

method⁹ of computing I - H curves, which neglects K_2 , is reasonably successful. Assuming I - H along $[111]$ as a basis, several points have been computed for I - H along $[011]$ and $[100]$. These are plotted on Fig. 1 and fall near the curves actually found.

One other peculiarity should be mentioned. As the temperature rises above room temperature the value of N which is apparently best at room temperature does not make the I - H curve rise vertically from the origin. A smaller value of N is called for. The variation of N with temperature for a typical case is as follows:

| Specimen | Temperature | N |
|----------|-------------|-------|
| K35 | 14°C | 0.761 |
| | 150 | 0.759 |
| | 298 | 0.754 |
| | 490 | 0.749 |

This variation makes W_0 uncertain, so that its values have not been presented in Table II. No satisfactory explanation for this behavior presents itself. It may be due to a variation in the thickness of a surface film magnetically very different from the interior. If so, the nature of this film and the factors upon which its thickness

⁹ N. S. Akulov, *Zeits. f. Physik* **67**, 794-807; **69**, 78-99 (1931).

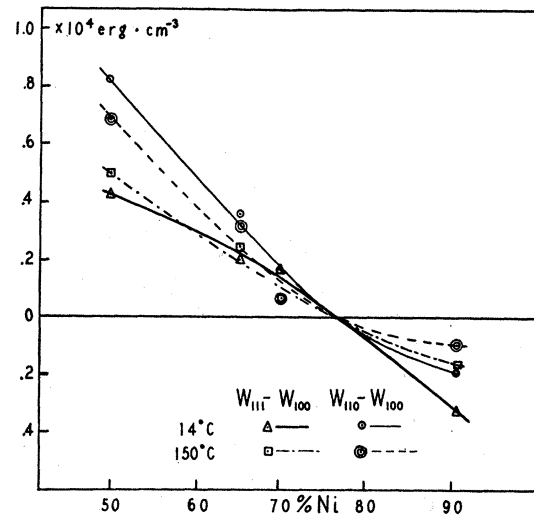


FIG. 5. Variation of energy differences with composition.

depends remain mysterious. A film of nonmagnetic material, everywhere of the same thickness, and thicker at higher temperatures, would change the apparent value of N in the observed manner.

It is with great pleasure that the author takes this opportunity to thank Professor L. W. McKeehan, who suggested this problem, for his advice and aid throughout the entire investigation.

Electrical Resistivity of Single Crystals of Some Dilute Solid Solutions in Zinc

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Sets of single crystals were grown of binary alloys consisting of dilute solid solutions of Cd, Cu, Ag, Au, Ni and Fe, each in zinc. Electrical resistivities at 20°C are expressed in terms of principal resistivities, ρ_0 and ρ_{90} , these values coming from the usual $\cos^2\theta$ (θ =orientation) plot of measured resistivities of a set of crystals. The resistance increases in a given series of alloys with increasing concentration, in a nonlinear fashion. The initial increase in

resistivity (above that of pure zinc) in micro ohm-cm per atomic percent of solute is: Cd 0.94, Cu 0.4, Ag 1.1, Au 2.3, Ni 51.0, Fe 300.0. This is correlated with the nearness of the solute metal to zinc in the periodic table. The ratio of principal resistivities is slightly higher than that for the zinc crystal. Temperature coefficients decrease in such a way that Mathiessen's rule is satisfied (with a maximum deviation of 4 percent) for all the alloys.

INTRODUCTION

THE resistivity and temperature coefficient of resistivity of dilute solid solutions of one metal in another have been studied frequently and the type of result to be expected is known at least qualitatively. Such studies in the past are apparently lacking for metals crystallizing in the nonregular system, probably due to the difficulty

of obtaining polycrystalline samples with grains oriented completely at random. It seemed worth while, therefore, to make a somewhat systematic study of single crystal samples, not only for the above reason, but because of the more fundamental nature of the approach using single crystals. Zinc was chosen as the solvent material. Binary alloys were made, each of zinc and some

TABLE I. Designation of alloys and concentration of the solute material.

| Designation of alloys | Percent by weight | | | Atomic percent | | |
|-----------------------|-----------------------|-------|-------|---------------------------|--------|--------|
| | | | | | | |
| Cd ₁ | 0.125 | | | 0.0721 | | |
| Cu _{1, 2, 3} | .125 | 0.250 | 0.500 | .1285 | 0.2571 | 0.5142 |
| Ag _{1, 2, 3} | .125 | .250 | .500 | .07575 | .1515 | .3030 |
| Au _{1, 2, 3} | .125 | .250 | .500 | .04144 | .08289 | .1657 |
| Fe _{1, 2} | .005 | .010 | | .00585 | .01171 | |
| Ni _{1, 2} | .005 | .010 | | .00557 | .01114 | |
| FeNi | .005 (Fe) + .005 (Ni) | | | .00585 (Fe) + .00557 (Ni) | | |

one other metal in various concentrations. The resistivity and the temperature coefficient of resistivity from 0° to 40°C were measured for sets of single crystals of the unalloyed zinc and the various alloys.

PREPARATION OF CRYSTALS

The zinc used was "Bunker Hill," a commercial zinc of exceedingly high purity, obtained from Platt Brothers and Company in the form of a single 50 lb. slab. By spectroscopic comparison with a test sample¹ of known purity it was estimated that the B. H. zinc contained: Cd, appreciably less than 0.0008 percent; Pb, slightly less than 0.0047 percent; Cu, slightly less than 0.002 percent; Ni, Au and Ag, none detected; Fe, appreciably more than 0.0004 percent (estimated by resistivity data, as shown later, to be about 0.002 percent), altogether certainly less than 0.01 percent impurity.

Binary alloys were made of zinc and certain selected concentrations of each of the following: Copper, silver, gold, iron, nickel and cadmium. See Table I. The method of preparation was usually to add to a known weight of the molten zinc the appropriate weight of the second constituent. Occasionally the most concentrated alloy (of a series) was first prepared and the lesser concentrations made by dilutions from it. Where both methods were used to prepare a certain concentration a good check on their equality was obtained in terms of the resistivity measurements. A single ternary alloy (Fe Ni in Table I) was prepared by mixing in equal proportions by weight the 0.01 percent Fe and 0.01 percent Ni alloys, thus giving an alloy of 0.005 percent by weight of each.

For the pure zinc and for each alloy a set of single crystals (from four to six) was grown with

¹ A. W. Hanson, Phys. Rev. **45**, 324 (1934), Table I.

orientations evenly distributed within the possible range of orientation,² 0°–90°. The crystals were prepared as described by Cinnamon³ and in the same furnace. They were about 10 centimeters long and with trapezoidal cross-sectional area of about 0.65 cm². For the pure zinc Cinnamon's "growth conditions" were substantiated, but for each alloy it was found necessary to determine appropriate growth conditions, which were toward higher gradients for about the same rates of growth used by Cinnamon. Keeping the ratio of gradient to rate of growth constant solely by decreasing the rate of growth did not produce single crystals. Moreover, it was found that for the alloys of lowest concentration single crystals were grown more easily than for pure zinc, both because the width of the range of successful growth was increased and also because "optical mosaics,"⁴ were easily prevented. This was particularly noticeable with the smallest concentration (0.005 percent) of iron. With increasing concentrations growth conditions became more and more critical and it was not found possible to prepare a full set of crystals for greater concentrations than those given in Table I.⁵ Also in most cases the highest concentrations were close to the probable limit of solid solubility.

MEASUREMENT OF RESISTIVITY AND TEMPERATURE COEFFICIENT

The resistance of a known length (about 8 cm) of the crystal was measured by comparison with a standard resistance using the customary potentiometer set-up. The crystal was placed in a wooden box and allowed to come to a constant temperature (room temperature, about 25°C) before resistivity measurements were made. The temperature was measured to 0.01 degree C by three thermocouples placed at each end and in the middle below the crystal. The distance between the potential contacts on the crystal was measured with a micrometer microscope and the cross-sectional area of the same part was meas-

² The angle between the length of the specimen and the vertical axis of the crystal.

³ C. A. Cinnamon, Rev. Sci. Inst. **5**, 187 (1934).

⁴ H. K. Schilling, Physics **5**, 1 (1934) and **6**, 111 (1935); W. J. Poppy, Phys. Rev. **46**, 815 (1934).

⁵ With the exception of Cd, for which only one concentration was tried since a more thorough investigation would duplicate work known to be in progress elsewhere.

ured by the immersion method described by Hanson.⁶ Resistivity at 20°C was computed from these measurements and the temperature coefficient.

The temperature coefficient was measured by placing the crystal in a large, sealed, brass tube which was immersed in water. The temperature was again measured by means of three spaced thermocouples, the leads being brought out through a small brass tube joined on the larger one and projecting above the surface of the bath. Resistivity measurements were made at three temperatures. For the first, ice was placed in the water surrounding the tube and stirred with a mechanical stirrer until the temperature of the crystal was constant as measured by the three thermocouples. Water at about 40°C was then substituted for the ice water and when equilibrium conditions were reached a second measurement was made. The third measurement was made after the crystal had come to, and remained for some time at, the temperature of the room. A resistance-temperature plot of these three points lay, within experimental error, along a straight line. The temperature coefficients of at least three crystals of each concentration were measured. The results for each concentration appeared constant within possible experimental error, there being indicated in particular no evident dependence on orientation.

RESULTS AND DISCUSSION

The resistivities of the Bunker Hill zinc and the zinc-copper alloys are shown in Fig. 1, each

TABLE II. Principal resistivities in micro ohm-cm, their ratio and their difference, all at 20°C.

| Material | ρ_0 | ρ_{90} | ρ_0/ρ_{90} | $\rho_0 - \rho_{90}$ |
|-----------------|----------|-------------|--------------------|----------------------|
| B.H. Zn | 6.253 | 5.902 | 1.059 | 0.351 |
| Cd ₁ | 6.345 | 5.970 | 1.063 | .375 |
| Cu ₁ | 6.352 | 5.966 | 1.065 | .386 |
| Cu ₂ | 6.406 | 6.023 | 1.064 | .383 |
| Cu ₃ | 6.466 | 6.086 | 1.062 | .380 |
| Ag ₁ | 6.348 | 5.986 | 1.060 | .362 |
| Ag ₂ | 6.425 | 6.062 | 1.060 | .363 |
| Ag ₃ | 6.598 | 6.212 | 1.062 | .386 |
| Au ₁ | 6.357 | 5.988 | 1.062 | .369 |
| Au ₂ | 6.436 | 6.072 | 1.060 | .364 |
| Au ₃ | 6.608 | 6.219 | 1.063 | .389 |
| Fe ₁ | 6.450 | 6.070 | 1.063 | .380 |
| Fe ₂ | 6.590 | 6.203 | 1.062 | .387 |
| Ni ₁ | 6.301 | 5.940 | 1.061 | .361 |
| Ni ₂ | 6.336 | 5.954 | 1.064 | .382 |
| Fe Ni | 6.490 | 6.111 | 1.062 | .379 |

⁶ A. W. Hanson, Rev. Sci. Inst. 7, 109 (1936).

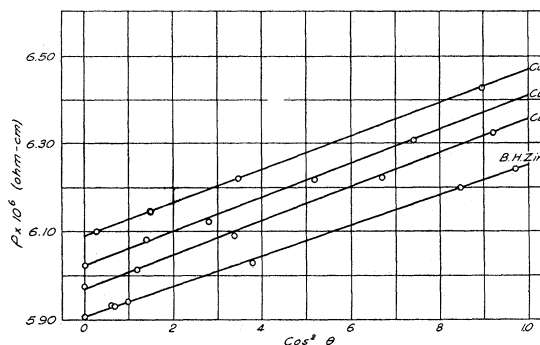


FIG. 1. Resistivity at 20°C as function of square of cosine of orientation θ for B.H. zinc and series of alloys containing copper. $Cu_1=0.129$, $Cu_2=0.257$, $Cu_3=0.514$ atomic percent.

plotted point representing one single-crystal specimen. Similar sets of curves were obtained for the other alloys. From these curves were read the values of the two principal resistivities, ρ_0 and ρ_{90} , parallel and perpendicular, respectively, to the vertical axis of the crystal. Table II includes these principal resistivities and other data for the B.H. zinc and the various alloys.

It will be noted that the ratio ρ_0/ρ_{90} is appreciably increased (about 0.4 percent) by the smallest addition of any solute and is not changed very much by further additions. The behavior of the difference $\rho_0 - \rho_{90}$ is not so regular. The first addition causes an increase (3 percent to 8 percent) but there is a further increase in some cases as additional alloying material is added. The writer thinks it exceedingly probable that all the alloys are solid solutions with the solute atoms replacing zinc atoms in an entirely random fashion. The initial changes in ρ_0/ρ_{90} and $\rho_0 - \rho_{90}$ show that the crystal is slightly altered, supposedly in lattice dimensions, from the true zinc lattice by the addition of small amounts of solute atoms. The disturbance due to further additions is not so marked, as witness the constancy of ρ_0/ρ_{90} . The alloy designated Fe Ni was prepared to check the additiveness of the resistance change. Thus considering ρ_{90} , the addition of 0.005 percent Fe (Fe₁) and 0.005 percent Ni (Ni₁) cause an increase in resistance of 0.168 and 0.038, respectively, summing to 0.206. For the Fe Ni the resistance change is 0.209 or the total effect of two additions is equal to the sum of the individual effects within experimental error.

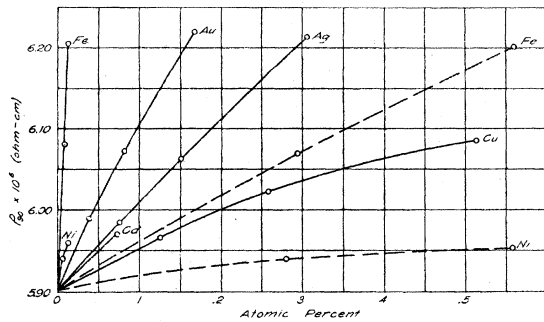


FIG. 2. Principal resistivity ρ_{90} at 20°C, as a function of atomic percent of solute. For dashed curves multiply abscissa scale by 2×10^{-2} .

Although it seemed unlikely that any type of "ordered alloy"⁷ would be produced with these small concentrations of solute, this possibility was tested. Since the attainment of an ordered condition would depend on the rate at which the alloys were cooled after solidification it might be that the cooling during growth of the crystals was too fast.⁸ A subsequent anneal and even slower cooling would test this point. Therefore, twenty-seven representative crystals had their resistivities remeasured several weeks after the first measurement.⁹ Twenty-four of these not only checked the first measurement but also showed no change in resistivity after two anneals, one at 200°C for 72 hours and the other at 400°C for 36 hours. The cooling to room temperature after these anneals was extended over

TABLE III. Relative effects of added elements.

| Material | Group | Initial $\Delta\rho$ per atomic percent | Reciprocal* effect |
|----------|-------|---|--------------------|
| Cd | 2 | 0.94 | |
| Zn | 2 | | |
| Cu | 1 | .4 | 0.29 |
| Ag | 1 | 1.1 | .5 |
| Au | 1 | 2.3 | .9 |
| Ni | 8C | 51.0 | |
| Fe | 8A | 300.0 | |

* The figures in the last column are taken from Norbury's work and show the reciprocal effect, i.e., one atomic percent of zinc in copper produces an increase in resistivity of 0.29×10^{-6} ohm-cm etc. Norbury's work was done with polycrystalline specimens.

⁷ W. L. Bragg and E. J. Williams, Proc. Roy. Soc. **A151**, 540 (1935).

⁸ Actually the crystals were left in the furnace for a period of fifteen hours while cooling from the melting point to room temperature.

⁹ First measurements were made directly after the growth of the crystals. The remeasurement was made, first as a check that no change had occurred due to a very slow relaxation at room temperature, and second to guard against possible changes due to accidental strains.

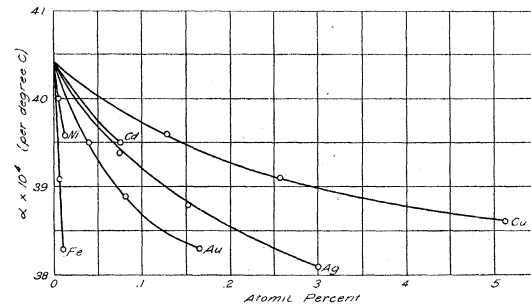


FIG. 3. Temperature coefficient of resistivity as function of atomic percent of solute.

about 48 hours. To test the reverse point, i.e., whether an ordered condition had been attained during growth of the crystals, seven crystals were kept at 400°C for 24 hours and then quenched to 0°C by dropping them into iced water. No departure from the original resistivity occurred. It, therefore, seems likely that a simple random arrangement is stable both for slow and fast cooling.

In Fig. 2 the resistivities are shown as a function of atomic percent of the solute materials. Only one of the principal resistivities, ρ_{90} , is plotted but the other, ρ_0 , would yield a similar plot. The relation between resistivity and concentration is definitely not linear, the effect becoming less for equal additions as the concentration increases. Nor do these curves fit a relation of the type proposed by Guertler:¹⁰ $R = R_0 + K(C - C^2)$ in which R_0 is the resistance of the pure solvent, K a constant, and C the concentration of the solute. The curves in fact bend towards the concentration axis more rapidly than the above relation predicts. The relative effects of the different added elements can be compared by computing (from the lowest concentration in each case) the increase in resistivity per atomic percent. This has been done and the results are arranged in Table III, the materials being listed in order of closeness to zinc in the periodic table, both horizontally and vertically. The data in the table could also be plotted to give a diagram similar to some given by Norbury¹¹ for various solutes in a single solvent metal.

The relation between temperature coefficient

¹⁰ W. M. Guertler, J. Inst. Metals **6**, 135 (1911).

¹¹ A. L. Norbury, Trans. Faraday Soc. **16**, 570 (1921) and J. Inst. Metals **33**, 92 (1925).

and atomic percent of solute is given in Fig. 3. The decrease in temperature coefficient with increased concentration and with the nature of the solute is very similar to the increase of resistivity previously discussed. The relation between these two effects is, however, brought out much better in Table IV, in which a test is made of Mathiessen's rule. This rule states that $\alpha_m \rho_m = \alpha \rho^{12}$ in which α_m and ρ_m are temperature coefficient and resistivity, respectively, of an alloy, computed solely by "law of mixtures" and α and ρ are the actual measured quantities for the same alloy. For all the above described work, α_m and ρ_m are practically exactly the values for pure zinc, because of the use of such small concentrations. Therefore, for Mathiessen's rule to be obeyed the product $\alpha \rho$ for each alloy should be constant and equal to the value for the solvent material. The constancy of the last column in Table IV shows excellent agreement with this rule. The maximum variation from the value for the solvent (2206) is about 4 percent.

The resistivity of the B.H. zinc was appreciably higher than the resistivity determined by Poppy⁴ for two samples of zinc of approximately the same grade of purity. Moreover, Poppy's

TABLE IV. Principal resistivity, ρ_{90} , at 0°C, temperature coefficient and their product.

| Material | ρ_{90} at 0°C | α | $\alpha \rho_{90}$ |
|-----------------|--------------------|----------|--------------------|
| B.H. Zn | 5.461 | 0.00404 | 2206 |
| Cd ₁ | 5.533 | .00395 | 2185 |
| Cu ₁ | 5.514 | .00397 | 2189 |
| Cu ₂ | 5.601 | .00390 | 2184 |
| Cu ₃ | 5.648 | .00386 | 2180 |
| Ag ₁ | 5.575 | .00392 | 2185 |
| Ag ₂ | 5.674 | .00385 | 2184 |
| Ag ₃ | 5.768 | .00381 | 2198 |
| Au ₁ | 5.568 | .00394 | 2194 |
| Au ₂ | 5.673 | .00387 | 2195 |
| Au ₃ | 5.777 | .00383 | 2213 |
| Fe ₁ | 5.630 | .00391 | 2201 |
| Fe ₂ | 5.762 | .00383 | 2207 |
| Ni ₁ | 5.500 | .00400 | 2200 |
| Ni ₂ | 5.517 | .00396 | 2185 |
| Fe Ni | 5.676 | .00383 | 2174 |

¹² See Hume-Rothery, *The Metallic State*, p. 51, but note that his α 's are temperature coefficients of conductivity. However, the similar relation for temperature coefficient of resistance is easily derived. It may also be shown that the relation $\alpha_m \rho_m = \alpha \rho$ follows by considering that the resistivity of the alloy is made up of two parts, one having the resistivity and temperature coefficient of pure zinc (for these small concentrations) and the other being an additional resistance unaffected by temperature.

TABLE V. Comparison of various samples of zinc.

| | ρ_0 | ρ_{90} | ρ_0/ρ_{90} | Fe lines detected |
|----------------|----------|-------------|--------------------|-------------------|
| E.W.B. (Poppy) | 6.161 | 5.842 | 1.055 | none |
| E.W.B. (Way) | 6.170 | 5.842 | 1.056 | none |
| E.W.R. (Poppy) | 6.218 | 5.882 | 1.057 | 18 ¹³ |
| B.H. (Way) | 6.253 | 5.902 | 1.058 | 37 |

two samples differed somewhat, which he attributed to a difference in the iron content. It seemed worth while therefore to check up on this point. A set of crystals was grown of the material of lower resistivity used by Poppy (designated E.W.B.) and their resistivities were determined. Spectrographic comparisons were made between this material, the B.H. zinc and the test sample¹³ previously referred to.

The results are summarized in Table V. It will be noted that the resistivities are qualitatively consistent with the difference in iron content. Moreover, the E.W.B. is practically iron-free. In the light of the present work the other impurities¹⁴ in any of the zincs are believed to have negligible effect on the resistivity. Also, the E.W.B. sample agrees very nicely in ρ_{90} with the determination of ρ_{90} for spectroscopically pure zinc,¹⁵ ($\rho_{90} = 5.847 \times 10^{-6}$ ohm-cm). Assuming thus that the values for E.W.B. are correct for 100 percent zinc, it is possible to extrapolate backwards from the iron resistivity-concentration curve (Fig. 2) and determine the actual iron content of the B.H. zinc. The result is that the B.H. zinc contained 0.0019 percent Fe.

Professor E. P. T. Tyndall's kind suggestions and cooperation in the development of this research problem are deeply appreciated by the author.

¹³ None of Poppy's material of higher resistivity (designated E.W.R.) was available. The test sample was said by Hanson (reference 1) to contain about the same amount of iron as the E.W.R. and it was used therefore in the spectrographic comparison.

¹⁴ Lead should perhaps be excepted since it is an impurity in all the samples of Table V. However, a second sample of B.H. zinc, obtained after the completion of this work and differing from the first only in the fact that it had less lead (2 lead lines, as against 8 in first sample), had precisely the same resistivity.

¹⁵ E. P. T. Tyndall and A. G. Hoyem, *Phys. Rev.* **38**, 820 (1931). The value quoted above is corrected to a density of 7.13 g/cm³, the authors having computed cross section of crystals by weighing a measured length and using a density of 7.15 g/cm³.