ANNIHILATION OF POSITRONS WITH BOUND ELECTRONS OF ATOMIC CORES IN METALS OF THE SILVER AND GOLD SERIES

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(Received May 14, 1970)

This work deals with the problem of the annihilation of positrons with electrons bound in atomic cores in metals with a simple core electronic configuration. Angular correlations of annihilation quanta were measured for metals of the silver series, Ag, Cd, Ir, Sn and Sb, and metals of the gold series, Au, Tl, Pb and Bi. On the basis of the simple electronic model of a metal the obtained experimental distributions of the z-th momentum component of the annihilating electrons was divided for each metal into a part corresponding to annihilation with valence (free) electrons and a part corresponding to annihilation with electrons bound in the atomic core. It was found, by analyzing the obtained results, that the percentage participation of electrons bound in a core with stable electronic configuration in the annihilation decreases with increasing number of valence electrons. This is true of both the silver and the gold series. An increase in the number of atomic core electrons (and a change in its electronic configuration) with an unchanged number of valence electrons, leads to an increase in the percentage participation of bound electrons in annihilation. The observed dependences are put into mathematical form. They imply that the mutual participation of the two groups of electrons in the annihilation is decided by the number of valence electrons, the number of bound electrons and the ionic radius of the atomic core. On the other hand, it is relatively weakly affected by the electronic configuration of the atomic core. The results obtained for Sb differ strongly from those for the other metals if the number of valence electrons per atom for this element is assumed to be five. Satisfactory conformity is received when this quantity is assumed to be equal three.

1. Introduction

Already the first measurements of angular correlation of annihilation radiation for metals showed that not only free (valence) electrons, but also electrons bound in atomic cores partake in annihilation. This conclusion was reached by Lang *et al.* [1] when interpreting the angular correlation curves for the so-called B and C group metals.

Angular correlation curves obtained with the use of conventional measurement geometry [2] are distributions of the z-th component of the momentum of electron-positron

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annihilating pairs. By introducing some minute approximations stemming from the well-satisfied assumptions regarding positron annihilation in metals it is possible to interpret these curves as distributions of the z-th momentum components of the annihilating electrons. The identity between the angular and momentum distributions follows from the linear dependence between the measured small angle θ, which is a measure of the angular deviation from colinearity of the flight paths of the two annihilation quanta, and the z-th component of the annihilating electron's momentum p_z; it is given by the formula

$$\theta \simeq \frac{p_z}{mc} \tag{1}$$

where m is the mass of the electron.

In the approximation of an ideal gas of free electrons (a spherical Fermi surface with constant state density) the distributions of the z-th momentum component $N(p_z)$ are described by the formula

$$N|p_z|dp_z = \text{const} \left| 1 - \frac{p_z}{p_F^2} \right| dp_z \tag{2}$$

where p_F is the maximum momentum of the annihilating electrons, *i.e.* the so-called Fermi momentum.

Figure 1 depicts a typical angular correlation curve for a metal. The central part of the distribution is almost always shaped similarly to the reversed parabola described by formula (1); this is particularly apparent in the case of non-transition metals. Deviation from the parabolic curve is primarily due to a nonspherical shape of the Fermi surface. The remaining part of the distribution, the "tails", is brought into existence by a number of factors. Here are some of them:

a. deviation from a spherical Fermi surface and constant state density in the momentum space,

b. temperature blurring of the momenta of the annihilating particles, primarily positrons,

c. annihilation with the bound electrons in the atomic cores, and

d. to a certain extent, the limited resolving power of the measuring equipment

A theoretical determination of the participation of each of these factors, is, in principle, a solvable problem, but actual attempts of finding a numerical characteristic have thus far encountered considerable difficulties. These mainly arise from the choice of appropriate wave functions for the annihilating positron and annihilating bound electrons.

It is now believed that the decisive factor in the formation of the "tail" parts of the correlation curves is the annihilation of positrons with the bound electrons of atomic cores. The effect of this factor has attracted the most attention. For example, already in 1956 Ferrel [3] computed the expected angular distributions for bound s, p and d electrons on the basis of simple wave functions. Comparison with experimental data for some metals led to the conclusion that these distributions are indeed like the "tail" parts of the correlation curves. Others who worked on this problem were, among others, Gustafson *et al.* [4],

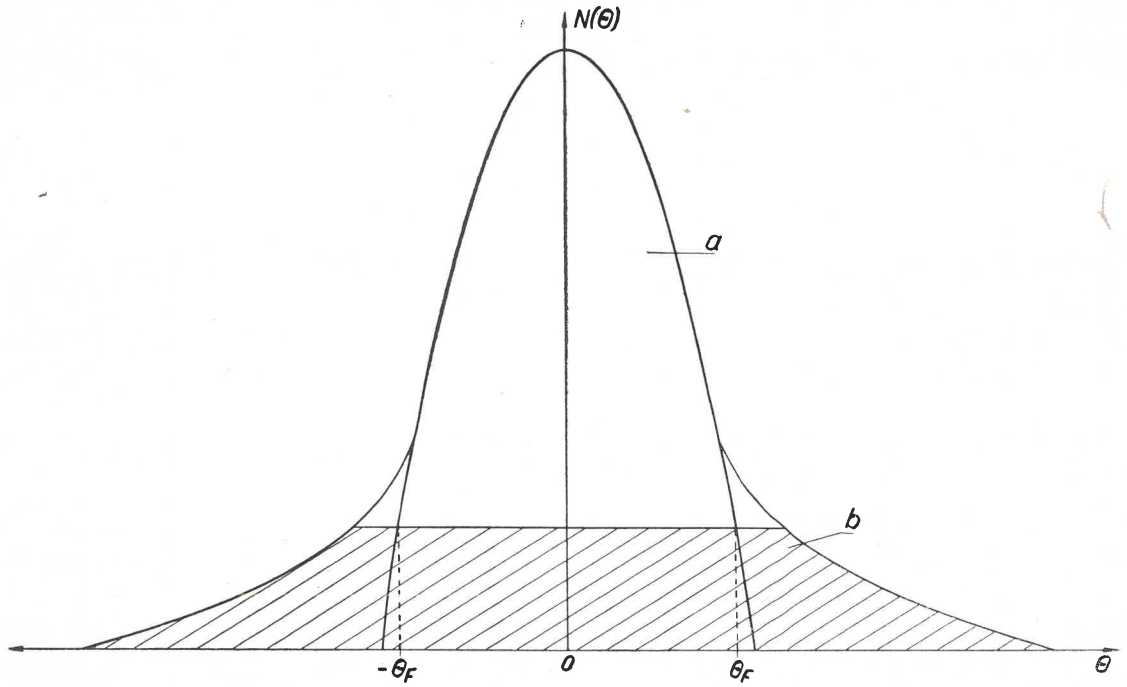

Fig. 1. Typical angular correlation curve for a metal. a — parabolic central part, b — "tail" part. $\theta_F = \frac{p_F}{mc}$, where p_F is Fermi momentum, and m is electron mass

Gustafson and Mackintosh [5], Carbotte [6], Rackmore and Stewart [7], West *et al.* [10] and Dekhtyar [11].

Dividing the experimentally procured angular distributions into parts corresponding to annihilation with electrons in various states is a rather crucial operation in the method of angular correlation of annihilation quanta. Research on the electronic structure of metals, the shape of the Fermi surface, the distribution of the density of states, *etc.*, require skillful separation of the part of the distribution corresponding to annihilation with bound electrons in atomic cores. A properly singled out part of the distribution corresponding to annihilation with bound electrons may, in turn, provide abundant information about the core electrons, which lie at the root of many properties of a metal, *e.g.*, magnetic.

2. Objective of this study

The intention of this study was an attempt to find an answer to the question: How does the participation of bound electrons change in the two-photon annihilation with positrons when going from one metal to another within a single series (*i.e.* the change with increasing atomic number)? In other words, how does this participation change when the electronic configuration of the atomic core is maintained while the number of peripheral electrons increases? Considered are metals of two series, one beginning with silver and the other with gold. The choice of two series lets us compare metals within one group from an interesting aspect, namely, with a maintained number of peripheral electrons and varying electronic structure of the atomic core.

The results of research are based on our own experimental data, except for mercury, and concern the following metals: Ag, Cd, In, Sn and Sb with $4s^24p^64d^{10}$ configuration of the core's N-shell, and Au, Hg, Tl, Pb and Bi with a $5s^25p^65d^{10}$ configuration of the core's O-shell.

The participation of bound electrons in annihilation was determined for each of the above-mentioned metals on the basis of a simplified model, but one which was consequently applied to all of the elements. The results presented here should thus be regarded as approximate ones and it is not assumed that they give a full answer to the question put forth at the beginning of this section.

3. Apparatus and results of measurements

The angular distributions of radiation from the two-photon annihilation of the electron-positron pair were measured by means of a scintillation spectrometer with employment of the typical "sample-detectors" geometry. An accurate description of the apparatus and other details may be found in the papers [8] and [9]. The samples were in the form of long bands about 8 mm wide and from 0.4 mm to 0.8 mm thick. The resolving power of the setup was somewhat better than in the case set forth in Ref. [9].

In Figs 2 and 3 there are the curves of angular correlation $N(\theta)$ for metals of the silver and gold series, respectively, except for the curve for antimony, which is shown in Fig. 4. The curves have been normalized to a mutual height at the point $\theta = 0$.

In subsequent considerations this height is conventionally accepted to be equal to unity, $N(0) = 1$. The half-width of the horizontal function of resolving power is about 0.8×10^{-3} radian. The maximum statistical error of the individual measurements is shown for points near $\theta = 0$; for the other points it decreases proportionally to the square root of the relative number of coincidendes.

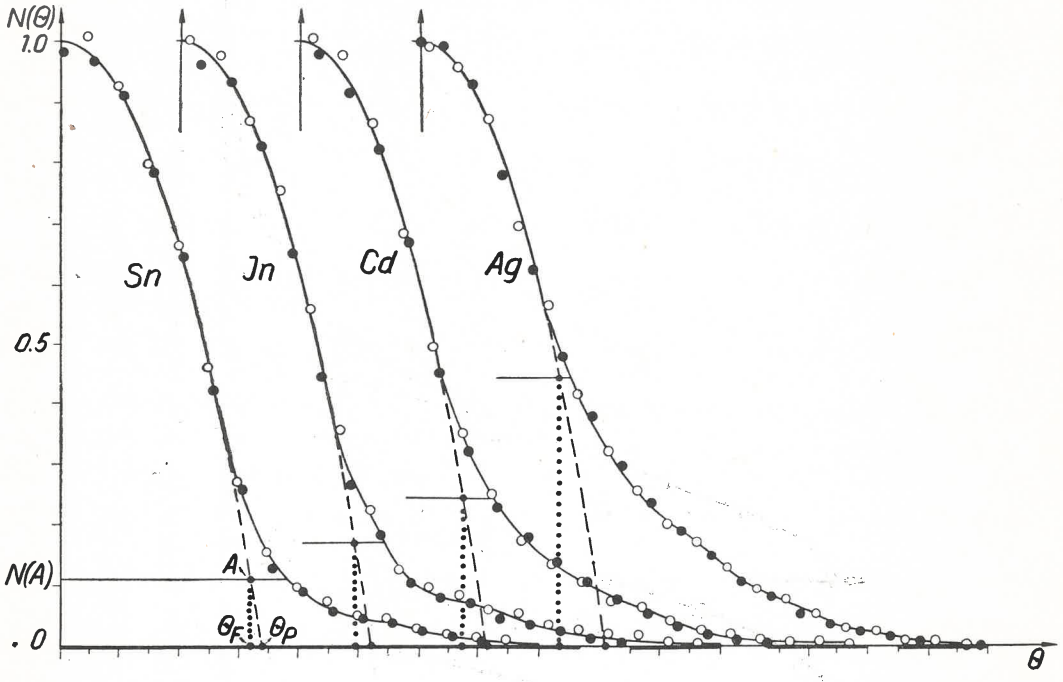

Fig. 2. Angular correlation curve $N = N(\theta)$ for metals of silver series. On axis of ordinates relative units with $N(0) = 1$; on axis of abscissae the angle θ in 10^{-3} radian. θ_p — angle of intersection of parabola with axis of abscissae; A — point of intersection of parabola with straight line $\theta = \theta_F$ (dotted line)

4. Analysis of results

The angular distribution of each of the examined metals was divided arbitrarily into two parts (Fig. 5) in the following manner. The parabolic central part was accepted as corresponding to annihilation with valence electrons, of which there are as many as the number of the group to which the given element belongs, except for antimony, for which a different number was assumed (details concerning antimony can be found in the last section of this paper).

The remaining part of the distribution, spreading out in the direction of large angles (momenta), are taken to correspond to annihilation with bound electrons of atomic cores. This division was accomplished by cutting through with a straight line parallel to the axis of abscissae and passing through point A. Point A lies on the parabola best fitted to the experimental points of the central part and at the same time has an angular coordinate $\theta_F = p_F/mc$, where p_F is the Fermi momentum calculated on the basis of the

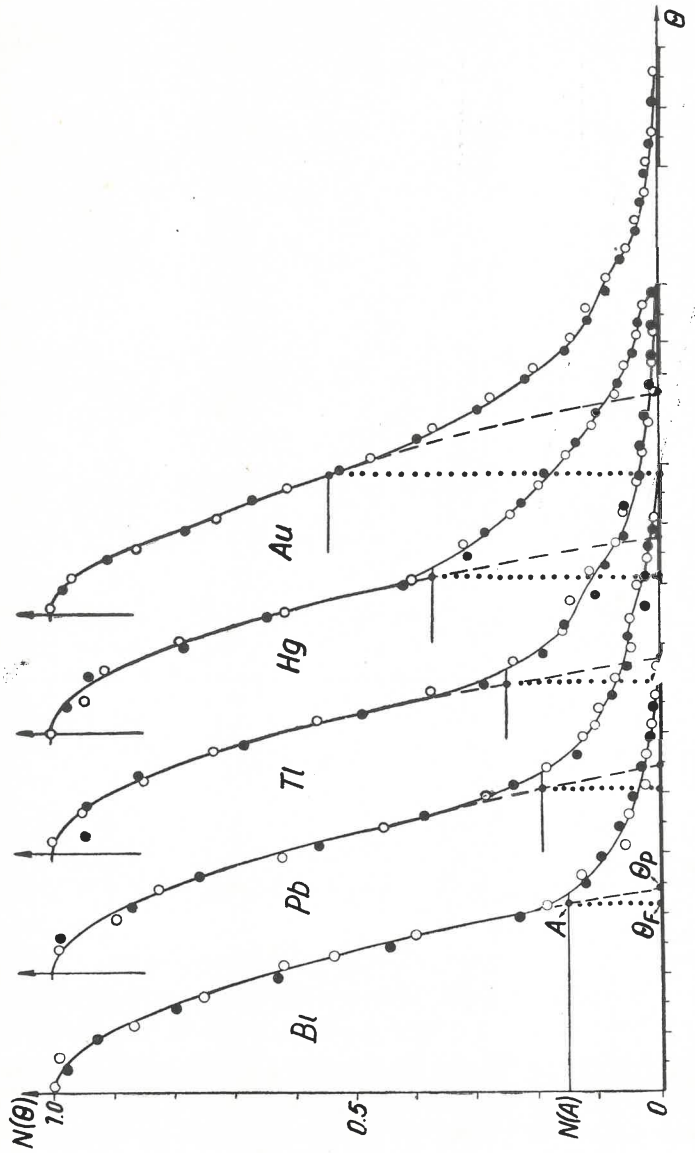

Fig. 3. Angular correlation curve $N = N(\theta)$ for metals of gold series. For explanation of notation see Fig. 2

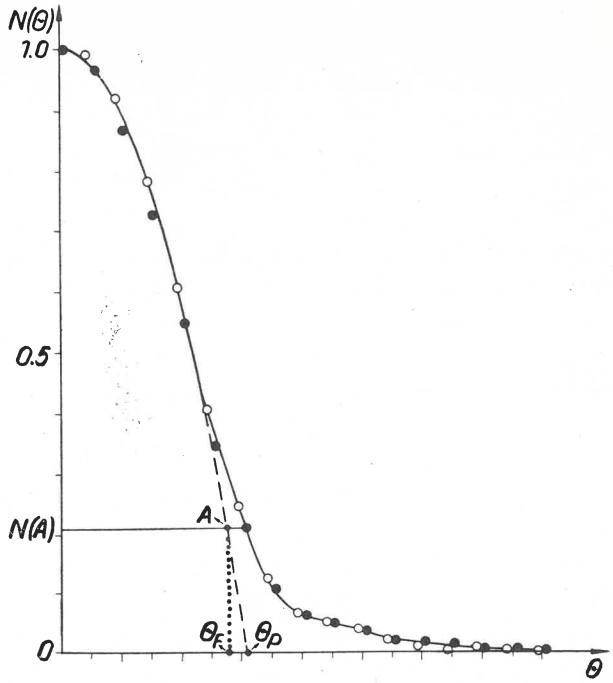

Fig. 4. Angular correlation curve $N = N(\theta)$ for antimony. For explanation of notation see Fig. 2

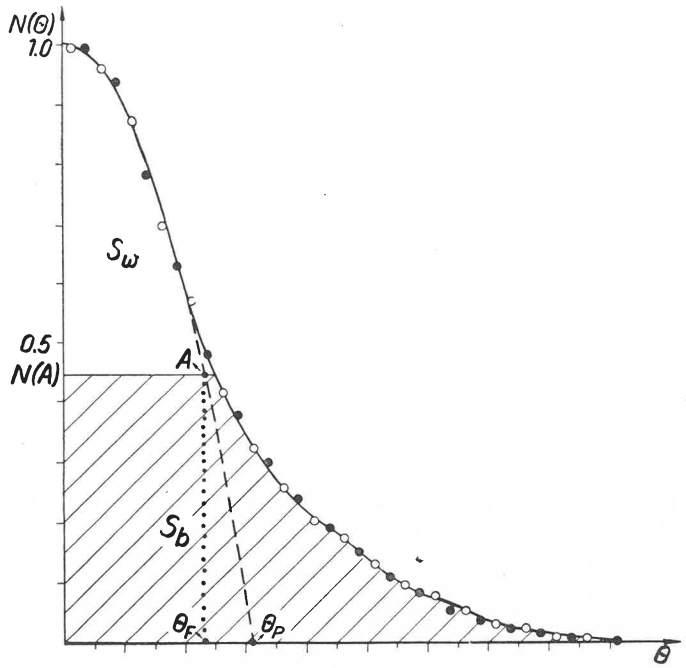

Fig. 5. Example of division of angular correlation curve $N = N(\theta$ into two parts. $N = N(A)$ (continuous line) separates region S_w (no hatching) from region S_b (hatched)

model of an ideal gas of free electrons. In this way the obtained central part corresponds to the idealized parabolic angular distribution of free electrons. The slight deviation of the experimental data from the parabolic curve at the parabola's base (near point A) is so small that it does not really shake the assumed model; indeed, it may be acknowledged to be the blur due to the finite resolving power of the apparatus.

Some authors, such as those of Refs [4] and [10], use a different method of dividing the angular distribution. They determine the part corresponding to annihilation with free electrons from the theoretically calculated Fermi angle, like is done in this work. However, they limit the distribution corresponding to annihilation with electrons of atomic cores by a Gaussian curve best fitted to the "tail" part of the angular correlation curve. This division also accepted *a priori*, generally does not lead to conformable results and is not unambiguous. For example, for solidified mercury 75 per cent of the annihilation events were with electrons in study [4], whereas in study [10] only 69 per cent. Results obtained by our method state a 61 per cent participation of this group of electrons.

Attempts of theoretically calculating the angular correlations for annihilation with the electrons of atomic cores or for annihilation with free and bound electrons together, as for example in Refs [10] and [12], have unfortunately been rather unsuccessful. The theoretical curves distinctly deviate from the distributions received experimentally.

The essential difference between the division accepted in this work and those used by others is primarily brought down to the fact that in the range of angles $(0, \theta_F)$ a constant value is assumed here for the distribution corresponding, to annihilation with core electrons. Having analyzed the various methods of dividing experimental distributions, the authors of this paper believe that the method they used does not lead to any greater systematic errors than those encountered in the other methods.

This work is not intended to give a comparison of experimental and theoretical data, but only tends to grasp some mutual regularities on the basis of experimental material achieved with a greater number of samples. The use of one or the other means of dividing the experimental distributions should not bear any substantial effect on the features of the sought regularities.

Tables I and II contain the following numerical values for the silver and gold series, respectively: θ_F — the calculated Fermi angle corresponding to the Fermi momentum in accordance with Eq. (1), θ_p — the angle of intersection of the central parabola with the axis of abscissae, and $N(A)$ — the height of the scission line.

Respectively for the two series, Tables III and IV hold the numerical values of the area S_w enclosed by the central parabola, this being a measure of the participation of valence electrons in annihilation, and values of the area S_b of the remaining part of the angular distribution, being a similar measure for the bound electrons (Fig. 5). The last columns give the ratio of the values of these two areas W, which provides information on the mutual participation of the two groups of electrons in annihilation.

Analysis of the data presented in Tables III and IV brings us to some simple, and indeed expected, conclusion. The share of valence electrons participating in annihilation increases with an increase of their number, with the number of bound electrons fixed. Likewise,

TABLE I

Numerical values of θ_F, θ_p, and $N(A)$ for silver series

Metal	θ_F mrad	θ_p mrad	$N(A)$
Ag	4.645	6.288	0.444
Cd	5.414	6.231	0.245
In	5.819	6.391	0.171
Sn	6.330	6.709	0.110
Sb[1]	5.519	6.193	0.206

[1] For Sb the number of valence electrons assumed is $n_w = 3$; details in last section

TABLE II

Numerical values of θ_F, θ_p and $N(A)$ for gold series

Metal	θ_F mrad	θ_p mrad	$N(A)$
Au	4.658	7.372	0.542
Hg	5.160	6.544	0.378
Tl	5.648	6.523	0.250
Pb	6.088	6.968	0.192
Bi	6.229	6.774	0.148

TABLE III

Numerical values of areas S_w and S_b and their ratio W for silver series

Metal	S_w^1 mrad	S_b^1 mrad	$W = \frac{S_w}{S_b}$
Ag	1.748	3.480	0.502
Cd	2.816	2.324	1.212
In	3.293	1.663	1.980
Sn	3.853	1.131	3.407
Sb	2.984	1.664	1.793

TABLE IV

Numercial values of areas S_w and S_b and their ratio W for gold series

Metal	S_w^1 mrad	S_b^1 mrad	$W = \frac{S_w}{S_b}$
Au	1.319	4.227	0.312
Hg	2.144	3.388	0.633
Tl	2.860	2.314	1.236
Pb	3.211	1.820	1.764
Bi	3.474	1.271	2.733

[1] Areas are measured in milliradians; the axis of ordinates carries the dimensionless relative values of number of coincidences; normalized by taking $N/0/=1$.

with a fixed number of valence electrons the participation of bound electrons in annihilation also grows together with an increase in the number of the latter.

Such behaviour of electrons of both groups in a metal with respect to annihilation only partially stems from their competition in numbers. As may be easily found, an assumption of a simple numerical competition is insufficient to justify the obtained numerical values. Each of the groups of electrons behaves differently owing to their specific features. The positive charge of the atomic cores will diminish the participation of bound electrons in annihilation as compared with the participation resulting from their numerical force.

A deeper analysis of the obtained results leads to the conclusion that a positron which has already penetrated into the core and moves inside it interacts with the core much more weakly because of its positive charge than would stem from simple Coulomb interaction. It may be assumed in first approximation that the positron surrounded by a certain number of electrons screening it forms with them a neutral system and moves into the interior of the core without any greater difficulties. These conclusions may be justified by the final numerical interpretation of the obtained results. This interpretation is satisfactory when all of the core electrons are treated equally, independently of their status in the core, and it is moreover assumed that their participation in annihilation depends only on the conditions pervading in the core peripheries, *i. e.* in the region to which a positron penetrates into the core.

All this enables us to postulate the following dependences. Firstly, the probability of annihilation with valence electrons w_w is directly proportional to their density in the atom, *i. e.*

$$w_w \sim \frac{n_w}{r_a^3} \tag{3}$$

where n_w is the number of valence electrons per atom, and r_a denotes the linear dimensions of the atom. Secondly, the probability of annihilation with bound electrons w_b is also directly proportional to their density in the atom and, in addition, is inversely proportional to the Coulomb potential at the core surface:

$$w_b \sim \frac{n_b}{r_a^3} \tag{4}$$

and

$$w_b \sim \frac{1}{V_c} \tag{5}$$

where n_b is the total number of bound electrons per atom, and V_c is the potential at the core surface. Putting $V_c = \frac{Q_{ef}}{r_c}$, where r_c is the radius of the core and Q_{ef} is the effective charge of the core, we get for the ratio of the participation of the two groups of electrons in annihilation W the following expression:

$$W = \frac{K n_w}{n_b \cdot r_c} \tag{6}$$

K is a proportionality constant which, as will be seen, depends weakly on Q_{ef}, and $\frac{K}{n_b}$ plays the role of the same type of constant within one series.

The numerical values of coefficient $\frac{K}{n_b} = W\frac{r_c}{n_w}$ are given for the two series respectively in Tables V and VI.

The numerical values of the coefficients K/n_b for the silver series, without *Sb*, fluctuate about the arithmetical mean of 0.590 Å (according to Pauling) *viz.*,

$$\left(\frac{K}{n_b}\right)_{Ag} = (0.590 \pm 0.021) \times 10^{-8} \text{ cm} \tag{7}$$

Analogously, we get for the gold series the mean value of 0.388 Å and mean deviation of 0.014 Å, or

$$\left(\frac{K}{n_b}\right)_{Au} = (0.388 \pm 0.014) \times 10^{-8} \text{ cm} \tag{8}$$

The assumptions (6) of the linear dependence between the quantity W (the ratio of the number of annihilation events with valence electrons to the number of such events with bound electrons in the atomic core) and the expression n_w/r_c, made for the examined

TABLE V

Metal	n_w	according to Pauling			according to Goldschmidt		
		r_c	$\frac{r_c}{n_w}$	$\frac{K}{n_b}$	r_c	$\frac{r_c}{n_w}$	$\frac{K}{n_b}$
		10^{-8} cm			10^{-8} cm		
Ag	1	1.26	1.260	0.632	1.13	0.130	0.567
Cd	2	0.97	0.485	0.588	1.03	0.515	0.624
In	3	0.81	0.270	0.534	0.92	0.307	0.607
Sn	4	0.71	0.178	0.605	0.74	0.185	0.630
Sb	5	0.90	0.300	0.538	0.90	0.300	0.538

TABLE VI

Metal	n_w	according to Pauling			according to Goldschmidt		
		r_c	$\frac{r_c}{n_w}$	$\frac{K}{n_b}$	r_c	$\frac{r_c}{n_w}$	$\frac{K}{n_b}$
		10^{-8} cm			10^{-8} cm		
Au	1	1.37	1.370	0.427	—	—	—
Hg	2	1.10	0.550	0.348	1.12	0.560	0.354
Tl	3	0.95	0.317	0.391	1.05	0.350	0.433
Pb	4	0.84	0.210	0.371	0.84	0.210	0.371
Bi	5	0.74	0.184	0.405	—	—	—

metals of a single series, is satisfied in the light of the performed research more than satisfactorily.

The numerical values of the proportionality coefficient K between the measured quantity W and the postulated expression $n_w/n_b r_c$ (Eq. (6)), which is common for metals of both series, can be obtained immediately from Tables V and VI. This is done by putting for the metals of the silver series (except Sb) the value $n_b = 46$ and for metals of the gold series $n_b = 78$; these values are contained in Table VII.

TABLE VII

Metal	according to Pauling	according to Goldschmidt
	10^{-8} cm	10^{-8} cm
Ag	29.072	26.082
Cd	27.048	28.704
In	24.564	27.922
Sn	27.830	28.980
Sb	25.824	25.824
Au	33.306	—
Hg	27.144	27.612
Tl	30.448	33.774
Pb	28.933	28.933
Bi	31.590	—

The arithmetic mean value of the coefficient K according to Pauling (without Sb) is 28.882 Å, with a mean square deviation from the mean of 0.907 Å, that is,

$$K = (28.882 \pm 0.907) \times 10^{-8} \text{ cm} \tag{9}$$

Deviations from the mean value for the individual metals are not very large and fit within the limits of experimental error, except perhaps for Au and In.

The mean coefficients K calculated separately for the silver series (without Sb) and gold series are as follows:

$$K_{Ag} = (27.128 \pm 0.957) \times 10^{-8} \text{ cm} \tag{10}$$

and

$$K_{Au} = (30.284 \pm 1.062) \times 10^{-8} \text{ cm} \tag{11}$$

The differences between the mean coefficients K for the two series imply that the phenomenon of annihilation with electrons of the atomic core is affected not only by the global number of bound electrons but also to some extent by their configuration. The study described here was not intended to deal with the effect of core configuration. It may just be noticed that identically filled outer shells of the core of the silver and gold series lead to coefficients K very close to each other.

Coefficients K/n_b and K obtained from measurements for Sb with the assumptions that $n_w = 5$, $n_b = 46$ and Sb^{5+} ion radius $r_c = 0.62$ Å are very different from the mean values obtained for the other metals. A much better agreement may be reached by putting

for Sb the following values: $n_\omega = 3$, $n_b = 48$ and Sb^{3+} ion radius $r_c = 0.90$ Å. Below are given the characteristic values for Sb obtained on the basis of the data just mentioned and experimental data (they may be found in the respective tables):

$S_w = 2.984$ milliradians, $S_b = 1.664$ milliradians adn $W = 1.793$.

These values yield

$$\frac{K}{n_b} = 0.538 \text{ Å and } K = 25.824 \text{ Å} \tag{12}$$

The performance of similar research for other elements may perhaps enable us to generalize the accepted assumptions for metals of an identical core to be made for the remaining metals, with the specific electronic structure of the atomic core now being accounted for.

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