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Effect of impurities of normal metals on the residual electric resistance of Na, K, Rb, and Cs

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The effect of 12 impurities (Li, K, Rb, Cs, Ca, Sr, Cd, Hg, In, Tl, Sn, Pb) on the residual resistivity ρ_0 of sodium, and of Cs impurities on the ρ_0 of potassium is studied experimentally. It is found that the dependence $\Delta\rho/c = 4.75\,(\Delta Z - 1.1)^2 + 5.15$ is valid for sodium with impurities of the V period. The values of $(\Delta\rho/c)_{exp}$ for alloys with Na, K, Rb, and Cs bases are compared with those of $(\Delta\rho/c)_{calc}$ determined by using the phase shifts and making allowance for lattice distortions by means of the Blatt correction. The agreement between experiment and calculation is just barely satisfactory (a discrepancy by a factor of 2–4). It is suggested that the Blatt correction is insufficient for obtaining good agreement, and that the deviation of the real Fermi surface of the matrix from spherical is not the principal cause of the discrepancy.

In the study of residual electric resistance of dilute alloys based on normal polyvalent metals Sn,[1] Pb,[2] Tl,[3] In, Ga,[4] Zn, Cd, Mg,[5] and Hg,[6] it has been established by the authors that the calculated values of the electric resistance agree with the experimental values by no better than barely satisfactory. In Ref. 7, where we studied the residual resistance of alloys based on lithium, whose Fermi surface is close to spherical (in comparison with polyvalent metals), a rather good agreement between theory and experiment was obtained; therefore, it has been suggested there that an important role in the impurity scattering of conduction electrons is played by the anisotropies of the Fermi surface of the metal matrix. Inasmuch as all our calculations were made within the framework of the free-electron model, and the contribution to the scattering connected with anisotropies of the Fermi surface was nowhere taken into account, a better agreement of the theoretical and experimental results should be expected for metals in which the Fermi surface is closer to spherical. Sodium and potassium belong to such metal matrices. The present research was undertaken with the aim of testing the assumptions stated above.

Prior to the beginning of our investigations, there were a series of papers in the literature on the effect of impurities of Na, Rb, and Cs on the residual resistivity ρ_0 of calcium;[6, 8-11] however, the data on the system of alloys K + Cs were unreliable because of a great scatter of the experimental points among the various authors and greater precision is required. For the other alkali metals, the researches of Refs. 12 and 13 are known to us, in which the resistance of dilute alloys of Cs + Rb, Rb + K, and K + Cs were studied (the boldface indicates the metal-matrices).

Researches devoted to the study of ρ_0 of dilute alloys on a sodium base were not known to us at all. Therefore, to perform the undertaken task, it was first necessary to obtain reliable data on the change in the residual resistivity $(\Delta\rho_0)$ of sodium or potassium in which one impurity or another is dissolved. The problem was appreciably complicated by the fact that, according to known binary diagrams of state only Cs, Rb and some quantity of Na dissolve in solid potassium, and only Tl and Ba in sodium. With the aim of studying the possibility of formation of binary solid solutions of sodium and potassium with various metals, exploratory research was performed by us,[14] in which a noticeable solubility of ten impurity metals in sodium and practically none for impurity metals (except Rb, Cs, and Na) in potassium were first noted.

METHOD OF EXPERIMENT

All the alloys were prepared on the base of pure (~99.99%) metals with electric resistance ratio $\delta_{4.2} = R_{4.2}/R_{293}$ ($R_{4.2}$ and R_{293}—resistance of the sample at 4.2 and 293 K, respectively) equal to $(1.2 - 1.6) \times 10^{-4}$ for sodium and 3.6×10^{-4} for potassium. The quantity $\delta_{4.2}$ differed from δ_0 (relative residual resistance) by not more than 15% for potassium and not more than 2–3% for sodium. The method of preparation of the alloys and of the wire samples (diameter 3 mm and length ~180 mm), and of also the measurements of their electric resistance at 4.2 and 293 K was reported in detail in Ref. 14.

The error of measurement of R_T did not exceed 0.7%. To increase the reliability of the determination of the quantity $\Delta\rho/c$—the change in ρ_0 of the metal-matrix up-

TABLE I.

Impurity	ΔZ	$\Delta\delta_0/c$, (at.%)$^{-1}$	$\Delta\rho/c$ *, μohm·cm·(at.%)$^{-1}$
		Na matrix	
Li	0	~0.033	~0.16
K	0	0.115±0.008	0.546±0.04
Rb	0	0.125±0.01	0.595±0.05
Cs	0	0.26±0.03	1.23±0.14
Ca	1	~0.25±0.1	~1.2±0.5
Sr	1	~0.75±0.25	~3.6±1.2
Cd	1	1.10±0.08	5.22±0.4
Hg	1	1.15±0.05	5.46±0.2
In	2	1.9±0.1	9.0±0.4
Tl	2	1.75±0.1	8.3±0.5
Sn	3	4.7±0.8	22.3±3.8
Pb	3	2.20±0.1	10.9±0.5
		K matrix	
Na	0	–	0.54 [10] / 0.62±0.07 [9] / 0.68 ** [6]
Rb	0	–	0.12 [10, 11] / 0.132±0.007 [9]
Cs	0	–	0.865±0.015 / 0.48±0.3 [10] / 1.1±0.2 [9] / 0.7 [13] ***
		Rb matrix	
K	0	–	0.13 [12], 0.01 [11]
		Cs matrix	
K	0	–	0.9 [13] ***
Rb	0	–	0.28 [12]

*The heavy type indicates those values of $\Delta\rho/c$ which were obtained by us from the corresponding published experimental data.
**Unfortunately, in the recalculation of the correct value of $\Delta\delta_0/c$ in Ref. 6, a value $\Delta\rho/c = 1.73$ was obtained in error.
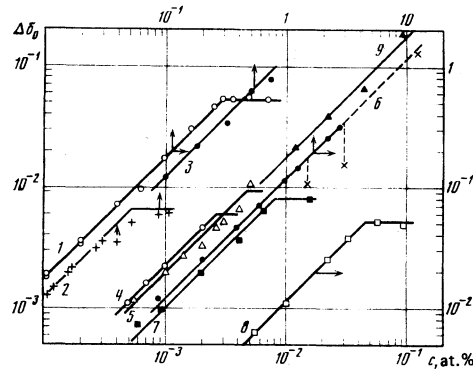***The value of $\Delta\rho/c$ was obtained at 190 K in Ref. 13 and at 4.2 K in the remaining works.

FIG. 1. Dependence of $\Delta\delta_0$ of sodium and potassium on the concentration of dissolved impurities. Sodium alloys: 1—impurity Tl, 2—Rb, 3—K, 4—Pb, 5—In, 7—Cd, 8—Hg. Potassium alloys: 6—impurity Cs (our data), 9—Cs (data from Ref. 8), ×—data from Ref. 10.

phase on $\Delta\rho/c$, as in the work with lithium.[7] Potassium does not undergo a polymorphic transition down to 1.2 K.[16]

RESULTS AND THEIR DISCUSSION

Finding $\Delta\rho/c$. The quantity $\Delta\delta_0$ of interest to us—the change in the relative residual electric resistance of sodium or potassium with dissolved impurities with concentration c—was found in the form

$$\Delta\delta_0 = \left(\frac{R_{4.2}}{R_{293}-R_{4.2}}\right)^{alloy} - \delta_{4.2}^{pure} = \left(\frac{\delta_{4.2}}{1-\delta_{4.2}}\right)^{alloy} - \delta_{4.2}^{pure}. \quad (1)$$

The dependences of $\Delta\delta_0$ on the atomic concentration c of the introduced impurity are shown in Figs. 1–3 in logarithmic coordinates. For most impurities, the experimental points lie well along a straight line making an angle of 45° with the coordinate axes, which indicates a linear relation between $\Delta\delta_0$ and c. The breaks in the lines correspond to the limit of solubility of the given impurity in solid sodium (similar data on the solubility are given in Ref. 14). From these sloping lines, the values of $\Delta\delta_0/c$ given in Table I were found. For the impurities Li, Ca, and Sr in sodium, we did not succeed in finding the exact locations of the corresponding lines in the region of existence of the solid solutions.

on solution in it of 1 at.% of a given impurity (as $c \to 0$)—the interval of impurity concentrations in the region of existence of the solid solution was chosen to be as large as possible (1–15 orders of magnitude). This interval was bounded, on the one hand, as a rule, by the narrow limit of solubility, and on the other, by the purity (ρ_0 or $\delta_{4.2}$) of the metal-matrix. The error in finding the quantity $\Delta\rho/c$ amounted to 2–10% (see Table I), with the exception of alloys of sodium with tin (~17%), and also the system of alloys with impurities of Sr, Ca, and Li. For the latter three impurities, because of the large scatter of the experimental points, due basically to the error in the determination of the impurity concentration, the value of $\Delta\rho/c$ must be regarded as tentative, requiring further experimental refinement.

It should be observed that sodium below 40 K undergoes a polymorphic transition of the martensitic type: its *bcc* lattice transforms into a low-temperature *hcp* lattice. The amount of the *hcp* phase is determined by the degree of deformation of the sample and can change in the thermocycling. According to the data of Ref. 15, in which experiments were carried out on thermal cycling of samples of pure sodium and the alloy Na+K, in spite of the fact that in broad samples with $d \approx 0.1$ cm the effect of the transition on the ideal resistivity can reach 10% at 30 K (in samples-capillaries with $d \approx 50–150\mu$ this change is much less and reaches 5% at the same temperature), the residual resistivity is practically independent of the phase composition and differs for *bcc* and *hcp* phases by not more than 1%. Therefore, we have neglected the effect of the second *hcp*
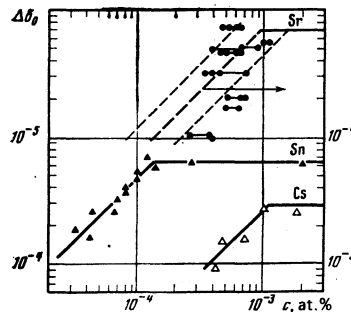

FIG. 2. Dependence of $\Delta\delta_0$ of sodium on the concentration of dissolved impurities Sr, Sn and Cs. The concentration of Sr was determined by chemical analysis. The horizontal lines connect points of different concentration and correspond to analysis data of different segments along the length of the same sample.
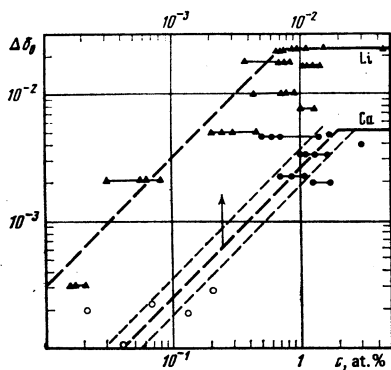
FIG. 3. Dependence of $\Delta\delta_0$ of sodium on the concentration of the impurities Li and Ca. The points ▲ and ● correspond to concentrations found with the aid of chemical analysis, ○—calculated from the initial batches of the two components. The horizontal lines connecting several points have the same meaning as in Fig. 2 for the impurity Sr.

Impurities in Li:

Li ●	Be ●													B	C	N	O
Na	Mg 1.2													Al 7.1	Si	P	S
K —	Ca	Sc ●	Ti ●	V ●	Cr ●	Mn ●	Fe	Co ▲	Ni ●	Cu	Zn 2.0	Ga 7.4	Ge	As ●	Se ●
Rb —	Sr	Y ●	Zr ●	Nb ●	Mo ●	Tc	Ru ●	Rh ●	Pd	Ag 1.3	Cd 2.5	In 5.8 (11)	Sn (10)	Sb ● (28)	Te ●
Cs —	Ba	La	Hf ●	Ta ●	W ●	Re ●	Os	Ir ●	Pt	Au 4.8	Hg 3.6	Tl 7.3	Pb 12.3 (21)	Bi (21)	Po (33)

Impurities in Na:

Li 0.16	Be ●												B ●	C	N	O
Na	Mg —												Al	Si	P	S
K 0.55	Ca 1.2	Sc ●	Ti ●	V ●	Cr ●	Mn ●	Fe ●	Co ●	Ni ●	Cu ●	Zn —	Ga	Ge	As ▲	Se
Rb 0.6	Sr ~3.6	Y ●	Zr ●	Nb ●	Mo ●	Tc	Ru ●	Rh ●	Pd	Ag (11)	Cd 5.2	In 9.0	Sn 22.3 (45)	Sb (45)	Te (72)
Cs 1.2	Ba	La	Hf ●	Ta ●	W ●	Re ●	Os	Ir ●	Pt	Au	Hg	Tl 5.5	Pb 8.3	Bi 10.9	Po

FIG. 4. Data on $\Delta\rho/c$ (in μohm-cm/at. %) for element-impurities in lithium and sodium: ●—impurities are not dissolved in lithium 650 °C and in sodium at 750 °C; ▲—impurities are not dissolved in lithium at 250 °C and in sodium at 150 °C. *Correction.* The last three figures in the lower right corner should be shifted to the left by one square.

Only a certain "corridor" was established, through which the desired line passes. The most reasonable location of such a line is noted in Figs. 2 and 3 by the heavy dashed lines, from which the value of $\Delta\delta_0/c$ was estimated for each impurity. The value of $\Delta\rho/c$, found by multiplication of $\Delta\delta_0/c$ by the resistivity of very pure sodium and potassium at 293 K, equal respectively to 4.75 and 7.2 μohm-cm,[17] is shown in Table I for each of the 12 impurities in sodium and for the impurity Cs in potassium (see Fig. 1).

There are no values of $\Delta\rho/c$ for impurities in sodium in the literature; therefore our data cannot be compared. A criterion for the degree of reliability of the obtained values of $\Delta\rho/c$ are the errors indicated in Table I. However, it should be remarked that $\Delta\rho/c \approx 3.6$ μohm-cm/at. % for the Sr impurity is very large. Starting from the position of Sr and Na in the periodic table, we can assume that the actual value of $\Delta\rho/c$ should evidently lie between 1.5 and 2 μohm-cm/at. %. From this viewpoint, the quantity $\Delta\rho/c$ for the Pb impurity should be 1.5–1.7 times larger.

Our data for the alloys of the system K + Cs can be compared with results from Refs. 8 and 10. For comparison, the corresponding points from these researches are shown in Fig. 1. It is seen that the points from Ref. 8 cluster on a line passing above ours, with a significant scatter (one point at $c \approx 0.07\%$ is omitted altogether, since it falls far out). It is difficult to draw a line with a slope of 45° through the points of Ref. 10 because of the great scatter. All our eight experimental points cluster well on a single straight line and for that reason we regard our value of $\Delta\rho/c$ as the more reliable. The value $\Delta\rho/c = 0.7$ from Ref. 13 was estimated and obtained at a high concentration of Cs (22 at. 5).

Thus, for comparison with theory, we had the values of $\Delta\rho/c$ for 12 impurities (see Table I) in sodium, for the impurities Na, Rb, and Cs in potassium and also for K and Rb in cesium and K in rubidium. According to what was said in Ref. 14, in addition to these 18 experimental values of $\Delta\rho/c$, detailed information can be obtained only for the system of alloys Rb + Cs, since Rb and Cs have unlimited solubility in one another.

From the viewpoint of the estimation of the possibility of obtaining data on $\Delta\rho/c$ for various impurities in lithium and sodium, Fig. 4 is of interest, in which are shown all the data on $\Delta\rho/c$, and also the elements are noted that do not dissolve in both metals even in the liquid phase at sufficiently high temperatures.[7,14,18] It is seen from this figure that there remains a small number of elements-impurities for which there are no data on $\Delta\rho/c$. Thus the information obtained in the present work and in Ref. 7 (investigations on the basis of lithium) represent at the present time practically all the possible data on $\Delta\rho/c$ for impurities dissolving in alkali metals. For any other impurities in cesium, rubidium, potassium, sodium, and lithium, it will be very difficult to obtain $(\Delta\rho/c)_{exp}$ because of the very small ($\sim 0.001\%$) solubility of them in the alkali metals. The quantity $\Delta\rho/c$ for other impurities in lithium, sodium, and potassium can be obtained experimentally only under the condition of a significant increase in the purity of the metal-matrix (by about 1–2 orders of magnitude) and the application of high-sensitivity ($10^{-5}\%$) methods of analysis.[7,14]

One regularity is clearly seen from a consideration of the existing experimental values of $\Delta\rho/c$ for homovalent impurities in alkali metal-matrices (see Table I): if the matrix and the impurity exchange places (Na–K, K–Rb, Cs–K), the value of $\Delta\rho/c$ remains practically unchanged. This fact allows us to predict a value $\Delta\rho/c = 0.2$–0.3 μohm-cm/at. % for the impurity Cs in rubidium, since experimental studies of these alloys are unknown to us, but the value of $\Delta\rho/c$ for Rb in cesium is known. Moreover, it follows from Tables II and III that $(\Delta\rho/c)_{exp}$ increases for homovalent impurities as the impurity lies farther (in the period) from the metal-matrix in the periodic table.

Linde's rule. According to the empirical Linde's rule,

$$\Delta\rho/c = a\Delta Z^2 + d, \tag{2}$$

where $\Delta Z = Z_{imp} - Z_{mat}$ is the difference in valence of the

TABLE II.

Impurity in sodium	ΔZ	$(\Delta\rho/c)$ exp, μohm·cm at.%	$(\Delta\rho/c)_{calc.}$ μohm·cm at.%		K', atomic units	β_{theor}	V, atomic units
			$N=\Delta Z$	$N=\Delta Z-\beta$			
Ag	0	(10.9) *	0	0.39	0.558	0.363	115.1
Li		~0.16		0.23	0.538	−0.289	145.6
K		0.55		0.44	0.416	0.582	510
Rb		0.6		0.82	0.390	0.860	626
Cs		1.23		1.40	0.367	1.239	784 ***
Ca	1	~1.2	1.31	1.12	0.598	0.058	290
Sr		~3.6		0.60	0.563	0.269	378
Cd		5.2		2.60	0.684	−0.290	145.5
Hg		5.46		2.46	0.676	−0.264	156.2
In	2	9.0	3.91	5.16	0.752	−0.217	176
Tl		8.3		4.90	0.739	−0.175	193.2
Sn	3	22.3	7.51	8.71	0.814	−0.202	182.2
Pb		10.9		8.39	0.797	−0.147	204.7
Sb	4	(45.5) *	10.75	11.26	0.860	−0.149	204.2
Te	5	(72.5) *	13.9 **	14.4 **	−	−0.088	229.3

*The predicted values of $\Delta\rho^\circ c$ are shown in parentheses (see text).

**The values of $\Delta\rho/c$ for Te impurity were obtained by extrapolation of the corresponding graphs of the dependence of $\Delta\rho/c$ on β to the points $\beta=0$ and $\beta=-0.09$.

***We calculated the atomic volume of Cs, assuming the density of cesium equal to 1.90 g/cm³. For sodium V = 267 atomic units.

impurity and the matrix, a and d are certain constants. On the basis of the experimental material for 14 metallic matrices, it was shown in Ref. 19 that for impurities not in the same period as the matrix the following dependence is observed:

$$\Delta\rho/c=a\Delta Z^2+b\Delta Z+d=a(\Delta Z-\alpha)^2+\beta, \tag{3}$$

where a, b, d, α, β are coefficients dependent on the numbers of the periods of the matrix and the impurity. For impurities in the same period as the matrix, the dependence (2) is observed at $d = 0$. It is of interest to test the validity of these dependences for sodium alloys as well. For this purpose, the experimental values of $\Delta\rho/c$ for three impurities belonging to period V were represented as functions of ΔZ, as shown in Fig. 5. The continuous curve describes an equation of type (3):

$$\Delta\rho/c=4.75(\Delta Z-1.1)^2+5.15. \tag{3a}$$

Consequently, the conclusion drawn in **Ref. 19** is also valid for sodium alloys. Attention is called to the large shift of the minimum of the parabola to the right from the ordinate axis (by 1.1) and away from the abscissa (by 5.15), which was observed previously in lithium with impurities of period VI.[7] One must also note the

TABLE III.

Impurity	$(\Delta\rho/c)$ exp, μohm·cm at.%	$(\Delta\rho/c)_{calc}*$, μohm·cm at.%	K', atomic units	β_{theor}
Matrix K				
Na	0.68	0.38	0.443	−0.331
Rb	0.12	0.054	0.369	0.157
Cs	0.865	0.255	0.349	0.372
Matrix Rb				
K	0.13	0.051	0.380	−0.130
Cs	(0.2–0.3) **	0.071	0.344	0.177
Matrix Cs				
K	0.9	0.22	0.369	−0.245
Rb	0.28	0.066	0.353	−0.141

*Calculated at $N = \Delta Z - \beta$.

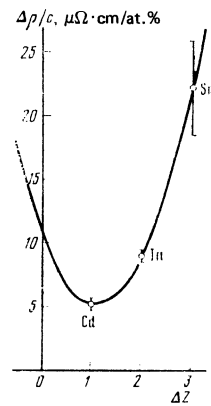**The expected value of $(\Delta\rho/c)_{exp}$ is given (discussion in the text).

FIG. 5. Dependence of $\Delta\rho/c$ on ΔZ for impurities of elements of period V in sodium.

large slope of the parabola $(a = 4.75)$, which was observed previously only in gallium with impurities of period VI.[19] Using this equation, we found (predicted) values of $\Delta\rho/c$ equal to 10.9, 45.5, and 72.5 μohm-cm/at.% respectively for the impurities Ag, Sb, and Te (see Fig. 4), which one could not to date measure experimentally because of the very small solubility of these elements in solid sodium.

A similar reduction of the data on $\Delta\rho/c$ for the three impurities belonging to the VI period gives a parabola with a negative coefficient a in Eq. (3) which makes no physical sense. Evidently this is connected with the underestimate of $\Delta\rho/c$ for the impurity Pb, about which we spoke above. For an estimate (in first approximation) of the coefficient a for the impurities of the VI period, this coefficient was found as the slope of the straight line passed through the points for Hg and Tl in the coordinates $\Delta\rho/c=f(\Delta Z^2)$, assuming the coefficient b in (3) to be equal to zero. Such an estimate gives the value $a=0.94\approx1$, which is completely reasonable for the matrix of an alkali metal.[19]

Calculation of $\Delta\rho/c$ by the method of phase shifts.
The change of the residual resistivity of a metal when 1 at.% of an impurity is dissolved in it (in the form of a substitutional solid solution) is equal to[2,3]

$$\frac{\Delta\rho}{c}=\frac{2.73}{nk_F}\sum_{l=0}^{\infty}(l+1)\sin^2[\eta_l(k_F)-\eta_{l+1}(k_F)], \tag{4}$$

where k_F is the Fermi wave vector of the metal-matrix, equal to 0.4806, 0.3877, 0.3629, 0.3359 atomic units, respectively, for sodium, potassium, rubidium, and cesium (the Fermi surface was assumed to be a sphere); η_l is the phase shift of the lth partial wave, n is the number of electrons per atom. It is known[20] that for alkali metals $n\approx1$. The quantity n is closest to unity in Na and K at room temperatures and falls off somewhat with decrease in temperature. According to the investigation of the Hall effect on pure Na and K, the minimum n occurs at a temperature $\sim\Theta/5$, and at $T\sim 6$ K, $n=1.006$ for Na and 0.98 for K.[9] In this same research, measurements were carried out on alloys of K + 0.19 at.% Rb and K + 0.8 at.% Na, whence it can be estimated that upon introduction of 1 at.% Na in potassium n decreases by $\sim10\%$. Taking it into account that

in our alloys the concentration of the impurity was as a rule less than 0.2%, we have set $n=1$ everywhere in these calculations.

The procedure of calculation with the use of a high-speed computer is described in detail in Refs. 1–6. We note only that the phase shifts η_l necessary for the calculation of $\Delta\rho/c$ were found to be such that in the chosen value of K', which characterizes the depth of t the potential well (or the height of the barrier) that approximates the impurity potential they satisfied the Friedel sum rule:

$$N = \frac{2}{\pi} \sum_{l=0}^{\infty} (2l+1)\eta_l(k_F), \qquad (5)$$

where $N = \Delta Z$ if we do not take into account distortions of the lattice by the impurity atoms. Summation was carried out over $l = 0, 1, 2, 3, 4$; the remaining terms could be disregarded because of the rapid convergence of the series. The distortion of the lattice-matrix was taken into account according to Blatt[21] in the form of some change in the excess charge ΔZ because of the re-screening:

$$N = \Delta Z - \frac{1+\sigma}{1-\sigma} \frac{\Delta a}{ac} = \Delta Z - \beta. \qquad (6)$$

Here σ is Poisson's ratio, equal to 0.315 for sodium, 0.350 for potassium, and 0.356 for rubidium and cesium,[22] and $\Delta a/ac$ is the relative change in the lattice parameter of the alloy (in per cent) for a 1 at. % of dissolved impurity.

The values of $\Delta a/ac$ for sodium alloys are not known to us, but can be obtained from x-ray investigations of binary alloys only for the impurities Li, K, and Tl, the limit of solubility of which is sufficiently great (0.3–0.8 at. %).[14] For the other impurities in sodium (see Table II) it is not possible to obtain these data by the most exact x-ray method because of the very small ($\ll 0.1\%$) value of their solubility. Therefore, for most of the impurities (9 out of 12) in Table II, it is not possible even to expect to obtain the value of $\Delta a/ac$ by the x-ray method. Consequently, the correction for the lattice distortion (according to Blatt) for sodium alloys could be made only using the difference between the atomic volumes of sodium and the impurity. In the case of alloys based on K, Rb, and Cs, the values of $\Delta a/ac$ can be obtained in principle for all the impurities considered in Table III, since they form an unlimited series of solid solutions with the metal-matrices or have a sufficiently large solubility (K+Na). However, in connection with the experimental data on $\Delta a/ac$, we, as earlier,[1-7] have taken $\Delta a/ac$ to be equal to $\Delta V/3V_{mat}$, where $\Delta V = V_{imp} - V_{mat}$ (V_{imp} and V_{mat} are the atomic volumes of the impurity and matrix, respectively). The values of β, calculated by means of ΔV, we have called "theoretical." They are shown in Tables II and III with the corresponding values of the parameter K'.

It is seen from Table II that the values of $(\Delta\rho/c)_{calc}$ for sodium without account of lattice distortions are much smaller than the experimental ones. Allowance for the distortion of the lattice made it possible first to distinguish between impurities of the same valence, in-

cluding homovalent ones; second, it essentially increased the values of $(\Delta\rho/c)_{calc}$, bringing them closer to the experimental. It is worthy of note that for homovalent impurities in sodium, the difference does not exceed 40%, something not observed earlier in polyvalent matrices,[1-6] where the difference, as a rule, was severalfold or even an order of magnitude. In the case of impurities of valence 2–4 (with the exception of Sr), the values of $(\Delta\rho/c)_{calc}$ are as a rule smaller than the experimental, but this difference does not exceed ~2.5 times. In alloys with the base of K, Rb, and Cs and with homovalent impurities (see Table III), the values of $(\Delta\rho/c)_{calc}$ turn out to be much smaller (by a factor of 1.8–4) than the experimental.[1)]

As before,[1-7] we have found, by the method of least squares, the value $n = n_{eff}$ at which $(\Delta\rho/c)_{calc}$ agrees best with $(\Delta\rho/c)_{exp}$ for sodium and potassium alloys. Such a calculation gives $n_{eff} = 0.53$ for sodium and 0.44 for potassium. In the case of sodium alloys we have not used in these calculations the value of $\Delta\rho/c$ for Sr, since it is the least reliable. At such n_{eff} the difference between the calculation and experiment naturally becomes smaller; however, the found n_{eff} contradicts the known (from the Hall effect) values $n \approx 2n_{eff}$ for pure sodium and potassium; therefore, the calculations at $n = n_{eff}$ are not considered further.

We can thus assert that for the alloys of sodium and potassium that we have considered the agreement of the calculated values of $\Delta\rho/c$ at $n=1$ with the experimental is only barely satisfactory, i.e., similar to what was observed for alloys with a lithium base. If we take it into account that of all the alkali metals, the most anisotropic Fermi surfaces are possessed by lithium and cesium, and for sodium and potassium the departure of the Fermi surface from a sphere is very slight, then we can make the important conclusion that the departure of the real Fermi surface of the metal-matrix from a sphere is not an important reason for the poor (or only satisfactory) agreement of the calculated $\Delta\rho/c$ with the experimental for the given method of calculation.

One of the possible causes of such a wide difference can in some measure be associated with the replacement $\Delta a/ac \rightarrow V/3V_{mat}$; however, it is hardly the princi-
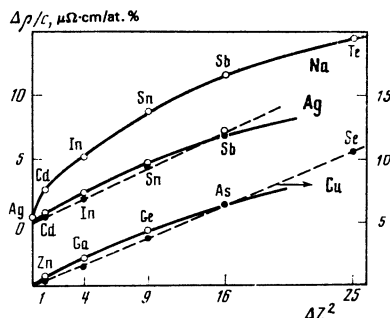

FIG. 6. Dependence of $(\Delta\rho/c)_{cal}$ on ΔZ^2 with account of the distortion of the lattice for three metal-matrices: N, Cu, Ag (for Cu, the scale is at the right). For the latter two metals, the ratio $\Delta a/ac$ is taken from experimental investigations. The black circles are experimental,[19] the open circles, calculated.

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pal cause, since a similar insufficient effect of the Blatt correction was observed according to Ref. 21 earlier on magnesium alloys, where only the experimental value of $\Delta a/ac$ was used in the calculation.[5] Evidently the principal reason of such a great discrepancy between calculation and experiment is the imperfection of the employed theory and, in the first degree, the insufficiency, and, in a number of cases, even the incorrectness of the introduced Blatt correction for the distortion of the lattice of the metal-matrix, in the form (6).[2)] An attempt at checking the validity of a relation $\Delta\rho/c = f(\Delta Z^2)$ of the type (2) or (3) for the values of $\Delta\rho/c$ calculated with account of lattice distortion. (Without account of the lattice distortion, the indicated relation does not hold.) The results of such an attempt are shown in Fig. 6 for alloys based on sodium with impurities of period V, where, for comparison, we have put similar data for alloys on the bases of copper and silver, with the use of the experimental values of $\Delta a/ac$ in the calculations. The latter data were selected for comparison because it is universally assumed that the calculation of $\Delta\rho/c$ for them with the Blatt correction[21] gives excellent agreement with the experimental data.

It is seen from the graph that the calculated dependences $f(\Delta Z^2)$ for alloys of copper and silver are much weaker than the experimental ones described by the equation $\Delta\rho/c = a\Delta Z^2$ at $a = 0.40$ for Cu and 0.46 for Ag.[19] The nonobservance of a quadratic law (departure from a straight line) appears very clearly for sodium alloys, and its character (as we have verified) does not change when $\Delta\rho/c$ is plotted not against ΔZ^2 but against $(\Delta Z - 1.1)^2$ (see Ref. 19). A significant departure from a straight line should be observed also for Se and Te impurities (in Cu and Ag, respectively); however, experimental data for $\Delta a/ac$ for these impurities are lacking. The deviation from a quadratic dependence, which is clearly evident in the experimental data of Ref. 19, is also additional proof of the imperfection of the method of calculation with use of phase shifts.[3)]

Thus, we can now say unambiguously (there is no fitting parameter of the type n_{eff} as was the case earlier in Refs. 1 and 6) that the theory of phase shifts with the Blatt correction cannot give a good description of the experimental results on $\Delta\rho/c$ for metallic matrices and impurities of the B subgroup of the periodic table.

It was proposed in Ref. 19 on the basis of analysis of empirical rules pertaining to purely experimental values of $\Delta\rho/c$ that the lattice distortion of the metal-matrix is not the only reason (besides the scattering of electrons from the excess charge of the impurity) affecting the value of $\Delta\rho/c$ of dilute alloys. The difference in the ionic composition of the matrix and the impurity, which is not at all considered in the theory, can be another possible reason.

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1)In these alloys, the calculation could be carried out only with account taken of the distortion of the lattice.

2)In a number of alloys (Ag + Zn, Al, Ga, Tl; Au + Zn, Al, Ga; Mg + Sn, Pb, Bi) it has been noticed that the Blatt correction with use of $\Delta a/ac$ does not decrease, but rather increases the difference between the calculation and the experiment.

3)However, it should be noted (see Tables II and III) that, in spite of the significant difference between $(\Delta\rho/c)_{calc}$ and $(\Delta\rho/c)_{exp}$ for each set of alloys, $(\Delta\rho/c)_{calc}$ just as $(\Delta\rho/c)_{exp}$ undergoes practically no change upon interchange of places of the matrix and the homovalent impurity (Na-K, K-Rb, Cs-K, Cs-Rb).

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