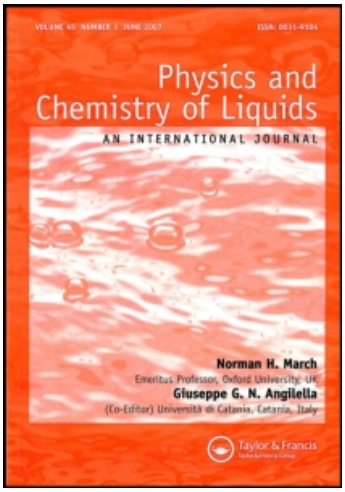

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S. Steeb[a]; U. Maier[a]; D. Godel[a]
[a] Max-Planck-Institut für Metallforschung Institut für Sondermetalle, Stuttgart

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Temperature- and Concentration-dependency of the Electrical Resistivity of Molten Ag-Mg-, Cu-Sb-, and Zn-Sn-alloys

S. STEEB, U. MAIER, and D. GODEL

Max-Planck-Institut für Metallforschung
Institut für Sondermetalle
Stuttgart

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Abstract—The electrical resistivity was measured in the liquid systems Ag–Mg, Cu–Sb, and Zn–Sn. With the eutectic system Zn–Sn the resistivity shows a convex smooth run between the values of the pure components. With the systems Cu–Sb and Ag–Mg the resistivity shows maxima at the concentrations of the solid intermetallic compounds. The relative superelevation of these maxima decreases with rising temperature, corresponding to the decay of "compound-molecules" in the melt.

With the system Zn–Sn the small maxima found by Roll and Motz could not be confirmed. Also no influence of the magnetic susceptibility on the run of resistivity *vs.* concentration could be detected during the measurements in a rotating field apparatus.

A convincing consistency of the measured values of the electrical resistivity in the system silver–magnesium with those values, which were obtained by calculation from X-ray data is shown.

1. Introduction

The number of papers published on measurements of the electrical resistivity with molten two component alloys is rather large and contained in the bibliographies.[1–4] The following results are essential :

1. The isothermes of resistivity always show a maximum at those concentrations, where intermetallic compounds exist.

2. At certain valency electron concentrations the run of isothermes of resistivity in two component alloys shows anomalies. The corresponding concentrations depend on the position of the components in the periodic table.

3. The run of resistivity *vs.* temperature shows a jump at the melting point and a positive or negative temperature coefficient in the molten state. The negative values especially are observed near intermetallic

compounds. Some hundred degrees above the liquidus however, the negative values change to positive ones.

In the present paper the number of experimental data for these effects shall be augmented by investigation of further two component systems. Furthermore the influence of specific magnetic susceptibility on the accuracy of the experimental method used will be determined. Also the measured data of resistivity will be compared with those obtained by calculation from X-ray data.[5]

2. Experiments

The experiments were done in a rotating-field-apparatus described by Roll and Motz.[6] With this method the electrical resistivity can be measured without electrodes within a temperature range up to 1200 °C. The theory of this method was given by Braunbek[7] for the first time. According to this paper for the calculation of the specific electrical resistivity ρ the following expression is obtained :

$$\rho = C\frac{i^2 r^4 l}{\alpha} \tag{1}$$

with : C = constant of the apparatus
i = current used for the production of the magnetic rotating field around the specimen
α = angle, by which the specimen is turned by the rotating field
r = radius of the specimen
l = length of the specimen

Equation (1) was derived under the assumption, that the ratio l/r is very large. For the specimens investigated during this work the deviation of this condition was taken into account by the half-empirical corrected equation (1a) :

$$\rho_{\mathrm{corr}} = C\frac{i^2(r^4 + 5)(l - 3.5)}{\alpha} \tag{1a}$$

Consideration of possible mistakes during the application of the rotating field method yields an error of about 6% for absolute and of about 3% for relative measurements.

From each of the systems under investigation the resistivity of 25 to 30 single alloys was measured. The preparation of specimens varied from

system to system : With Cu–Sb the alloys were brought into the apparatus as powder mixtures and then they were molten inside the apparatus. The Sn–Zn specimens were molten in a larger crucible and then turned to template. The Ag–Mg-alloys finally were sucked into a tube from quartz-glass. By this way the specimens with proper diameters were obtained immediately. The purity of the metals was Cu (99.9%), Sb (99.9%), Ag (99,995%), Mg (99.99%), Sn (99.95%), and Zn (99.9%).

3. Results

1. System Cu–Sb

The phase diagram of Cu–Sb shows the intermetallic compounds Cu_2Sb and Cu_3Sb being those, whose phase regions nearly touch the liquidus. The compound Cu_3Sb is retained nearly up to the melting point, whereas Cu_2Sb decomposes at 586 °C. Measurements of electrical resistivity in the system Cu–Sb were reported by Bornemann and Rauschenplat[8] as well as by Matuyama.[9] The values of Bornemann and Rauschenplat lie for about 8% higher than the values reported here. It should be mentioned, that the densities of molten Cu–Sb alloys were taken from the paper of Bornemann and Sauerwald.[10]

The run of resistivity versus temperature for 26 different specimens is shown in Fig. 1. At the left side of every curve the starting value of electrical resistivity is given. All curves show a linear run with positive temperature coefficient. Only the alloys with 22 and 25 At.–% Sb show a negative temperature coefficient.

In Fig. 2 the resistivity-concentration-isothermes for the two temperatures 700 and 1100 °C are shown. The maximum shifts according to these curves with rising temperature to higher Sb-concentrations and furthermore its height relative to the minimum at about 70 At.–% Sb diminishes.

2. System Ag–Mg

No densities were reported for the molten alloys of this system. Therefore according to Eq. (2) the densities D_{alloy} were calculated from the densities D_i of the pure components, v_i being the volume parts:

$$D_{alloy} = v_1 D_1 + v_2 D_2 \qquad (2)$$

$$(v_1 + v_2 = 1)$$

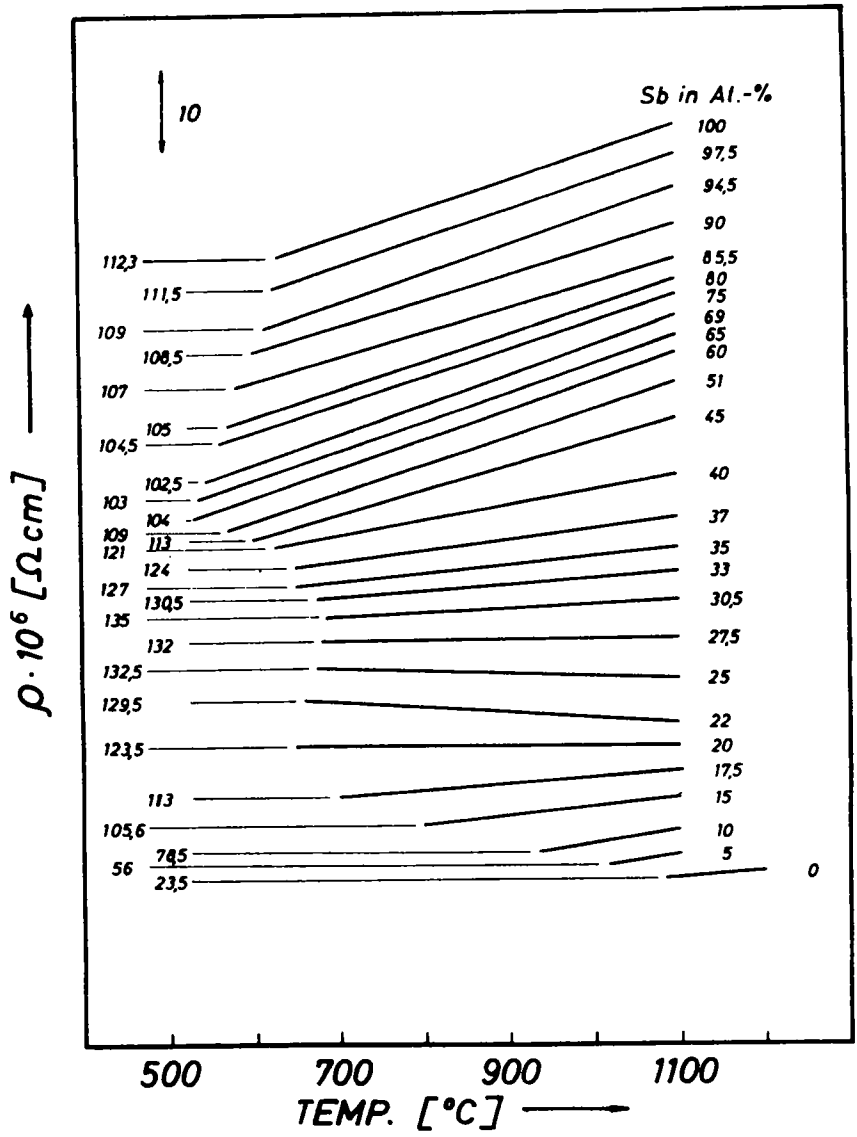

Fig. 1. Resistivity of molten Cu–Sb alloys.

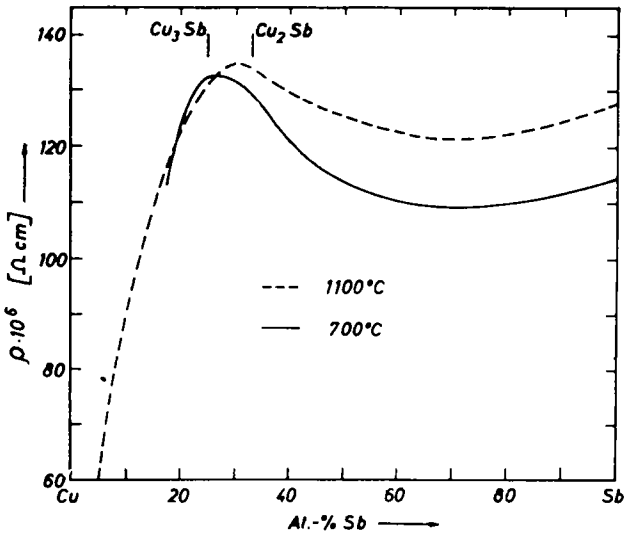

Fig. 2. Isothermes of resistivity in the system Cu–Sb.

The run of resistivity versus temperature for different specimens is shown in Fig. 3. All curves show a linear run. The temperature coefficient of resistivity is negative between 30 and 70 At.–% Mg. This is shown in Fig. 4. The diagram of temperature coefficient versus Mg-concentration shows two minima at those concentrations, where the resistivity-concentration-isotherme of Fig. 5 exhibits two maxima. This curve in Fig. 5, which is marked with "exp." shows a large and broad maximum at 50 to 65 At.–% Mg and a smaller and narrower maximum at about 77 At.–% Mg.

3. System Sn–Zn

The electrical resistivity in this system was measured by Roll and Motz[11] as well as by Matuyama.[9] Furthermore in this system the specific magnetic susceptibility was measured by Wachtel and Übelacker.[13]

There are two reasons for measuring the electrical resistivity in this system once more. First of all, the influence of specific magnetic susceptibility on the measurement of electrical resistivity using the rotating field method should be determined. Furthermore the maxima at certain valency electron concentrations reported by Roll and Motz,[11] which up to date cannot be explained theoretically, should be tested. The densities of molten Sn–Zn-alloys were taken from a paper of Matuyama.[12]

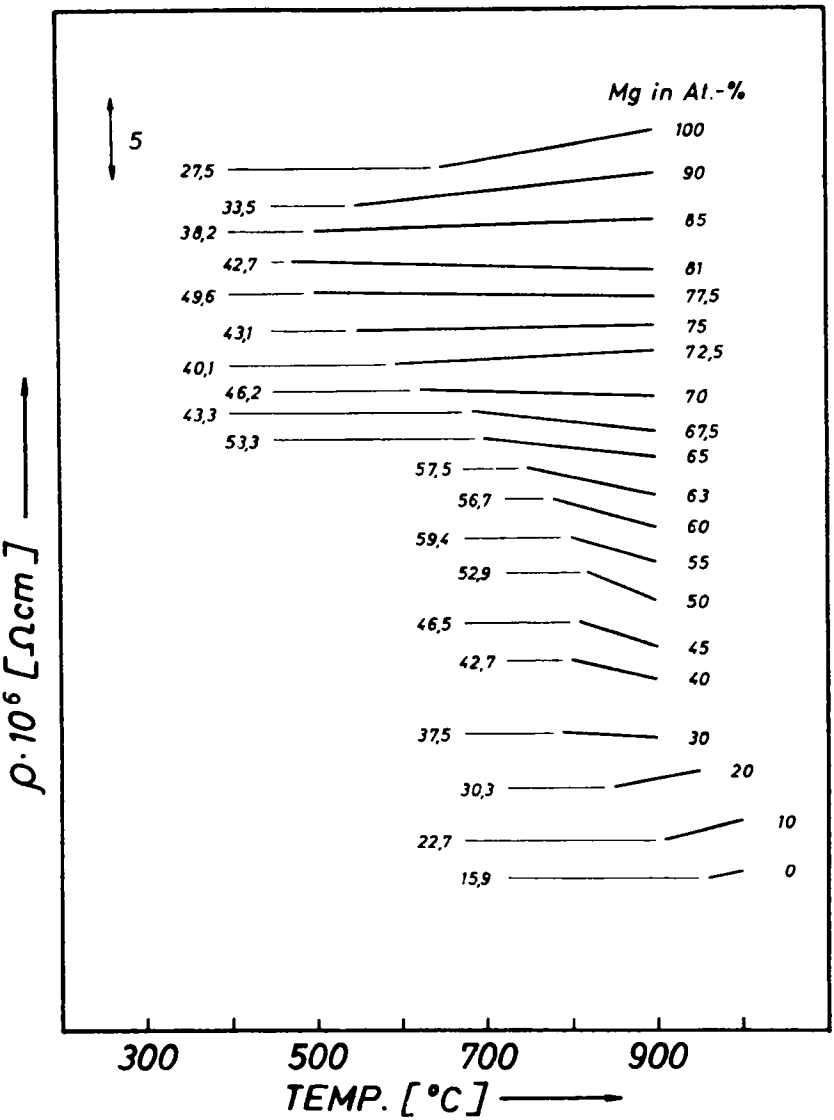

Fig. 3. Resistivity of molten Ag–Mg alloys.

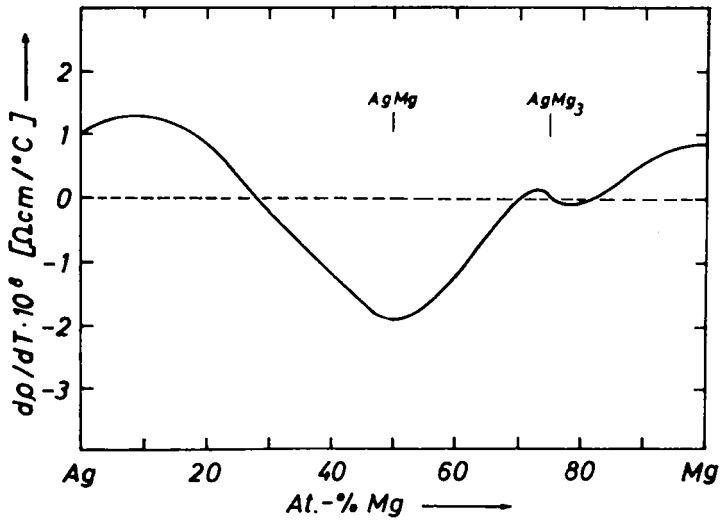

Fig. 4. Temperature coefficient of resistivity in the system Ag–Mg.

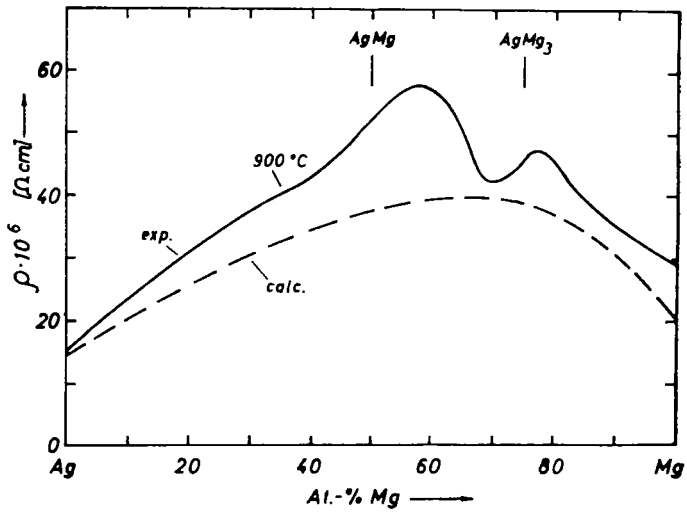

Fig. 5. Isothermes of resistivity in the system Ag–Mg. "exp." means measured curve, "calc." means curve calculated from x-ray data according to reference (5).

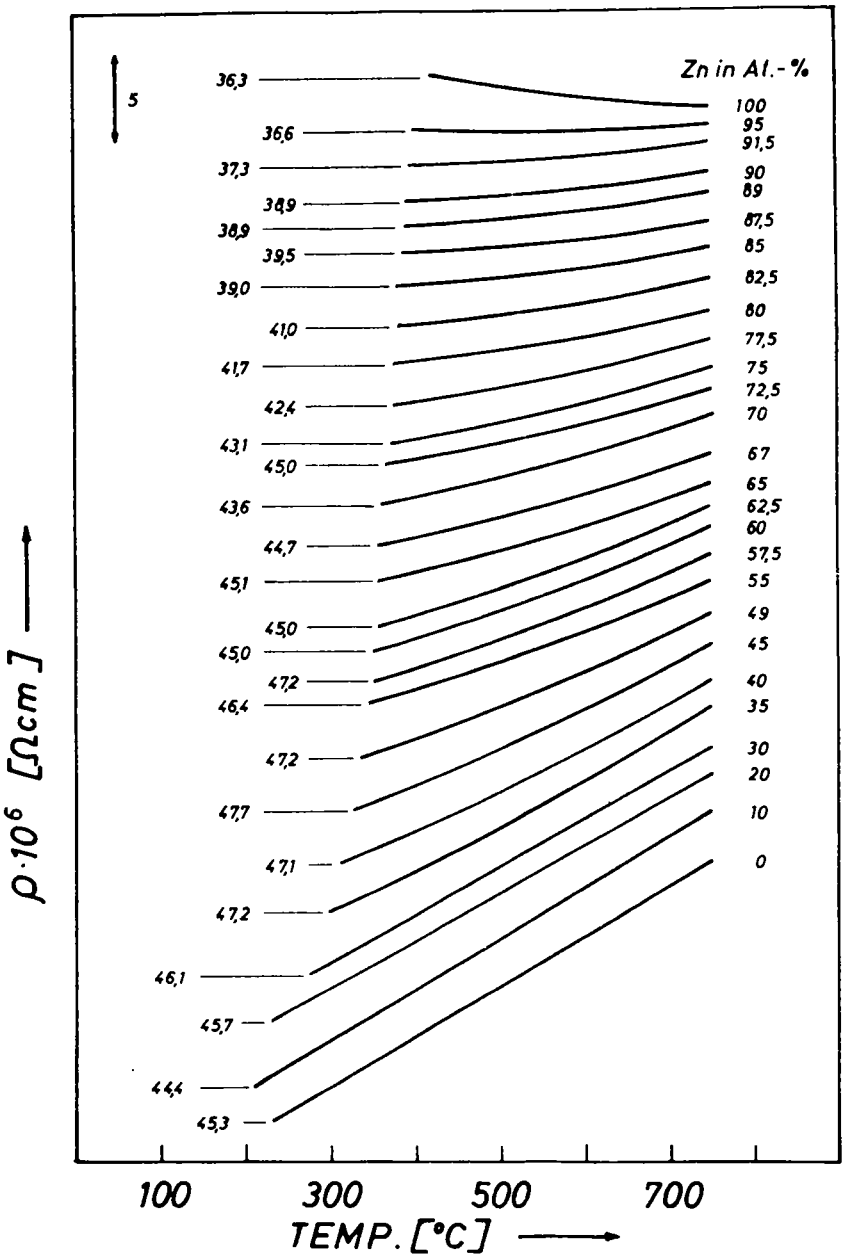

Fig. 6. Resistivity of molten Zn–Sn-alloys.

Figure 6 shows the run of the resistivity of 27 specimens versus the temperature. Zinc shows a negative temperature coefficient up to about 750 °C. The run of resistivity versus temperature is concave. All the other curves show the same curvature but they exhibit a positive temperature coefficient. The curves between 0 and 20 At.-% Zn show a linear run.

Four isothermes of resistivity are shown in Fig. 7. They show no anomalies and have a smooth run between the values of the pure components.

The values measured by Matuyama[9] as well as Roll and Motz[11] are in accordance within about 3% with the values of this work. However, the two maxima measured by[11] could not be confirmed by our result in spite of the fact, that numerous measurements were done. There is also no abnormality at that point, where the specific magnetic susceptibility measured by Wachtel and Übelacker[13] shows a minimum. The run of specific magnetic susceptibility according to[13] is shown in Fig. 7 (marked with κ).

Since the resistivity versus concentration, as shown in Fig. 6, shows no linear run in this system, in Fig. 8 two isothermes of the temperature coefficient versus the concentration are shown. The one was obtained at 450 °C, the other at 750 °C. These isothermes show a smooth run. With rising temperature also the temperature coefficient increases.

4. Discussion of Results

1. System Cu–Sb

In the system Cu–Sb the resistivity versus concentration shows the expected run. The maximum of resistivity, which corresponds to the intermetallic compound Cu_3Sb becomes flat with increasing temperature and might be disappeared at about 1300 °C. From this observation it is evident, that the decay of Cu_3Sb increases rapidly with increasing temperature. At the concentration of Cu_2Sb at lower temperatures no maximum can be detected, but the decrease from the maximum at Cu_3Sb in direction to Cu_2Sb is much more flat than in direction to pure Cu. So a hidden maximum, arising from Cu_2Sb could exist under the flat run of the curve. With increasing temperature the maximum shifts towards higher Sb-concentrations. At 1100 °C it lies at about 31 At.-% Sb. This shift of a maximum is in good accordance with the observations of Gebhardt

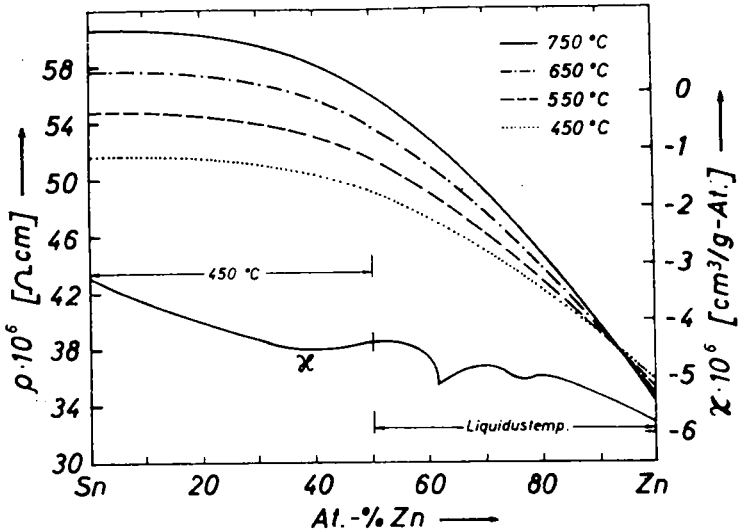

Fig. 7. Isothermes of resistivity and run of specific magnetic susceptibility at different temperatures in the system Zn–Sn.

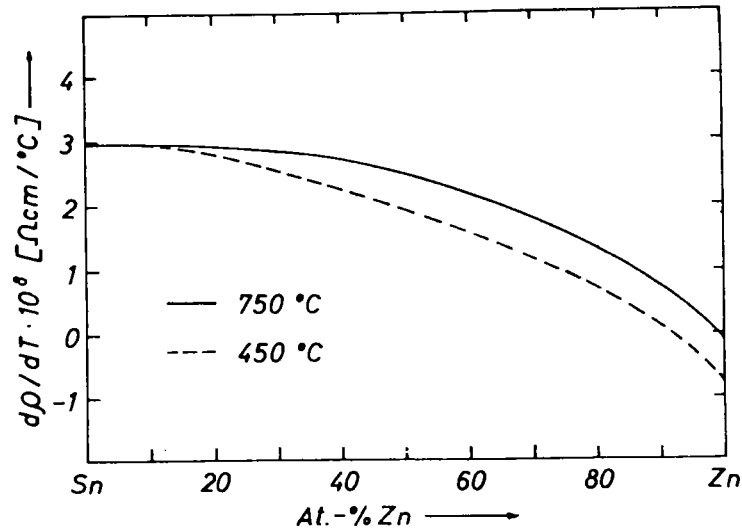

Fig. 8. Isothermes of temperature coefficient of resistivity in the system Zn–Sn.

et al.[14], who measured the viscosity. Also with these measurements the maxima of the viscosity isothermes shifted with rising temperature above the liquidus.

To the maximum of the resistivity curve a minimum in the run of temperature coefficient corresponds. The position of this minimum, however, not exactly lies at the concentration of Cu_3Sb, but at 23 At.-% Sb. The formation of the strong negative temperature coefficient near the intermetallic compound can be understood in the following way :

In solid state, the intermetallic compound Cu_3Sb exhibits a positive temperature coefficient. Assuming, that this coefficient also would exist in the molten state, for the explanation of the experimental manifested negative coefficient with increasing temperature further charge carriers must be formed. This would be done by decay of Cu_3Sb "alloy molecules" in the melt. Eventually, the decay of Cu_3Sb takes place by the formation of Cu_2Sb. Thereby, always more copper forms, whose high conductivity leads to a decrease of the resistivity and at the same time to the negative temperature coefficient.

Diffraction experiments[4] with melts show, that "compound molecules" exist at concentrations near the intermetallic compounds. The formation of such molecules could be connected with a diminution of the effective number of free electrons. By this way, the maximum of resistivity could be formed. This would mean, that part of the free electrons in the melt is used for the bond in the "compound molecules".

Measurements of the density in the system Cu–Sb were done by Bornemann and Sauerwald.[10] In Fig. 9, the relative difference between experimental and calculated density (Eq. 2) is given versus the concentration. From this run it can be seen, that this difference exhibits a maximum at 25 At.-% Sb and decreases to both sides nearly linear. This run can be understood well, because it confirms the result obtained by resistivity measurements, that in the molten state "alloy molecules" exist, which have a greater density than the surrounding melt.

2. Ag–Mg

Also this system contains intermetallic compounds. Therefore the effects observed in the system Cu–Sb are to be expected with Ag–Mg, too. Maxima of resistivity occur at the concentrations of intermetallic compounds. In this system, the two maxima can be separated, because there is a larger concentration difference between the compounds. Not only the

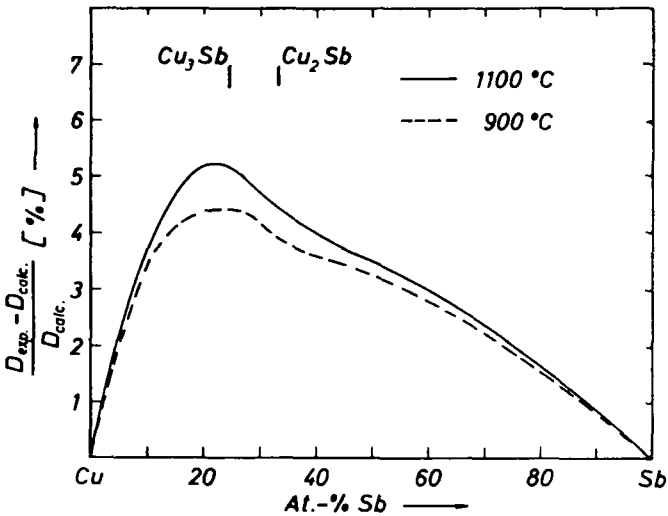

Fig. 9. Relative difference between measured[10] and calculated density in the system Cu–Sb for two different temperatures.

relative, but also the absolute height of the maxima decreases with rising temperature. The considerations on the decay of maxima and the run of temperature coefficient, mentioned above, stands accordingly. It is to be mentioned that with some alloys the originally negative temperature coefficient at temperatures above 1000 °C finally becomes positive.

Figure 5 contains in addition to the measured curves a further curve, which was calculated according to the Faber–Ziman theory[15] from the structure factors and pseudopotentials. The values of the structure factors were taken from a paper of Bühner and Steeb.[5] In the region near pure silver the calculated and measured values are in very good accordance. Also the accordance in the remaining concentration range is well, if one considers the mistakes in pseudopotentials, structure factor- and resistivity-determination.

3. Shift of maxima of resistivity

The shift of maxima of resistivity with increasing temperature in the systems under consideration to higher Sb- or Mg-concentrations can be understood by the results of diffraction experiments:

From an unpublished paper[16] results, that the shift of maxima with increasing temperature can be understood from the point of view of

structure of molten alloys. This was shown for the systems Mg–Sn and Mg–Pb and probably can be transferred to the systems of the present paper.

4. Zinc–Tin

No peculiarities can be observed in the resistivity of the eutectic system Zn–Sn. The negative temperature coefficient of the pure Zn was explained by Wallace.[17] The two maxima observed by Roll and Motz[11] could not be confirmed. The small deviations of the measured points lie within the error limit, so that no anomalies could be stated. The relative superelevation with the measurements of Roll and Motz amounted to 1–2% and therefore was inside the experimental error limit.

No influence of susceptibility could be probed. This can be understood by the following consideration: A specimen with magnetic moment $\vec{m}$ is deviated by a homogeneous magnetic field $\vec{H}$ with a rotating moment $\vec{M}$:

$$\vec{M} = \vec{m} \times \vec{H} \tag{3}$$

Since the magnetic dipoles existing in the specimen in every moment lie parallel to the outer magnetic field, $\vec{M}$ must be zero in every moment. So the magnetic field can exhibit no influence on the determination of the electrical resistivity. The experimental evidence for the failure of an influence of the magnetic field given by Fig. 7 should be tested with further alloy systems, to get more precise knowledge on the occurrence of maxima at certain valency electron concentrations also in those systems.

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