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INTERPRETATION OF HYPERFINE STRUCTURE IN SPECTRAL TERMS

By H. E. White*
Physikalisch-Technische Reichsanstalt, Berlin

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Abstract

Interpretation of hyperfine structures in cadmium, bismuth and lanthanum. Term analysis of the hyperfine structure of cadmium indicates, as suggested by Schüler and Brück, that the fine structures of λλ5086, 4800 and 4678 are due to isotopes some with an angular momentum 0 and some with an angular momentum $\frac{1}{2}h/2\pi$. This is verified by the fine-structure $\Delta\nu$'s when each level f is assigned a weight $2f+1$. The inverted terms indicate a positively charged nuclear spin.

Some of the fine-structure terms in bismuth and lanthanum are inverted while others are not. The process of inversion within multiplet terms is shown in process by Figs. 2, 3 and 4. The data are taken from the work of Back and Goudsmit for Bi, and from Meggers and Burns for La. A possible explanation of term inversion is given. This is based upon the penetration of an s valence electron, since part of the time it is found near the nucleus and part of the time outside all of the other electrons. In this way the penetrating electron acts as a carrier in that it strengthens the coupling between J of the valence electrons and the nuclear spin i. For multiplet terms, which involve an s electron and which show LS coupling, the total fine-structure separations for each term should be proportional of cos Si when cos $Ji=1$, provided $J>i$, while at the same time the relative separations within each term should be given by the cos Ji.

At THE present time the most satisfactory explanation of the hyperfine structure in spectral lines and terms is obtained by assigning an angular momentum, or spin, to the nucleus of an atom. This nuclear angular momentum, i, which for some elements must take on whole integer values of $h/2\pi$ while for other elements must take on half integer values, is space quantized with the total angular momentum, J, of all of the electrons outside of the nucleus in such a way as to give resultant values, f, different from each other by $h/2\pi$. In this way each energy level in the ordinary energy level scheme of an atom should be broken up into $2i+1$ components (except for $J<i$). In a previous report on the hyperfine structure of praseodymium[1] it was shown how such fine-structure separations should be expected to follow the Landé interval rule. In the singly ionized praseodynium spectrum, the fine structure of nearly two hundred lines show six components which do follow very closely the Landé interval rule. These fine-structure groups, which in each case are the diagonal lines of a tiny multiplet, have also been found in the spectra of manganese, bismuth, lanthanum, bromine, and iodine. Numerous other elements show different types of fine structure.

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* National Research Fellow.

[1] White, Phys. Rev. **34,** 1397 (1929).

CADMIUM

With the fine-structure measurements of several cadmium lines, made by Schrammen,[2] Ruark and Chenault[3] constructed a tentative fine-structure term scheme. A further study of the Cd I fine structure by Schüler and Brück[4] indicated that an angular momentum of $\frac{1}{2}\,h/2\pi$ should be assigned to the cadmium atom.

It has been indicated previously[1] by the author that in an atomic system where fine structure appears, the widest fine-structure term separations can, in nearly every case, be attributed to a single *s* electron. The lowest term in the Cd I spectrum is a $^1S_0$ term arising from $5s^2$. This $^1S_0$ term, with $\Sigma s = S = 0$, $\Sigma l = L = 0$, $\Sigma j = J = 0$, can only give one fine-structure term with $i = \frac{1}{2}$, namely $f = \frac{1}{2}$, where f is the vector sum of J and i. Next above this $^1S_0$ term comes the $^3P_{0,1,2}$ terms arising from *5p5s*, shown on the left side of

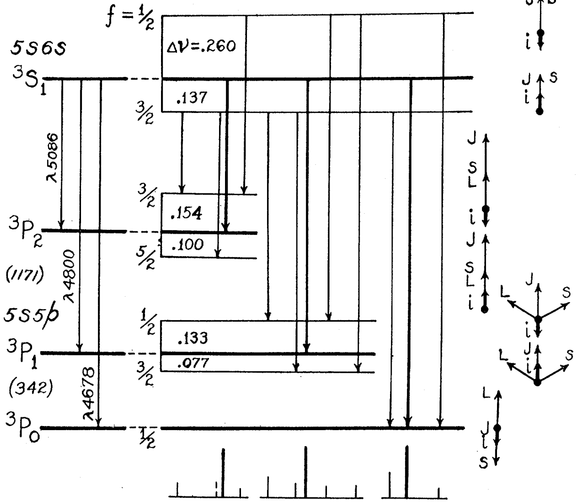

Fig. 1. Hyperfine structure in cadmium terms.

Fig. 1. Still higher the $^3S^1$ term of *5s5s* is found. This $^3S_1$ term combines strongly with the $^3P_{0,1,2}$ terms in the lines λλ 4678, 4800, 5086. The fine structures of these three lines are shown at the bottom of Fig. 1. Since cadmium has at least six isotopes, masses 110, 111, 112, 113, 114, and 116, Schüler and Brück have attributed the strong component in each of the three groups of fine structure to the isotopes 110, 112, 114 and 116 with $i = 0$ and the remaining components to the two isotopes 111 and 113 with $i = \frac{1}{2}$. An energy level diagram for the fine-structure levels is given in the center of Fig. 1. The heavy lines represent the unshifted energy levels arising from the isotopes with $i = 0$. For these atoms $^3S_1$ combines with $^3P_{0,1,2}$ giving the three strong lines near the center of each group, shown at the bottom of the

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[2] Schrammen, Ann. d. Physik **83,** 1161 (1927).

[3] Ruark and Chenault, Phil. Mag. **50,** 937 (1925).

[4] Schüler and Brück, Zeits. f. Physik **56,** 291 (1929).

figure. The cadmium isotopes with $i=\frac{1}{2}$ splits each energy level, except where $J=0$, into two components. Combinations may now take place between those terms where f changes by ± 1 or 0, excluding 0 to 0. At the right of Fig. 1 is given the vector space quantizations of the various angular momenta for each f level. If the above explanation is correct, then the center level of each set of three levels should lie at the "center of mass" of the two outside components, the relative weights for each level f being given by $2f+1$. For the $^3S_1$ term these weight ratios are 2:1 which is borne out by the $\Delta\nu$'s 0.137 and 0.260. For the $^3P_2$ and $^3P_1$ levels these ratios are 3:2 and 2:1, and here again they are borne out by the $\Delta\nu$'s 0.154, 0.100 and 0.133, 0.77 respectively.

Careful observations on the fine-structure intensities, by Dr. Schüler, of λ 4678 show that the fine-structure terms must be inverted as shown. The total (${}_{3/2}{}^3S_1-{}_{1/2}{}^3S_1$) separation ($5s6s$) is 0.397 cm^{-1}. From Schrammen's data on cadmium, the fine structures of the first, second and third members of the $^3S_1$ series ($5s6s$, $5s7s$, and $5s8s$) have total separations of 0.397, 0.375 and 0.364. These separations, as well as those from $5s5p$, are strong evidence for the role played by the s electron in fine structure. Since the third member of $^3S_1$ is so near the series limit, a doublet S term, the normal state of Cd II, $^2S_{1/2}(5s)$ should have a doublet separation not far from 0.350 cm^{-1}. This again is evidence for the strong coupling of an s electron with the nuclear spin.

THALLIUM

The normal state of thallium is given by a single $6p$ electron. The resultant ^2p terms have a separation of about 7800 cm^{-1}. The next term above ^2p is the $^2S_{1/2}$ term of $6s$ followed by the ^2D terms of $5d$. Fine-structure observations on the three lines λ5352($^2P_{3/2}-{}^2S_{1/2}$), λ3776 ($^2P_{1/2}-{}^2S_{1/2}$) and λ2768 ($^2D_{3/2}-{}^2P_{1/2}$) have been made by several investigators.[3] Schüler and Brück[4] have quite definitely shown from Zeeman patterns that for the thallium atom the nucleus must have an angular momentum of $\frac{1}{2}h/2\pi$. Recent observations on the line λ3766 by Jackson[5] show four components. The other two lines mentioned above have already been found to have four components. These components in each case, by analogy with the Cd I fine structure, indicate that thallium must have a weak isotope with $i=0$. In order to arrange a definite term scheme for the four lowest levels in thallium more accurate measures of the fine structures must be obtained. This is being undertaken at present by Dr. Schüler.

BARIUM

The gross structure of Ba I and Ba II has long been known. Investigation of the hyperfine structure is being investigated by Dr. Ritschl and the author. The normal state of Ba I, a^1S_0 term ($6s^2$), is sharp. Next above this come the ^3D and ^1D terms ($6s5d$) which reveal fine structure. The normal state of Ba II is given by $^2S_{1/2}(6s)$ followed by $^2D(5d)$ and $^2P(6p)$. As would be expected,

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[5] Jackson, unpublished data.

the $^2S-^2P$ combinations show quite wide fine-structures, while the $^2D-^2P$ combinations appear quite narrow.

Bismuth

Many lines in the bismuth spectrum are known to be complex, some of them containing as many as 15 components. Although we have quite definite knowledge of the gross structure, it is difficult to assign very many levels to definite electron configurations. The normal state, a $^4S_{3/2}$ term ($6p^3$) $\nu=58741$, according to Goudsmit and Back,[6] is quite narrow. Undoubtedly the next two terms, $^2D_{3/2}$, $\nu=47323$ and $^2D_{5/2}$, $\nu=43304$, arise from the same electron configuration $6p^3$. With some degree of certainty it can also be said that the term $^2S_{1/2}$, $\nu=26153$ arises from $6p^27s$. Using the fine-structure measurements of bismuth lines as given by Nagaoka and Mishima,[7] Goudsmit and Back[6] have been able to give definite knowledge as to the fine-structure term scheme of some six or seven levels. Three of these sets of levels are shown in Fig. 2. At the left in Fig. 2 the gross-structure is given with corresponding electron origins, while in the middle the fine structure is given with relative term separations. The admirable work of Back and Goudsmit[8] on the Zeeman effect of the hyperfine structure components of λ4722, which in Fig. 2 is the transition from $^2S_{1/2}$ to $^2D_{3/2}$, definitely assigns to the nucleus an angular momentum of $(9/2)h/2\pi$. At the right side of Fig. 2 the space quantizations between i and J are shown for each of the three levels. For each J, since i is so large, there results $2J+1$ fine-structure components, the relative separations between which should follow the Landé interval rule. This has been shown previously by the author in connection with praseodymium hyperfine structure, a graphical representation having been given.[1] The theoretical and observed ratios for $^2D_{5/2}$, 7:6:5:4:3, and $^2D_{3/2}$, 6:5:4, as may be seen from the figure, are in excellent agreement.

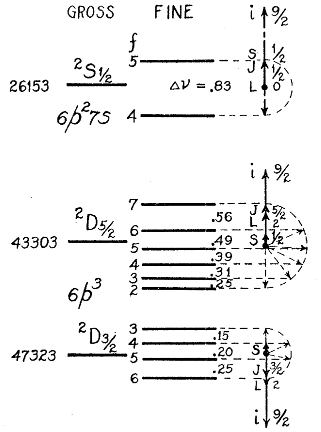

Fig. 2. Hyperfine structure of bismuth terms.

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[6] Goudsmit and Back, Zeits. f. Physik **43**, 321 (1927).

[7] Nagaoka and Mishima, Proc. Imperial Acad. Japan **2**, 249, 1926.

[8] Back and Goudsmit, Zeits. f. Physik **47**, 174 (1928).

LANTHANUM

The normal state of La I, a ^2D term ($6s^25d$) has been verified by Meggers.[9] The normal state of the ionized atom, also given by Meggers,[10] is not given by $6s5d$, as would be expected, but by $5d^2$. It has been pointed out by Meggers and Burns[11] and by the author[1] that in most cases where hyperfine structure has been observed in the heavier elements the energy levels arise from electron configurations involving one unbalanced s electron. Excellent examples are found in La I and La II. For La I the normal state $^2D(6s^25d)$ shows no fine structure, while $^4F(6s5d^2)$ does. For La II the normal state $^3F(5d^2)$ shows no fine structure, while both ^1D and $^3D(6s5d)$ do. The fine structures of the terms just mentioned are shown in Figs. 3 and 4 with graphical representations of the vector space quantizations. The levels as shown in the center of each figure are taken in part from published data[11] and part from communications with Dr. Meggers. As given by Meggers, the $^3D_3$ term has five components which means that for the nucleus of lanthanum, $i=2$. As yet the exact number of components for the $^4F_{3/2, 5/2, 7/2, 9/2}$ terms are not known. The observed fine structures are so close together on one side or the other that it is, as yet, difficult to say whether, for example, $^4F_{9/2}$ has four, five or six components. The wider components are sufficiently far apart, however, to say that the Landé interval rule is for $^4F_{9/2}$, $^4F_{3/2}$, $^3D_3$, $^3D_1$, and $^1D_2$ definitely in operation and that the relative intervals decrease in one direction for one set and in the other direction for the other. It is very likely that for lanthanum the nucleus has a value $i=(5/2)h/2\pi$ as in the case of praseodymium.[1]

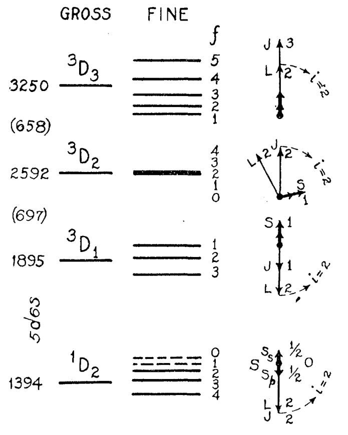

Fig. 3. Hyperfine structure in lanthanum terms, La II.

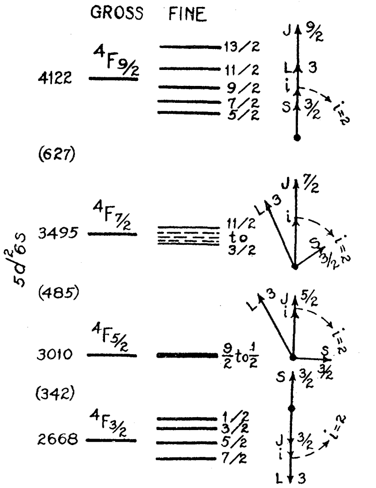

Fig. 4. Hyperfine structure in lanthanum terms, La I.

[9] Meggers, Jour. Wash. Acad. Sci. **17,** 25 (1927).
[10] Meggers, J.O.S.A. & R.S.I. **14,** 191 (1927).
[11] Meggers and Burns, J.S.O.A. & R.S.I. **14,** 449 (1927).

In Cd I and Tl I, (excluding isotopes with $i=0$) $i=\frac{1}{2}$. In Pr II[1] and probably in La I and La II, $i=5/2$, while in Bi I, $i=9/2$. These values, different from each other by $4h/2\pi$ may be significant in the theory of nuclear structure.

In Fig. 2 it may be seen that for the $^2D_{3/2}$ term the fine structures are inverted, while for $^2D_{5/2}$ they are not. In La II a middle step in this turning over process is seen with the $^3D_1$ term, which appears quite sharp. In La I, an additional step is seen. In Pr II, where quintet multiplets occur, there are fine-structure groups of many different widths, some degrading toward the violet while others degrade toward the red. There is evidence in praseodymium for five steps in the above process of term inversion.

THEORETICAL INTERPRETATION

It has been stated before that the widest fine structures appear in the heavier elements of the periodic table. In a simple case like caesium, where one valence electron is responsible for the spectroscopic terms, and the nucleus has an angular momentum, the coupling between the electron spin and the nucleus is almost entirely screened off by a cloud of 54 electrons With caesium in its normal state the one and only valence electron is a *6s* electron. This electron is part of the time found on the outside of all of the other 54 electrons and part of the time near the nucleus. At the time of deepest penetration there must occur the strongest coupling between electron spin, S, and nuclear spin, i, and hence a doubling of the resultant $^2S_{1/2}$ term, The one term due to the electron spin $S=+\frac{1}{2}$, the other term to $S=-\frac{1}{2}$. If the nuclear spin is positive (i.e. due to a spinning proton or α-particle) then for $S=+\frac{1}{2}$ and $-\frac{1}{2}$ the fine structure terms should be inverted, as is quite definitely the case in cadmium, Fig. 1. On the other hand, if the nuclear spin is negative (i.e. due to electrons) then the terms should not be inverted.[12] For a *6p* electron in caesium the penetration into the cloud of 54 electrons is less than that for a *6s* electron and hence the coupling between S and i and the resultant doubling of both of the $2P$ terms is not as great.

In cases where more than one valence electron is responsible for the resultant spectroscopic terms, as for example lanthanum, bismuth and praseodymium, the explanation is certainly more complex. An excellent example is found in the $^4F(5d^26s)$ terms of La I, Fig. 4. That strictly an LS and not a jj coupling is here in operation is seen by the term intervals 627, 485, and 342 in almost perfect agreement with the theoretical ratios 9:7:5. The angular momentum vectors, J, L and S, when the *6s* electron is outside the other electrons, are screened off from the nuclear momenta i and there can only be a very weak coupling between i and J. When the *6s* electron penetrates the cloud of electrons then the coupling between nucleus and *6s* electron is strong and at the same time both are screened from the two *5d* electrons. Thus it is seen that the *6s* electron acts as a carrier which

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[12] When the valence electron spin is in the same direction as the proton spin, then the two angular momenta are in the same direction, while the two magnetic moments are in the opposite direction.

strengthens the coupling between nuclear spin, i, and electron resultant, J.[13]

For the ${}^4F_{9/2}(13/2)$ term, in Fig. 4, the vectors J, S and i are all in the same direction. The i vector, space quantized with electron resultant J, gives five fine-structure levels, separations between which follow the Landé interval rule. For the ${}^4F_{5/2}(11/2)$ the vectors J and i are in the same direction while S makes an angle of about 90° with them. As the i vector now may take discreet quantized positions with J, the cosine of either ji or Si is small or else one is positive while the other is negative. Hence the levels appear almost as one. For the ${}^4F_{3/2}(7/2)$ term, J and i are in the same direction, while S and i are in opposite directions, (cos $Ji=+1$ and cos $Si=-1$). Here the space quantization of i with J gives inverted terms.

For multiplet terms which show LS couplings and for which there is but one deeply penetrating valence electron involved, (*an s electron,*[14]) (*a*) *the total fine structure separations for each term should be proportional to cos Si when cos* $Ji=1$ *(Fig. 4), provided* $J>i$, *and at the same time* (*b*) *the relative separations of fine structure for each term should be given by the cos Ji.* (*c*) *When the cos Si is positive and i is positive*[15] *the fine-structure terms should be inverted while for negative i they should be normal; for cos Si negative and positive i the terms should be normal while for negative i they should be inverted.* When more than one valence electron is quite deeply penetrating, the vector sum of the separate electron couplings with i determines the total fine-structure width. In bismuth, Fig. 2, the resultant couplings of three similar $6p$ electrons is sufficient to produce the quite wide fine structures observed.

Note added October 30, 1929. The fine-structure measurements in singly ionized thallium, Tl II, made by McLennan, McLay and Crawford[16] are shown by the author in another paper[17] to be in excellent agreement with the above theory of normal and inverted fine structure, and the part played by a single s electron in revealing fine structure.

The weighing of fine structure terms in Cd I, as is done above and graphically shown in Fig. 1, is also suggested by Goudsmit in a short article,[18] as a confirmation of the isotope effect in cadmium which was first pointed out by Schüler and Brück[4] from intensity relations.

A preliminary investigation of the fine-structure lines in manganese (to be published later) shows that the fine-structure terms follow very nicely the Landé interval rule and are normal or inverted where predicted.

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[13] The number of resultant fine-structure terms must be given by i and J and not by i and s alone.

[14] For a penetrating p electron (for example $6p$) the coupling must depend on both s and l of the electron. This means that a p electron may, in some cases, produce as large fine-structure separations as an s electron ($l=0$) which is more tightly bound.

[15] If i is due to a spinning proton or α-particle it is positive, if due to electrons it is negative.

[16] McLennan, McLay and Crawford, Proc. Roy. Soc. **A125**, 570 (1929).

[17] White, Proc. Nat. Acad. Sci., in publishers hands.

[18] Goudsmit, Naturwiss. **41**, 805 (1929).