

EFFECT OF IMPURITIES ON THE RESIDUAL ELECTRIC RESISTIVITY OF CADMIUM

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The degree of influence of fifteen impurities (Pb, Sn, Pd, Rh, Ge, Pt, Tl, Au, In, Ga, Ag, Cu, Mn, Hg, Zn) on the residual resistivity ρ_0 of cadmium is studied. The alloys were prepared with 99.9999% pure cadmium possessing $\rho_0/\rho_{293} = (1-2) \times 10^{-5}$ and impurity concentrations ranging from 2×10^{-4} to 2%. Homogenizing annealing at 250-280°C was carried out in helium for at least 14 days. It is demonstrated that the Linde rule holds only for impurities of period V (which includes cadmium). For impurities of periods IV and VI the dependence $\Delta\rho/c = a(\Delta Z)^2 + b\Delta Z + d$ is valid, the coefficient a increasing with the number of the period. A calculation of $\Delta\rho/c$ for normal metals by the phase shift technique yields satisfactory agreement with the experimental values. Allowance for lattice distortion by impurity atoms does not improve the agreement. The limits of solubility of In, Cu, Tl, Rh, Pd, Ga, Sn, Pt, Ge, and Pb in cadmium at 250°C are estimated. It is found that for Ni, As and Sb the solubilities are $(1-2) \times 10^{-3}\%$ and for Mn it is $<0.1\%$.

It is known from the published experimental papers that the influence of dissolved impurities on the residual electric resistivity ρ_0 of metals is very large. For a given metal matrix, this influence depends on the kind of impurity, and the maximum difference reaches one order of magnitude. This reveals the individual behavior, connected with the singularities in the screening of the impurity atoms by the conduction electrons, of each impurity in a given metal matrix. The degree and character of the impurity-ion screening depend both on the metal matrix and on the type of impurity, or more accurately on the position of the latter in the periodic table. An experimental study of the influence of different impurities on ρ_0 and a comparison with the existing theories should therefore contribute to correct ideas concerning the character and details of the interaction of the impurity atoms with the lattice and with the conduction electrons. Unfortunately, the existing theory, using phase shifts^[1], can describe the experimental data satisfactorily only for noble univalent metals. This agreement was improved by Blatt by taking into account the degree of lattice distortion by the introduction of the impurity ion^[2]. This theory, however, describes poorly the results for the polyvalent metals Hg^[3] and Sn^[4]. For further development of the theory, it is necessary to have reliable experimental data for different metal matrices with as many investigated impurities as possible. Such information will help reveal more subtle empirical relations than the Linde rule observed on the basis of noble metals (which further study has shown not to hold in all cases), and will contribute by the same token to the development of a correct theory of the phenomenon in question.

It is indeed the diversity of the experimental data, which frequently disagree with each other in the results of different authors, and the scarcity of the data, which apparently hinder further development of the theory at the present time. To obtain reliable information on the variation of the residual resistivity $\Delta\rho/c$ per atomic per cent of dissolved impurity it is necessary to per-

form as a rule special investigations, as was done for the noble metals^[5], Al^[6], Hg^[3], and Sn^[4], since the preparation of a homogeneous solid solution in each metal has its own peculiarities. Otherwise, many obtained values of $\Delta\rho/c$ are unreliable for various reasons^[4]. We note that an obstacle to the acquisition of plentiful data on easy-melting metals is the non-solubility of most metals with high melting points, a situation we encountered in the case of tin, mercury, and, as will be shown here, also cadmium. The present paper, which is a continuation of our earlier publications^[3,4,7], is devoted to the study of the influence of 15 impurities on the resistivity ρ_0 of the polyvalent metal cadmium and to a comparison of the obtained $\Delta\rho/c$ with the existing theory.

THEORY

A neutral impurity atom placed in a metallic host leaves the metal, on the whole, neutral as before. The impurity atom, however, gives up valence electrons to the conduction band Z_{imp} , whereas the atom of the host metal matrix gives up Z_M electrons (Z_{imp} and Z_M are the valences of the impurity metal and of the base metal). As a result, the ion core of the impurity atom, placed in the metallic matrix, has a charge that differs from that of the core of the host-metal atom. This excess charge of the impurity core is screened at a relatively short distance by the conduction electrons. The Friedel sum rule^[1] expresses this excess charge in terms of the phase shifts of the conduction electrons scattered by the impurities:

$$\Delta Z = \frac{2}{\pi} \sum_{l=0}^{\infty} (2l+1) \eta_l(K_F), \quad (1)$$

where ΔZ is the excess ion charge and η_l is the phase shift of the l -th partial wave (in radians). Blandin^[8] generalized Friedel's sum rule to include scattering of Bloch waves and to include bands with nonspherical Fermi surfaces.

The residual resistivity of a metallic alloy in the

solid-solution region, per atomic per cent of dissolved impurity, is given with sufficient accuracy by the first-approximation solution of the Boltzmann transport equation

$$\frac{\Delta\rho}{c} = 9,0 \cdot 10^{15} \frac{\hbar K_F}{ne^2} \sigma(K_F), \quad (2)$$

where the wave vector K_F of the metal matrix, Planck's constant \hbar , and the electron charge e are in cgs esu, the scattering cross section $\sigma(K_F)$ is in cm^2 , and $\Delta\rho/c$ is in $\Omega\text{-cm/at.}\%$. Here n is the number of conduction electrons per atom. The scattering cross section $\sigma(K_F)$ can be expressed in terms of the phase shifts of the partial waves scattered by a spherically symmetrical potential^[9]:

$$\sigma(K_F) = \frac{4\pi}{K_F^2} \sum_{l=0}^{\infty} (l+1) \sin^2[\eta_l(K_F) - \eta_{l+1}(K_F)]. \quad (3)$$

Then, substituting in (2) the expression (3) for $\sigma(K_F)$, we obtain

$$\frac{\Delta\rho}{c} = \frac{2,73}{nK_F} \sum_{l=0}^{\infty} (l+1) \sin^2[\eta_l(K_F) - \eta_{l+1}(K_F)], \quad (4)$$

where K_F is in atomic units.

The wave vector K_F of electrons on the Fermi surface with energy E_F can be calculated in the free-electron approximation directly from the density γ of the solvent metal

$$K_F^2 = 2E_F = (3\pi^2 N_A Z_M A^{-1} \gamma)^{2/3}, \quad (5)$$

where N_A , Z_M , and A are respectively Avogadro's number, the valence of the solvent, and the atomic weight.

EXPERIMENTAL PART

In the main, the technique of preparing alloys based on cadmium and of measuring the resistivity of metallic samples in the form of cylindrical wires 5–10 cm long and 1–1.8 mm in diameter was the same as in the tin-base alloys^[4,7]. We shall discuss here certain technological features of the new metallic matrix.

The alloys were prepared from cadmium ~99.9999% pure with resistivity ratios in bulk $\delta_0 = R_0/R_{293} = (1-2) \times 10^{-5}$ and $\delta_{4,2} = (2-4) \times 10^{-5}$. Since the impurity concentration in the alloys could be determined only from knowledge of the initial batches of the two components, particular attention was paid to preventing loss of any component during the smelting. The impurity was alloyed with the cadmium in an inert atmosphere of high-purity helium in an ampule of molybdenum glass for 20–25 minutes at a temperature approximately 100° higher than the melting temperature of pure cadmium. The melt was mixed by constant stirring. At such a temperature (250–430°C) all the impurities with the exception of mercury and zinc can be regarded as non-volatile, so that there was no danger of losing some amount of them by evaporation. Usually a piece of impurity, placed in the sufficiently cold lower end of the ampule, was rapidly covered with molten cadmium at ~350°C. Such alloying was particularly important in the case of the zinc impurity. The series of alloys with the highly volatile mercury as impurity was prepared with greatest accuracy. To

this end, weighed pieces of cadmium and drops of mercury were kept in contact at room temperature in the evacuated ampule for 3–5 minutes, which sufficed to let the mercury wet the cadmium well and become partly dissolved on it, after which pure helium was admitted and the ampule was heated in an oven to 325–250°C. The melt was kept at this temperature for 5–6 minutes. Alloys with concentration ≥ 0.1 wt.% were prepared by melting directly the weighed components (the impurity content was not less than 20 mg in this case), and all concentrations lower than 0.1% were prepared by diluting an alloy containing $\geq 0.1\%$ impurity in pure cadmium. For greater assurance that a set of correct concentrations was obtained, this dilution was carried out in most cases for two alloys with different concentrations.

The obtained samples were homogenized by annealing at 250°C¹⁾ for 14–26 days. To prevent the samples from becoming oxidized by air at this temperature, they were placed in sealed glass ampules filled with pure helium. The chosen minimum annealing time (14 days), the significance of which was discussed in detail in^[7], was considered by us to be fully sufficient to homogenize the alloys, for the following reason. It is known that the homogenization processes are realized mainly by a diffusion-vacancy mechanism, and the closer the annealing temperature (t_{ann}) to the melting temperature (t_{melt}) of the solvent metal, the more rapid (exponential) these processes. We have therefore tried to use as high an annealing temperature as possible. For homogenization of a tin-based alloy, annealing at a temperature ~60°C lower than t_{melt} for two weeks turned out to be quite sufficient, and moreover could even be reduced by one-half^[4]. It can be assumed on this basis that annealing at ~70°C below t_{melt} for two weeks should also be quite sufficient. An indirect proof of the correctness of this statement is the fact that the resistance of a number of alloys (Ga, Ge, Pt) remains unchanged when the annealing time is increased to 25–27 days. Moreover, the annealing time can apparently be reduced to 6–7 days, since the points obtained for Cd-In alloys after six days' annealing fit well the main line $\delta_0 = f(c)$ obtained with 15 and 45 days' annealing.

After the annealing, the ampule and sample were cooled in liquid nitrogen, the end of the ampoule was broken, and the sample was extracted and mounted on a plastic block^[7] that was constantly cooled with liquid nitrogen. The electric resistance was then measured first in a helium bath at 4.2°K and then at room temperature. The samples were cooled to nitrogen temperature after a homogenizing annealing, to prevent rapid decomposition of the alloy at room temperature, and then to conserve the homogeneity of the solid solution as well as possible up to the instant when the resistance was measured in the liquid helium^[7].

To simplify the measurement procedure, we determined not the resistivity $\rho_{4,2}$ of the alloy, but its relative value, $\delta_{4,2} = R_{4,2}/R_{293}$. The minimal value δ_0 for the alloys was $\sim 1 \times 10^{-4}$. Therefore, the residual re-

¹⁾ Cadmium samples containing Zn, Cu, and Mg were annealed at ~280°C for 10–11 days.

sistivity δ_0 of most alloys having $\delta_{4.2} \geq 5 \times 10^{-4}$ was obtained by measuring the resistivity not at zero, but at 4.2°K, when it can be assumed with assurance that $\delta_{4.2} = \delta_0$. The value $\delta_{4.2} \sim 1 \times 10^{-4}$ of cadmium exceeds δ_0 by $\sim 10\%$ ^[10], and therefore the residual resistivity of five alloys with $\delta_{4.2} = (1-4) \times 10^{-4}$ was determined at 2°K, when $\delta_2 = \delta_0$. We note that for the purest alloys the resistance size effect^[11] in samples of 1–1.5 mm diameter was small (5–10%) and was therefore neglected. In the case of the series of alloys with Pb, Pt, and Rh, which were prepared from initially more contaminated cadmium with $\delta_{4.2\infty} = (6-8) \times 10^{-5}$, it was necessary to subtract from $\delta_{4.2} < 1 \times 10^{-3}$ of the alloy the value $\delta_{4.2} \sim 1 \times 10^{-4}$ corresponding to an initial sample of 1–15 mm diameter.

RESULTS

Solubility of elements in solid cadmium. It is known from the binary phase diagrams that only Mg, Hg, Ag, Au, and Zn have appreciable solubility in cadmium, and that of Sn and Pb is low ($\sim 0.25\%$)^[12]. Nothing definite is known concerning the solubilities of the remaining elements, although there are data indicating that 23 elements are not soluble in cadmium at 450°C, mainly the high-melting-point transition metals^[23]. For most alloys it was therefore necessary to find the solubility limit c_{lim} at 250°C from the kinks on the curves of Fig. 1, in analogy with the procedure used for tin-based alloys^[7]. These data are listed in Table I, from which it follows that all elements have negligible ($\leq 0.4\%$) solubility in solid cadmium, and for most

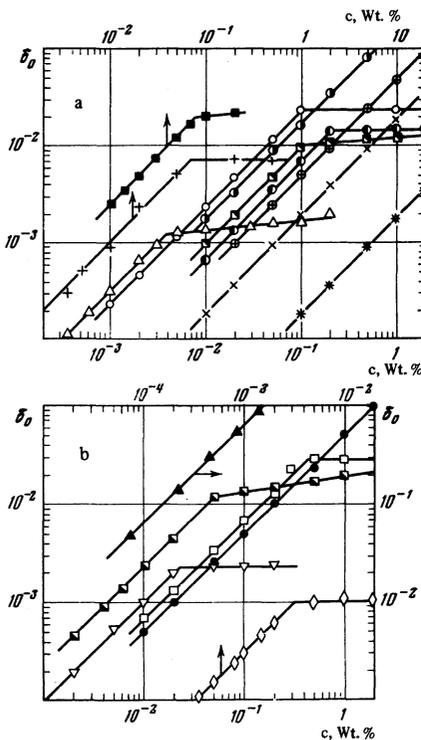


FIG. 1. Relative residual resistivity vs concentration c for 15 impurities in homogenized alloys: \square —In, \blacksquare —Tl, \blacksquare —Sn, \blacksquare —Pd, \circ —Rh, \bullet —Mg, \bullet —Cu, \diamond —Pb, $*$ —Hg, \oplus —Au, \bullet —Ag, Δ —Ge, ∇ —Pt, \times —Zn, \dagger —Ga, \blacktriangle —Mn^[14]. For most lines, the coordinates are marked on the lower and right-hand axes. In all other cases the arrows point of the appropriate axes.

Table I

Impurity element	c_{lim} , wt. %	(wt. %) ⁻¹	$\Delta\rho/c$, $\mu\Omega\text{-cm/at.}\%$	
			Our data	Published data
Pb	$3.3 \cdot 10^{-3}$	0.3	4.17	—
Mn	≤ 0.1	≥ 1	≥ 3.7	2.45 ^[14] *
Sn	$5 \cdot 10^{-2}$	0.25	2.0	0.007 ^[15]
Pd	$8 \cdot 10^{-2}$	0.25	1.78	—
Rh	0.1	0.23	1.58	—
Ge	$4 \cdot 10^{-3}$	0.3	1.47	—
Pt	$2.3 \cdot 10^{-2}$	0.1	1.31	—
Tl	0.1	$9.5 \cdot 10^{-2}$	1.30	—
Au	—	$4.8 \cdot 10^{-2}$	0.64	—
In	0.4	$7 \cdot 10^{-2}$	0.54	—
Ga	$7 \cdot 10^{-2}$	0.1	0.47	—
Ag	—	$5 \cdot 10^{-2}$	0.36	—
Cu	0.2	$6.6 \cdot 10^{-2}$	0.28	—
Mg	—	0.17	0.28	0.4–0.45 ^[16]
Hg	—	$1.7 \cdot 10^{-2}$	0.24	1.0 ^[17]
Zn	—	$1.8 \cdot 10^{-2}$	0.08	0.018; 0.027 ^[18] ; 0.026 \pm 0.002 ^[15] ; 0.016 \pm 0.004 ^[17]

Note. The alloys were annealed at 250°C, with the exception of Cu, of Cu, for which the annealing was at 280°C. Alloys containing Sn were annealed also at 185°C, corresponding to $c_{lim} = 0.02\%$. For In, Tl, Ga, and Mn, the values of c_{lim} are estimated at 0.09%, 0.015%, 0.01%, and $\leq 0.1\%$, respectively, at 320°C, since all these alloys were weakly doped and were rapidly cooled to room temperature after solidification. They were not subjected to high-temperature annealing.

*This mean value was obtained by using minimal values of R_T/R_{293} and corresponding to 6 concentrations (0.014–0.38 at. %) Mn, obtained by us from the plot of δ_T vs T .

impurities c_{lim} could be determined by using the method of residual resistivity. To establish the degree of solubility of some other metals in solid cadmium, a small piece of the investigated impurity was kept in molten cadmium for 25–40 min at 350–400°C in a helium atmosphere. The sample was then prepared and its $\delta_{4.2}$ measured. It turned out that Mo, Nb, Ta, V, Ti, and Cr caused no change whatever in $\delta_{4.2}$ of pure cadmium, the impurities W, Al, Fe, and Te increased $\delta_{4.2}$ to 1×10^{-4} , while C increased $\delta_{4.2}$ to 3.4×10^{-4} . On the basis of these data and of the purity of the initial cadmium, it can be assumed that the solubility of most of these metals is $< 1 \times 10^{-4}\%$ and that of cobalt is $\sim 1 \times 10^{-4}\%$, so that the influence of these metals on δ_0 of cadmium could not be investigated.

The annealed cadmium alloys containing As, Sb, and Ni were investigated in the concentration intervals $2 \times 10^{-3} - 0.1$, $1 \times 10^{-3} - 2$, and $2 \times 10^{-3} - 0.2$, respectively. For As and Sb, δ_0 had constant values 6×10^{-4} and $(1-3) \times 10^{-3}$, respectively, while for Ni we obtained a straight line inclined 3.5° to the abscissa axis, with δ_0 equal to 2×10^{-3} at the minimal concentration. Further study of $\delta_0(c)$ was hindered by the excessively low concentration, $(1-2) \times 10^{-3}\%$. All that could therefore be established for these impurities was that their solubility limit in cadmium at 250°C is smaller than or equal to the lowest concentration of the corresponding alloy²⁾.

An attempt was made to prepare an alloy containing $\sim 0.1\%$ Mn, by fusing 20 g of cadmium with 22 mg of

²⁾ If we use the proposed values $\Delta\rho/c = 3$ for As and 8.6 for Sb from the appropriate equations in Table II below at $\Delta Z = 3$, corresponding to $\delta_0 = 6 \times 10^{-4}$ and $(1-3) \times 10^{-3}$, then we can estimate c_{lim} . This turned out to be about 7×10^{-4} for As and $1 \times 10^{-3} - 3 \times 10^{-4}$ for Sb, which agrees well with the proposed values given in Table I.

Mn at 400–700°C for 40 min. As a result, all the Mn was dissolved (not less than 80% of the initial weight as observed visually). This indicates that the solubility of Mn in cadmium is low and apparently does not exceed 0.1% at ~320°C. The cylindrical sample prepared from this alloy for the measurement of δ_0 was not annealed. Thus, 15 is the largest number of impurity elements whose influence on δ_0 of cadmium could be investigated with the employed procedure to prepare the alloys and to monitor their composition.

Determination of $\Delta\rho/c$. The concentration dependence of the relative residual resistivity δ_0 of solid alloys based on cadmium is shown in a logarithmic scale in Fig. 1. The data on δ_0 of Mn were taken by us from the plots of ρ against T for T_{\min} in^[14], where no mention is made of the annealing and of the procedure used to prepare the alloys, and a value $\Delta R_{4.2}/cR_{273} = 0.385/\text{at.}\%$ is cited. The Mn content was determined spectrally at only two unknown points. It is seen from Fig. 1 that for all 16 impurities the experimental points fit well straight lines inclined 45° to the coordinate axes (for some impurities these lines were observed below a definite concentration). The 45° inclination is the consequence of the linear dependence of δ_0 on the impurity concentration c ($\delta_0 = Bc$). To determine B with high reliability, the concentration interval was chosen to be large enough (1–2 orders of magnitude). Just as in the case of tin^[4], the concentration of the prepared alloys was either limited by the solubility or confined to a maximum 1–2%, above which not only ρ_0 but also ρ_{293} became dependent on c . The lower limit, on the other hand, was imposed by the value $\delta_{4.2} = 1 \times 10^{-4}$ or by the sufficiently large number of experimental points (8–10). The value of $\Delta\rho/c$ was determined by multiplying δ_0/c by the mean value of the resistivity of pure polycrystalline cadmium at room temperature, $\bar{\rho}_{293} = 7.55 \mu\Omega\text{-cm}$. The values of δ_0/c and $\Delta\rho/c$ are listed in Table I together with some information obtained from the literature for four impurities.

We see that satisfactory agreement (a difference by a factor 1.5) is observed only for Mg (experimental data dating from 1921). The difference for Zn and Hg is larger—by a factor of 4, and for Sn the results cannot be compared. We note that information on $\Delta\rho/c$ of the last three impurities were obtained by us for one concentration (Sn) or 2–3 concentrations (Zn, Hg) of the impurity and from the corresponding ρ_0 cited in the papers (the authors themselves do not give the values of $\Delta\rho/c$ and the published ones for Sn and Hg is apparently due to insufficient care in the preparation of the alloys and the small number of concentrations used in the published studies (for example, the alloy with Sn contains 3–5 times more impurities than the limiting solubility at 200°C). The large difference for Zn may be due also to the insufficient length (7–12 days) of the homogenizing annealing at 200°C in all three papers, and this should lead to a decrease of $\Delta\rho/c$ in comparison with the results for the homogeneous alloys^[7]. The values $\Delta\rho/c = 2.45$ and > 3.7 for Mn are apparently not final and should increase after a homogenizing annealing.

As shown by us earlier in the case of tin^[7], an important role is played in the determination of the cor-

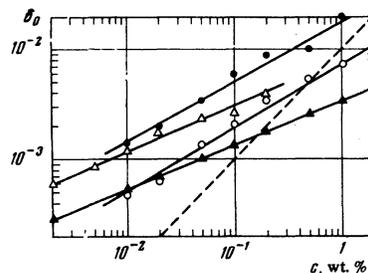


FIG. 2. Relative resistivity δ_0 vs c for non-annealed alloys containing: ●—Cu, Δ —Ge, \circ —Zn, \blacktriangle —Sn. The dashed line is inclined 45°

rect $\Delta\rho/c$ is played by homogenizing annealing of the samples immediately before the measurement of δ_0 . Figure 2 shows four series of cadmium samples with Cu, Ge, Zn, and Zn impurities, in which there was no linear dependence on the concentration c prior to annealing, so that the inclination angles of the lines, plotted in a logarithmic scale, are less than 45°. All the samples were measured several days after they were prepared. The angles of the lines obtained for the alloys with Ge and Sn equal 23°, and those for Cu and Zn are 28° and 30°, respectively (average ~26°). In the case of Ag, Rh, Pd, Au, and Mg, the angles of the lines are 41–43°. After two weeks of annealing at 250°C, the resistivity δ_0 of all these alloys fitted well a straight line inclined 45° (see Fig. 1). We note that in the case of Hg and Pt annealing changed neither the angle nor the value of $\Delta\rho/c$ itself, and in the case of In this quantity without annealing is ~45% lower than after annealing. We see thus that for cadmium alloys, just as for the tin alloys, it is very important to homogenize by annealing. It is still unclear, however, why for some alloys δ_0 depends linearly on c even before annealing (angle 45° in logarithmic coordinates), and in others only after homogenization, and also why for some alloys the angle of the line prior to annealing differs little from 45°, and for others it differs greatly. Nonetheless, the results show that the previously observed relation $\delta_0 = Ac^{1/2}$ (angle of line 26°)^[16] for alloys based on cadmium is due to the absence of homogenization by annealing. It is obvious that for the same reason a nonlinear dependence of δ_0 on c was observed for zinc-based alloys^[19,20].

DISCUSSION OF RESULTS

The Linde rule. To verify the validity of the Linde rule, the obtained values of $\Delta\rho/c$ are shown in Fig. 3

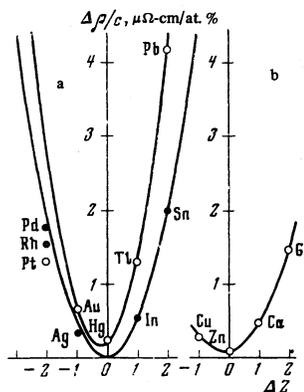


FIG. 3. Residual resistivity per atomic per cent of impurity vs the difference between the valences of the impurity and of cadmium; a—periods V and VI, b—period IV.

Table II

Period No.	Equations describing solid curves in Fig. 3	Coordinates of the minimum of the curve
IV	$\Delta\rho/c = 0.30(\Delta Z)^2 + 0.096\Delta Z + 0.08$	$\Delta Z = -0.16; \Delta\rho/c = 0.07$
V	$\Delta\rho/c = 0.49(\Delta Z)^2$	$\Delta Z = 0; \Delta\rho/c = 0$
VI	$\Delta\rho/c = 0.82(\Delta Z)^2 + 0.35\Delta Z + 0.19$	$\Delta Z = -0.21; \Delta\rho/c = 0.15$

as functions of ΔZ (the difference between the valences of the impurity and of the main metal). The solid lines are described by the equations given in Table II. The equations were obtained by least-squares reduction of the experimental points, with the transition-metal (Rh, Pd, Pt) impurities not taken into account. It is seen from Fig. 3 that for non-transition impurity metals the values of $\Delta\rho/c$ are well described by the parabolic equations listed in Table II. However, as in the case of alloys based on tin^[4], the Linde rule $\Delta\rho/c = a(\Delta Z)^2 + d$ is observed only for impurities that lie in the same period as the main metal. For impurities from other periods, a term linear in ΔZ appears in the dependence of $\Delta\rho/c$ on ΔZ . Attention is called also to the fact that, just as in the case of tin alloys^[4], for the periods that do not contain cadmium the positions of the minima of the curves shift to the left of $\Delta Z = 0$. However, if the alloy base is cadmium, whose valence is lower than that of tin (i.e., it is closer to noble metals, for which the Linde rule was established), this shift is smaller by a factor 5–7. We note that, unlike tin alloys, the coefficient a of $(\Delta Z)^2$ increases for the cadmium base with increasing number of the period.

Calculation of $\Delta\rho/c$ by the phase-shift method. The phase shifts were calculated in the same manner as in the earlier work^[3]. Since the residual resistivity of the alloy is insensitive to the form of the screening potential of the dissolved substance^[2], we choose it in the form of a square well of radius r_0 and depth $K_0^2/2$ (for the potential well we have $K_0^2 = (K')^2 - (K_F)^2$, and for the barrier we have $K_0^2 = (K_F)^2 - (K')^2$). The parameter r_0 was chosen equal to the radius of the Wigner-Seitz unit cell, which is connected with the Fermi wave vector K_F by the relation

$$K_F r_0 = (9\pi Z_M/4)^{1/3} \approx 1.92 Z_M^{1/3}. \quad (6)$$

The wave vector K' was obtained by choosing the phase shifts η_l at l equal to 0, 1, 2, 3, and 4 such as to satisfy the sum rule (1), assuming $K_F = 0.7468$ a.u. for cadmium. The results of such a calculation for ΔZ equal to -1, +1, +2, +3, and +4, performed with an ÉVM-20 computer, are given in Table III. Knowing the phase shifts, we calculated $\Delta\rho/c$ from formula (4), putting $n = 1$. These results are given in Table IV (fourth column). A comparison of the calculated values

Table III

ΔZ	K'	η_0	η_1	η_2	η_3	η_4	$\Sigma^* - \Delta Z$
-1	0.6735	-0.5664	-0.2363	-0.0505	0.0057	0.0004	$6 \cdot 10^{-9}$
1	0.8483	0.3928	0.2842	0.0567	0.0055	0.0003	$2 \cdot 10^{-9}$
2	0.9708	0.6451	0.5979	0.1237	0.0112	0.0007	$6 \cdot 10^{-5}$
3	1.0675	0.8259	0.9047	0.2085	0.0172	0.0010	$5 \cdot 10^{-9}$
4	1.1507	0.9740	1.1710	0.3231	0.0241	0.0014	$4 \cdot 10^{-5}$

* Σ is the Friedel sum (the first part of Eq. (1)), obtained as a result of using the chosen phase shifts η_l .

Table IV

Impurity	ΔZ	$(\Delta\rho/c)_{\text{exp}}$, $\mu\Omega\text{-cm/at.}\%$	$(\Delta\rho/c)_{\text{calc.}}$, $\mu\Omega\text{-cm/at.}\%$			$N_2 = \Delta Z - 1.86\beta Z_M$	K' , at. un.
			$n = 1$ ($N = \Delta Z$)	$n = 1^*$ ($N = N_2$)	$n = n_{\text{eff}} = 0.60$ ($N = N_2$)		
Cu	-1	0.28	0.65	0.18	0.31	-0.438	0.6564
Ag		0.36		0.42(0.41)	0.73	-0.741	0.6159
Au		0.64		0.41	0.71	-0.733	0.6170
Mg		0.28		0.004(0.01)	0.007	-0.094	0.7297
Zn		0.08		0.08	0.14	0.364	0.7922
Hg	0	0.24	0	0.004(0.001)	0.007	-0.094	0.7297
Ga		0.47		0.58	1.00	1.113	0.8644
In		0.54		0.23	0.40	0.741	0.8142
Tl		1.30		0.14	0.24	0.594	0.7973
Ge		1.47		1.55	2.68	1.937	0.9229
Sn	+2	2.00	1.69	1.09	1.89	1.688	0.8888
Pb		4.17		0.81	1.40	1.496	0.8657

*The parentheses contain the resistances computed with N_2 determined from Eq. (7). The values of $\delta\alpha/\alpha$ averaged over the orientation were defined as $1/3(2\Delta a/a + \Delta c/c)$, where a and c are the cadmium-lattice parameters along and across the six fold axis.

of $\Delta\rho/c$ with the experimental ones shows good agreement for Au, Ga, In, Ge, and Sn and satisfactory agreement for Cu, Ag, Pb, and Tl (difference by a factor 2–3). This method, however, “does not distinguish” that the individual peculiarities of impurities have the same valence.

Has shown by Blatt^[2], allowance for the distortion of the metal-matrix lattice by introduction of the impurity atoms leads, in the case of noble metals, to a better agreement between theory and experiment. In this case ΔZ in (1) should be replaced by N_2 :

$$N_2 = \Delta Z - \frac{1 + \sigma \delta\alpha}{1 - \sigma \alpha} Z_M, \quad (7)$$

where σ is the Poisson coefficient obtained under the assumption that the lattice is an elastic continuum; this coefficient is equal to 0.30 for cadmium^[21]. $\delta\alpha/\alpha$ is the relative change of the lattice parameter of the alloy in per cent per atomic per cent of the dissolved matter. The screening radius r' (with allowance for the lattice distortion) will now be connected with the preceding radius r_0 by the relation

$$r' = r_0 \left[1 + \frac{1 + \sigma \delta\alpha}{1 - \sigma \alpha} \right]^{1/2}, \quad (8)$$

which is used in the determination of η_l . The difficulty in introducing this correction lies in the fact that information on $\delta\alpha/\alpha$ is known only for Ag, Mg, and Hg^[22]. The results of the calculation are given in Table IV (fifth column), which an improvement for Ag and a very large deviation for Mg and Hg. To supplement the missing experimental data for $\delta\alpha/\alpha$ we replaced, just as in^[4,23], $\delta\alpha/\alpha$ by the quantity $\beta = (V - V_0)/3V_0$, where V and V_0 are the atomic volumes of the impurity and the host metal, respectively, although such a replacement is not quite accurate ($V_0 = 2.17 \times 10^{-23}$ cm). We chose for this case new values of K' (and the corresponding new phase shifts) and again calculated $\Delta\rho/c$ at $n = 1$ (see Table IV). It is seen from Table IV that the use of the parameter β improved the agreement between calculation and experiment only for Cu, Ag, and Ge, and made it worse for Au, Ga, In, Tl, Sn, and Pb. This difference was not larger than by a factor of two for seven impurities, and by a factor 5 and 9 for Tl and Pb respectively, i.e., the agreement became in general worse. A particularly large discrepancy was observed for the homovalent

impurities Mg and Hg, regardless of whether the experimental value of $\delta\alpha/\alpha$ or β was chosen for the calculation. This indicates that allowance for only the lattice distortions by impurity atoms, for which $\Delta Z = 0$, is patently insufficient to obtain relatively large values of $\Delta\rho/c$ commensurate with the experimental values. There obviously exist some other factors the allowance for which improves the agreement between theory and experiment for all ΔZ . To improve the agreement of the theory (with allowance for the lattice distortion via the quantity β) with experiment we chose n as the second fitting parameter (in addition to K'), as was done for Zn^[23] and for Sn^[4]. To this end we obtained by least squares the optimal n_{eff} , which is in satisfactory agreement with $n = 0.40$ obtained from the resistance size effect^[11], and coincides with n_{eff} for Zn^[23]. The values of $\Delta\rho/c$ using $n = n_{\text{eff}} = 0.60$ in formula (4) are given in Table IV. As expected, the agreement between the calculated and experimental values became better (in six out of nine cases), including the homo-valent impurities, than for those calculated with $N = N_2$ and $n = 1$.

In conclusion it can be stated that in the case of cadmium the phase-shift theory describes satisfactorily the available experimental data on $\Delta\rho/c$, and to a better degree than for tin. However, just as in the case of the tin alloys, allowance for the lattice distortion by the impurity atom is by far insufficient to improve the agreement between theory and experiment. Our calculation of $\Delta\rho/c$ with the aid of the known published pseudopotential form factors of Animalu^[24], Shaw^[25], and Shyu and Wehling^[26] has shown^[27] that the experimental values of $\Delta\rho/c$ (for nine impurities in cadmium and fifteen impurities in tin) differ greatly from the calculated values, namely, $(\Delta\rho/c)_{\text{calc}}$ is less than $(\Delta\rho/c)_{\text{exp}}$ in most cases (83%) by 1–2 orders of magnitude. All this leads to the conclusion that the question of calculating the residual resistivity of dilute metallic atoms per atomic per cent of the dissolved impurity is still open.

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