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„Thermodynamic investigations of the ternary
Al-Ge-Zn system“

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Chapter 1: Introduction

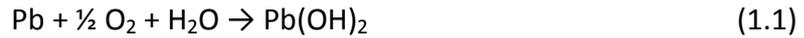
1.1 Background

1.1.1 Health and environmental concerns about lead

Lead and its compounds belong to the most problematic chemicals with regard to the consequences it may have on human life and environment [94Woo]. The accumulation of lead in the body over a long period can cause serious health problems. The function of the human body might be disturbed because lead has the property to bind strongly to proteins. Known effects are disorders in the nervous and reproductive system, delays in the neurological and physical development, cognitive and behavioral changes, reduced production of hemoglobin which can cause anemia and hypertension [84Mon]. Lead poisoning is assumed, when the level of lead exceeds 50mg/dl [95Nap]. It should be noted, that also a level of lead below this official threshold can be dangerous especially for children and their neurological and physical development [06Zuo].

Due to the fact, that lead and its compounds pose a great risk to the human population and its well-being, a lot of effort is made to reduce the exposure to these substances. Potential risks occur from occupational exposure, lead waste derived from the manufacturing process and the disposal of electronic assemblies. Primary sources for occupational exposure are soldering processes. In this case, the inhalation of lead vapors represents one of the greatest risks. The problems arising from the disposal of lead containing waste will be probably even more important. Especially the rapidly increasing amounts of electronic assemblies like personal computers, television sets and mobile phones could cause serious problems of lead contamination in the future, when they are discarded. Lead which is disposed in this form in landfills can be washed out and may cause a contamination of water sources, terrain and as a consequence it might cause a disruption of the human ecosystem in general [06Zuo], [11Hin].

There is no clear scientific prove about the mechanisms of how lead from electronic waste reaches our ecosystem, but one possible explanation is, that lead reacts with oxygen, water and carbon dioxide.



This way, water soluble compounds can be formed. Especially $\text{Pb}(\text{HCO}_3)_2$ can be easily dissolved in water. Due to these reactions it is possible, that lead is washed out and gets into the environment (see Fig. 1.1) [10Mik]. It should also be mentioned, that these reactions are suspected to be catalyzed by chloride ions [10Mik], [10Uni].

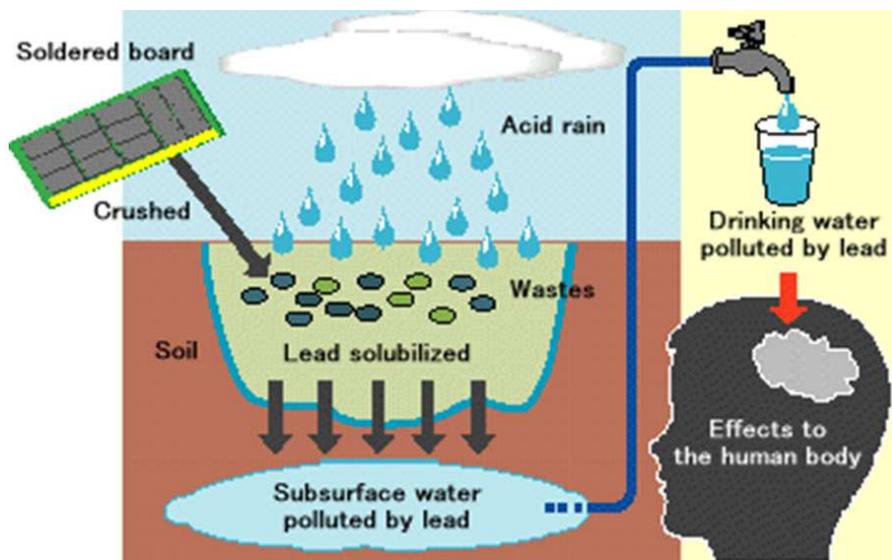


Fig. 1.1 Path of lead from soldered board to the human body via drinking water [10Mik]

1.1.2 Legislation

According to the RoHS (Restriction of Hazardous Substances Directive) 2002/95/EC which is updated periodically, the use of lead in the manufacture of electrical and electronic equipment in the European Union is restricted from July 1st 2006 [03Eur]. This RoHS is not a law, it is simply a directive and it is closely linked with the WEEE (Waste Electrical and Electronic Equipment Directive) 2002/96/EC which regulates the collection, recycling and recovery for electrical goods. Similar restrictions were also set in China. The United States of America introduced a law in the Senate and the House of

Representatives which should regulate the points mentioned above. Japan did not forbid the use of lead directly but sending lead or lead containing materials to landfills will be prohibited. This way, Japan is trying to prevent lead from reaching our ecosystem. Manufacturers have two possible options. Either they conceive the complete recycling of lead from their products or they establish the use of lead-free solder alloys. Since a lot of Japanese companies started to proclaim the use of new lead-free solders, the trend seems to be conclusive [06Zuo].

1.2 New lead-free solders

1.2.1 Function of lead in eutectic tin-lead solders

The reason why lead is frequently used for solders is that there are a lot of technical advantages for the manufacturing processes of electronic devices. The popularity of the classical Sn-37Pb alloy has several reasons:

- I. The melting temperature of 183°C is quite low. This allows very mild soldering conditions. Furthermore the SMT (Surface Mount Technology) can be applied.
- II. The wettability (solderability) is improved because lead reduces the surface tension of pure tin.
- III. The addition of lead reduces the possibility of the transformation of the grey α -tin to the white β -tin which is also known as “tin pest”. This reaction reduces the structural integrity of the tin and therewith the stability of the soldered parts.
- IV. Lead promotes the fast formation of intermetallic bonds by acting as a solvent metal.
- V. Lead is a low cost material which is sufficiently available.

These are common reasons why lead-based soldering materials are still widely used for the manufacture of electronic devices [00Abt].

1.2.2 Lead-free solders

During the last years, a number of different lead-free solders were investigated which are mostly based on tin-alloys. It is probably not possible to substitute lead containing solders completely but the new solders may be used as an environmentally friendly alternative [11Hin]. Possible intermetallic compounds are for example Sn-Ag and Sn-Cu. One of the biggest disadvantages of these new solders is their higher melting point, in comparison to alloys which have been used until now. The higher melting point causes a lot of technical problems during the manufacture processes. The processes of soldering have to be adapted for higher temperatures and the materials used (e.g. printed circuit boards) must resist these high temperature conditions. For this reason the reduction of the melting temperature is a current subject of research. If elements like Indium and Bismuth are added to the new intermetallics ternary alloys with much lower melting points are formed [01Sug].

Recent works of our group have shown, that intermetallic systems on the basis of Cu-In-Sn have good wettability and improved mechanical properties [06Zuo]. With regard to melting properties, wettability and mechanical properties, previous investigations suggested Ag-Bi-Sn Systems as good alternatives to currently used lead containing solders [98Kar1], [98Kar2], [99Via1], [99Via2], [02Xia].

1.3 Research Objectives

The aim of this work is to obtain information about the thermodynamic properties of the ternary Al-Ge-Zn system. The primary reason for the investigation of this particular system was the fact, that studies concerning this system are quite rare. Especially reports about experimental works on this system are very limited. There are few publications [76Tad], [81Sto], [91Sri] with thermodynamic calculations on that system.

The measurement of the electromotive force (EMF) of an appropriate galvanic cell represents a highly accurate method to determine thermodynamic properties of metallic systems. It is possible to measure the partial Gibbs energies directly and to derive the Gibbs energies of formation of alloys [97Mik].

Chapter 1: Introduction

The activity of aluminum in the Al-Ge-Zn intermetallic system can be determined by the measurement of the electromotive force (EMF) in an electrochemical cell containing a liquid electrolyte. Thermodynamic data are very significant for the calculation of phase diagrams, for the development of new lead-free solders and for the prediction of their physical and chemical properties such as surface tension and viscosity [98Sau]. Furthermore the evaluated parameters can be included into a database of lead-free solders [06Zuo].

This work was part of the COST MP0602 action. The previous COST 531 action for the investigation of lead free solder alloys was originally founded in 2001 by H. Ipser and A. Mikula. The goal of this program is to create a database of important results of different investigations in this particular area. It should help to create new useful alloys and to avoid the repetition of complicated and time-consuming experiments.

Chapter 2: Experimental techniques

2.1 Methodology

2.1.1 Electromotive force (EMF) method

A chemical system, which is able to produce electric current, is named “galvanic cell” or “electrochemical cell”. A chemical reaction in such a cell can be obtained by a concentration difference between two electrodes. According to that, this cell-type is called “concentration cell”. In this case, the thermodynamic properties of the chemical reaction inside the cell can be calculated from the measured electromotive force (EMF) which is provided by the particular cell. Furthermore the activity of one metal in an alloy system (eg. binary or ternary intermetallic systems) can be determined. As mentioned in 1.3 the measurement of EMF is a widely used technique and one of the most accurate methods for investigating thermodynamic properties of alloys [11Hin].

In general there are two possible methods of measuring the EMF to obtain thermodynamic data of an intermetallic system: One possibility is to work with solid electrolytes, which normally allows the work at high temperatures (over 800°C). The other option is to work with liquid electrolytes at temperatures below 800°C [06Zuo]. In 1923, aqueous electrolytes were replaced with molten salt-mixtures by Taylor [23Tay]. In this way, it was possible to measure the activities of Zn, Cd, Sn, Pb and Bi in binary alloys. Many further publications, [52Wag], [58Chi], [73Kom] refer to galvanic cells which work with molten salts. An extensive summary of the EMF-technique was compiled in 1997 by A. Mikula [97Mik]. With the aid of the EMF measurement in liquid electrolytes, a number of potential lead-free solders like Ag-Sn-Zn [94Kar], Cu-Sn-Zn [97Pen], Al-Sn-Zn [02Kno], Cu-In-Zn [06Kno1], Ag-Bi-Sn [06Li1] and Pd-Sn-Zn [06Li2] Ag-Au-Sn [10Hin], Au-Sb-Sn and Au-Sb [11Hin] were investigated extensively by our group.

2.1.2 Principle of the EMF method

Basically the concentration cells which are used to study thermodynamic properties of liquid alloys consist of an electrode which is a pure metal A and a second electrode which is an alloy containing metal A [97Mik], [06Zuo], [11Hin].

According to this, we can write for a typical cell-setup:



The cell-reaction can be written as follows:



If pure $\text{A}_{(l)}$ is used as a reference, the change of the chemical potential for this reaction is described by the following equation [97Mik]:

$$\overline{\Delta G}_A = -zFE = RT \ln a_A \quad (2.3)$$

z.....Number of transferred electrons in the cell reaction

F.....Faraday constant ($96486 \text{ C} \cdot \text{mol}^{-1}$)

E.....measured electromotive force (EMF) of the cell

R.....universal gas constant ($8,314 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$)

T.....absolute temperature (K)

a_Athermodynamic activity of component A in the alloy

If the subscript A is substituted by i, the partial molar Gibbs free energy $\overline{\Delta G}_i$ and the activity of the component i in the alloy can be determined directly by the measured EMF [06Zuo]:

$$\overline{\Delta G}_i = -zFE \quad (2.4)$$

$$a_i = \exp\left(\frac{-zFE}{RT}\right) \quad (2.5)$$

The temperature dependence of the EMF allows us to calculate the partial molar enthalpy $\overline{\Delta H}_i$ and also the partial molar entropy $\overline{\Delta S}_i$ using the Gibbs-Helmholtz relation [97Mik], [06Zuo]:

$$\overline{\Delta H}_i = \overline{\Delta G}_i + T\overline{\Delta S}_i = -zF \left[E - T \left(\frac{\partial E}{\partial T} \right)_{x,P} \right] \quad (2.6)$$

$$\overline{\Delta S}_i = zF \left(\frac{\partial E}{\partial T} \right)_{x,P} \quad (2.7)$$

It is known, that the thermodynamic properties of real solutions differ from ideal ones. According to this, the mixing thermodynamic properties of real solutions are described as the sum of an ideal contribution and an excess contribution [06Zuo], [11Hin].

If this definition is applied to partial molar properties, the following expressions are obtained:

$$\overline{\Delta G}_i^E = RT \ln \gamma_i \quad (2.8)$$

$$\overline{\Delta S}_i^E = -R \ln \gamma_i - \left(\frac{\partial \ln \gamma_i}{\partial T} \right)_P \quad (2.9)$$

$\overline{\Delta G}_i^E$ partial excess Gibbs free energy

$\overline{\Delta S}_i^E$ partial excess entropy

In this case γ_i is the activity coefficient of the component i.

In the multi-component solution, the molar quantity ΔZ is the sum of the individual partial molar quantities multiplied by the mole fraction:

$$\Delta Z = \sum_i x_i \overline{\Delta Z}_i \quad (2.10)$$

The integral properties cannot be obtained directly by using equation 2.10 because only the partial molar properties of one component in the multi-component solution can be measured by the EMF-method. To solve this problem, the Gibbs-Duhem equation can be used [97Mik], [06Zuo], [11Hin]:

$$\sum_i x_i d \overline{\Delta Z}_i = 0 \quad (2.11)$$

After carrying out a partial differentiation of the equation (with respect to x_i while keeping x_j, x_k, x_l, \dots constant) and combining the result with the Gibbs-Duhem equation the following expression can be obtained:

$$\left[\frac{\partial}{\partial x_i} \left(\frac{\Delta Z}{1-x_i} \right) \right]_{x_j, x_k, x_l, \dots} = \frac{\overline{\Delta Z}_i}{(1-x_i)^2} \quad (2.12)$$

In this case x_j, x_k, x_l, \dots means, that the relative amounts of all components except i are constant.

In a ternary system, where the partial molar properties of component 3 are measured by the EMF method, the integration of equation 2.12 from $x_1=0$ to x_3 at a constant molar ratio of x_1 to x_2 results in the following equation [51Ell], [06Zuo], [11Hin]:

$$\Delta Z = (1 - x_3) \left[\Delta Z_{x_3=0} + \int_0^{x_3} \frac{\overline{\Delta Z}_3}{(1-x_3)^2} dx_3 \right]_{x_1/x_2} \quad (2.13)$$

From this equation, molar thermodynamic properties can be calculated if the partial molar properties of one component are measured over the whole concentration range. $\Delta Z_{x_3=0}$ represents the starting value of the binary 1-2 system [06Zuo].

If this relationship is applied to the excess Gibbs free energy and enthalpy of mixing, the following two equations can be derived [50Dar], [51Ell], [06Zuo]:

$$\Delta G^{XS} = (1 - X_{Me}) \left[\Delta G_{Me=0}^{XS} + \int_0^{X_{Me}} \frac{\overline{\Delta G}_{Me}^{XS}}{(1-X_{Me})^2} dX_{Me} \right]_{X_1/X_2} \quad (2.14)$$

$$\Delta H = (1 - X_{Me}) \left[\Delta H_{Me=0} + \int_0^{X_{Me}} \frac{\overline{\Delta H}_{Me}}{(1-X_{Me})^2} dX_{Me} \right]_{X_1/X_2} \quad (2.15)$$

$\Delta G_{Me=0}^{XS}$ and $\Delta H_{Me=0}$ are representing the limiting excess Gibbs energy and enthalpy values of the binary system. X_{Me} is the mole fraction of Al in the alloy.

According to [Hin11] an additional function is used for the integration of the partial excess Gibbs free energy:

$$\overline{\Delta G}_{Me}^{XS} = RT \ln \gamma_{Me} \quad (2.16)$$

In this case γ_{Me} represents the activity coefficient.

According to this, the integrand becomes the so called alpha function:

$$\alpha = \left(\frac{\ln \gamma_{Me}}{(1-x_{Me})^2} \right) \quad (2.17)$$

When this alpha function is inserted into 2.14 the following expression can be obtained [Hin11]:

$$\Delta G^{XS} = (1 - X_{Me}) \left[\Delta G_{Me=0}^{XS} + RT \int_0^{X_{Me}} \alpha dX_{Me} \right]_{X_1/X_2} \quad (2.18)$$

2.1.3 Requirements for accurate EMF measurements

There are several points, which should be taken into account if EMF measurements are performed. These are important to obtain accurate and reliable data:

- I. The cell reaction has to be reversible. No drift or polarization effects should be shown. At the same temperature the value of the measured EMF must be constant and reproducible.
- II. It is important to know the charge of the electropositive ion A^{Z+} .



This should also represent the only charge transfer through the electrolyte and the only reaction on the surface of the used electrodes.

- III. The conduction through the electrolyte should be pure ionic. Attention must be paid to prevent displacement reactions.
- IV. Reactions between the lead wires, the electrodes, the electrolyte, the containment and the alloy must be averted. During the investigation of the ternary Al-Ge-Zn system, a reaction between the molybdenum electrodes and the liquid alloys was observed. The problem was solved by using graphite rods as electrodes which touched the liquid alloys. This way, a direct contact between the Mo-wires and the samples was prevented (see also 3.2.3). Similar phenomena of unwanted side reactions were noticed in our group during the measurement of liquid Sn-Zn-Al alloys with tungsten electrodes [02Kno].
- V. Potential reactions of the electrolyte and the electrodes with materials which the cell consists of must be taken into account.

- VI. For heating the cell, a furnace should be used, which is not wired inductively. In this way electrical interferences during the measurement can be prevented. For the present investigations a metallic, grounded shield was placed around the cell. In this way electrical interferences (induction effects) could be minimized.
- VII. Eventually concentration changes because of the vapor pressure of the electrodes and the electrolyte must be taken into consideration.
- VIII. During the measurement of the EMF, it is mandatory to prevent the passage of electrical current through the cell. This can be accomplished by using a voltmeter with an input impedance greater than 10^{10} ohms.
- IX. A protecting atmosphere consisting of an inert gas must be provided. In the case of the Al-Ge-Zn system, Ar-gas was used to fill the cell with a pressure of 0,5bar.
- X. The temperature should be high enough to avoid changes in the composition of the alloy.
- XI. The appearance of thermoelectric voltage must be prevented.

It is essential that these conditions are fulfilled for successful experiments. If this is the case, adequate EMF-measurements are possible and as mentioned in 2.1.2 a relationship between the reversible cell potential E and the Gibbs free energy change ΔG can be found in a simple equation [79Kub], [96Mik], [06Zuo], [10Ips].

2.2 EMF measurements with liquid electrolytes

This kind of measurement is done by using a liquid electrolyte (molten salt-mixture), which is normally composed of different alkali chlorides with a small addition of Me-ions of the investigated alloy-compound in the form of a suitable Me-salt. This means, that for the investigation of the ternary Al-Ge-Zn system, where the focus of research is set on the activity of the aluminum in the liquid ternary alloy, Al^{3+} is added to the electrolyte in the form of a suitable salt. A widely used electrolyte is the eutectic salt mixture of LiCl and KCl which starts to melt at $354^{\circ}C$ [10Ips].

The use of molten salts is a standard method for measurements at elevated temperatures [10lps]. The setup of the measuring cell which uses liquid electrolytes consists of a reference electrode which is a pure metal A and another electrode which is an alloy containing the metal A. The electrodes are covered completely by the molten salt electrolyte. This form of the setup works like a classical, chemical concentration cell and the electromotive force between the electrodes can be measured in dependence of the temperature by using a voltmeter [97Mik], [06Zuo], [11Hin].

2.2.1 The EMF apparatus for liquid electrolytes

The general setup of an EMF apparatus which works with liquid electrolytes is shown in Figure 2.1. The experimental details concerning the apparatus which was used for the investigation of the ternary Al-Ge-Zn system can be found in 3.2.3. This type of apparatus represents the measuring setup, which is currently used in our group.

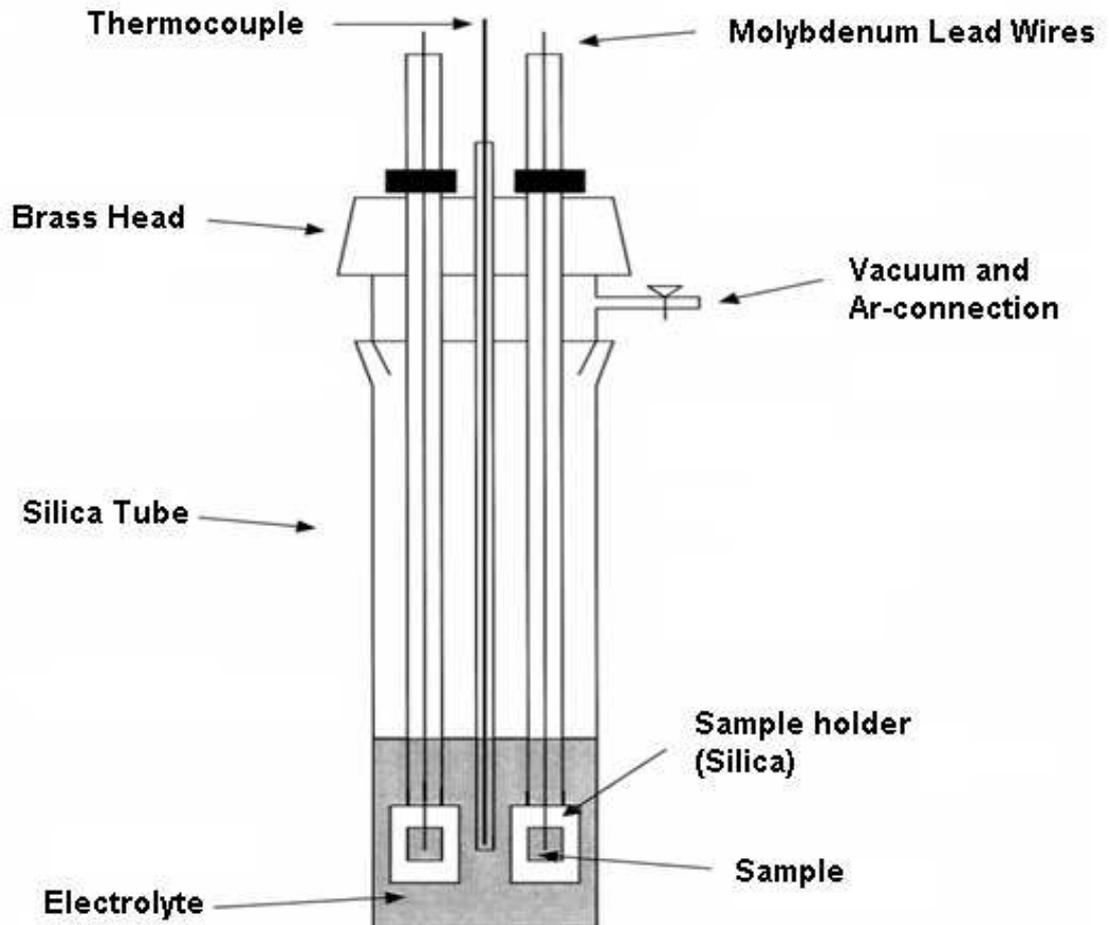


Fig. 2.1 The EMF apparatus for measurements with liquid electrolytes [11Hin]

The whole cell is made of quartz (silica). The sealing at the top of the cell is made of brass and has five inlets at the top and a glass valve attached at the side which is used as a connection to the vacuum-pump and the argon-bottle. Four of the inlets are used for the lead wires, and the central one is used for the sample holder which is also made of quartz. The lead wires and the sample holder are all introduced through the inlets. In this way a steering of the alloys during the measurement is possible. Furthermore it is possible to insert a thermocouple into the sample holder to monitor and record the temperature while measuring it.

For the measurement the setup of the whole cell is prepared first. During each measurement four electrodes are used. One of them is the reference and the other three are the alloy samples. With this cell arrangement three samples can be

measured during one experiment. The contact is provided by wires with a protection made of thin quartz capillaries.

After everything has been prepared, the electrolyte, which should have been prepared previously (see 3.2.2) is inserted into the quartz tube. The apparatus is closed immediately and evacuated. After this, the cell is purged with Argon gas. This procedure is repeated for 4 times. Finally the container is filled up with Argon gas to about half standard atmosphere. Subsequently the cell is heated in a vertical furnace to melt the electrolyte. The electrodes and the sample holder are kept at the top of the cell during the heating process. This prevents the evaporation of volatile compounds of the alloys. After the electrolyte has melted, the sample holder and the electrodes are pushed down into the molten salt. When the temperature reaches a maximum of 800°C the lead wires are connected with the data acquisition system, the thermocouple is inserted and the measurement can be started.

Generally the measurement is done by slowly cooling the cell down and simultaneously measuring the temperature and the EMF values. This way, a function which is dependent on the temperature and the EMF, can be recorded. The cooling rate normally is about 0.1°C to 0.2°C per minute. Furthermore it is also common, to keep the temperature for a longer period of time at different constant levels. In this case, the EMF-values also have to be constant. The temperature and the EMF-values are monitored with a computer and automatically recorded for the evaluation.

2.2.2 Preparation of the liquid electrolyte

The following part will give a general overview of the preparation of a liquid electrolyte. Also a list of advantages and disadvantages concerning the use of liquid electrolytes is given. The experimental details for the investigation of the Al-Ge-Zn system are described in 3.2.2.

The liquid electrolytes, which are commonly used for the investigation of various alloys, often consist of eutectic mixtures of different alkali chlorides. A small amount of a salt (normally also a chloride) of the metal whose activity is investigated is added to

this mixture to ensure that only ions of this particular metal can migrate through the electrolyte during the measurement. The choice of the particular electrolyte-composition depends on the alloys, which shall be investigated and further on the experimental parameters like the temperature range, in which the cell is going to be operated. A very common electrolyte is a eutectic mixture of 46 wt.% LiCl and 54 wt.% KCl with a melting temperature of 354°C [96Mik].

The use of liquid electrolytes during the study of intermetallics has several advantages [96Mik], [06Zuo], [10Ips], [11Hin]:

- I. Systems with liquid electrolytes reach the equilibrium much faster than those, which are working with solid electrolytes. This has the advantage, that diffusion processes don't have to be taken into account.
- II. The liquid electrolyte covers the molten alloys and prevents evaporation. This is very useful, if alloys containing a volatile compound (e.g. zinc) are investigated.
- III. Eutectic mixtures of LiCl and KCl have a melting point of about 354°C. Compared to other salt mixtures this is quite low, and opens up the possibility of working at lower temperatures.
- IV. Solid electrolytes sometimes can suffer microcracks. This can falsify measurements. If liquid electrolytes are used, this kind of error source does not occur.

At this point it must be mentioned, that there are also limitations when liquid electrolytes are used [96Mik], [06Zuo], [11Hin]:

- I. The preparation of the electrolyte must be done very carefully. Any impurities can cause serious problems during the measurement because of side reactions, which leads to incorrect results.
- II. Liquid electrolytes should not be used at temperatures which are higher than 800°C. The reason for this is that the molten salt mixture can get some electronic conductivity at higher temperatures.
- III. As mentioned in 2.1.3 reactions between lead wires, the electrodes, the electrolyte, the containment and the alloy have to be taken into account.

The aim of the process for preparing the liquid electrolyte is to remove impurities such as water and hydroxides from the used salts. The experimental setup is shown in Fig. 2.2. The apparatus has to be made of glass to resist the reaction-conditions and it also has to be completely vacuum tight.

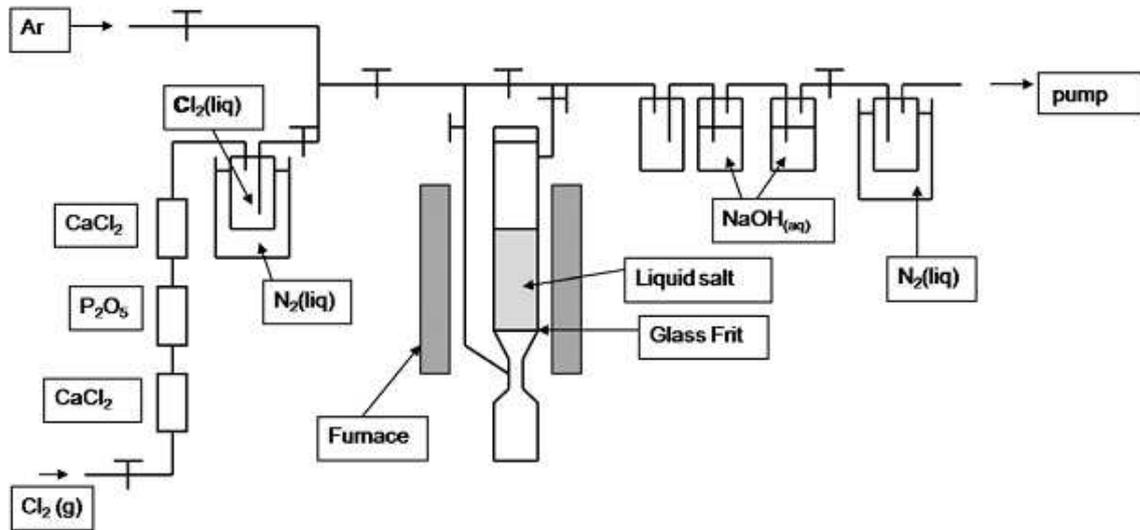


Fig. 2.2 Apparatus for the preparation of liquid electrolytes [10lps]

For the purification, the single components of the electrolyte are mixed together and then filled into the apparatus. After that, the whole setup is evacuated. By heating the eutectic mixture up to 600°C the salt becomes liquid. As this happens, chlorine gas is passed through the molten salt for about 30-45 minutes. Often this causes a slightly yellow-greenish color of the molten salt. The process of chlorination leads to the purification of the electrolyte according to the following reactions:



It is also possible to use other gases like hydrogen chloride for this process. However, chlorine gas is preferred because it gives a lower residual water and hydroxide content [06Zuo].

After the step of chlorination, all remaining chlorine gas must be removed from the electrolyte. Therefore, the residue of chlorine is removed from the molten salt with argon gas which is bubbled through the electrolyte for about four hours until the previously developed color disappears. When this is finished, the molten salt is filtered through the frit at the bottom of the apparatus into an ampoule. This is subsequently sealed under vacuum. An electrolyte, which is prepared according to this procedure, can be stored for several months until it is used [96Mik], [06Zuo], [10Ips], [11Hin].

2.2.3 Preparation of the alloys for EMF measurements with liquid electrolytes

The detailed process and the compositions of metals which were used for investigating the Al-Ge-Zn system can be found in 3.2.1. There are many different ways to prepare alloys for EMF measurements. Common methods are simply to melt the single components together in crucibles using a standard laboratory furnace or an induction furnace. It is also possible to use a commercial arc-melter to prepare the alloys on laboratory scale. Another possibility for preparing intermetallics for research experiments is to use a modified version of an electron gun which is normally used for physical vapor deposition experiments [02Pas], [05Goz], [07Goz].

However, it might be necessary to prepare larger quantities of alloys to have the possibility of repeating some experiments. For this reason, the alloys can be prepared by melting the appropriate quantities of the pure metals together using large alumina crucibles. This can be done in a common laboratory furnace during one week. To prevent oxidation of the metals, the alumina crucibles are placed and sealed into quartz ampoules under vacuum. After heating these ampoules for six days in a furnace 50-100K above the melting temperature, the temperature is lowered, so that it is close

to the melting temperature of the particular alloy. After another day of heating, the alloys can be quenched and kept for further experiments.

2.3 EMF measurements with solid electrolytes

EMF measurements with solid electrolytes are often carried out by using CaF_2 crystals as electrolyte. The ionic conductivity at higher temperatures of this electrolyte makes it suitable for this kind of measurements. Although there are some differences between the EMF technique with liquid and solid electrolytes, the obtained data can be used in each case in the same way. The EMF values which are measured in dependence of the temperature can be used to derive thermodynamic properties of different intermetallic materials.

As mentioned before, the current work was partly established at the “Dipartimento di chimica – Università degli studi di Roma la Sapienza” in Rome/Italy. There will be a review of the technique of EMF measurements with solid electrolytes which is currently used by Prof. Daniele Gozzi and his team at the faculty of chemistry at la Sapienza University in Rome for the investigation of alloys consisting of rare-earth elements and Fe, Co or Ni.

The work achieved work during the semester abroad in Rome can be summarized as follows:

It was possible to assemble a working setup for the investigation of rare-earth elements and transition-metal elements with the EMF technique with solid electrolytes (see 2.3.1). The apparatus was equipped with new holders for the tungsten resistor of the cell. These holders were made of copper and cooled by water. Due to the different thermal expansion of copper and tungsten, mechanical forces occurred and caused problems which finally led to a break of the resistor. Further problems were that the resistor-holders could not be mounted into the vacuum chamber in a leak tight way due to mistakes which were done during the manufacture process. The problems were solved by a modification of the resistor by the US based manufacturing company. Also the holders for the resistor were modified and the new ones were completely made of

tungsten metal. The whole setup was checked for several days for leak tightness by heating up the cell to normal operation temperatures of about 800°C. To prove the correct function of the whole system, the temperature controller was set to a stepwise cooling. Several temperature steps were programmed, keeping each temperature constant for 10 minutes and the temperature of each isothermal section was recorded. The measured values were then evaluated by plotting them on a PC. The results showed a very good isothermal behavior of the cell for each previously set temperature. Based on these measurements further calculations could be carried out to calculate the exact runtimes for the following EMF measurements of the alloys.

Another part of the work was the preparation of the investigated intermetallics. Several alloys were prepared during the work on the system. The alloys for this particular study were intermetallic systems formed by different rare-earth elements and cobalt. The fusion of the metals was achieved by using an electron-gun (see also 2.3.3). After the preparation of the alloys, the correct composition was proved by an X-ray diffraction analysis.

The author of the current work had the possibility to investigate the Pr₂Co₁₇ intermetallic with the setup which is mentioned below. The results of this measurement are listed together with the results of two further investigations (Nd₂Co₁₇ and Gd₂Co₁₇) in 2.3.4.

2.3.1 The EMF apparatus for measurements with solid electrolytes

The basic setup for the investigation of alloys consisting of rare-earth elements and iron is an EMF cell of the following type:



In this case Fe_{ss} is the rare earth saturated solution of Fe in equilibrium with the RE₂Fe₁₇ + Fe_{ss}. REF_y is the rare earth fluoride [05Goz], [07Goz]. Figure 2.3 shows the whole measuring unit (dismantled) at the laboratory of Prof. Gozzi.

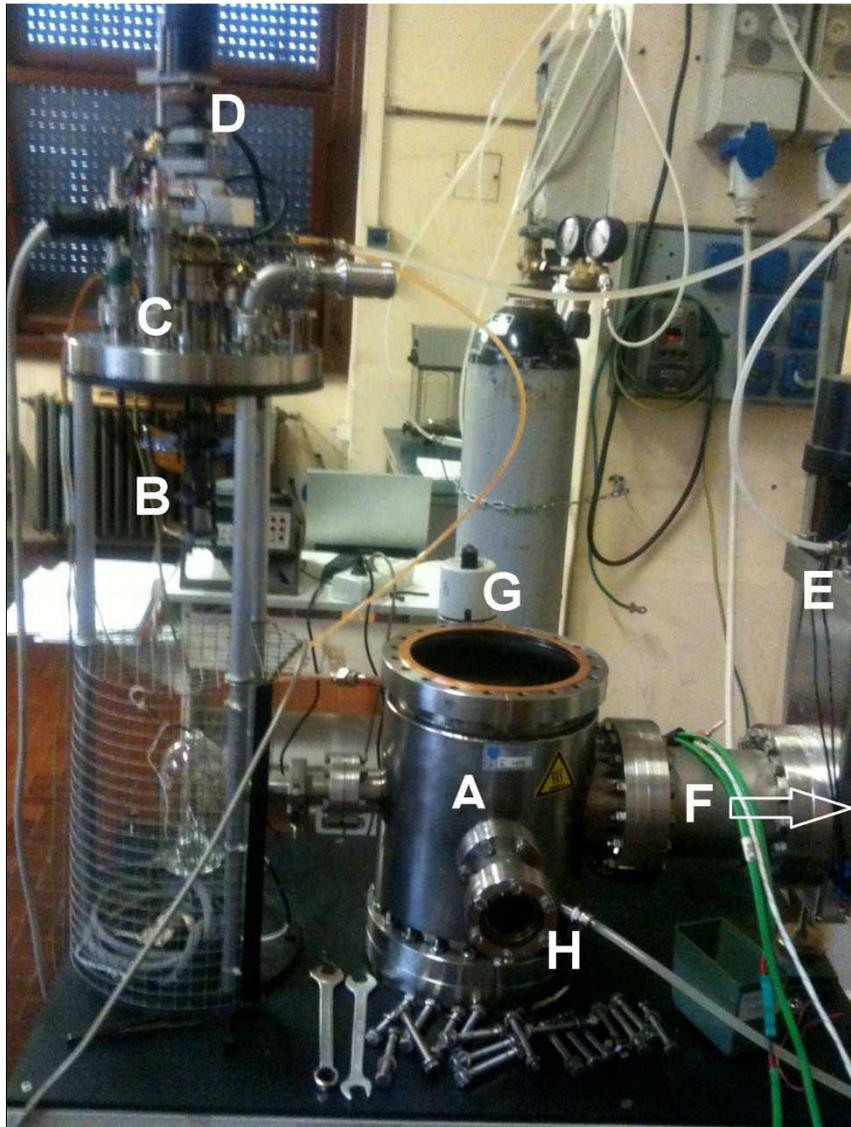


Fig. 2.3 Opened apparatus for EMF measurements with a solid CaF_2 electrolyte for the investigation of alloys consist of rare-earth elements and transition-metal elements.

A- vacuum chamber, B- holder for the electrodes and the electrolyte, C- Head of the measuring setup, D- feedback-motion device, E- guillotine type vacuum valve, F- connection to the vacuum pump, G- vacuum sensor, H- window for visual control [photo: Virgilio Genova]

The electrolyte, which is used for this particular cell is a CaF_2 single crystal, which is shaped as a disk with a diameter of 8mm and 2mm thickness. The surfaces of the crystal are polished [05Goz], [07Goz]. A setup, where the cell is assembled in a Knudsen cell-like holder with a sandwich-type arrangement is currently used by the

group of the RIM-lab (Reactivity of Inorganic Materials) at la Sapienza University (Fig. 2.4).



Fig. 2.4 Knudsen cell-like holder with a “sandwich-type” arrangement for the electrodes and the electrolyte [photo: Virgilio Genova]

This specially designed holder-arrangement is placed as a whole in the center of a massive tungsten resistor which is used to heat the cell. The setup was used in the past to measure Ni-rich and Fe-rich intermetallics along the rare earth series [02Pas], [05Goz], [07Goz]. At the moment, the group is carrying out investigations of Co-RE (rare earth elements) alloys. It is of great importance to mention that the system was improved by the scientific group of Prof. Gozzi by performing the EMF measurements under molecular effusion conditions. For this reason a very high vacuum is required.

Attention should be paid to this aspect especially when the vapor pressure of at least one of the galvanic cell components is high at operating temperatures [02Pas].

For this kind of cell a resistor which is completely constructed of tungsten is used for heating the sample (Fig. 2.5). The resistor is connected to a transformer which supplies the system with a very high current of up to 700 amperes. As mentioned above, the whole sample holder is placed in the center of this resistor.

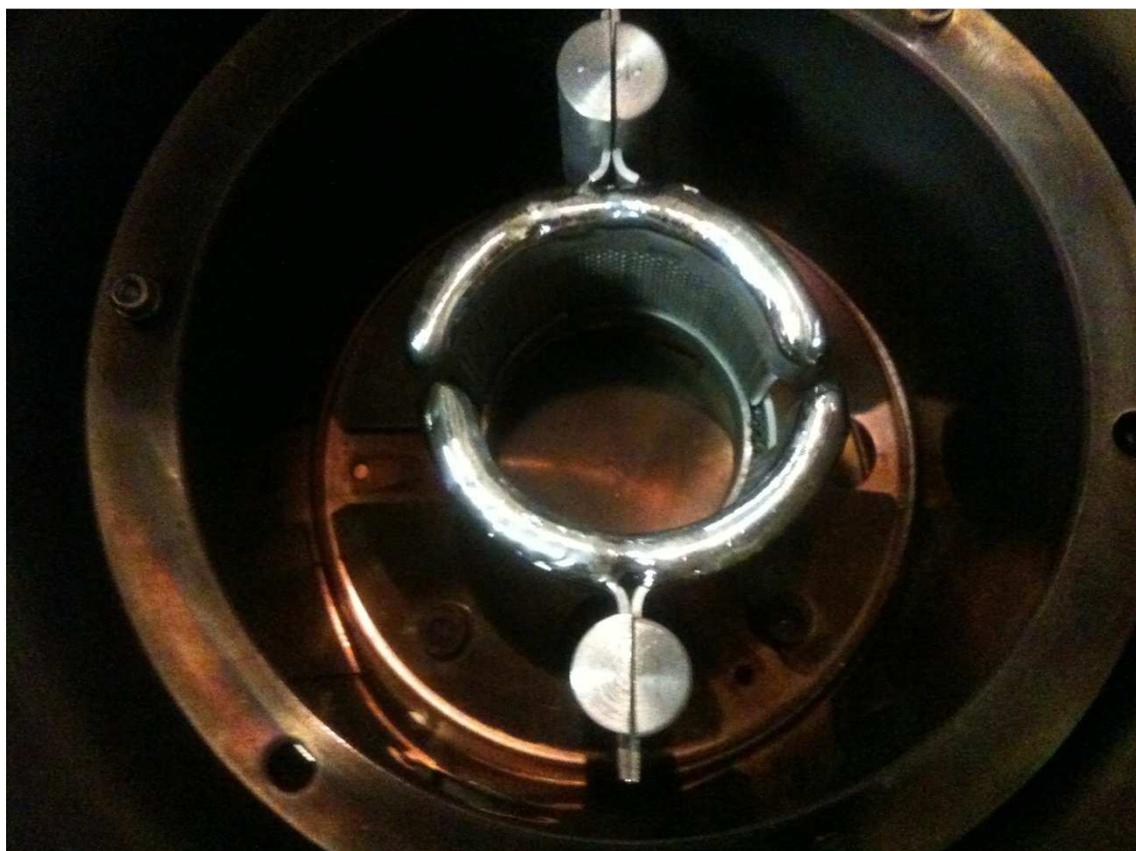


Fig. 2.5 Tungsten-resistor [photo: Virgilio Genova]

A spring loaded latticework is utilized to place the electrochemical cell in the isothermal zone of the furnace. Size changes of the sample and other parts of the electrochemical cell setup are measured by a force-sensor and compensated by a feedback-motion device (Fig. 2.6). This is important, because by doing so, it can be ensured, that the contact pressure at the electrode-electrolyte interface is independent of the temperature [07Goz].



Fig. 2.6 Feedback-motion device for the compensation of size changes of the electrodes and the electrolyte due to the high temperatures [photo: Virgilio Genova]

The measurement itself is done by stepwise cooling down the cell from a high temperature (about 800°C). This means, that several temperature steps are programmed where each temperature is kept constant for about 10 minutes and the EMF of this isothermal section is recorded.

The measurement of compounds which contain rare earth- and transition-metal elements is of great interest because the interaction of d and f orbitals forms relevant properties. Such compounds can be used as superconductors, permanent magnets, catalysts, hydrogen storage materials or other promising structural materials. For this reason, it is interesting to determine the thermodynamic properties of these materials

by the EMF technique. Publications in this particular field of research are quite rare [07Goz].

2.3.2 Solid electrolytes for EMF measurements

The following part of this thesis gives a general overview of possible solid electrolytes which can be used for EMF measurements. Also the advantages and disadvantages concerning the use of this particular type of electrolytes will be given.

In general there are many different classes of substances which are suitable to be used as a solid electrolyte, for instance oxides, halides, sulfides and other types of solid materials [10Ips]. A very common type of solid electrolytes is CaF_2 which is normally used in the form of a single crystal [73Ske], [01Kle]. Solid electrolytes are more and more important in various scientific and technological applications because they can be used in electrochemical cells for the measurement of chemical potentials in gases, liquids and solids [10Ips].

A big advantage of solid electrolytes is the possibility to use them at temperatures above 800°C . While liquid salt mixtures (liquid electrolytes) are not suitable for these high temperatures (see also 2.2.2), galvanic cell setups with solid electrolytes can be easily used also under these conditions and deliver reliable data [97Mik], [06Zuo].

Another important aspect is that current cells with solid electrolytes remain very stable during an experiment and can be operated for more than a week.

Finally it is important to mention, that it is not necessary to perform the time consuming and labour-intensive preparation and purification of the electrolyte like it is necessary for liquid salt mixtures as electrolyte.

It should be mentioned, that there are also some limitations concerning the use of solid electrolytes during EMF experiments:

Due to the solid state of the electrolyte-material, the system needs much longer to reach an equilibrium. This should be taken into account when planning a particular experiment. Furthermore the solid electrolyte does not provide any protection against

evaporation of material or the oxidation at the surface of the electrodes like liquid electrolytes do. This should be taken into account, especially if the alloys contain volatile components like for example zinc. Finally it has to be mentioned, that solid electrolyte materials can suffer so called microcracks. As mentioned before in 2.2.2 this can falsify measurements. If liquid electrolytes are used, this kind of error source does not occur.

One of the most important aspects concerning the use of solid electrolytes is their predominantly ionic conductivity. The ionic transference number t_{ion} , which is defined as the ratio of the ionic conductivity σ_{ion} to the total conductivity σ_{total} should be near to 1 for an ideal solid electrolyte [10lps].

$$t_{ion} = \sigma_{ion} / \sigma_{total} \quad (2.24)$$

A simple setup of a measuring cell was constructed by Schweitzer et. al. [04Sch] for the determination of the activities of Indium in the intermetallic compound $InPt_3$. The cell for this purpose had a sandwich type arrangement, where the solid electrolyte was placed between the two electrodes which were contacted by Ir foil for separating the leading wires to avoid any unwanted side reactions. The experimental setup of solid electrolyte cells which are commonly used for EMF measurements is very frequently similar to this arrangement. Some details to this particular system can also be found in [10lps].

2.3.3 Preparation of the alloys for EMF measurements with solid electrolytes

There are different possibilities for the preparation of samples for EMF measurements. Some of them were already mentioned and described in 2.2.3. Normally the samples are prepared by melting a mixture of the different components together. Melting can be achieved by standard laboratory furnaces, induction furnaces or electric arc furnaces. A special, not very common method is the use of a modified electron gun (e-gun) which is normally used for physical vapor deposition. This particular technique is currently used by the RIM-lab in Rome/Italy [05Goz], [07Goz].

The procedure for preparing the alloys is quite simple. The single components are mixed together by stirring them gently in a mortar. To prevent loss of material due to the formation of a fine metal dust and to obtain a better result concerning the homogeneity of the composition, the mixture is wetted by some drops of pure acetone. The finished compound is placed on a support in the e-gun. To prevent the formation of oxides on the surface of the sample during the melting process, a commercially available getter material is also placed in the chamber of the e-gun. After the chamber is evacuated, the getter material is heated for several hours. Then the preparation process of the intermetallic is carried out. To ensure homogeneity, each sample is heated repeatedly [07Goz].

2.3.4 Measurements of $\text{Re}_2\text{Co}_{17}$ alloys with a solid electrolyte based EMF cell

As mentioned above, EMF investigations of $\text{Re}_2\text{Co}_{17}$ intermetallics (Re=Pr, Nd, Gd) were carried out with a galvanic cell which was equipped with a solid CaF_2 single crystal as electrolyte. The author of this work had the possibility to examine the $\text{Pr}_2\text{Co}_{17}$ intermetallic system. In this case, the $\text{Re}_2\text{Co}_{17}$ alloys were measured in a solid state. The following figures and tables show the results of this measurement and also the data which were obtained from two further investigations ($\text{Nd}_2\text{Co}_{17}$ and $\text{Gd}_2\text{Co}_{17}$).

The following intermetallic systems were examined [11Gen]:

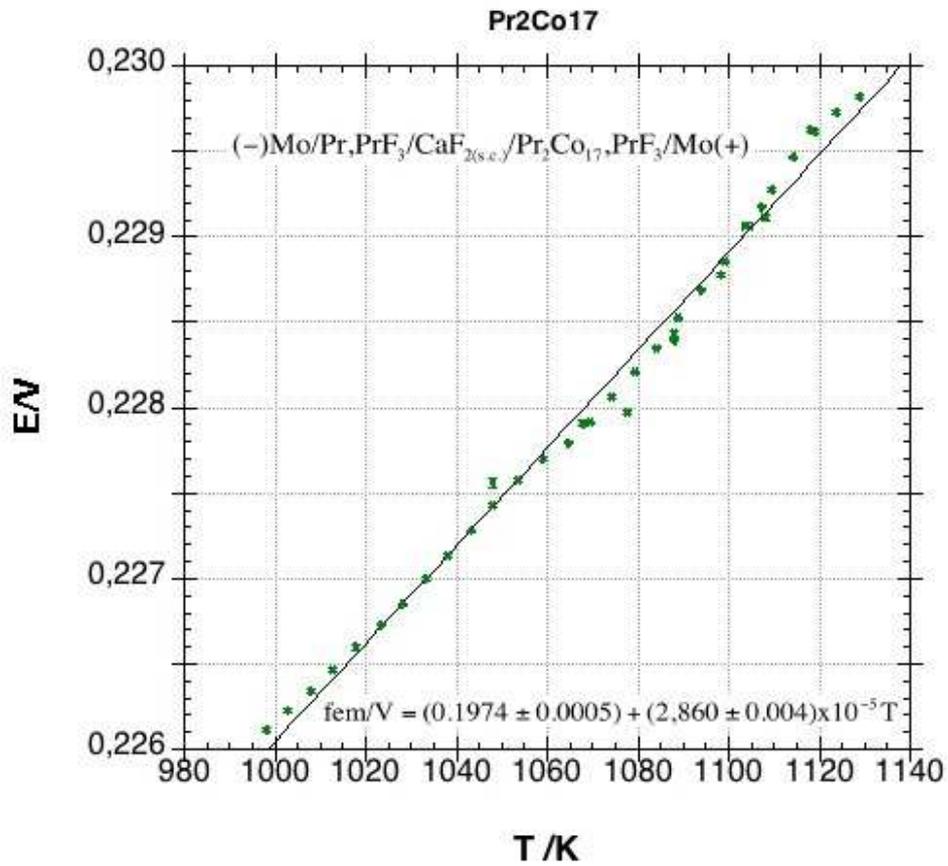


Fig. 2.7 Linear interpolation of EMF vs T for the system Pr₂Co₁₇ [diagram: Virgilio Genova]

$$(-)Mo/Pr, PrF_3/CaF_{2(s.c.)}/Pr_2Co_{17}, PrF_3/Mo(+) \quad (2.25)$$

$$EMF (V) = (0.1974 \pm 0.0005) + (2.860 \pm 0.004) \times 10^{-5} T \quad (2.26)$$

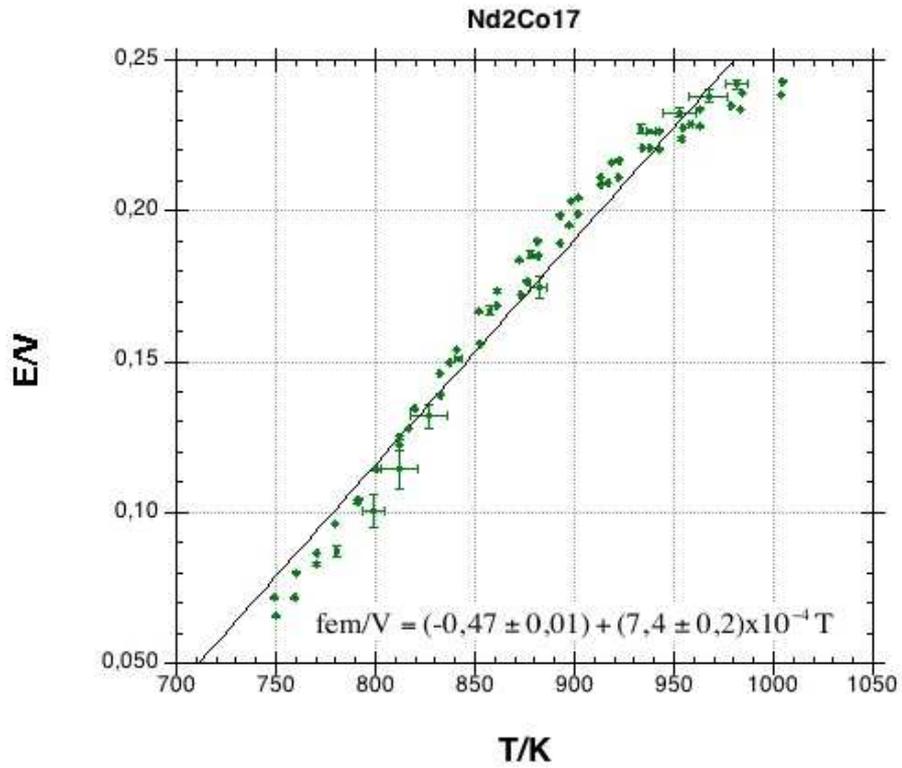


Fig. 2.8 Linear interpolation of EMF vs T for the system Nd₂Co₁₇
[diagram: Virgilio Genova]

$$(-)Mo/Nd, NdF_3/CaF_{2(s.c.)}/Nd_2Co_{17}, NdF_3/Mo(+) \quad (2.27)$$

$$EMF (V) = (-0.47 \pm 0.01) + (7.4 \pm 0.2) \times 10^{-4} T \quad (2.28)$$

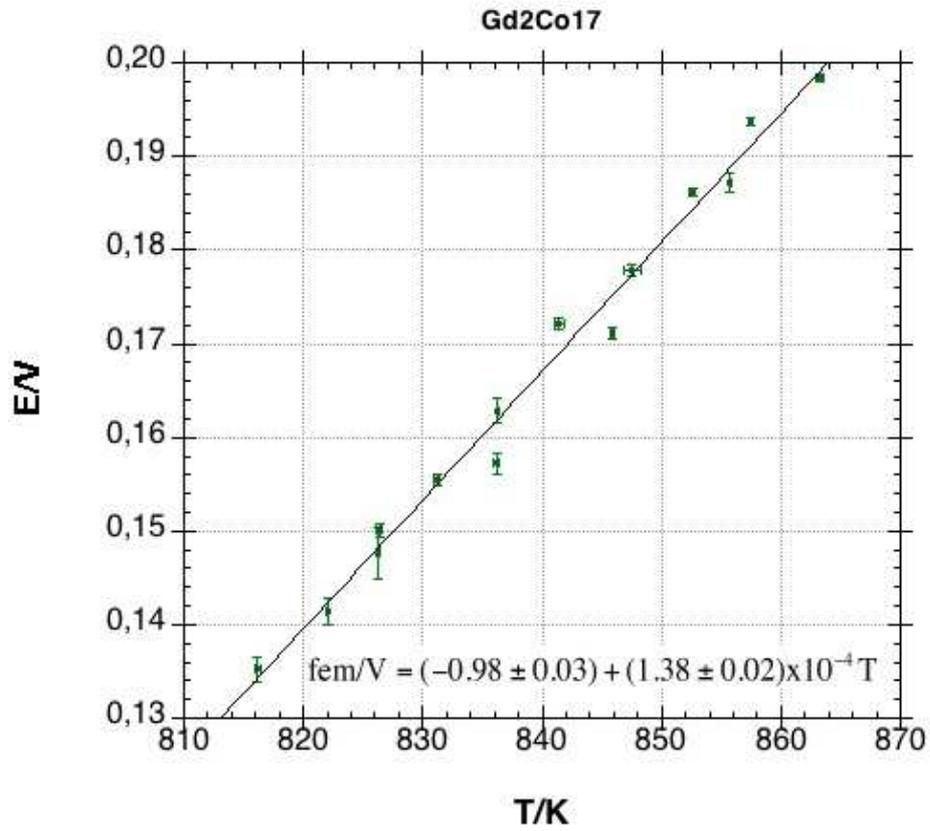


Fig. 2.9 Linear interpolation of EMF vs T for the system Gd_2Co_{17}
[diagram: Virgilio Genova]

$$(-)Mo/Gd, GdF_3/CaF_{2(s.c.)}/Gd_2Co_{17}, GdF_3/Mo(+) \quad (2.29)$$

$$EMF (V) = (-0.98 \pm 0.03) + (1.38 \pm 0.02) \times 10^{-4} T \quad (2.30)$$

The measured EMF values can be used to calculate the activity of the Re and the change of the partial Gibbs free energy $\overline{\Delta G_{Re}}$ according to the equations of chapter 2.1.2.

Furthermore, it is possible to calculate also the partial molar enthalpy $\overline{\Delta H_{Re}}$ and the partial molar entropy $\overline{\Delta S_{Re}}$ by using the equations mentioned in chapter 2.1.2.

The table below shows the calculated thermodynamic properties [11Gen]:

<i>Re in Re₂Co₁₇</i>	<i>T (K)</i>	<i>-log a_{Re}</i>	$\overline{\Delta G_{Re}}$ (kJ/mol)	$\overline{\Delta H_{Re}}$ (kJ/mol)	$\overline{\Delta S_{Re}}$ (J/K)
Pr	1070	17.107	-6.948	-6.0152	8.72
Nd	878	15,631	-5.313	16.433	26.21
Gd	840	14.25	-5.085	30.125	4.922

Tab. 2.1 Calculated thermodynamic properties of Re₂Co₁₇ alloys (Re=Pr, Nd, Gd)

Chapter 3: EMF investigations of the ternary Al-Ge-Zn system

3.1 Literature review

3.1.1 The Al-Ge binary system

This particular system is interesting because it shows superconducting and semiconducting metastable phases which can be formed by rapid cooling [11Spr1]. Figure 3.1 shows the calculated phase diagram by A. J. McAlister and J. L. Murray (1984) with a simple eutectic. It is based primarily on the work of [26Kro], [39Sto], [62Gla], [66Wil], [79Es1] and [79Es2].

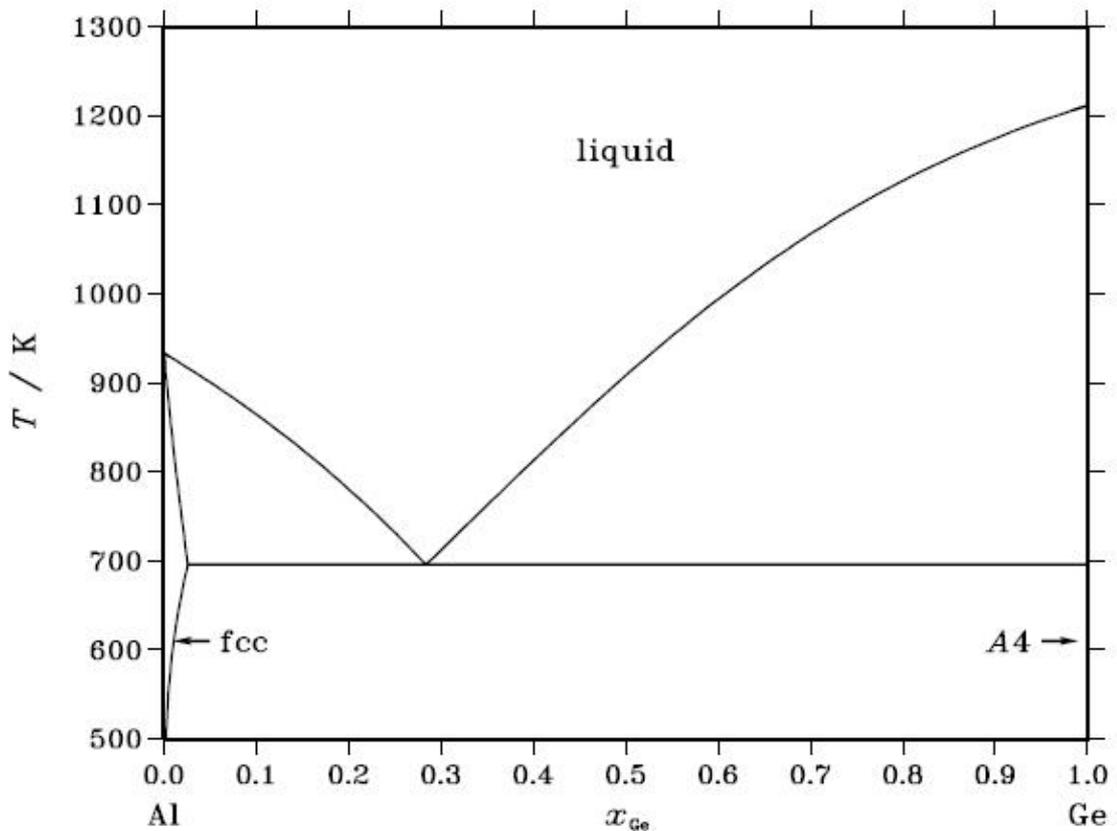


Fig. 3.1 Calculated phase diagram for the system Al-Ge

[A.J. McAlister and J.L. Murray, 1984]

The eutectic temperature has not been determined reliably [86Mas1]. Estimates have been done based on the electrochemical cell data of [79Es1] of $417^{\circ}\text{C} \pm 3^{\circ}\text{C}$. The mean of these estimates agrees quite well with the value of 420°C resulting from the present thermodynamic calculation [86Mas1].

3.1.2 The Al-Zn binary system

Al-Zn alloys are of great interest, because they form the basis of many technically important alloys. Figure 3.2 shows the calculated phase diagram by J. L. Murray (1983) of the Al-Zn binary system. Some further information about this particular system can be found in [11Spr2].

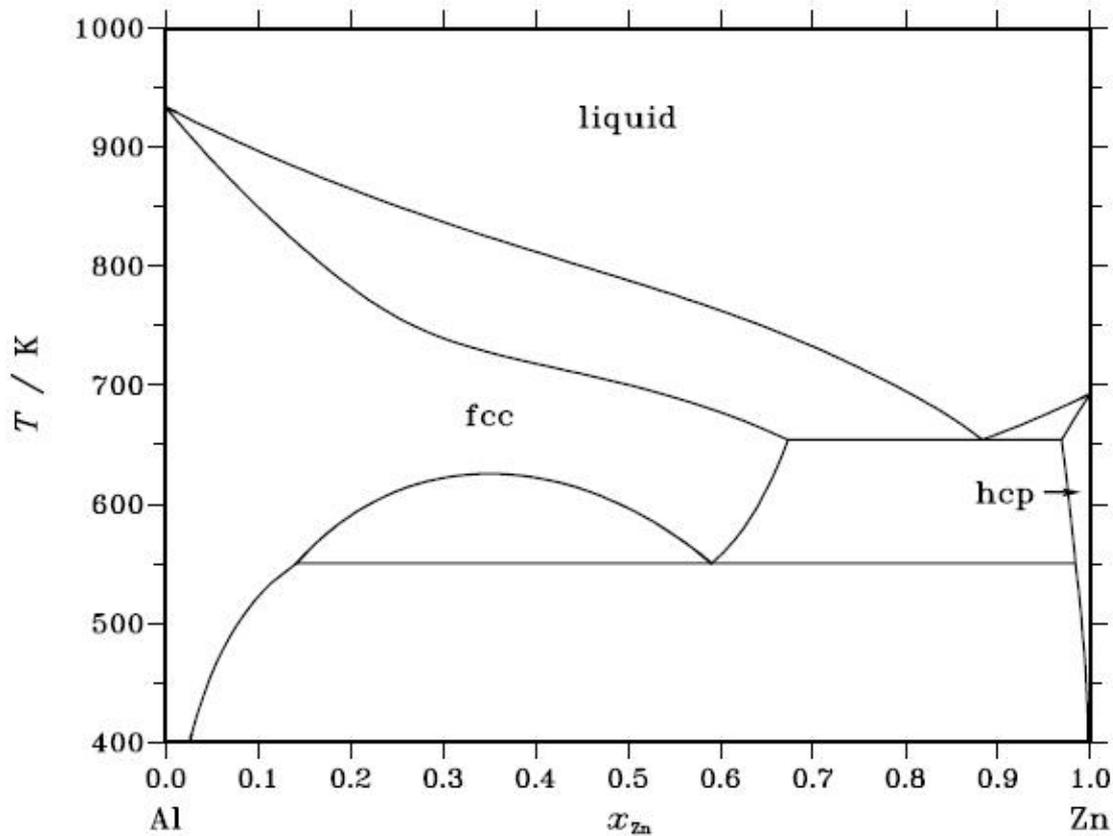


Fig. 3.2 Calculated phase diagram for the system Al-Zn

[J.L. Murray, 1983]

3.1.3 The Ge-Zn binary system

The Ge-Zn system is characterized by a eutectic reaction at 394°C and 94,7 at. % Zn [86Mas2]. A thermodynamic assessment of this particular system was carried out by Chevalier [89Che], [11Spri3]. Figure 3.3 shows the calculated phase diagram by G. W. Olesinski and G. J. Abbaschian (1985) of the Ge-Zn binary system.

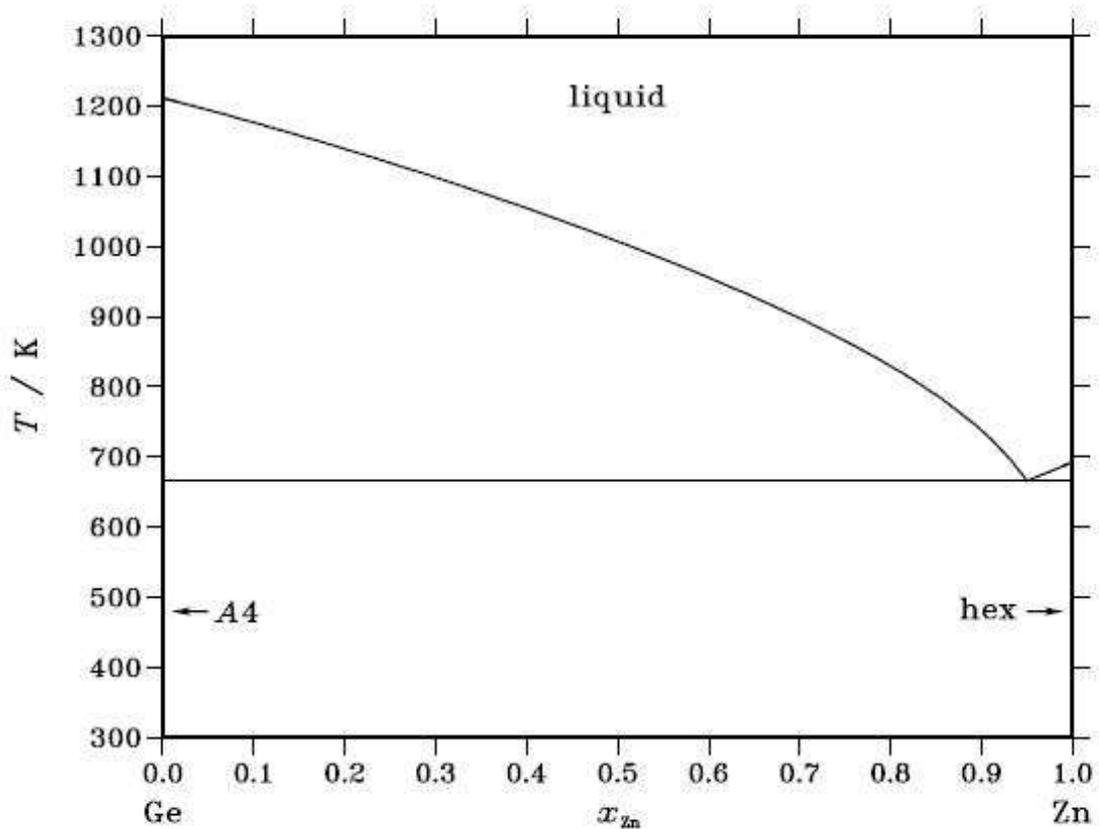


Fig. 3.3 Calculated phase diagram for the system Ge-Zn

[R.W. Olesinski and G.J. Abbaschian, 1985]

Previous works, which were based on EMF measurements, were carried out to determine the partial free energy of Zn in liquid alloys [72Pre], [11Spri3]. Also Batalin et al. obtained thermodynamic properties of the liquid phase by using EMF measurements [70Bat].

3.1.4 The Al-Ge-Zn ternary system

Thermodynamic data of the ternary Al-Ge-Zn system are quite scarce in the literature. There is to be found just some information about the thermodynamic calculation of phase equilibria in Al-Ge-Zn system [91Sri], but also in this case, the calculations were based on the data of the binary alloys Al-Ge, Al-Zn and Ge-Zn [11Sci]. Up to now, it has not been possible to find any reports about experimental work concerning the ternary Al-Ge-Zn system.

3.2 Experimental procedures

3.2.1 The Al-Ge-Zn alloys

The alloys were prepared by melting the appropriate quantities of aluminum, germanium and zinc together in a standard laboratory furnace. To avoid oxidation of the metals, the alumina crucibles, which were used, were sealed into quartz ampoules under vacuum. Leak tightness was ensured using a test with a small Tesla transformer. Aluminum was obtained in small rods from Alfa Aesar with a purity of 99.999%. Pure 99.999% germanium was also bought at Alfa Aesar and zinc with a given purity of 99.999% was used from Johnson Matthey Chemicals Limited. The alloys were molten for 6 days at 850°C. Subsequently the alloys were quenched.

Figure 3.4 shows the measured cross-sections and alloy compositions of the ternary Al-Ge-Zn alloys. Altogether 30 different alloys were prepared. It is apparent from the diagram, that three different sections with varying ratios of germanium and zinc were defined (Ge:Zn=3:1, Ge:Zn=1:1, Ge:Zn=1:3). Each section was subdivided so that ten compositions with a variable concentrations of aluminum (from 5 to 90 atomic %) were defined for every section. This results in a total number of 30 different ternary Al-Ge-Zn alloys.

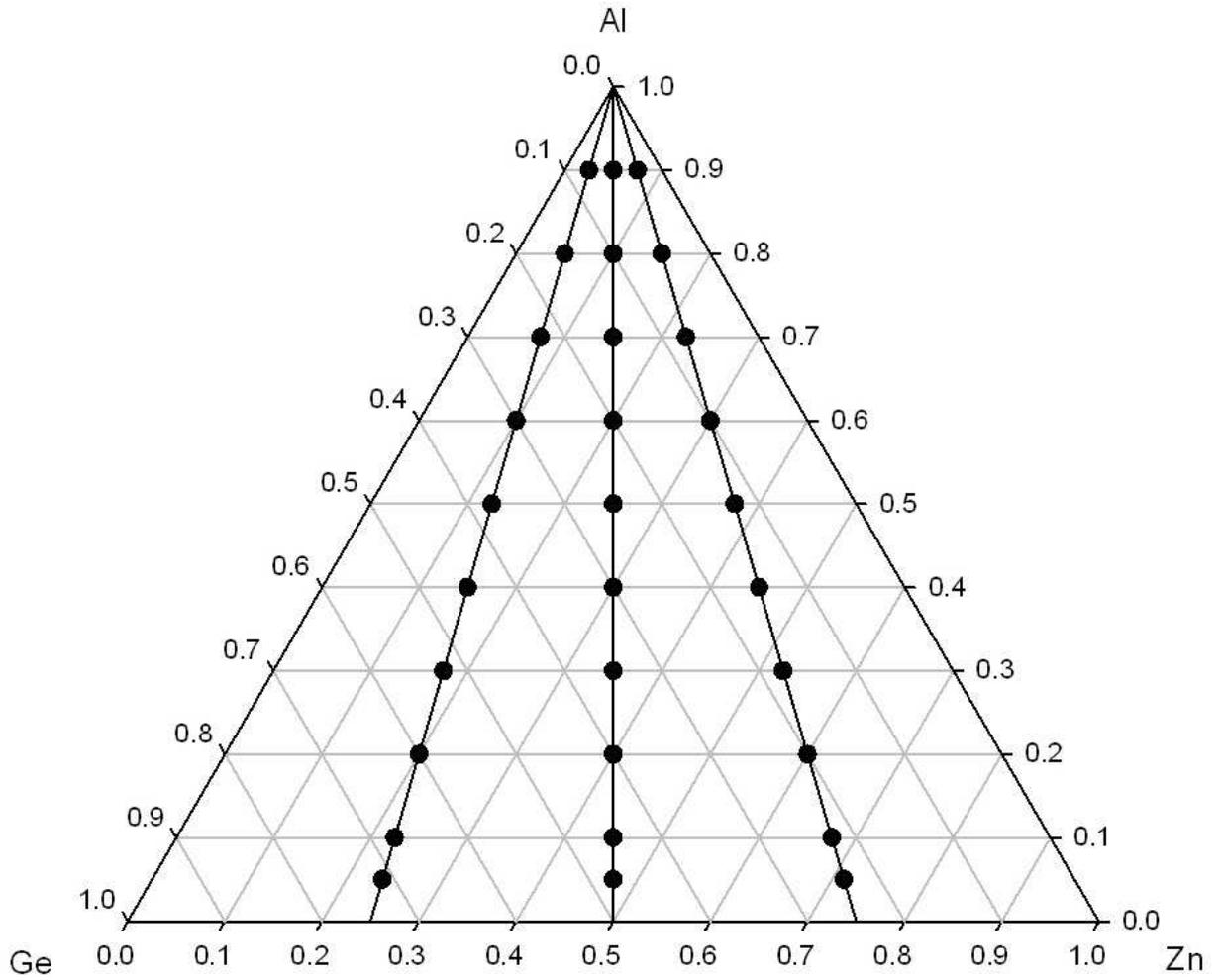


Fig 3.4 Measured cross-sections and alloy compositions in the ternary Al-Ge-Zn system

The following tables give a detailed overview of the composition of each single alloy which was prepared:

<i>ID</i>	<i>wt Al (g)</i>	<i>wt Ge (g)</i>	<i>wt Zn (g)</i>	<i>Al at. %</i>	<i>Ge/Zn</i>	<i>Total wt</i>
1	0.07869	3.01661	0.90506	5.004	3.000	4.00036
2	0.16244	2.95206	0.88552	10.000	3.001	4.00002
3	0.34771	2.80925	0.84322	19.993	2.999	4.00018
4	0.56166	2.64525	0.79357	30.008	3.001	4.00048
5	0.81001	2.45347	0.73614	39.998	3.000	3.99962
6	1.10348	2.22800	0.66829	50.003	3.001	3.99977
7	1.45432	1.95796	0.58725	59.999	3.001	3.99953
8	1.88242	1.62911	0.48861	70.000	3.001	4.0014
9	2.41508	1.21928	0.36569	79.999	3.001	4.00005
10	3.09786	0.69498	0.20849	90.001	3.001	4.00133

Tab. 3.1 The compositions of Al-Ge-Zn alloys (Ge:Zn=3:1)

<i>ID</i>	<i>wt Al (g)</i>	<i>wt Ge (g)</i>	<i>wt Zn (g)</i>	<i>Al at. %</i>	<i>Ge/Zn</i>	<i>Total wt</i>
11	0.08056	2.06264	1.85705	4.994	1.000	4.00025
12	0.16660	2.01750	1.81627	10.003	1.000	4.00037
13	0.35605	1.91779	1.72632	19.994	1.000	4.00016
14	0.57406	1.80325	1.62315	29.998	1.000	4.00046
15	0.82710	1.66974	1.50332	40.002	1.000	4.00016
16	1.12437	1.51367	1.36232	50.000	1.000	4.00036
17	1.47925	1.32725	1.19493	60.002	1.000	4.00143
18	1.90852	1.10098	0.99126	69.999	1.000	4.00076
19	2.44065	0.82126	0.73935	80.001	1.000	4.00126
20	3.11634	0.41961	0.41961	90.000	1.000	4.00198

Tab. 3.2 The compositions of Al-Ge-Zn alloys (Ge:Zn=1:1)

<i>ID</i>	<i>wt Al (g)</i>	<i>wt Ge (g)</i>	<i>wt Zn (g)</i>	<i>Al at. %</i>	<i>Ge/Zn</i>	<i>Total wt</i>
21	0.08258	1.05866	2.85897	4.988	3.000	4.00021
22	0.17060	1.03456	2.79403	9.990	3.000	3.99919
23	0.36510	0.98254	2.65369	20.005	3.000	4.00133
24	0.58727	0.92204	2.49010	30.005	3.000	3.99941
25	0.84487	0.85262	2.30280	40.007	3.000	4.00029
26	1.14634	0.77144	2.08334	50.003	3.000	4.00112
27	1.50320	0.67443	1.82125	60.003	3.000	3.99888
28	1.93384	0.55784	1.50632	70.001	3.000	3.99800
29	2.46584	0.41495	1.12042	80.000	3.000	4.00121
30	3.13685	0.23454	0.63354	90.000	3.001	4.00493

Tab. 3.3 The compositions of Al-Ge-Zn alloys (Ge:Zn=1:3)

3.2.2 The liquid electrolyte

The preparation of the liquid electrolyte for the investigation of the ternary Al-Ge-Zn system was done according to the procedure described in 2.2.2. In this case a mixture of 77.3g LiCl, 90.7g KCl and 2.975g KAlCl_4 was used. The KAlCl_4 (Fig. 3.5) was prepared in a separate experiment. According to [63Moo] it was found that the use of this salt, leads to much better results than the use of AlCl_3 . KAlCl_4 is less hygroscopic than AlCl_3 and also has a lower vapor pressure at high temperatures (At 650°C the vapor pressure of pure AlCl_3 is about 10 atm., that of KCl- AlCl_3 is < 0.02atm.) [63Moo].



Fig. 3.5 Handling of moisture sensitive $KAlCl_4$ inside of the glovebox

One day before the purification, the first two components (LiCl and KCl) were mixed together and stored in a dry box at 100°C over night. The mixture was then filled into the glass apparatus for the purification. At this moment the $KAlCl_4$ was removed from the glove box and added to the other components. As mentioned before, the whole apparatus (Fig. 3.6) was constructed of glass.



Fig. 3.6 The apparatus for the preparation of the $KCl-LiCl-KAlCl_4$ electrolyte

The procedure of the chlorination was done according to the steps which were described in the previous chapter. For safety reasons, only a small amount of chlorine gas was transferred from a gas bottle into a cooling-trap which was cooled down under the exhaust hood (Fig. 3.7). The cooling of the trap was accomplished with liquid nitrogen.



Fig. 3.7 Transfer of chlorine gas into a cooling trap under the exhaust hood

Then the cooling trap was attached to another one, which was permanently fixed to the purification-apparatus. The chlorine was transferred from the first to the second trap (Fig. 3.8) by removing the dewar container with the liquid nitrogen.

This way, only a small amount of the needed chlorine gas could be transferred to the apparatus for the purification.



Fig. 3.8 Chlorine gas inside of the purification-apparatus

The salt was heated up to 600°C. After the eutectic mixture was melted, chlorination was accomplished in 45 minutes. The remaining chlorine gas which passed the molten salt was dissolved in washing bottles which contained aqueous solutions of sodium hydroxide. The light green color of the aqueous solution showed that chlorine gas was absorbed (Fig. 3.9).



Fig. 3.9 Chlorine gas bubbling through aqueous sodium hydroxide solutions. The slightly green color of the solution in the right bottle shows the presence of dissolved chlorine

This particular salt mixture seems to have a kind of viscosity which causes the formation of foam. For this reason the cold parts of the apparatus were heated periodically from the outside with a hydrogen torch to melt down the parts of the electrolyte which condensed at the cooler part of the tube (Fig. 3.10).



Fig. 3.10 Melting down the condensed parts of the electrolyte with a hydrogen torch

After that a continuous flow of pure argon gas was passed through the molten salt for about four hours. Finally the molten salt was filtered under vacuum through a frit and sealed into a glass ampoule (Fig. 3.11).



*Fig. 3.11 Sealing the purified electrolyte into an ampoule
[photo: Michael Hindler]*

3.2.3 The setup of the cell

The general setup of the measuring cell was accomplished according to the way described in 2.2.1. Figure 3.12 shows the setup of a typical cell which was used for the current investigations.

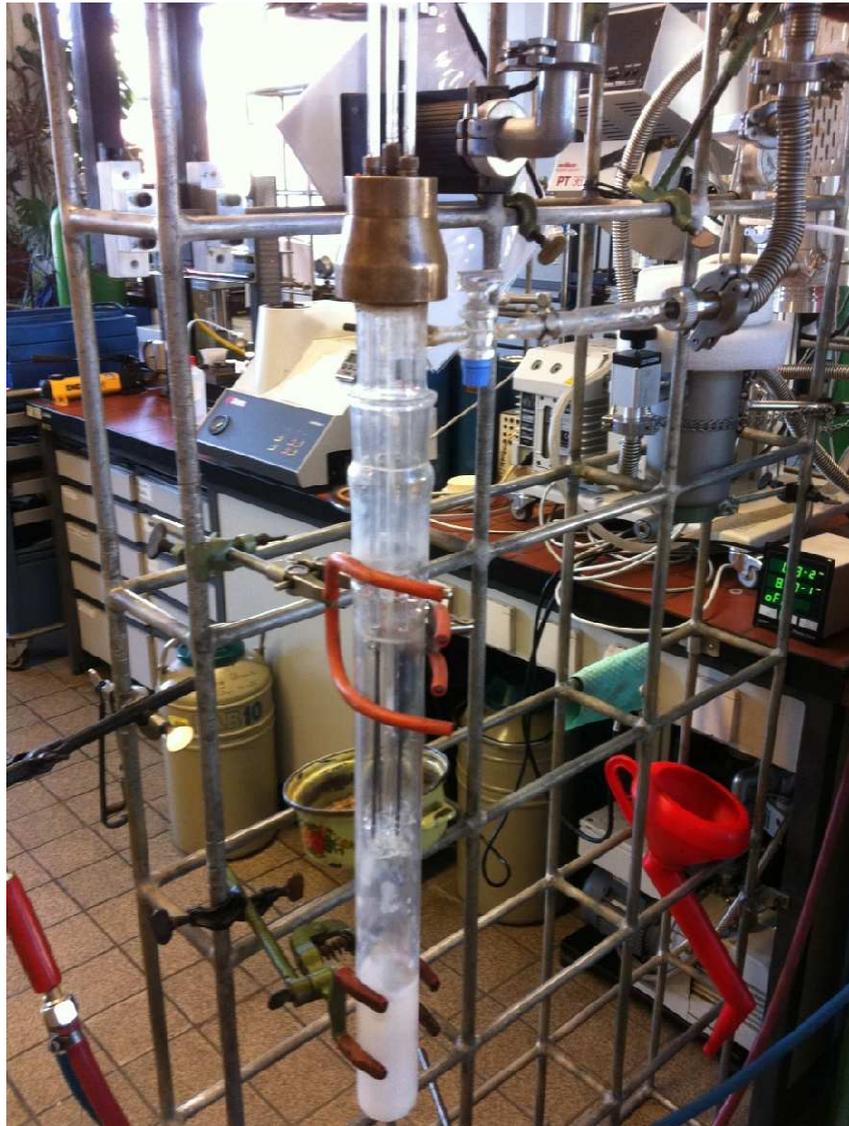


Fig. 3.12 EMF cell for the investigation of Al-Ge-Zn alloys with liquid electrolytes

The alloy samples were placed in small alumina crucibles which themselves were inserted into the sample holder (Fig 3.13).



Fig. 3.13 Sample holder

This procedure seemed to be important because reactions between the alloys and the quartz material were observed in previous experiments. By placing the alloys into the alumina crucibles, this kind of interaction could be prevented. The investigated alloys were of various compositions. The details concerning the preparation of the alloys and their exact formation are described in 3.2.1. Pure aluminum was used as a reference electrode.

The lead wires which established the connection to the liquid electrodes were made of molybdenum. In the course of first tests, an interaction of the molybdenum wire with the alloys was observed. For this reason, graphite rods were attached at the end of the lead wires using commercially available electrical connectors (Fig. 3.14).



Fig. 3.14 Graphite rods at the end of the molybdenum lead wires to prevent interactions between the Mo and the investigated alloys

The graphite rods were of sufficient length, so that only the graphite dipped into the liquid electrolyte and touched the alloys. This way, an interaction between the molybdenum wire and the investigated intermetallics could be avoided.

For the present investigation a K-type Ni/NiCr thermocouple was used to monitor the temperature inside the cell. After heating up the cell to about 800°C the temperature control of the furnace was set to establish a cooling rate 0.1 °C per minute. Thus the temperature was gradually lowered to 500°C. During this process, the EMF values in

dependence of the temperature were recorded with a PC. The cooling curve was used to evaluate the thermodynamic properties.

Chapter 4: Results and discussions

The following chapter shows the measured data and their evaluation. It is to be mentioned, that in the course of the experimental work some problems occurred which caused some fluctuations of the recorded values. It might be that the electrolyte is not stable enough to work at high temperatures of about 800°C for a longer period of time. Interactions of germanium with any compound of this particular setup also cannot be excluded. The fact, that the measurement of the Ge-rich compounds turned out to be more difficult supports this assumption. This is also the reason, why it was not possible to obtain reasonable data in all cases (for all previously set Al-concentrations from 5 at. % to 90 at. %) of each cross section. According to that it is suggested to carry out further investigations concerning the Al-Ge-Zn system. A possibly suitable way could be the measurement of EMF values with solid electrolytes. This could be achieved by a setup like the one, which is described in chapter 2.3 of the current work.

Despite of the mentioned problems, a reasonable data evaluation has been accomplished, by careful analysis and interpretation of the measured values.

4.1 Measured EMF values

The following figures show the measured EMF values in dependence of the recorded temperature. These data were obtained through the measurements and used for the evaluation. It is apparent from the figures, that some of the recorded curves are shorter than the others. The previously described experimental problems caused a lack of values and resulted in shorter curves.

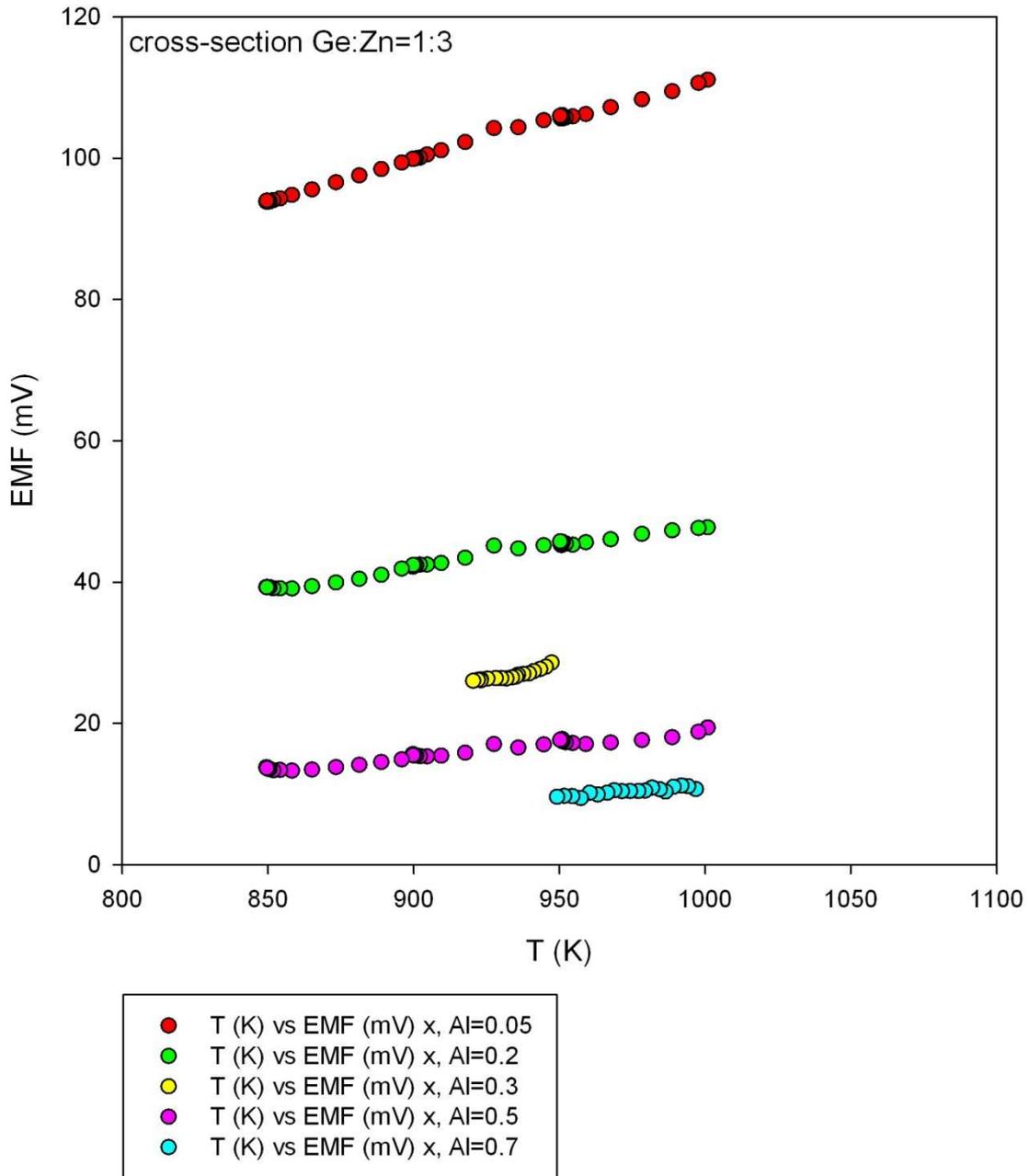


Fig. 4.1 Measured EMF values in dependence of the temperature for the cross section Ge:Zn=1:3

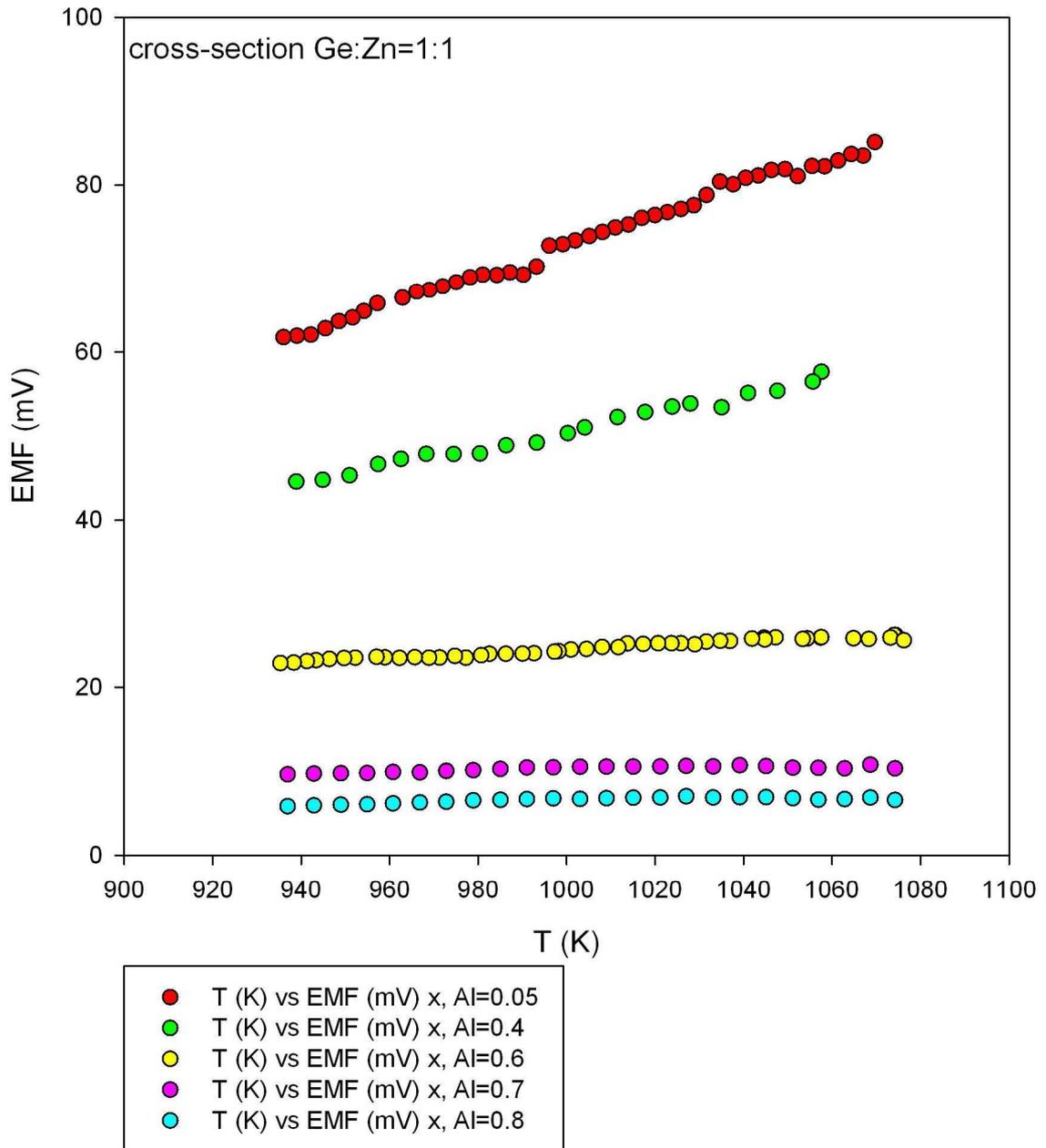


Fig. 4.2 Measured EMF values in dependence of the temperature for the cross section Ge:Zn=1:1

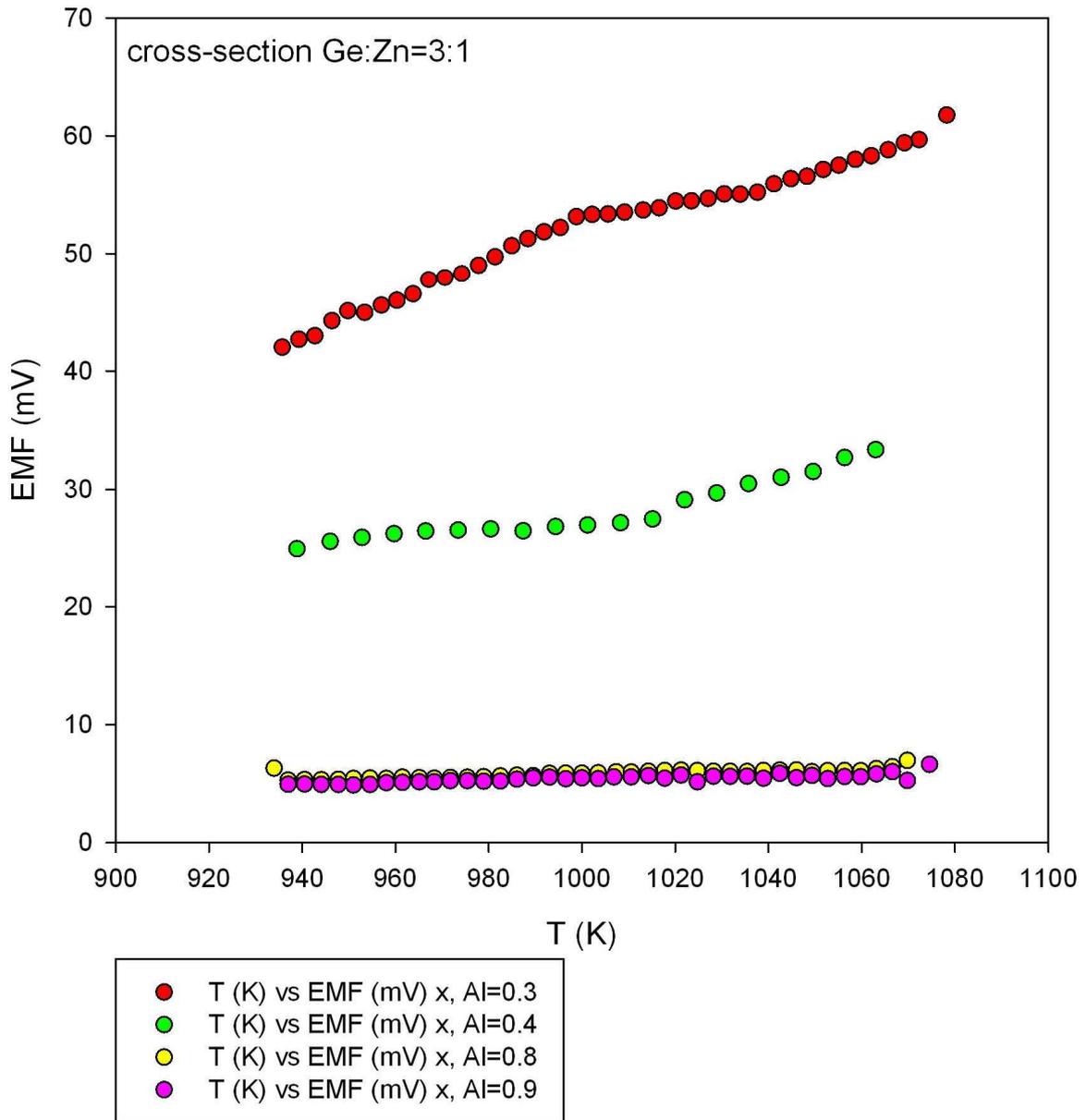


Fig. 4.3 Measured EMF values in dependence of the temperature for the cross section Ge:Zn=3:1

The linear parts of the temperature vs. EMF curves were used for the evaluation. The EMF values were fitted with a square fit according to the following equation:

$$E \text{ (mV)} = a + bT \text{ (K)} \quad (4.1)$$

The tables below show the obtained parameters:

x_{Al}	$E \text{ (mV)}$
0.05	$-4.95 + 0.1164 T/K (\pm 0.27)$
0.2	$-12.93 + 0.0613 T/K (\pm 0.30)$
0.3	$-45.51 + 0.0775 T/K (\pm 0.24)$
0.5	$-20.04 + 0.0394 T/K (\pm 0.35)$
0.7	$-7.37 + 0.0181 T/K (\pm 0.36)$

*Tab. 4.1 Measured EMF data of liquid Al-Ge-Zn alloys. Cross-section
Ge:Zn=1:3*

x_{Al}	$E \text{ (mV)}$
0.05	$-103.23 + 0.1759 T/K (\pm 0.60)$
0.4	$-53.20 + 0.1039 T/K (\pm 0.40)$
0.6	$1.02 + 0.0234 T/K (\pm 0.22)$
0.7	$3.73 + 0.0065 T/K (\pm 0.19)$
0.8	$-0.15 + 0.0067 T/K (\pm 0.21)$

*Tab. 4.2 Measured EMF data of liquid Al-Ge-Zn alloys. Cross-section
Ge:Zn=1:1*

x_{Al}	E (mV)
0.3	$-70.60 + 0.1220 T/K (\pm 0.90)$
0.4	$-30.75 + 0.0588 T/K (\pm 0.82)$
0.8	$-8.17 + 0.0141 T/K (\pm 0.64)$
0.9	$-8.96 + 0.0143 T/K (\pm 0.70)$

Tab. 4.3 Measured EMF data of liquid Al-Ge-Zn alloys. Cross-section
Ge:Zn=3:1

4.2 Partial molar quantities of aluminum in liquid Al-Ge-Zn alloys

By using the measured EMF values, the activity of aluminum and the change of the Gibbs free energy were calculated according to the equations of chapter 2.1.2.

As mentioned above (see 2.1.2), it is possible to calculate also the partial molar enthalpy $\overline{\Delta H_{Al}}$ and the partial molar entropy $\overline{\Delta S_{Al}}$ by the following equations:

$$\overline{\Delta H_{Al}} = -zF \left[E - T \left(\frac{\partial E}{\partial T} \right)_{x,P} \right] = \overline{\Delta G_{Al}} + T \overline{\Delta S_{Al}} = -3aF \quad (4.2)$$

$$\overline{\Delta S_{Al}} = zF \left(\frac{\partial E}{\partial T} \right)_{x,P} = 3bF \quad (4.3)$$

The calculated results are listed in the following tables:

x_{Al}	EMF (mV)	a_{Al}	$\overline{\Delta G_{Al}}$ (J/mol)	$\overline{\Delta H_{Al}}$ (J/mol)	$\overline{\Delta S_{Al}}$ (J/mol K)
0.05	108.305	0.0212	34429	1434 ^{*3}	33.69
0.2	46.793	0.1892	14879	3744	17.74
0.3	158.07	0.0035 ^{*1}	45431 ^{*2}	13174	22.43
0.5	17.633	0.5339	5607	5801	11.40
0.7	11.27	0.6618	917	2133	5.23

Tab. 4.4 Activities and partial molar quantities of aluminum at 677°C for the cross-section Ge:Zn=1:3

*1 value was not taken into account for the plot a vs x_{Al} (Ge:Zn=1:3, T=677°C)

*2 value was not taken into account for the plot ΔG_{Al} vs x_{Al} (Ge:Zn=1:3, T=677°C)

*3 value was not taken into account for the plot ΔH_{Al} vs x_{Al} (Ge:Zn=1:3, T=677°C)

x_{Al}	EMF (mV)	a_{Al}	$\overline{\Delta G_{Al}}$ (J/mol)	$\overline{\Delta H_{Al}}$ (J/mol)	$\overline{\Delta S_{Al}}$ (J/mol K)
0.05	10.403	0.0863	-20882	29882	50.91
0.4	45.64	0.1825	-3798	15691	30.07
0.7	9.826	0.6989	3044	1081	1.88
0.8	6.037	0.7953	-1870	44	1.93

Tab. 4.5 Activities and partial molar quantities of aluminum at 677°C for the cross-section Ge:Zn=1:1

x_{Al}	EMF (mV)	a_{Al}	$\overline{\Delta G}_{Al}(\text{J/mol})$	$\overline{\Delta H}_{Al}(\text{J/mol})$	$\overline{\Delta S}_{Al}(\text{J/mol K})$
0.3	44.671	0.1785	12930	20437	35.31
0.4	25.837	0.3867	-8425	8903	17.02
0.8	5.408	0.8208	-1764	2366	4.08
0.9	4.858	0.8295	-1585	2593	4.13

Tab. 4.6 Activities and partial molar quantities of aluminum at 677°C for the cross-section Ge:Zn=3:1

The following figure shows the activities of aluminum at 677°C of the three cross sections. The binary values for Ge-Al and Zn-Al were taken from [73Hul]:

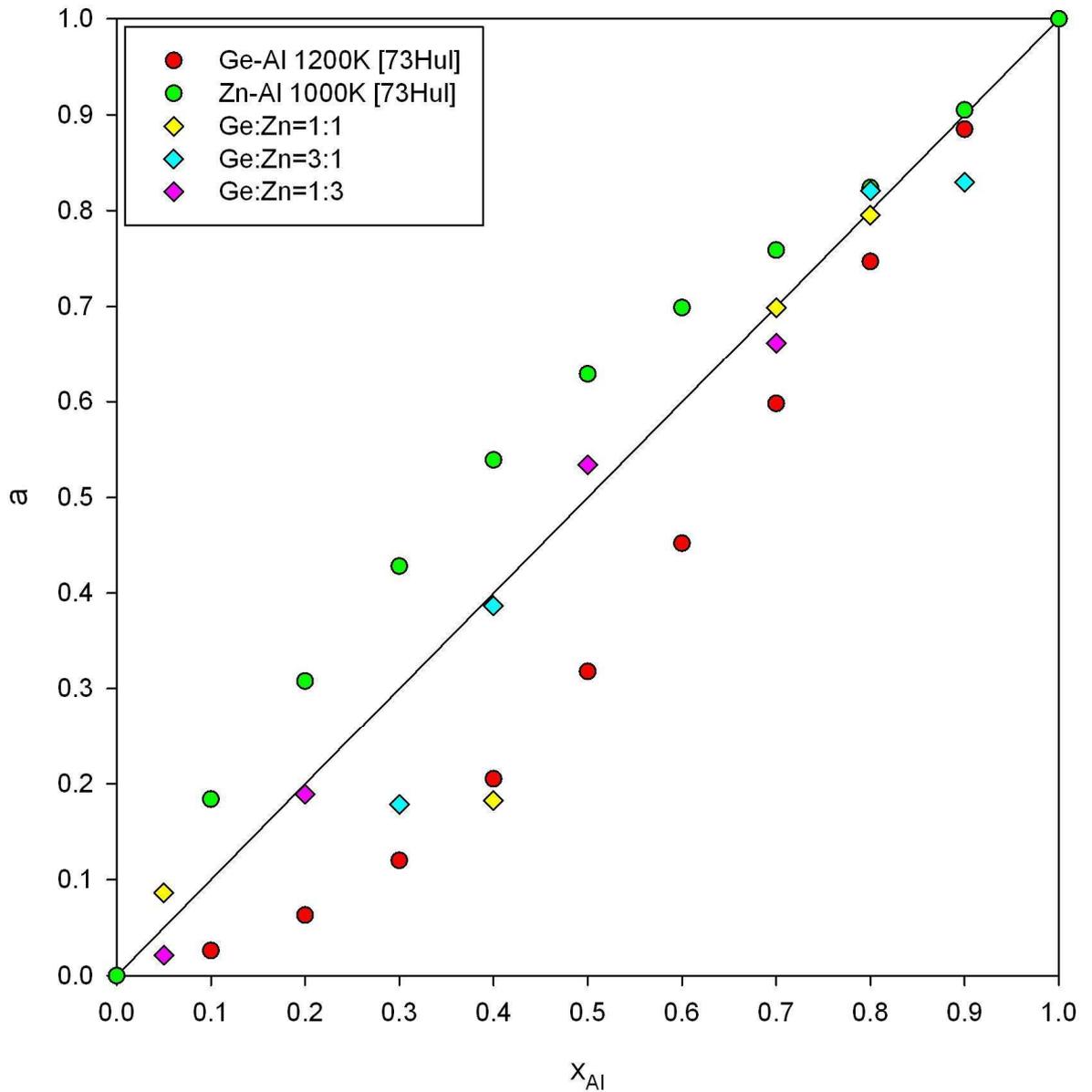


Fig. 4.4 Activities of aluminum at 677°C for three cross sections

The figures below show the curves of the partial thermodynamic quantities $\overline{\Delta G_{Al}}$, $\overline{\Delta H_{Al}}$ and $\overline{\Delta S_{Al}}$. The results seem to be reasonable, even with the apparent deviations of the theoretical trend of the curves.

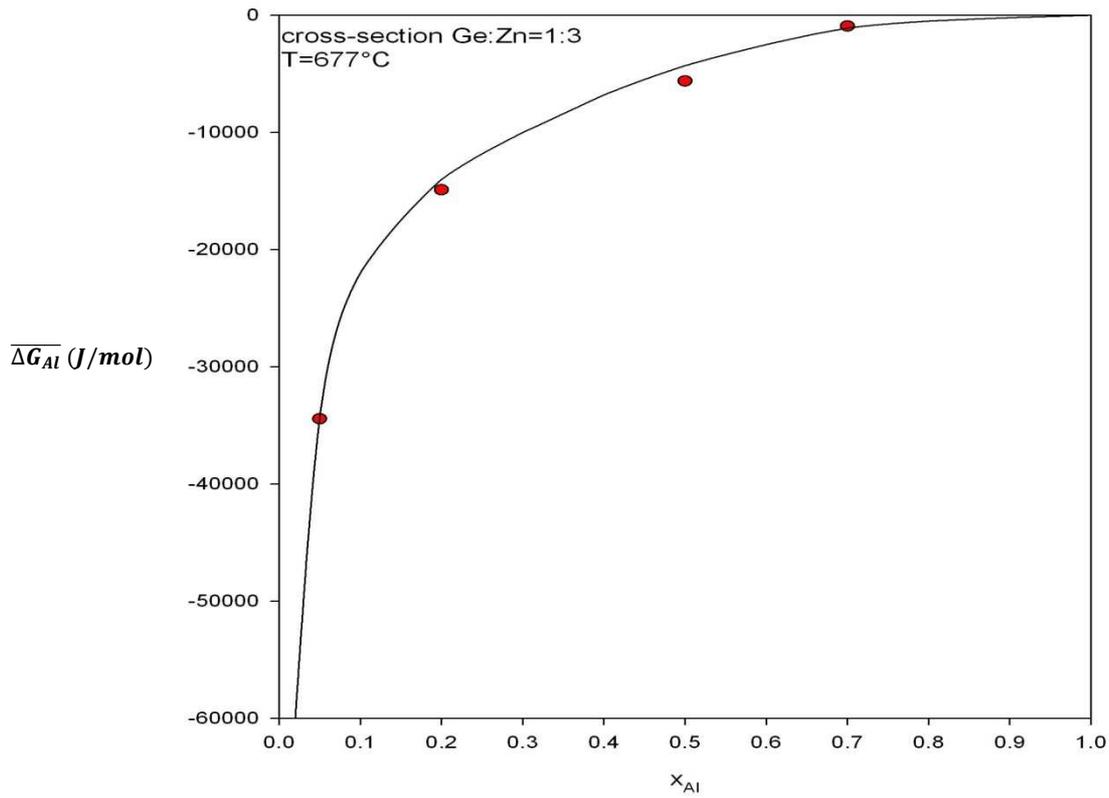


Fig. 4.5 Partial Gibbs free energy of aluminum for the cross section Ge:Zn=1:3 at 677°C

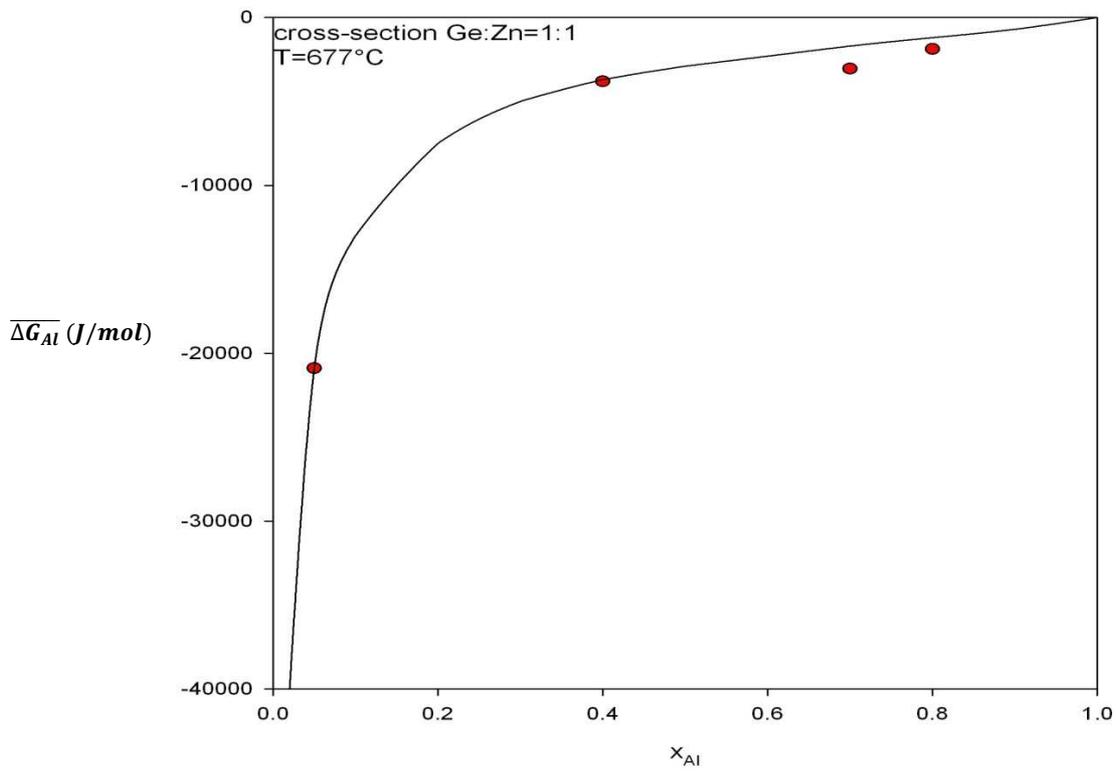


Fig. 4.6 Partial Gibbs free energy of aluminum for the cross section Ge:Zn=1:1 at 677°C

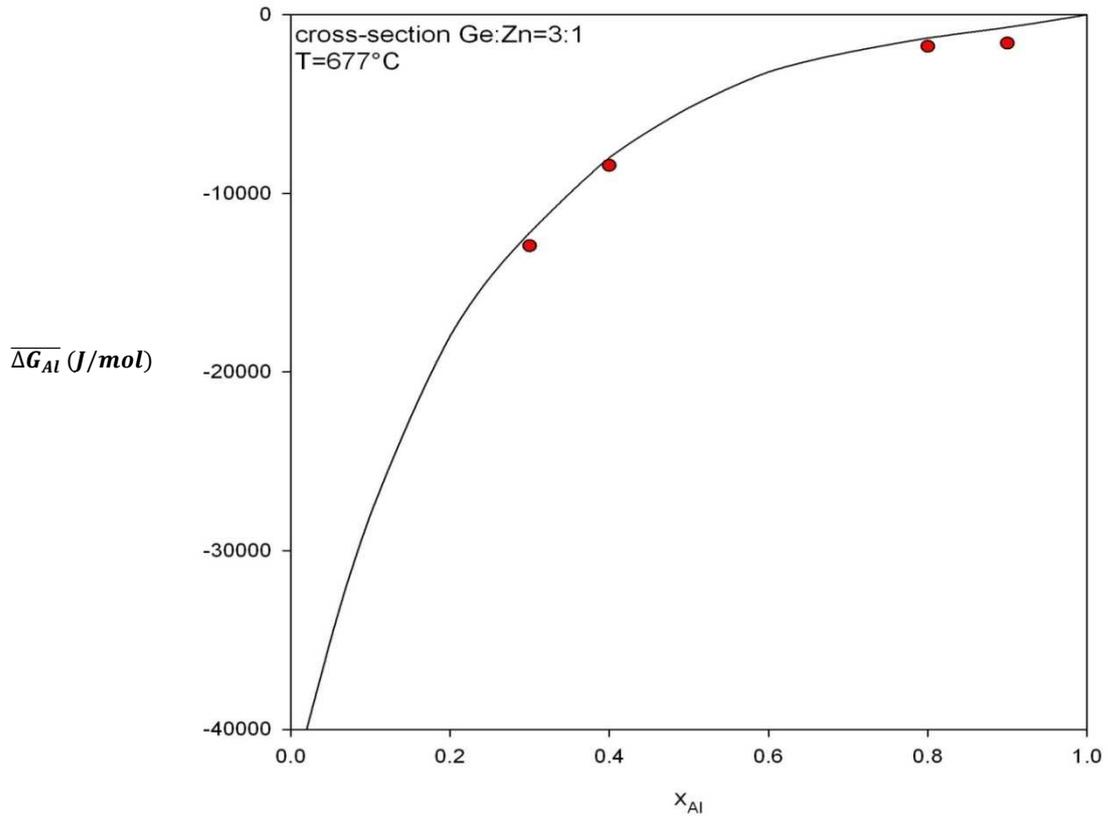


Fig. 4.7 Partial Gibbs free energy of aluminum for the cross section Ge:Zn=3:1 at 677°C

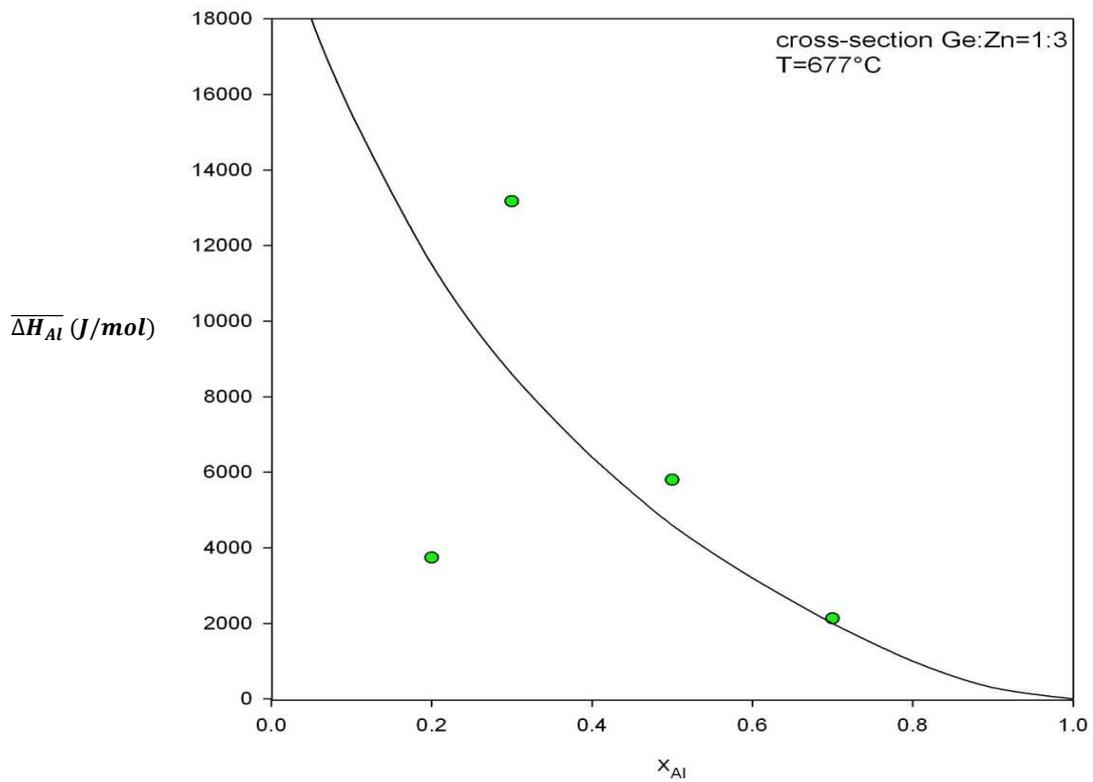


Fig. 4.8 Partial enthalpy of aluminum for the cross section Ge:Zn=1:3 at 677°C

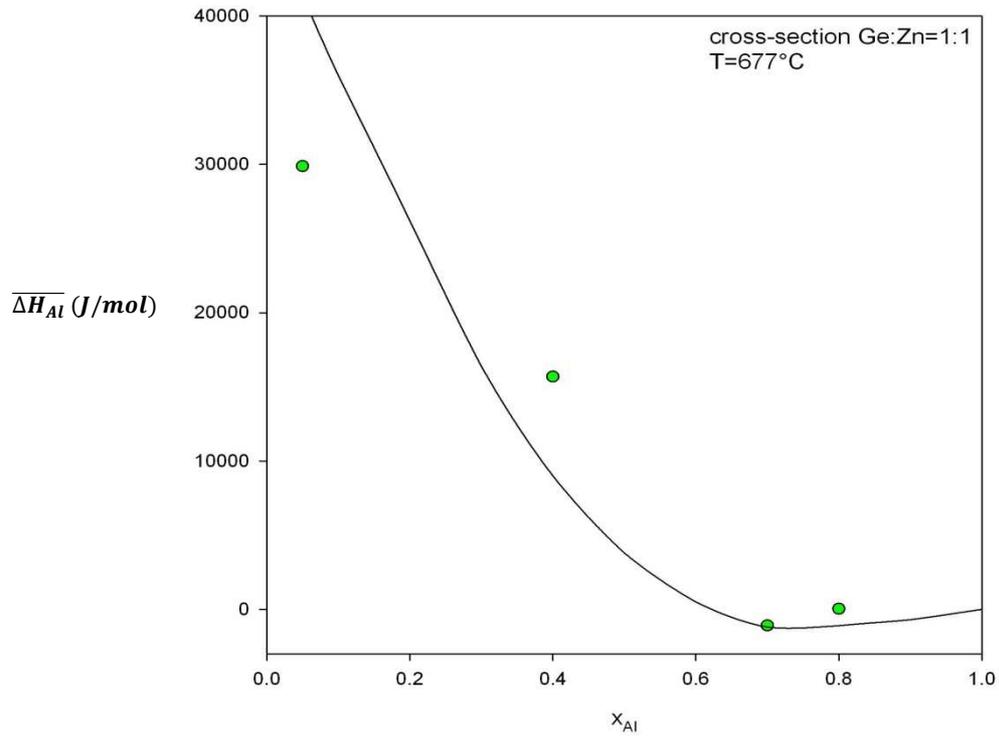


Fig. 4.9 Partial enthalpy of aluminum for the cross section Ge:Zn=1:1 at 677°C

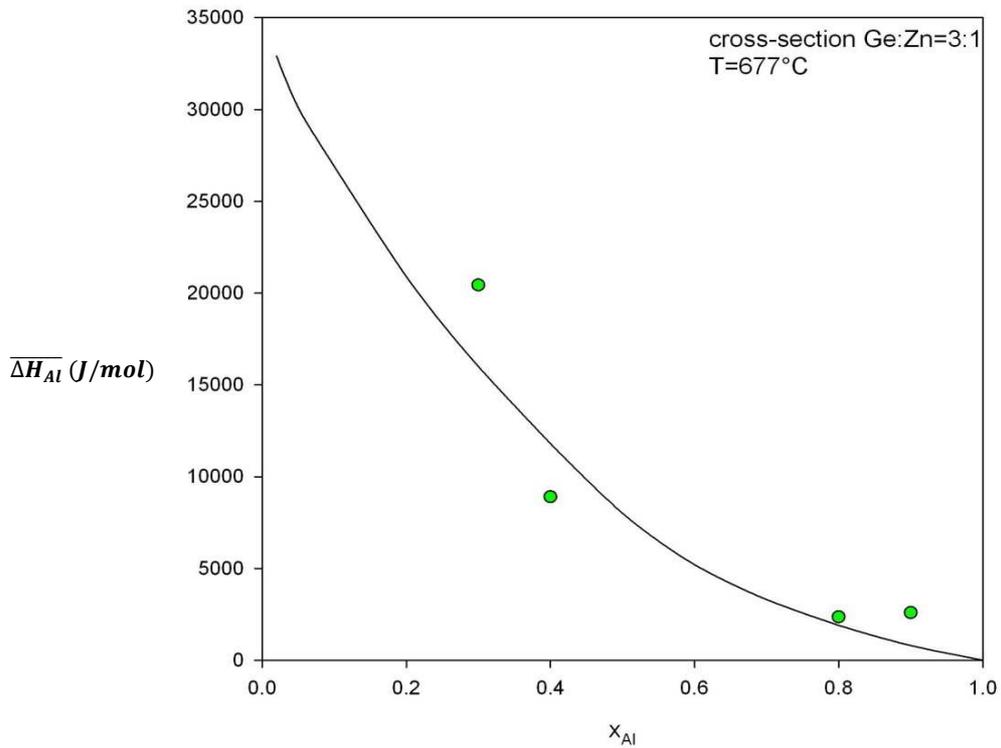


Fig. 4.10 Partial enthalpy of aluminum for the cross section Ge:Zn=3:1 at 677°C

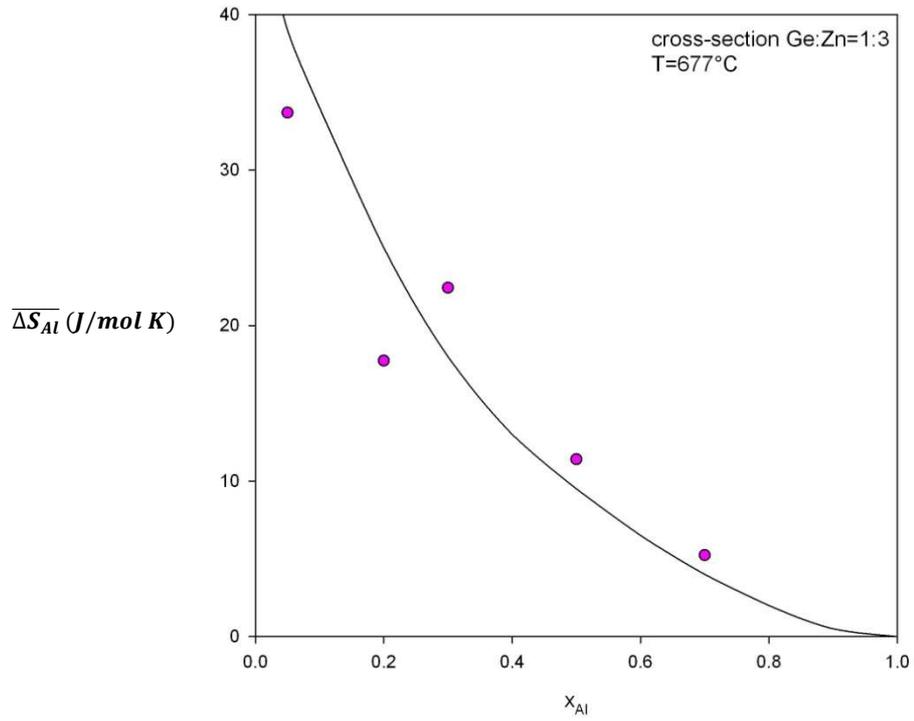


Fig. 4.11 Partial entropy of aluminum for the cross section Ge:Zn=1:3 at 677°C

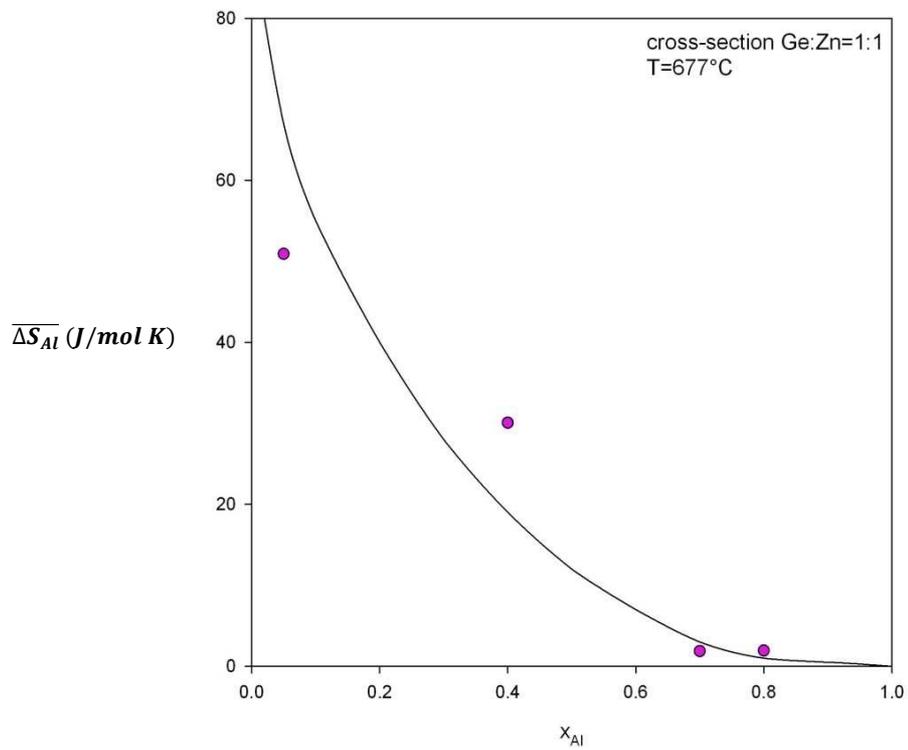


Fig. 4.12 Partial entropy of aluminum for the cross section Ge:Zn=1:1 at 677°C

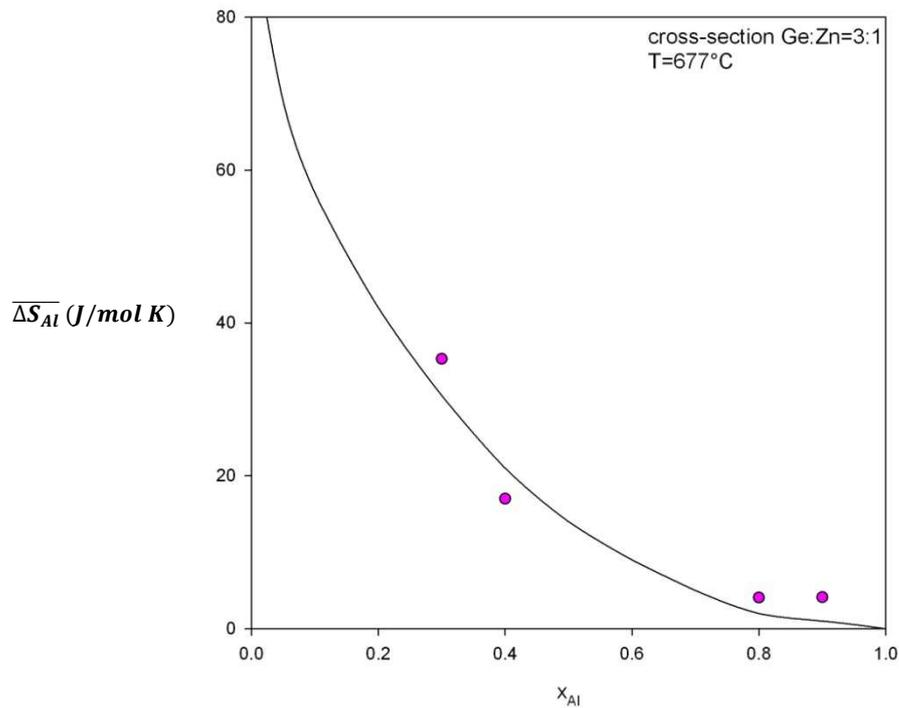


Fig. 4.13 Partial entropy of aluminum for the cross section Ge:Zn=3:1 at 677°C

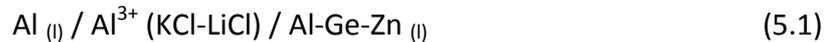
4.3 Conclusion

The investigation of the ternary Al-Ge-Zn system with a suitable galvanic cell made it possible to determine the activity and the partial thermodynamic quantities of Al in liquid Al-Ge-Zn alloys as a function of concentration and temperature. Although the apparent fluctuations of the experimental parameters which were caused by the previously described problems (see chapter 4 and 5), the obtained results seem to be reasonable. A total amount of 47 alloys was investigated with the EMF technique. Due to the difficulties described above it was not possible to evaluate all of the measured data. According to that, it was practicable to receive thermodynamic data for 13 different alloys of the ternary Al-Ge-Zn system. As described in 3.2.1 the studied intermetallics consisted of compositions with the constant ratios of Ge:Zn=3:1, Ge:Zn=1:1 and Ge:Zn=1:3 which had a variable content of 5 to 90 atomic percent aluminum.

Chapter 5: Summary

In terms of the possible use of the ternary Al-Ge-Zn alloys as lead free solders, the thermodynamic properties of these intermetallic systems were investigated with the EMF (electromotive force) method. The data received in these experiments were then evaluated mathematically to obtain information regarding the thermodynamic properties of this particular system. The major accomplishments achieved in the present work can be summarized as follows:

The activities and the partial molar Gibbs free energies of Al in liquid Al-Ge-Zn alloys were determined as a function of concentration and temperature. This was achieved by using a suitable electrochemical cell with the following compilation:



In sum it was possible to obtain thermodynamic data for 13 different alloys of the ternary Al-Ge-Zn system which were located on three cross sections of the phase diagram. These previously defined sections had constant molar ratios of Ge:Zn=3:1, Ge:Zn=1:1 and Ge:Zn=1:3. The individual alloys had variable contents of aluminum from 5 to 90 atomic percent.

From the experimental point of view, the following aspects are to be mentioned:

A suitable electrolyte for the measurement of the particular Al-Ge-Zn system could be found in the form of an eutectic mixture of KCl, LiCl and KAlCl_4 . It was discovered, that the use of KAlCl_4 leads to much better results than the usually used AlCl_3 , due to the lower vapor pressure and the higher stability of the KAlCl_4 at elevated temperatures.

Furthermore it was found, that graphite can be used as suitable material for the electrodes contacting the liquid alloys. This prevents interactions between the intermetallics and the electrodes for the measurement. It was important, that the investigated alloys were placed into small alumina crucibles. Otherwise there might have been the possibility of interactions between the liquid alloys and the sample holder, which was made of quartz.

It should also be also mentioned, that some problems occurred while carrying out the experimental work. If it is compared to other ternary intermetallic systems, it seems that this particular system is much more difficult to investigate with the commonly used EMF technique. It is suspected, that problems with the electrolyte lead to inaccurate EMF values. Also an interaction of Germanium with the electrolyte cannot be excluded completely because the measurements seemed to be more difficult with the Ge-rich compounds. The problems during the measurement were reflected in the evaluation of the data nevertheless the results seem to be reasonable, even with the apparent deviations of the theoretical trend of the curves. For this reason, the interpretation became more difficult in this particular case. According to that, further investigations should be carried out to get more information about the Al-Ge-Zn alloys, also due to the fact that publications of experimental works concerning this system are practically nonexistent.

Concerning the work, which was carried out in Rome, the major accomplishments achieved for this thesis can be summarized in the following way:

A suitable EMF cell for measurements with solid electrolytes was set up. The apparatus was checked for leak tightness and the correct function was proved by the measurement of a previously set temperature program. After the evaluation of the measured values by plotting them on a PC, the results showed a very good isothermal behavior of the cell.

Based on these measurements further calculations were carried out to calculate the exact runtimes for the following EMF measurements.

The preparation of the investigated intermetallics was achieved by a modified electron-gun. The correct composition of the prepared alloys was proved by an X-ray diffraction analysis.

Finally it was possible to investigate the thermodynamic properties of 3 different $\text{Re}_2\text{Co}_{17}$ (Re=Pr, Nd, Gd) alloys.

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Abstract (English version)

The present thesis gives a review about the current need of new lead free solder alloys. A short introduction into the EMF (electromotive force) technique is also given. The practical aspects of EMF measurements with liquid and solid electrolytes are described. Requirements as well as advantages and disadvantages of the different methods are explained.

Concerning the ternary Al-Ge-Zn system the current work deals with the following aspects:

In terms of the possible use of Al-Ge-Zn alloys as lead free solders, the thermodynamic properties of this intermetallic system were investigated by using the EMF method with liquid electrolytes. This work describes the setup of the galvanic cell and the execution of the measurements. Also the preparation of the electrolyte for the galvanic cell is described. A suitable salt for the investigation of the particular Al-Ge-Zn system was found in the form of an eutectic mixture of KCl, LiCl and KAlCl_4 .

The preparation of the investigated alloys is also described.

The experimental data were mathematically evaluated to obtain information regarding the thermodynamic properties of this particular system. By using the measured EMF values, the activity of aluminum and the change of the Gibbs free energy were calculated. It was also possible to determine the partial molar enthalpy $\overline{\Delta H_{Al}}$ and the partial molar entropy $\overline{\Delta S_{Al}}$.

Since parts of this work were carried out during an Erasmus semester abroad at the RIM-Lab (Reactivity of Inorganic Materials Laboratory) of the Facolta di Chimica at the Universita La Sapienza di Roma, measurements with solid electrolytes which I performed during my stay in Italy are also described.

The focus of this part of the work was set on the investigation of alloys consisting of rare-earth elements and cobalt. A suitable EMF cell for measurements with a solid CaF_2 electrolyte was set up. In this case, the preparation of the investigated intermetallics

was achieved by a modified electron-gun. It was possible to investigate the thermodynamic properties of the $\text{Pr}_2\text{Co}_{17}$ alloy.

Abstract (German version)

Die vorliegende Arbeit gibt einen Überblick über den derzeit bestehenden Bedarf für neue bleifreie Lotmaterialien und einige, für diesen Zweck bereits entwickelte intermetallische Systeme. Des Weiteren wird eine Einführung in die EMK-Messungen (Messungen der elektromotorischen Kraft) gegeben. Zusätzlich werden praktische Aspekte der EMK-Technik mit flüssigen und festen Elektrolyten erörtert. In der Arbeit werden die Voraussetzungen für derartige Messungen beschrieben und auch Vor- und Nachteile der einzelnen Methoden ausgeführt.

Bezüglich des ternären Al-Ge-Zn Systems behandelt diese Arbeit folgende Aspekte:

Im Hinblick auf den möglichen Einsatz von Al-Ge-Zn Legierungen als bleifreie Lotmaterialien wurden deren thermodynamische Eigenschaften mit Hilfe von EMK-Messungen mit flüssigen Elektrolyten untersucht. Die Arbeit beschreibt den Aufbau der galvanischen Zelle und die Durchführung der entsprechenden Messungen. Weiters wird die Herstellung des verwendeten Elektrolyten erklärt. In diesem Zusammenhang konnte in einer eutektischen Mischung welche aus KCl, LiCl und KAlCl_4 besteht, ein geeigneter Elektrolyt gefunden werden.

Zusätzlich wird die Herstellung der untersuchten Legierungen beschrieben.

Die experimentellen Werte wurden mathematisch ausgewertet um Informationen über die thermodynamischen Eigenschaften des Systems zu erhalten. Mit Hilfe der Messwerte konnten die Aktivität von Aluminium und die Änderung der Gibbsschen freien Enthalpie berechnet werden. Außerdem war es möglich die partielle molare Enthalpie $\overline{\Delta H_{Al}}$ und die partielle molare Entropie $\overline{\Delta S_{Al}}$ zu ermitteln.

Da Teile der vorliegenden Arbeit während eines Erasmus Auslandssemesters am RIM-Lab (Reactivity of Inorganic Materials Laboratory) der Fakultät für Chemie an der Universität La Sapienza in Rom entstanden sind, sind zusätzlich Beschreibungen von Messungen mit festen Elektrolyten welche während dieser Zeit in Italien durchgeführt wurden, enthalten.

Der Fokus dieses Teiles der Arbeit war auf die Untersuchung von Legierungen bestehend aus Seltenerdelementen und Cobalt gerichtet. Eine geeignete EMK-Zelle für Messungen mit festem CaF_2 als Elektrolyt wurde hierfür aufgebaut. In diesem Fall wurden die entsprechenden Legierungen unter Zuhilfenahme einer modifizierten Elektronenkanone hergestellt. Es war möglich die thermodynamischen Eigenschaften einer Legierung mit der Zusammensetzung $\text{Pr}_2\text{Co}_{17}$ zu untersuchen.

Conference contributions

First EuChemMS Inorganic Chemistry Conference-United Kingdom/Manchester April 2011

Dr. Mag. Michael Hindler, MSc. Zhongnan Guo, Jakob Steiner, Ao. Univ.-Prof. i.R. Dr. Mag. Adolf Mikula; "Lead Free Solder Alloys: Thermodynamic properties of the Au-Sb-Sn system"

Curriculum Vitae

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Professional Experience

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