a large-size Du Bois magnet, of whichithe endplanes of the conic pole tops were circular with a section of generally 8 mm . The distance between the poles was never greater than 4 mm The magnetizing current was measured with a thermic Ampèremeter of Hartmann and Braun, and generally amounted to 15 Ampères.

As source of light was used a spark between electrodes of the metal under examination, or alloys of it. The spark was, parallel to a condenser, in the secondary circuit of a transformator (of Koch and Sterzel at Dresden), of which the primary circuit was fed by the municipal alternating current. Besides in the secondary circuit there was found an auxiliary spark, and an adjustable selfinduction, in series with the spark. The particulars of the spark discharge (intensity of light, sharpness of the spectrum lines formed, melting of the electrodes) and the influence on this of self-mduction, capacity and auxiliary spark will be fully discussed in my Thesis for the Doctorate.

As photographic plates I mostly used "Agfa Rontgen" plates, which I made previously sensitive to colour by bathing them in "Pynachrom." The plates prepared in this way were preferable in my opinion to the commercial colour-sensitive plates.

The measurements were performed with a Zeiss comparator. The results were divided into four groups according to their greater or less accuracy; which I gave in the tables the weight: 4, 3, 2, 1. The first group had a probable error of $1 \%$ or less, the second from $1 \%$ to $5 \%$, the third from $5 \%$ tot $10 \%$, the fourth of more than $10 \%$. For the precautions taken in the measurements and the determination of the error I refer to my Thesis.

Also the preliminary experiments: the focussing of the plate-holder, the determination of the dissolving power, and the scalar value will not be treated further here, but may be found in my Thesis. The resolving power was certainly not smaller than the theoretical.

[^1]3. Observations. The different intensities of the field were always determined by measuring the resolutions which were caused by them for $Z n 4680$, in which the degree of resolution of this line was compared with that obtained with the well-known absolute measurements of Gmeian, Weiss and Cotton ${ }^{2}$ ), and Fortat ${ }^{2}$ ): As standard value for $\frac{2 d \lambda}{\lambda^{2} H} \cdot 10^{5}$ I took the mean of the values obtained by them, viz. 9,376 . I mostly worked with fields that lay in the neighbourhood of 30000 Gauss.

For tin and lead the electrodes were flexible strips of these metals, which were stretched cross-wise over the pole tops. For tin the spark was still cooled by blowing with a Fohn, because otherwise the electrodes were melted through too quickly, and the discharge passed into a continuous one. This method was discarded for lead, because with the Föhn there wonld often be a hitch, and an auxilary spark was inserted in the secondary circuit in series with the illuminating spark. By regulating the distance of this auxiliary spark, we have much better control over the action of the illuminating spark. The electrodes of the auxiliary spark must not oxidise, however, because then we get there a more continuous discharge, whereas the very function of the auxiliary spark is to obviate this drawback, which is met with for the illuminating spark, and is not to be avoided there; it has, therefore, to ensure an interrupted discharge. For this purpose the bulbs of brass, of which the auxiliary spark consisted, were coated with platinum hoods. The strips of lead were kept tightly stretched over the pole tops, as otherwise they are apt to bend over towards each other. thus rendering the spark length too small.

No flexible bands could be made of antimony on account of the brittleness of this metal, I therefore used small flat rods of this metal as electrodes, which were clasped in a spark stand of brass. An advantage of this metal is that it has a pretty high melting-point, and that therefore the electrodes do not so quickly melt through. I have only used Bismuth as electrode as alloy with antimony ( 60 percentages by weight of bismuth) else it combined the drawbacks of tin and lead that it melted soon, and that of antimony that it was brittle. In the alloy the first drawback was eliminated, and it could further be used as antimony.

I must state further that in the tables in which Schippers ${ }^{\text {a }}$ ) records

[^2]his measurements on the antimony spectrum, and which are inserted in Kayser's Handbuch der Spectroscopie, I came across some lines which I never found on my plates. They are the lines 4370,4295 , 4287, 4091, 4078, 4038, 4024, 4006, 4004, 3979, 3721, 3467, 3460. From some experiments which I made with the purpose of ascertaining whether these lines existed, I think I have to conclude that Schippers was mistaken, and took lines of the third order for lines of the second order. These lines are in my opinion successively the following lines of the thurd order - 2913, 2863, 2858, 2727, 2719, 2692, 2683, 2671, 2670, 2653, 2480, 2311, 2306.

Besides my own results I have recorded those of Purvis in the tables. I did not, however. ase the intensity of the field which he gave, because this ralue is undoubtedly too high. Instead of this I have ascertained by the aid of my results what field intensity Purvis used by comparing the average of his results with the average of mine, this separately for every element. Thus I found successively for tin, lead, antimony, and bismuth 30400, 31100, 28700,31100 Gauss. Cotron estimates the field intensity used by Purvis at 30800 , he himself gives 39980 Gauss. For the better mutual comparison of the results those of Purvis for $\frac{d \lambda}{\lambda^{3}}$ have been divided in the subjoined tables by the above mentioned field intensities.

The wavelengths are recorded in round values in international Ångström units.
4. Discussion of the Tables. On one of the photos for tin, on which the two kinds of components appeared at the same time, were further seen the quadruplets 2368 and 2762 (arc line), which had successively the values 34.6 (3), 48.0 (2), and $49 .(2), 56.6$ (3) as values for $\left(d_{l}: \lambda^{2} H\right) .10^{14}$. The values between parentheses indicate the weight. 2266 and 2408 are split up. The amount of the splitting up cannot be measured, but amounts successively to less than 76 and 59.2355 is probably split up.

For antimony the air line 3640 given by Schippers is also observed as split up. Of this $\left(d \lambda: \lambda^{2} H\right) \cdot 10^{14}=66.2$, weight 3 .

There are some among the Bismuth lines, for which we should be cautious when judging about the splitting up. In what follows I shall indicate by an $s$ everything that refers to vibrations normal to the lines of force, a $p$ marks what refers to vibrations parallel to the lines of force.
3068. The $s$-figure was on some photos a triplet of asymmetric intensity. Then the corresponding $p$-figure was a doublet, which
looked exactly like a reversed line, so that I supposed the s-triplet to he really a doublet of a reversed line, the two middle parts of which coincided. This appeared to be true when later on, probably through the increase of the self-induction, the $s$-triplet was transformed into an ordinary doublet, the $p$-doublet into a single line. Also a photo, made with an alloy in which there was less bismuth, presented this latter form, viz. an ordinary triplet. Compare also what Purvis says about this line.
4260. I suppose that the same thing applies for this line as for 3068. When the self-induction was carried up in order to get certainty, this line became, however, too faint to allow us to draw conclusions. In favour of the supposition pleads that the splitting up of the $p$-components is as great as that of the $s$-components.
4122. This is in my opinion a different case. Exner and Habchek give two lines here, 4121.75 and 4122.08 , the latter slightly heavier than the former. I too find two lines with a distance $0.24 \AA$. U., and the same ratio of strength. They do not look at all like one reversed line. The $s$-figure is a triplet which slightly changes in form when the circumstances change (see table). The difference in resolution between corresponding components in the two cases will no doubt be owing to the difficult and therefore unreliable observation. I think, however, that the difference in distance on either side of the middle component actually exists. A triplet is recorded for the $p$-figure. There is a blurred faint line, which towards red, and also but still fainter towards violet fades over some distance and then ceases more or less abruptly. I think, however, that I see a separation in some places. The measurements are of course worth little. Purvis states 72.3 for the splitting up. This is about equal to what I found for the splitting up of the outer components of the $s$-triplet.
4723. Wali Mohammad gives a description of this line as far as its behaviour is concerned for weak magnetic fields, studied by the add of an echelon. ${ }^{1}$ ) I myself find on the $s$ records 2 middle components, by the side of each of which there is a broad smudge, which stops pretty abruptly.

There is hardly any separation to be seen, which renders the measurement difficult. Nevertheless the different measurements of the outer components are in good harmony, those of the inner components not quite so good. The $p$-doublet is very close together, so that it is self-evident that a large comparative error arises there.

[^3]In the table the most violet component is marked by -, the most red by + . In this case the splitting up is not $=2 d \lambda$, as is given in the heading of the column, but $=d \lambda ; 0$ does not mean that the line is at the place of the original unsplit one, but only that there is a component there.
5. General results. When we compare the results in what precedes, it strikes us at once that though the general course of the results may be the same, there yet occur a good many deviations, which amount to more than the given probable error. Further it occurs occasionally that a quadruplet is mistaken for a triplet, which is not astonishing with the middle components of these often blurred lines, which are so very close together. That something similar may be the case with other lines which are given as triplet, is not impossible.

An agreement as Purvis gives between the quadruplets Hb 3740 , $\mathrm{Pb} 2873, \mathrm{Sb} 3723$, Sb 3638 , and possibly Sb 2668 , Bi 2989, does not exist according to my measurements, except perhaps that between Sb 3638 and Bi 2989 . When we examine whether there is perhaps some connection between the resolutions of the lines for which Kayser and Runge ${ }^{1}$ ) find the known constant differences of frequency, it appears that there is no such connection. $\mathrm{V}_{\text {an }}$ Lohuzen ${ }^{\prime}$ ) has given series in the spectra of tin and antimony. The correctness of this is, however, doubted by Saunders ${ }^{3}$ ) and Arnojids ${ }^{4}$ ). I have now examined whether the laws of Preston were valid for these series. Of series I, which v. Lohuzen gives for the tin spectrum, I have found the resolutions (i.e. the values for $\mathrm{d} \lambda: \lambda^{2} \mathrm{H}$, see table) 29,6 and 56,1 for the lines 3656 and 2785 ; in this series 2408 has a resolution smaller than 59. 'In series VII I find for the lines 3801, 2851, 2594, 2483,2422 successively the splittings up $40,5,42,5,44,7$ ( 56 and $46,8), 45,9$. In this 2483 gives a quadruplet, the other lines give triplets. Series VIII: 3175 and 2483 give successively 69,7 (56 and 46,8 ) as splitting up. Antimony. Series XIII: the lines 3268 and 2574 have successively a resolution of 40,9 and 45 . Series XIV: 3505 has the splitting up 63,7 and 2719 has 51.5. Series XX: 3233, 2653, 2478 have the resolutions $60,0,63,68,7$.

[^4]For the other tin and antimony serjes I have obtained no line that was split up or only one.

When we study the above results, we see that of the series for which it is possible to give an opinoon in how far they follow Preston's laws, only series XIII is not in conflict with these rules. In series VII the resolutions gradually increase; the first and the last splitting up lie farther apart than the limit of errors. Besides a quadruplet occurs there in the midst of the triplets. Even if these triplets were at bottom quadruplets, of which only the middle component was seen unsplit, which is very improbable, even then the amounts of the resolutions of the outer components would not be in agreement with each other. - The foregoing does not plead, in my opinion, in favour of v. Lonvizen's results, though there remains a possibility that there are serles that do not follow the rule of Preston. The efficacy of the Zeeman-effects for the discrimination of spectrum series was very apparent when Runge and Paschen found double lines in the spectra of $\mathrm{Mg}, \mathrm{Ca}, \mathrm{Sr}, \mathrm{Ba}$, which lines were changed in the magnetic field in the same way as double lines in principal and subordinate series in the spectra of the alkali-metals, while similar results were also found for some double lines from the Ra-spectrum. The hopes raised in 1902 and 1904 by the said researches with regard to the finding of series are accordingly not realized as far as the metals examined by me, are concerned.

I have further also tried to find regularities myself. For this purpose and also in what precedes I have made use of a graphical representation, which seemed convenient to me. I have arranged the resolutions in every element according to their amount, and then plotted them on the same scale vertically under each other, as is usually done when resolutions are to be compared inter se. Two successive resolutions on the whole differing but little in amount, there arises a curve. A vertical part represents a number of equal splittmgs $n p$. When the corresponding lines are indicated by the side of the resolution figure, we have at once a survey of all the lines that possibly belong to a series. Compare the graphical representation.

In this the resolution figures are only represented half, which, however, does not give rise to difficulties, as they are symmetrical. The components are not indicated by single lines; I have blackened the whole region, where they can be found according to the probable error. The vertical lines traced in the figure, are at distances $=$ half the normal splitting up. A sloping straight part of the curve means that between two definite amounts of splitting up the resolutions are regularly distributed. When I examined this for the resolutions
of the four elements exammed by me, I obtained four curves, each consisting for the greater part of a straight sloping part, which

Graphical representation of the resolutions.

therefore means that for each of the elements nearly all the resolutions are pretty well regularly distributed over a defimte region. For tin most resolutions he in this way between 40 and 70 , for lead between 45 and 70, antimony has a series of resolutions between 60 and 65 , and further some in the neighbourhood of 70 , of bismuth there exist, indeed, rather too few results, but these he pretty regularly between 45 and 70.
A distinctly rertical part, i.e. several equal resolutions does not
6. Tables.

Tin.

| $\lambda$ | $2 \mathrm{~d} \lambda(\mathrm{H}=34930)$ |  |  |  | ( $\mathrm{d} \lambda: \lambda^{2} \mathrm{H}$ ) $10^{14}$ |  |  |  | REMARKS. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | vibration $\perp$ 1. of f . |  | vibration // 1. of f . |  | my own observations |  | Purvis' observ.$\frac{\mathrm{d} \lambda}{\lambda^{g}}: 3,04$ |  |  |
|  | $2 \mathrm{~d} \lambda$ | g | $2 \mathrm{~d} \lambda$ | g | vibrat. $\perp$ l. of f. | vibrat. <br> / 1 . of f. | vibrat. 11. of f. | vibrat. <br> // l. of f |  |
| 2335 | 0.322 | 3 | 0 |  | 84.6 | 0 |  |  |  |
| 2422 | 0.188 | 3 | 0 |  | 45.9 | 0 |  |  |  |
| 2429 | 0.18 | 2 | 0 |  | 43 | 0 |  |  |  |
| 2483 | 0.24 | 2 | 0.202 | 3 | 56 | 46.8 |  |  |  |
| 2496 | 0.242 | 3 | 0.14 | 0 | 55.7 | 32 |  |  |  |
| 2547 | 0.227 | 3 | 0 |  | 50.2 | 0 |  |  |  |
| 2572 | 0.291 | 3 | 0 |  | 63.1 | 0 |  |  |  |
| 2594 | 0.210 | 3 | 0 |  | 44.7 | 0 |  |  |  |
| 2661 | 0.297 | 3 | 0 |  | 59.9 | 0 |  |  |  |
| 2707 | 0.357 | 3 | 0 |  | 69.9 | 0 | 72.2 | 0 |  |
| 2780 | 0.322 | 3 | 0 |  | 59.7 | 0 |  |  |  |
| 2785 | 0.304 | 3 | 0 |  | 56.1 | 0 |  |  |  |
| 2813 | split. up |  | 0 |  | split. up | 0 |  |  | The splitting up is |
| 2814 | 0.270 | 3 | 0 |  | . 48.9 | 0 |  |  | about as greatas |
| 2840 | 0.385 | 3 | 0 |  | 68.5 | 0 | 66.1 | 0 | that of 2814. |
| 2851 | 0.241 | 3 | 0 |  | 42.5 | 0 | 42.6 | 0 |  |
| 2863 | 0.372 | 3 | 0 |  | 65.0 | 0 | 64.5 | 0 |  |
| 2914 | 0.21 | 2 | 0 |  | 35 | 0 |  |  |  |
| 3009 | 0.429 | 4 | 0 |  | 67.9 | 0 | 66.1 | 0 |  |
| 3033 | 0.313 | 3 | 0 |  | 48.7 | 0 |  |  |  |
| 3034 | 0.463 | 3 | 0 |  | 72.1 | 0 , | 70.5 | 0 |  |
| 3142 | 0.368 | 3 | 0 |  | 53.2 | 0 |  |  |  |
| 3175 | 0.490 | 3 | 0 |  | 69.7 | 0 | 70.4 | 0 |  |
| 3219 | 0.261 | 3 | 0 |  | 36.1 | 0 |  |  |  |
| 3262 | 0.357 | 3 | 0 |  | 48.2 | 0 | 49.5 | 0 |  |
| 3283 | 0.30 | 1 | 0 |  | 40 | 0 |  |  |  |
| 3331 | 0.462 | 4 | 0.302 | 3 | 59.6 | 39.1 | 58.8 | 40.0 |  |
| 3352 | 0.39 | 2 | 0 |  | 49 | 0 |  |  |  |
| 3656 | 0.276 | 3 | 0 |  | 29.6 | 0 |  |  |  |
| 3801 | 0.409 | 4 | 0 |  | 40.5 | 0 | 40.0 | 0 |  |
| 4525 | 0.725 | 3 | 0 |  | 50.6 | 0 | 53.6 | 0 |  |
| 4586 | 0.59 | 2 | 0 |  | 40 | 0 |  |  |  |
| 4618 | 1.316 | 3 | 0 |  | 88.5 | 0 |  |  |  |
| 5563 | split. up |  | 0 |  | split. up | 0 |  |  |  |
| 5589 | 1.02 | 2 | 0 |  | 47 | 0 |  |  |  |

Lead.

| $\lambda$ | $2 \mathrm{~d} \lambda(\mathrm{H}=32810)$ |  |  |  | (d $\left.\lambda: \lambda^{2} \mathrm{H}\right) .10^{14}$ |  |  |  | REMARKS. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | vibration <br> $\perp$ l. of f . |  | vibration <br> // l. of f. |  | my own observations |  | Purvis' observ.$\frac{d \lambda}{\lambda^{2}}: 3.11$ |  |  |
|  | 2d $\lambda$ | g | $2 \mathrm{~d} \lambda$ | g | vibrat. <br> $\perp 1$. of f. | vibrat. <br> // 1 . off. | vibrat. $\perp 1$. of f . | vibrat. / 1 l. of f. |  |
| 2476 | 0.294 | 3 | 0 |  | 73.2 | 0 |  |  |  |
| 2577 | 0.277 | 3 | 0 |  | 63.6 | 0 |  |  |  |
| 2613.7 | 0.23 | 1 | 0.13 | 1 | 51 | 30 |  |  | 1 components: pro- |
| 2614 | 0.24 | 2 | 0.21 | 2 | 53 | 46 |  |  | here, 2 distinct ones and 2 faint ones; the two madre ones al |
| 2663 | 0.308 | 3 | 0 |  | 66.1 | 0 |  |  | most conncide. Probably the 2 faint ones |
| 2698 | 0.414 | 3 | 0 |  | 87.0 | 0 |  |  | belong to 2613.7, the two distunct ones to 2614. The distance |
| 2713 1) | 0.426 | 3 | 0 |  | 88.7 | 0 |  |  | middle faint one to middle distinct one |
| 2802 | 0.249 | 3 | 0.173 | 3 | 48.3 | 33.5 | 46.4 | 0 | $=0.45 \AA . U$.,the distance according to Klein's table between 2613.7 |
| 2823 | 0.318 | 3 | 0 |  | 60.6 | 0 | 41.5 | 0 | and $2614=052$ A. U , which corresponds |
| 2833 | 0.34 | 2 | 0.19 | 2 | 64 | 36 | 63.0 | 0 | with what I measure on the photo without |
| 2873 | 0.297 | 3 | 0.221 | 3 | 54.9 | 40.8 | 66.0 | 31.2 | 0.45 and 0.521 s bad, but was not to be expect- |
| 3573 | 0.492 | 3 | 0 |  | 58.9 | 0 |  |  | ed better in view of 2613.7, which are so difficult to measure. |
| 3576 2) |  |  |  |  |  |  | 62.1 | 0 |  |
| 3640 | 0.57 | 2 | 0 |  | 66 | 0 | 66.0 | 0 | spliting up 130 of 2613.7 rests on only |
| 3672 | 0.481 | 3 | 0 |  | 54.2 | 0 | 57.0 | 0 | one, very inaccurate measurement; the |
| 3683 | 0.609 | 3 | 0 |  | 68.3 | 0 | 69.2 | 0 | to middle amounted to 0.49 Å. U. |
| 3740 | 0.576 | 4 | 0.208 | 3 | 62.8 | 22.6 | 64.4 | 30.6 |  |
| 4020 | 0.501 | 3 | 0 |  | 47.3 | 0 |  |  |  |
| 4058 | 0.646 | 3 | 0 |  | 57.8 | 0 | 57.6 | 0 |  |
| 4062 | 0.729 | 4 | 0 |  | 67.3 | 0 | 68.2 | 0 |  |
| 4168 | 0.57 | 2 | 0.468 | 3 | 50 | 40.8 |  |  |  |
| 4245 | 0.537 | 3 | 0 |  | 45.3 | 0 | 42.2 | 0 |  |
| 4386 | 0.543 | 3 | 0 |  | 43.0 | 0 | 37.0 | 0 |  |
| 5609 | 1.706 | 3 | 0 |  | 52.0 | 0 |  |  |  |

1) Arc line.
${ }^{2}$ ) Should this perhaps be 3573 ?

Antımony


莫

Bismut


1) The reddest component is somewhat stronger than the two others, which are equally strong. They are equally sharp.
${ }^{2}$ ) The 2 outer components are about equally strong and sharp, the middle one is fainter and very vague.
2) The middle component is the strongest. The most violet component is fainter than the most red. Only when made more distinct by scratching with a needle this violet component could be measured.
occur. Hence in the search for series by the aid of equal resolutions hardly any result can be obtained by means of these curves. I have also tried it for tin and for antimony lines, which had a splitting up between 60 and 65, but likewise with no success.

I further examined whether there existed simple relations between the distances of the components for more than triple resolutions, which were rather accurately measured (weight 3 or 4). For Sb 3740, Sb 2671 , and Sb 2878 I did not find simple relations. For Sn 3331 the distances of the components are in the ratio of $3: 2$, when the values $\mathbf{5 9 , 3}$ and 39,5 , which lie within the limit of errors, are taken for them. For Pb 2802 the ratio is also as $3: 2$ with the values $49,1: 32,7, \quad \mathrm{~Pb} 2873$ gives $54,7: 41,0=4: 3$; $\quad \mathrm{Sb} 3723$ gives $72,6: 36,3=2.1$. There is, however, no mutual connection or a simple relation to the normal resolution.

The results may be briefly summarized as follows:
The Zeeman-effect was measured of 35 tin lines, 23 lead lines, 27 antimony lines, and 16 bismuth lines. In this deviations were found with Purvis' results which refer only to a few lines, probably in consequence of his less accurate measurements. No relation was found between the resolutions of those lines of the examined metals for which it was proposed to arrange them in series or those which are arranged according to the laws of the $2^{\text {nd }}$ kind of Kayser and Runge. The resolutions are pretty regularly distributed between values which amount to about 1 and 1,5 times the normal resolution. As an incidental result 1 found that a number of lines given by Schippers for antimony, are not real.


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