3. As the a-c discharge changes into a high-frequency one, and as the frequency is increased, a substantial role is played by the finite time of deionization occurring in the plasma of the a-c discharge when the voltage reverses polarity.

Translated by J. G. Adashko
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The Structure of Superconductors. IX. Roentgenographic Determination of the Structure of α - Bi_4Rh

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We have determined the structure of the low temperature modification of Bi_4Rh, which belongs to the space group O_h^{10} — $Ia3d$, with a lattice period $a = 14.928$ A. The positions of the bismuth and rhodium atoms were determined by a very precise method of constructing the cross sections and projecting the series of interatomic vectors (F^2-series) and the series of electron densities (F-series).

IN the work of one of us and Zhuravlev[1] it was shown that the compound Bi_4Rh has three modifications; α, β, and γ. The low temperature modification has a cubic lattice with a period $a = 14.928$ A and belongs to the space group O_h^{10} — $Ia3d$. In the simple lattice there are 120 atoms: 96 atoms of bismuth and 24 rhodium atoms. Alekseevskii[2] has shown that the low temperature modification α - Bi_4Rh does not exhibit superconductivity down to a temperature ~ 0.1 K, whereas the two other modifications - β - Bi_4Rh and γ - Bi_4Rh pass over into the superconducting state. In the same manner as in white and gray tin, the superconductivity in Bi_4Rh is a property of the high temperature modification which is metastable at low temperatures. The compound Bi_4Rh, having a considerable number of modifications and various superconducting properties, appears to be interesting, since a study of the structure of its polymorphic modifications may enable one to explain the connection between polymorphism and superconductivity. The problem in question in this work[3] was to determine the atomic structure of one of these modifications (α-Bi_4Rh), which contains a large number of atoms in the elementary cell. A short report of the results of this work was published previously[4].

An analysis of the regularity of the extinctions and the possible atomic positions shows that the bismuth atoms may occupy just the general position 96 h and the rhodium atoms — the one of the two 24 — fold positions 24 c or 24 d.

For determining the positions of the bismuth atoms, which forms the framework of the structure, we selected the method of constructing the cross sections of the F^2-series. A three dimensional assembly of the reflected intensity received from a series of oscillating-crystal roentgenograms, was taken by the method of irradiating in a RKV camera 86 mm in diameter. We derived the layer lines from zero to an eighth with a total number of independent reflections equal to 235. The reflected intensity was measured by a visual comparison of the spots for quality of blackening. For calculating $F^2(hkl)$ we took only angular factors into account; temperature and absorption factors were not considered.

The sections of the F^2-series were selected so that the number of maxima were as small as possible, with a small probability of over lapping, so that the connection between the coordinates of the maxima and the atomic coordinates was of a very simple form. There are three types of maxima: Bi-Bi,

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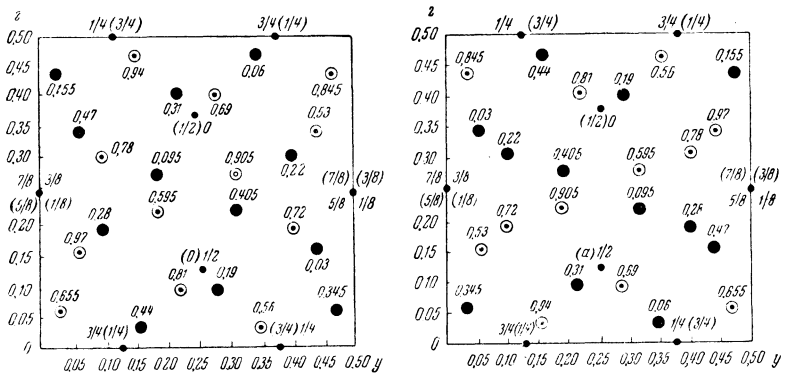

FIG. 1. • — Rh; ⊙ — Bi, $x > 0.5$; ● — Bi, $x < 0.5$

Bi-Rh, Rh-Rh; with the same factors and of relative weights: $Z^2_{Bi} : (Z_{Bi} \cdot Z_{Rh}) : Z^2_{Rh} = 3.4 : 1.8 : 1$. The appearance of maxima is principally characteristic of the spacing Bi-Bi, therefore the cross section can be found by considering only these maxima. We analyzed certain sections for flatness and for direction having simple indices, i.e., that were composed of pairs of the different coordinate positions 96 h, so that the values $u = x_i - x_j$, $v = y_i - y_j$; $w = z_i - z_j$ satisfied the relations for flatness and direction in every case selected. Sections were selected in the directions $[0, 1/2, w]$, from which 12 maxima are possible, corresponding to to the direction Bi-Bi, having a multiplicity of 8 and having coordinates $\pm 2x$; $\pm 2y$; $\pm 2z$; $\pm(1/2 - 2x)$; $\pm(1/2 - 2y)$; $\pm(1/2 - 2z)$; for both positions of the rhodium atoms it is possible to have Rh-Rh maxima with multiplicity 2, from the coordinates 0 and 1/2, and a multiplicity of 4 from the coordinates ¼ and ¾; Bi-Rh maxima are not possible.

As a result of constructing and analyzing the sections of the F^2-series there were derived 32 variations of the coordinates (xyz) of the bismuth atoms. A geometrical analysis eliminated 16 of the variations. From the remainder there were selected two variations of the positions of the bismuth atoms, for which the calculated value of $F(hkl)$ was very large and a single weak reflection with small indices agreed well with the experiments. A comparison of a large number of calculations for these two variations and the experimental value of $F(hkl)$ confirmed the selection, but did not indicate any preference for either of them. In Fig. 1 *a* and *b* are shown the projections of the nuclei of the bismuth and rhodium atoms on the (100) planes for both variations. We adopted that variation which corresponded to a greater uniformity in the distribution of the bismuth atoms over the volume of the cell (Fig. 1*a*). At the same time, the analysis of the interatomic spacing Bi-Rh gave for the rhodium atoms, the positions 24 c without any parameters. The coordinates of the bismuth atoms were: $x = 0.028$; $y = 0.437$; $z = 0.154$.

A direct check on the accuracy of the choice between the alternatives for the coordinates of the bismuth and rhodium atoms may be made by constructing any projection and section of the series of electron densities. The projections of the electron densities from all cells onto the (100) planes are of no interest, since they are alike for both variations. Aside from this, in these projections, the overlapping is a maximum.

We chose for the region of projection of the electron density (the projection of the electron cloud) that which was included between $x = 0$ and $x = 1/2$. In the projection, there appeared four sharp maxima and two very diffuse ones, whose distribution verified the accuracy of the choice of the coordinates of the bismuth atoms. Accordingly, the four greatest and sharpest maxima were used with the parabolic method to make more precise the coordinates of the bismuth atoms, i.e., $x = 0.026$; $y = 0.437$; $z = 0.151$. The rhodium atoms do not appear in this projection. The positions of the latter were determined by constructing the sections of a series of electron densities from the direction $[x, 1/4, 1/8]$. Calculation and construction of these sections confirmed the positions 24 c for the rhodium atoms.

From a second construction of a projected region of a series of electron densities the sign of $F(hkl)$ was calculated from the coordinates of the bismuth and rhodium atoms which were derived from the first construction. In Fig. 2 is shown the results of this second construction of the region of projection of the F-series. From it we derive sharper outlines of the maxima in those spots which were

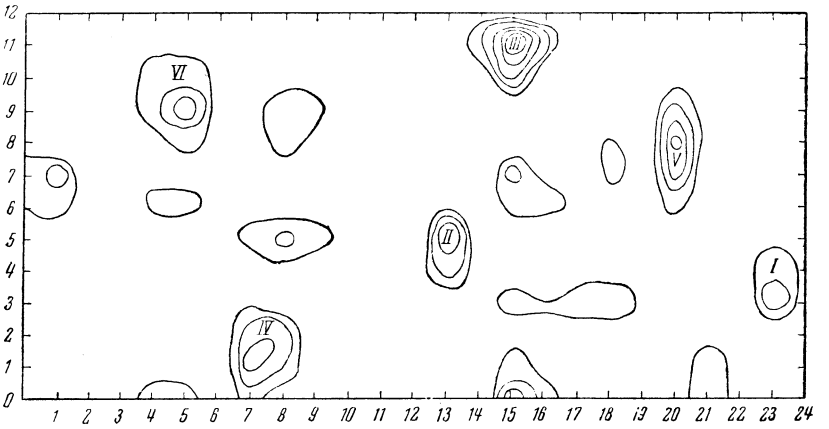

FIG. 2.

TABLE 1.

Calculation of the coordinate maxima-(u, v) and the derivation from them of the coordinates of the bismuth atoms from the second construction of the region of projection of the F-series.

No. of the maxima	u	v	Connection to xyz		x	y	z
			u	v			
I	0.478	0.086	$^1/_2-x$	$^1/_2-y$	0.022	0.434	—
II	0.272	0.100	$^1/_4+x$	$^1/_4-z$	0.022	—	0.150
III	0.314	0.225	$^3/_4-y$	$^1/_4-x$	0.025	0.436	—
IV	0.153	0.029	z	x	0.029	—	0.153
V	0.436	0.160	y	z	—	0.436	0.160
VI	0.100	0.187	$^1/_4-z$	$^3/_4+y$	—	0.437	0.150
	Average				0.024	0.436	0.153

found from the first construction. The coordinates u and v of the maxima were determined in this manner by the parabola method and from them were calculated the coordinates x, y, z of the bismuth atoms given in Table 1.

The coordinates given by the second construction of the projection differed from the coordinates obtained from the first construction by no more than 0.003. The final values of the coordinates of the bismuth atoms were: $x=0.024$; $y=0.436$; $z=0.153$.

In Table 2 are shown the interatomic spacings and the number of neighbor atoms in the structure α - Bi_4Rh.

The Bi-Rh spacing is less than the sum of the atomic radii by 3%. The coordination polyhedron of the rhodium atoms with eight vertices (a twisted cube) is shown in Fig. 3. In α - Bi_4Rh there are two forms of twisted cube, right and left handed, one of which is obtained from the other by a reflection through the center of symmetry. The tetragonal face of the eight-cornered figure which is parallel to the 110 planes appears as an external face of the α - Bi_4Rh crystal. An analogous coordination polyhedron is found in the series of structures of the compounds of the transition metals with elements of the B subgroup of the periodic table ($PtSn_4$, $PdPb_4$, $AuSn_4$, $CuAl_2$, $CoGe_2$).

Each bismuth atom has three neighboring atoms of bismuth arranged on one side of it as in the structure of pure bismuth. One of the Bi-Bi spacings is nearly equal to the shortest spacing in pure bismuth, two are somewhat larger, and the remaining six Bi-Bi spacings are near the largest spacings in pure bismuth.

N. V. Belov pointed out to us the analogy between the structure of α - Bi_4Rh and garnet

TABLE 2.

Interatomic Spacing and Number of Nearest Atoms

Atom	Atom	Spacing in A	Number of Neighbors
Bi	Bi 2Bi 2Bi 4Bi 2Rh	3,10 3,27 3,50 3,85 2,80	11 (9Bi + 2Rh)
Rh	8Bi	2,80	8Bi

$(Ca_3Al_2Si_3O_{12})$. The oxygen atoms in the structure of garnet occupy the same positions as the bismuth atoms in α - Bi_4Rh, and also form an eight-cornered figure – a twisted cube, in which are found octahedrons and tetrahedrons. In the garnet structure, the calcium atoms occupy an eight-cornered figure, the aluminum atoms – octahedrons, the silicon atoms – tetrahedrons formed by the oxygen atoms. In the structure α - Bi_4Rh the coordinates of the bismuth atoms nearly coincide with the coordinates of the atoms of oxygen in the garnet structure. The rhodium atoms occupy eight-cornered figures, octahedrons and tetrahedrons at the remaining vacancies.

RESULTS

1. The crystal α - Bi_4Rh has a cubic lattice with a period $a = 14.928 \pm 0.005$ A; and belongs to the space group $O_h^{10} - Ia3d$. The bismuth atoms occupy the positions 96 h with coordinates $x = 0.024$; $y = 0.436$; $z = 0.153$; the rhodium atoms – the positions 24 c.

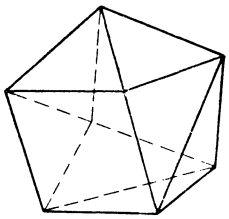

FIG. 3.

2. The coordination polyhedron of the rhodium atoms in α - Bi_4Rh is eight-cornered – a twisted cube, analagous to the coordination polyhedra in the structures

The bismuth atoms have a coordination number of 11 (9 bismuth atoms and two rhodium atoms).

3. The interatomic spacing Bi-Rh in α - Bi_4Rh is less than the sum of the atomic radii by 3%. Three of the Bi-Bi spacings are nearly equal to the shortest spacing, the remaining six near the largest values of the spacing in pure bismuth.

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