

Zeitschrift: Helvetica Physica Acta

Band: 41 (1968)

Heft: 6-7

Artikel: An experimental study of the resistivity-concentration dependence of alloys

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DOI: <https://doi.org/10.5169/seals-113963>

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An Experimental Study of the Resistivity-Concentration Dependence of Alloys

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(7. V. 68)

Abstract. The paper describes an experimental test of the concentration dependence of the additional resistivity of alloys applied to resistivity data for a number of Cu-, Ag- and Au-based alloys. The results obtained are compared with those required by the well-known resistivity-concentration rule of Nordheim, which according to the premises of Nordheim's theory expresses what should apply to alloy series with a random distribution of the alloy's atoms. The reported results display marked deviations from that rule in many cases, however, as well as agreement with the rule in some cases of the series. The reasons for the deviations observed are ascribed by the author to the well-known fact that the atomic distribution of metallic alloys frequently differs from that of an ideal random solid solution.

A formula for the resistivity-concentration dependence of alloys based on the experimental data of the investigation is proposed. The in the paper reported results also include renewed data for the atomic resistivity-increase for the alloy series treated. The work discusses also the effect of cold-working on the resistivity of the alloys.

1. Introduction

For systems of homogeneous random solid solutions the residual resistivity, $\Delta\varrho$, caused by a concentration c of solute atoms in the solvent metal is described by NORDHEIM's[1] concentration rule which we write here in the abbreviated form

$$\Delta\varrho = c (100 - c) F \quad (1)$$

where c is atomic percentage of the solute of a given binary alloy series, and F includes atomic constants and the remaining factors of the cross section of the impurity atoms.

According to Equation (1) the impurity-resistivity should for properly dilute alloys ($c/100 \ll 1$) be proportional to the concentration, c , which tallies fairly well with known experimental findings in this field. For non-dilute alloys, on the other hand, the resistivity-concentration dependence is not as a rule adequately described by (1). In fact the deviations occurring do not primarily concern the form of the $\Delta\varrho$, c relation which in reality is quadratic in c also according to experimental data up to moderately high c -values, in some cases 10 at.% or higher. They come instead into sight as divergencies in the absolute values of the coefficient for c^2 in the empirical relations compared with that appearing in (1). At still higher concentrations, c , other kinds of divergencies also appear. The reason for this non-conformity of Equation (1) to experimental data is most probably in the first place to be sought in the fact that the equation is properly adapted to conditions that are valid for a statistical distribution of the different atomic species on the lattice sites of the crystals while it now-

adays is generally recognized that deviations from that ideal form of distribution are often met with in alloys. These deviations as they come into sight in the resistivity properties of the alloys will be the main subject of the present investigation, which in addition includes some new determinations of values for the atomic resistivity-increase of the alloys at normal temperatures. A few data regarding the effect of cold-working on the resistivity of the alloys will also be reported.

2. Experiments

The available samples of mainly dilute alloys used by the author in the earlier investigations [2-5] have been completed for the present study with a number of alloys with appreciably higher solute concentrations, amounting, for some of the series, up to 20 at.%. After melting in sealed silica tubes the alloys were slightly cold-rolled and then homogenized by annealing for some hours at a high temperature. The need of an extension of the concentration region of the alloys for the present problem appears from the above-mentioned fact that the $\Delta\varrho, c$ relationship changes character in the higher concentration region. The measurements then also allow a higher accuracy in the determination of the atomic resistivity-increase ζ for the alloy series.

The resistance measurements occurred with a Thomson bridge at room temperature, occasionally also at 0 and 100°C for obtaining the resistance-temperature coefficient of the samples. The resistivities of the alloys drawn into wires were measured in the cold-worked state as well as after annealing in the 600-400°C temperature region in some cases also after annealing below 400°C.

We infer from the form of Equation (1) that for an alloy series to fulfil Nordheim's concentration rule regarding its resistivity properties it is necessary that the quantity $\Delta\varrho/c$ plotted against c must give a straight line the slope of which should be given by the quantity F in (1). A quantitative test of the rule can accordingly be achieved as follows: The $\Delta\varrho$ -values obtained as differences between the resistivity values of the alloys and that of the pure base metal for a certain temperature (20°C) are divided by the concentration value, c , and then plotted for each alloy series versus c . In the cases where the graphical representations of that kind (Fig. 1) result in straight lines, data for the atomic resistivity-increase, ζ , of the series are evaluated by extrapolating the lines to intercept the $\Delta\varrho/c$ axis. Deviations from Nordheim's rule may, however, exist for a given series notwithstanding an observed straight-line character of the experimental curves. These deviations can be visualized by plotting the corresponding theoretical curves given by Equation (1) in the same system of co-ordinate axes. This procedure will be further elucidated below.

3. Results

3.1. The Series $AuCu$, $AgCu$, $AgAu$, $AuAg$, $CuZn$, $AgZn$, $AuZn$ and $AgCd$. Development of the Formula for the Resistivity-concentration Dependence of Alloys

In the notations of alloy series employed in the present study the first component of the formula means the solvent of the series. The essential features of the resistivity-concentration relation for alloys according to results of the present experiments appear from the set of data given in the diagrams of Figure 1. The series represented in

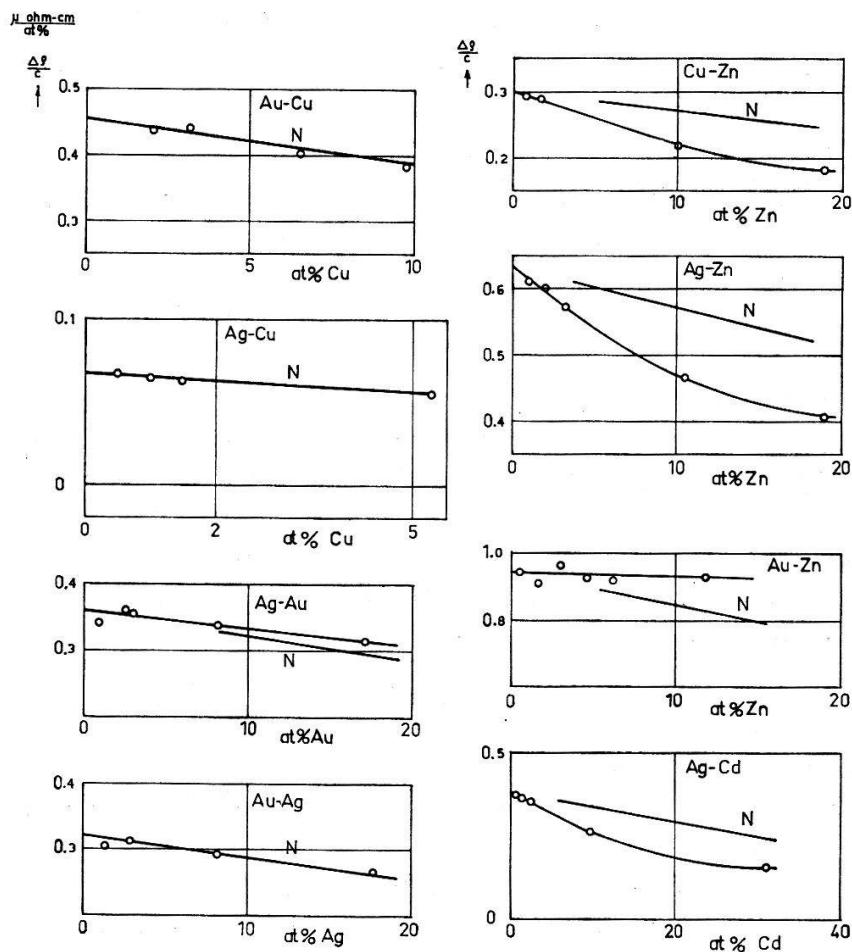


Figure 1

The $\Delta\varrho/c$, c relations for alloys containing an element with the valence of 1 or 2 as the solute.

this figure have been investigated up to a fairly high concentration of the solute elements. We recognize in the reproduced diagrams an initial straight-line behaviour of the curves, in some cases up to about 10 at.% of the solute, in others to essentially lower values, while the curves later in the course exhibit a marked upward-bend. It will be made clear below that the slope of the straight-line parts of the curves usually deviates from that required by (1), the magnitude of the deviations varying from alloy series to alloy series: For a quantitative analysis of the behaviour of the resistivity lines to the requirement of Nordheim's rule we proceed as follows: To begin with we put the atomic resistivity-increase, ζ , as a factor in Equation (1). This quantity we define by

$$\zeta = \lim \left(\frac{\Delta\varrho}{c} \right)_{c=0}. \quad (2)$$

Applied to (1) this gives

$$\zeta = 100 F. \quad (2a)$$

The divergencies in the slopes of the straight-line parts of the different curves in the graphs of this paper we take into consideration by introducing a factor A in the coefficient for c^2 in Equation (1) which relation is then written

$$\frac{\Delta\varrho}{c} = \zeta \left(1 - \frac{A c}{100} \right). \quad (3)$$

We determine conventionally the ζ -values of the series by extrapolating the lines concerned to intercept the $\Delta\varrho/c$ axis, while values of A are obtained from the slopes of lines. The data thus obtained are collected in Table 1 of Section 5. Also shown in Figure 1 for each alloy series are the theoretical lines deduced from (1) and corresponding to $A = 1$ in (3). They reproduce an assumed agreement with Nordheim's rule. These lines are denoted in the graphs by the letter N . The deviations from Nordheim's rule appearing as differences in the slopes of the experimental lines relative to the theoretical ones can evidently be expressed quantitatively as the differences of the experimental A -values from the number one.

A completion of (3) to apply also in the region of non-linearity of the curves appearing in the graphs can be achieved by adding terms of a higher degree in c to the given form of the equation. In a note published by J. S. LANGER and T. NEAL [6]

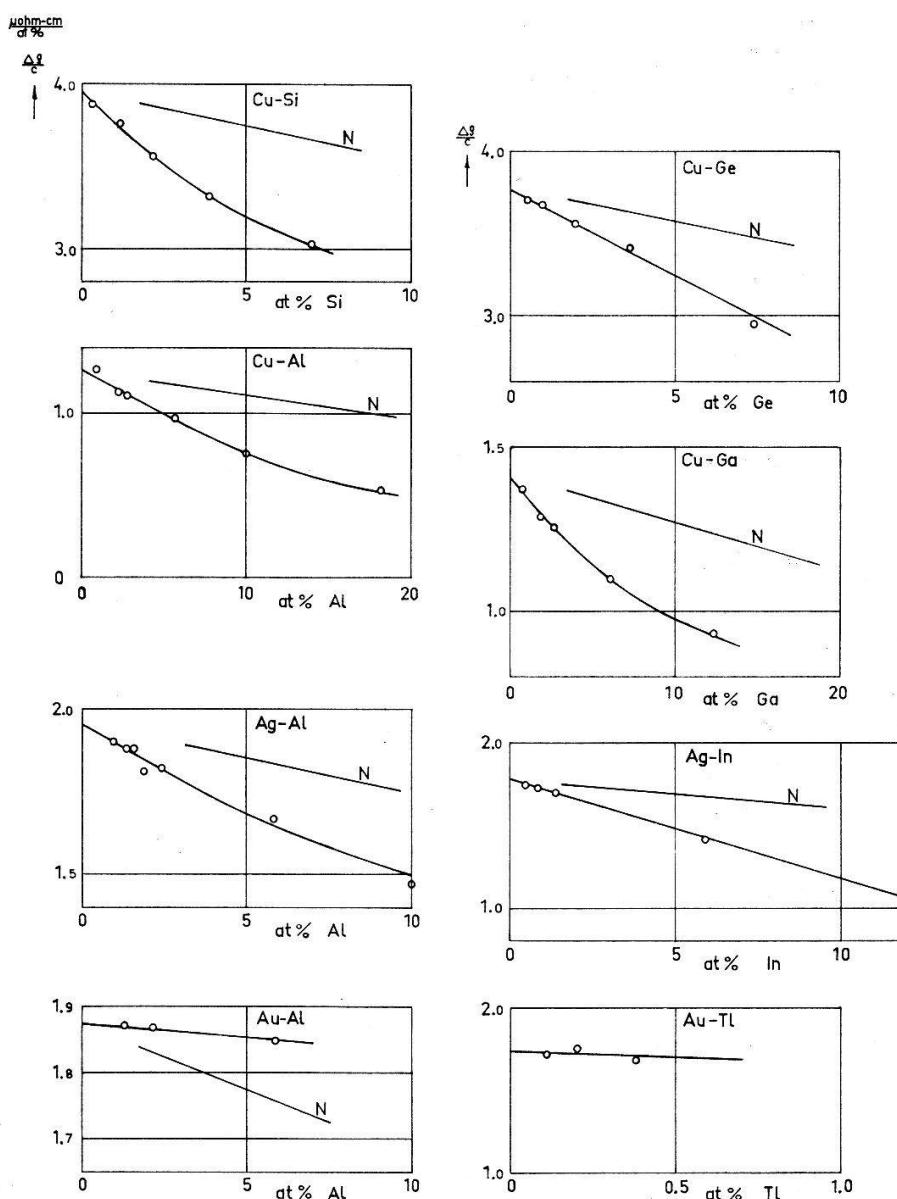


Figure 2

The $\Delta\varrho/c, c$ relations for alloys containing a b -element with the valence of 3 or 4 as the solute. *Note added in proof.* In the CuGa diagram the ordinate value at 12.25% Ga should read 0.80.

the authors claim that the leading term above that of c^2 in the expression for $\Delta\varrho$ should on theoretical grounds be of the form $c^3 \ln c$ instead of simply c^3 . Taking this theoretical requirement into account we write for the more complete form of (3)

$$\Delta\varrho/c = \zeta \left(1 - \frac{\Lambda c}{100}\right) - D c^2 \log \frac{c}{c_0} \quad (4)$$

where the quantity D is to be treated as a constant up to rather high values of c , generally not exceeding, however, 50 at.-%.

For lack of possibility to calculate theoretical values of D we restrict the testing of (4) to cases of alloy series where a value for D could be obtained empirically on the basis of the experimental $\Delta\varrho$ -value for an alloy of the series with a rather high concentration of the solute, the standardized $\Delta\varrho$ -value of the alloy being inserted in (4) in the calculation.

By way of further information we add the following remarks regarding the quantities appearing in (4). The purpose of the reference concentration, c_0 , of the equation is to render the number c , which is to be taken the logarithm of, free of physical

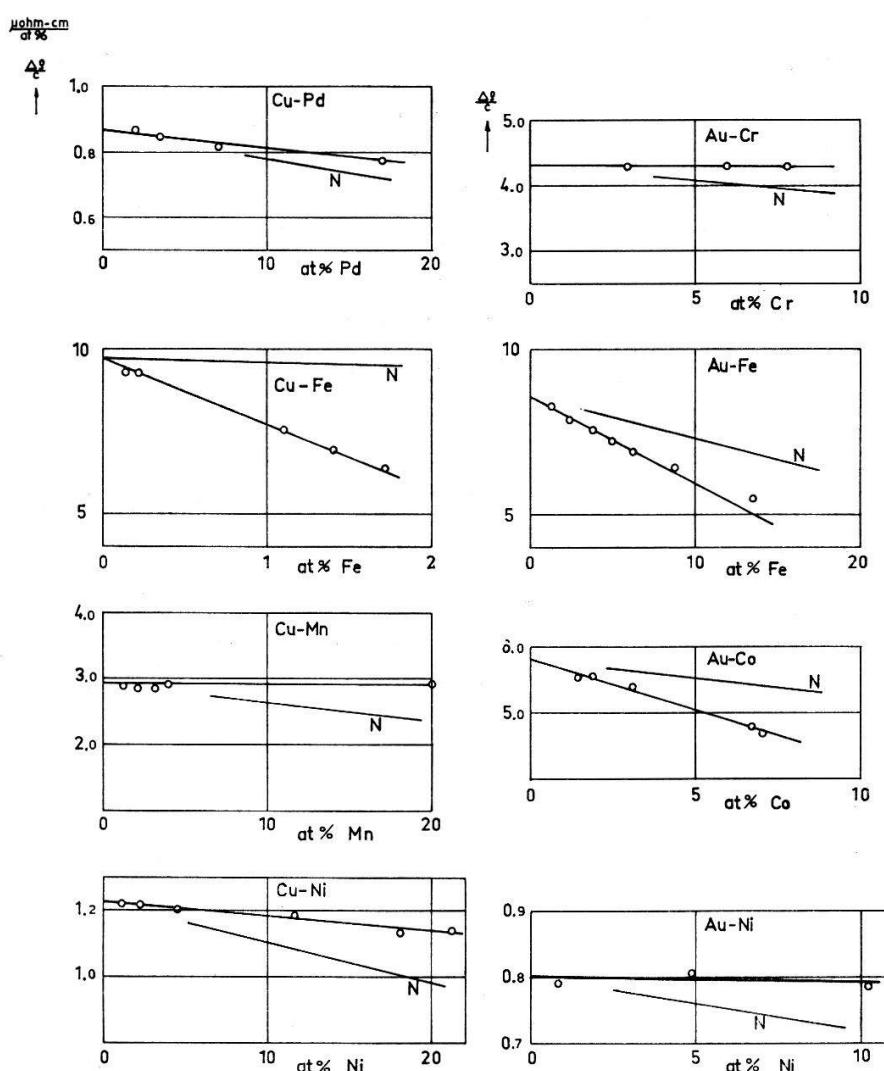


Figure 3

The $\Delta\varrho/c$, c relations for alloys containing a transition metal mainly of the first long period of the periodic table as the solute element.

dimensions. We have further to take into consideration that in the logarithmic factor of the equation the concentration values are to be entered in the unit of atomic fraction. This requirement is evidently fulfilled by adopting $c_0 = 100$ in (4), while the quantity c of the equation quite adequately is generally expressed in the unit of atomic per cent.

3.2. *The Series CuSi, CuAl, AgAl, AuAl, CuGe, CuGa, AgIn and AuTl*

Figure 2 gives $\Delta\varrho/c$ versus c for a number of Cu-, Ag- and Au-alloys pertaining to the group which has an element with the valence of 3 or 4 as the solute. Included in the figure are also the theoretical N -lines of the series applying to (1). We observe remarkably large deviations from Nordheim's rule for most of the series. Respecting the sign of the deviations we note that with exception of the series AuAl the absolute values of the slopes are larger for the experimental lines than for the theoretical ones. The numerical values of ζ and Λ evaluated for the different series are collected in Table 1 (Section 5). As regards the AuTl series it should be remembered that the solubility of Tl in Au is very low, which fact puts a determination of Λ for that series in the present investigation out of question.

3.3. *The Series CuPd, CuFe, CuMn, CuNi, AuCr, AuFe, AuCo and AuNi*

The solutes of the alloys of this section are transition elements from the first long period of the periodic table and in addition Pd belonging to the second long period of the table. The $\Delta\varrho/c$ data of the series are given in the diagrams of Figure 3. The results for the alloys of these metals apparently agree in their general character with those met with for the series of the preceding sections. The absolute values of the slopes of the experimental lines are, however, for most alloy series with a transition metal as the solute lower than for the corresponding theoretical lines, while the converse situation usually applies to alloy series with a *b*-metal as the solute.

4. Views on the Effect of Cold-Work on the Resistivity of the Alloys

The resistivity data given in the preceding sections refer generally to annealed specimens. The alloys had previous to the annealing been cold-worked to a degree of about 90%. The difference between the resistivity values at 20°C before and after that annealing we take as a measure for the resistivity cold-working effect related to a working-degree of the said 90%.

The most common effect of cold-working implies an increase of the resistivity values. Exceptions to this rule are, however, in this investigation, certain Au-based alloys in the first place those of the series AuCr and AuFe [4]. In these alloys cold-working causes a marked decrease of the resistivity, implying a negative value of what we can call the cold-working resistivity-coefficient of the alloys.

These effects have been the subject of isolated investigations in earlier works by the author [2-5]. More recently the problems concerned have at a great length been studied experimentally by KÖSTER and co-workers in Stuttgart [7-10].

A result of special interest achieved originally by the Stuttgart group is the discovery that a slight change in the resistivity occurs for most of the alloys investigated when annealed in the temperature region below about 400°C. This effect is inter-

preted by the authors as being caused by a short-range-order of the atoms developed by the annealing process. Taking into account the available publications by the mentioned authors, which concern the same class of alloys as those treated in the present investigation, we confine the presentation of our results to the discussions given above and in section 6.

5. Empirical Data for the Studied Quantities

Values of the quantity D of Equation (4) have been evaluated by the method outlined in Section 3.1 for a number of alloy series and are collected in Table 2. The table contains also calculated values of $\Delta\varrho/c$ for the non-dilute alloys of each series

Table 1

Compiled data for the atomic resistivity-increase, ζ , and the constant A of Equation (3) for the alloy series measured at 20 °C. Several of the series included in the table are not represented in the data of Figures 1-3.

Solvent	Cu		Ag		Au	
	ζ $\mu\text{ohm}\cdot\text{cm}$	A (at. fraction) $^{-1}$	ζ $\mu\text{ohm}\cdot\text{cm}$	A (at. fraction) $^{-1}$	ζ $\mu\text{ohm}\cdot\text{cm}$	A (at. fraction) $^{-1}$
Solute	at. %	at. %	at. %	at. %	at. %	at. %
Mg	0.6	—	0.5	2.8	1.30	1.2
Al	1.25	4.5	1.95	3.0	1.87	0.6
Si	3.95	4.9	—	—	—	—
P	6.7	—	—	—	—	—
Ti	—	—	—	—	12.9	—
V	—	—	—	—	12.6	—
Cr	(4.0)	—	—	—	4.30	0
Mn	2.90	0	1.60	0	2.41	0
Fe	9.66	20	—	—	8.5 (7.9)	3.1
Co	6.3	—	—	—	5.8 (6.1)	2.8
Ni	1.22	0.3	—	—	0.80	0.1
Cu	—	—	0.07	—	0.45	1.6
Zn	0.30	2.7	0.63	3.0	0.94	0
Ga	1.40	4.2	2.36	2.5	2.2	—
Ge	3.76	2.8	5.5	2.2	5.1	1.8
As	6.8	—	8.5	—	(8.0)	—
Zr	11.0	0	—	—	—	—
Rh	4.3	1.1	—	—	4.2	—
Pd	0.86	0.6	0.44	0.7	0.41	0.5
Ag	0.12	—	—	—	0.32	1.3
Cd	0.20 (0.30)	—	0.38	3.4	0.63	2.9
In	1.05	2.4	1.78	3.4	1.35	4.0
Sn	2.88	3.2	4.36	2.6	3.3	1.1
Sb	5.4	—	7.2	—	6.8	—
Ir	5.7	—	—	—	—	—
Pt	2.15	0.7	1.7	4.4	1.0	0.3
Au	0.54	1.0	0.36	0.7	—	—
Hg	—	—	0.79	—	0.4	—
Tl	—	—	2.26	0.7	1.7 (1.9)	—
Pb	—	—	5.1 (4.6)	2.4	(3.9)	—
Bi	—	—	(7.3)	—	(6.5)	—

obtained by means of (4) with the empirical D -values of the given series inserted in the equation. For the sake of comparison the corresponding experimental $\Delta\varrho/c$ -values are also included in the table.

Table 1 gives a summing up to numerical data obtained in this investigation for the atomic resistivity-increase, ζ , at 20°C in the studied alloy series as well as those of the constant Λ entering into Equation (3). To these data we add a few remarks. The values given for the atomic resistivity increase, ζ , in the table, generally show no conspicuous deviations from those earlier reported by the author, some of the appearing differences fall, however, outside the limit of accuracy of the present measurements. These cases are marked by also presenting the earlier ζ -values within parenthesis in the table. In cases characterized by a fairly narrow concentration region of the α phase of the alloy series no determination of values for Λ has been achieved. This restriction generally applies to those alloy series which contain an element with a valence of 5 as the solute. Data of Λ are therefore lacking for such alloy series in Table 1. We observe there the anomaly high value of Λ for the CuFe alloys. Results of primary paramagnetic measurements [11-12] indicate that the anomaly of the atomic distribution in this case most probably is due to clustering.

Table 2
Data for the quantities D and $\Delta\varrho/c$ of (4) as applied to the upper concentration region of the alloy series.

Alloy series	at. % solute	$D \times 10^4$ $\mu\text{ohm}\cdot\text{cm}$ (at. %) ³	$\Delta\varrho/c$ $\mu\text{ohm}\cdot\text{cm}$		Alloy series	at. % solute	$D \times 10^4$ $\mu\text{ohm}\cdot\text{cm}$ (at. %) ³	$\Delta\varrho/c$ $\mu\text{ohm}\cdot\text{cm}$	
			calc.	exp.				calc.	exp.
CuSi	2.10		3.55	3.56	CuGa	2.61		1.26	1.25
	3.86	7.4	3.22	3.32		6.04	9.1	1.08	1.09
	6.99		(3.02) ^{a)}	3.02		12.25		(0.80) ^{a)}	0.80
CuAl	5.6		0.98	0.975	AgZn	3.20		0.577	0.57
	10.0	11.8	0.80	0.76		10.5	5.3	0.49	0.47
	13.6		0.67	0.64		18.86		(0.407) ^{a)}	0.407
	18.1		(0.53) ^{a)}	0.53		9.71		0.28	0.26
CuZn	1.72		0.286	0.29	AgCd	19.79	3.5	0.22	0.19
	10.04	0.8	0.23	0.22		31.0		(0.153) ^{a)}	0.153
	18.92		(0.183) ^{a)}	0.183					

^{a)} Value used for the calculation of D .

6. Discussion

For an interpretation of the various resistivity effects studied in this paper a review of the most common facts regarding the nature of possible deviations from an ideal random distribution of the atoms of the alloys may be of essential interest. Among other things the following applies to this subject: In the cases where there is a tendency for the different atoms of a solid solution to surround themselves with identical neighbours a clustering is said to occur in the alloys. If, on the other hand, there exists a preference for dissimilar neighbours to the atoms this means that the alloy is apt to build up an ordered structure. If in the latter case the tendency is

confined to the immediate environment of a particular atom the alloy generally exhibits a short-range order (s.r.o.). According to a theory of FRIEDEL [13], s.r.o. should generally occur if a polyvalent metal is solved in a metal with a lower valence than that of the solute here concerned. Theoretical deductions by FLINN [14], on the other hand, give as result that s.r.o. should occur if the electron/atom ratio valid for the components of the alloy is less than 1.5, while in other cases clustering should occur. The responses of the alloys' electrical resistivity to these various disturbances of the atomic distribution is in the cases of clustering a decrease in this quantity while short-range-order is in some cases accompanied by a decrease, in others by an increase of the electrical resistivity. Most theories predict a decrease of the resistivity if the two components of a binary alloy have different valences but an increase if the valences are the same for both the components.

The implication of the quantity A in (3) we summarize as follows. A less than one means that the experimental $\Delta\varrho$ value is higher than the theoretical $\Delta\varrho$ value of a supposed alloy with ideal random distribution of the atoms. A greater than one on the other hand means that the experimental $\Delta\varrho$ value is lower than the theoretical $\Delta\varrho$ value. Results of the former kind ($A < 1$) evidently indicate a short-range order. Typical examples are AuCr, AuMn, CuMn, and AgMn. For AuCr this conclusion is further supported by the observed negative sign of the resistivity cold-work effect. The second kind of results ($A > 1$) can, however, be explained either by a clustering or a short-range order effect. Unfortunately a distinction between these both alternatives solely by means of resistivity measurements seems as yet not possible. Results of measurements of several other physical properties of alloys reported in the literature [15], however, favour the conclusion that short-range order, as a rule, applies to the atomic distribution of alloys. Somewhat varying definitions of that state seem, however, to occur in the literature.

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