Physics. — "*On the cristalstructure of white tin*". By A. E. VAN ARKEL.
(Communicated by Prof. P. EHRENFEST).

Continuing the research of Dr. BURGER [1]) on the properties of single-crystal-wires of tin, Röntgenograms were taken to determine the orientation of the crystals in relation with the axis of the filament. The results of this determination were not in agreement with the conclusions arrived at by BIJL and KOLKMEIJER [2]).

These authors found that the elementary cell of tetragonal tin contains three atoms, one of them forming the corners of the tetragonal prism, whilst the other two are placed in the centers of the four equivalent sides.

As the structure-factor [3]), by which the intensities are to be multiplied in this case is 9, when all indices of the reflecting spaces are either even or odd, and unity in all other cases, all faces will reflect in first order. Reflection-lines of all possible crystallographic faces therefore must be present, in any case those with small indices, as these for several reasons have a greater intensity.

Now on BIJL's films the reflections from the (100) and (110) faces are absent, whereas the reflection of (101) as BIJL indicates, is present. The reflection (310), also fails, whereas the reflection (410) which theoretically should be equally strong, is present.

Therefore there is some doubt whether the structure, as proposed by BIJL, is the true one.

In table I the values of $sin^2 \frac{\Theta}{2}$ are put together: (1°) as mentioned by BIJL, (2°) those given by JOHNSON [4]) and (3°) the mean of six films taken in this laboratory, partly by Dr. BURGER; also (4°) the relative intensities, as they should be according to the structure, proposed by BIJL and (5°) the estimation by the same author. The

[1]) H. C. BURGER. Physica **2**, 56 (1922).

[2]) A. J. BIJL and N. H. KOLKMEIJER. Proc. Roy. Soc. A'dam. **21**, 501 (1919).
A. J. BIJL. Diss. Utrecht 1918.

[3]) See a.o. DEBIJE and SCHERRER. Physik. Zeitschr. **18**, 293 (1917).

[4]) BIJL indicates only those lines, that are *not* in agreement with his own measurements.

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mean error of position in our measurements is about 0.3°/₀, except for the first lines. The position of the lines agrees fairly well with the other values, especially with those of JOHNSON.

TABLE I.

Intensity		$\sin^2\frac{\Theta}{2} \times 10^3$	$\sin^2\frac{\Theta}{2} \times 10^3$	$\sin^2\frac{\Theta}{2} \times 10^3$	$\sin^2\frac{\Theta}{2} \times 10^3$
(calc.)	(estim.)	(measured)	(BIJL)	(JOHNSEN)	(calc. by BIJL)
23	—	—	—		17.4
11	—	—	--		35
50	m	74	79	72	69
1.9	---	--	—		104
3.3	vw	—	124		121
78	vs	144	150	143	138
2.6	—	--	—		155
8.5	—	—	—		190
3.3	w	217	225		225
3.3	—	—	—		243
65	s	266	276		278
2.7	w	2-5	294		295
4.8	---	—	- -		328
20.8	vw	- -	343		347
2.2	m	356	365	348	382
4.0	—	—	—		399
4.2	vs	411	417	404	416
2.8	—	—	—		434
6.9	vw	—	466		451
14.6	—	—			486
4.8	m	496	508	491	502
4.4	—	—	..		538
47	s	560	556		555

BIJL and KOLKMEYER used the K-radiation of copper. Therefore on their films there are two series of lines, the ratio of the values of $sin^2\frac{\Theta}{2}$ of them for the same crystal face being 1 : 0.808. Half

of the lines observed by BIJL are ascribed to $K\alpha$ radiation, whereas the other part is ascribed to $K\beta$ radiation. In this laboratory the Röntgenradiation is usually filtered by a small nickel window, about $15\,\mu$ thick. In this way the $K\beta$ radiation is completely absorbed, as follows from about a hundred Röntgen-patterns of other materials. With tin we found accurately the same lines as BIJL did, three excepted, the squares of sines being 0.124, 0.343 and 0.466 respectively [1]).

It is very probable that only these three lines are to be considered as β lines, belonging to the very strong α lines 150, 417 and 556. In this case they should be 121, 338 and 450 respectively. JOHNSON also observed line 57. The latter is to be considered as the β line, belonging to the very strong line 72 (JOHNSON). From the small intensity of the β radiation it can be explained why the other β lines are missing. When all lines are to be considered as α reflections, then the agreement concerning the place of the lines, is certainly not sufficient for line 365. The nearest line is 382. The difference between the observed and calculated values of $sin^2\dfrac{\Theta}{2}$ is 4 °/₀, which cannot be ascribed to errors of measurement.

As to the intensities, however, the disagreement is still more pronounced. According to the table of the calculated intensities, we would expect some exceedingly dark lines together with many weak ones; yet the intensities of the lines are not very unequal. Only at great angles of reflection some very strong lines appear. On closer examination of the table, we see, that the first two lines are missing, though they should have intensities, resp. 7 and 3 times stronger than the line 225 which is present.

Line 225 shows a second deviation. For the lines, which should lay on both sides, a double and equal intensity respectively is found theoretically. The question arises why are both lines missing? The same applies to the line 294 with the intensity 2.7. Why does line 398 fail? Line 343 should be very strong (intensity 20.8). BIJL estimates the intensity as very weak; on our foto's the line fails entirely. For the next line which is present, and even is estimated of medium intensity, the calculated intensity is about 10 times smaller than that of 338. Line 417, which is estimated as very strong, should have the same intensity as line 398 which is missing.

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[1]) In the following we will call a reflection of which $sin^2\dfrac{\Theta}{2} = 0.124$, reflection (line) 124.

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We now compare the lines 343 and 417.

343, intensity calculated 20,8, estimated very weak

417,   ,,   ,,   4,2,   ,,   ,,   strong.

According to the intensities we should expect the very strong lines 451 and 486 to occur on the foto's. It is very important that only one line is observed, i.e. 466, described by BIJL as to be very weak. This criticism could be continued, in my opinion ,however, the intensity of the lines sufficiently proves, that the structure, as given by BIJL, cannot be right. Against this structure still more objections can be made, a.o. that the proportion of the axes, as given by BIJL, is not simply related to that found by MILLER [1]).

When we summarise the objections to the interpretation of BIJL, we have:

1. for the absence of a number of lines no explanation is given.

2. the observed place of some lines is not in accordance with the calculated one.

3. the intensities do not satisfy.

4. the structure does not explain but very unsatisfactorily the proportions of the axes measured by MILLER.

By the following reasoning we come to a structure satisfying in all respects. As tin cristallizes in the tetragonal system the squares of sines are given by:

$$sin^2 \frac{\Theta}{2} = A (h_1^2 + h_2^2) + B h_3^2.$$

Now the measured values satisfy this relation when we take:

$$A = 0.00875$$
$$B = 0.0588.$$

Hence the number of atoms per structure element is 8. When we take:

specific weight $= 7,285$

atomic weight $= 118,7$

$$N = 0,6062 \times 10^{24},$$

wave-length $Cu_{K\alpha} = 1,539$ Å (the average of K_{α_1} and K_{α_2}) we find by calculation:

$$A = 0,008745$$
$$B = 0,05878$$

when the value of the proportion of the axes given by MILLER (6,722) is accepted as being right.

The indices of the faces, which give lines of interference, as appears

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from the table, are all either even, having a sum divisible by **4**, or all odd. In the case of regular crystals this condition is characteristic for diamond structure. Hence white tin has a tetragonal diamond-structure. No other lines than the calculated ones are present; on the other hand, all calculated lines are observed. Partly, however, they are doublets, laying so closely together that they cannot be observed separately. These double-lines can partly be recognized, because they are wider than the other ones; for those of them where the distance is greatest, distinct indications of double-structure can be seen on some of our films, a.o. for the lines 74 and 144. The observed intensities too are in accordance with the structure proposed here. The strongest lines on the film are marked with S in table II. Indeed, for these lines the calculated intensity is greatest, partly because the lines are close doublets.

The reflections of the faces 004 and 553 (= 713) are double. This is, because at big angles of reflection the $K_{\alpha\alpha_1}$ doublet is separated into its components. When we calculate from both the doublets the proportion of the wavelengths, K_{α_1} and K_{α_2}, we find resp.:

$$1.0027 \text{ and } 1.0025$$

whereas from the values given by SOMMERFELD [1]) follows:

$$1.00254.$$

As BIJL [2]) pointed out, the grey tin possesses diamondstructure. Hence the structures of grey and white tin are very closely related.

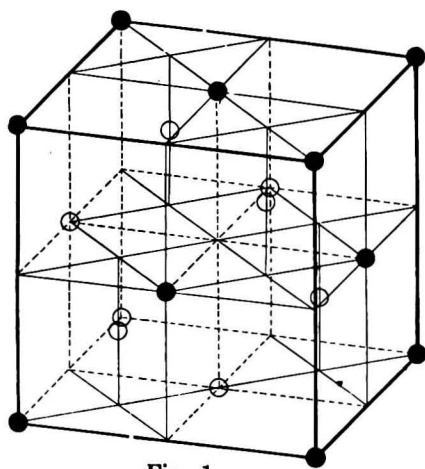In fig. 1 and 2 the structure-elements of grey and white tin are represented in natural proportion.
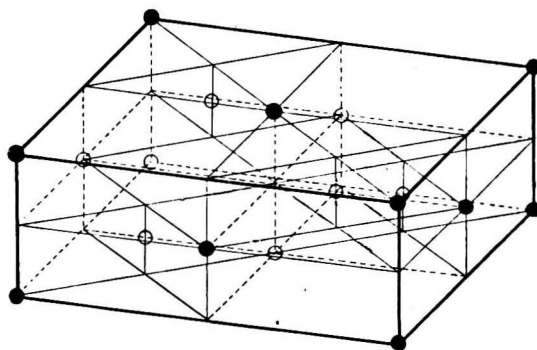

Fig. 1   Fig. 2

[1]) Atombau und Spectralliniën 3e Auflage Braunschweiz 1922, p. 188.
[2]) l. c.

TABLE II.

Distances	Intensity		$10^3 \times \sin^2 \frac{\Theta}{2}$	$10^3 \times \sin^2 \frac{\Theta}{2}$	Indices
	(estim.)	(calc.)	(calc.)	(meas.)	
4.54	s	22	70 76	74	220 111
6.40		17	140 146	144	400 311
7.96		4	216	217	331
8.98		6	270	266	202
9.24	s	9	280 286	285	440 511
10.50	s	9	350 356	356	620 531
11.42	s	8	410	411	422
12.85	s	5	496	496	711 and 551
13.69		4.3	547 550	548	113 602
13.87		4.2	560 564	560	800 731
14.79		1.3	617	615	313
15.11		1.3	630	634	660
16.08	s	5.8	687 690	690	333 642
16.41	s	4 6	700 706	703	840 751
17.30		2.1	757	755	513
17.71		2.0	776	777	911
18.73	s	5.8	827 830	827	533 822
19.05		1.9	846	840	931
20.97		2.7	910 914	917	1020 771
21.64 and 21.82		0.4	941	938 and 943	004
22.60 and 22.82		2.5	967	963 and 969	713 and 553

In fig. 3 a section is given according to a (110) face through both the structure elements, which coincide here with the central points. The atoms of the grey tin are represented by small circles, those of the white tin by spots.

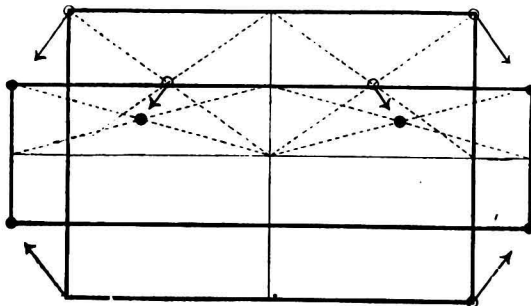The transition of grey tin into white we can describe as follows.

Fig. 3.

An elementary cube of grey tin, with a sidelength of 6.46 Å, is pressed together in a direction perpendicular to the (100) face till somewhat more than half of the height. At the same time the atoms slide sideways, without changing their mutual position. In this way the structure-element of white tin is formed with the length of the sides 3.17 and 8.22 Å. The smallest distance between two atoms changes with the transition from 2.23 Å to 2.35 Å. Notwithstanding the increase of specific weight with transition, the minimum distance between the atoms has increased.

Up to now tetragonal diamond-structure of elements has not yet been observed; some examples of compounds, however, are known. The structure which has most his resemblance with that of tin, is that of the copper-pyrites ($Fe\,Cu\,S_2$).

Burdick and Ellis [1] describe this structure as follows: on each corner of the structure-element there is an iron atom, a second is in the middle of the basis-faces. Two Cu atoms are in the centre of the side-faces, whereas four sulphur-atoms are on the same place as the four inside tin-atoms in fig. 1. The proportion of the axes of this body is $1:1:0.985$.

The main difference between the two structures lays in the axial ratio, which in the case of copperpyrite only slightly deviates from 1, whereas with tin this ratio is 2.602.

Practically at the same time as this paper was written there

[1] C. L. Burdick and J. H. Ellis Journ. Am. Chem. Soc. XXXIX. 2518. (1917).

appeared a publication of Mr. POLANYI's, about the structure of white tin also. Mr. POLANYI proposes a new structure for white tin. The elementary cell contains 4 atoms, with the relative coördinates (000) ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$) ($\frac{1}{2}0\frac{1}{4}$) ($0\frac{1}{2}\frac{3}{4}$).

The square of the axial ratio is $\frac{1}{2}$.6.772 instead of 6.772, as found here.

In truth there is no difference at all between the two structures, as Mr. POLANYI's structure-element is only the half of the element with 8 atoms, described above. The indices of table II are formed from Mr. POLANYI's notations by multiplying the first two by two.

From Mr. POLANYI's description the transition from white into grey tin seems somewhat complicated. Therefore I prefer the structure-element with 8 atoms.

Mr. KOLKMEYER kindly wrote me, that he made some new foto's with Copper K_α radiation only, and now also had found the same structure as given above.

Physical Laboratory of the "Philips" Glowlampworks.

Eindhoven, December 1923.