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Thermophysical Properties in the System Li-Pb

**Part I:
Preparation and characterization of
Li(17)Pb(83) eutectic alloy and the
LiPb intermetallic compound**

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**Part III:
Estimation of the thermophysical
properties in the system Li-Pb**

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General Abstract

This report describes the work performed on the determination of the thermophysical properties of alloys in the binary system lithium-lead, within the frame of the KfK-project of nuclear fusion technology.

The preparation of the Li(17)Pb(83) alloy and the intermetallic compound LiPb from the pure elements determines the contents of part I of the report, which includes too the characterization of the materials using chemical analysis, metallography, thermal and thermal differential analysis. The great importance of the characterization especially of the metallography is shown in presenting some results of the eutectic alloy fabricated by different producers under technical conditions. Because of the great importance of the thermophysical behaviour of the liquid eutectic Li(17)Pb(83) for the design of a liquid metal breeder blanket in the next European Torus, part II of the report describes the measurements and results of the thermodynamic properties (latent heat of fusion, specific heat, density, thermal expansion and surface energy) of this alloy. The results of the determination of the transport properties (thermal and electrical conductivity and viscosity) are presented, too.

In part III the methods are given, which lead to an estimation of thermophysical properties of Li-compounds with high Li-contents (> 50 at.%) in the solid state.

THERMOPHYSICAL PROPERTIES IN THE SYSTEM Li-Pb

Part 1

Preparation and Characterization of the Li(17)Pb(83)
eutectic alloy and the LiPb intermetallic compound

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Abstract

Li(17)Pb(83) and LiPb were prepared from the pure elements in amounts of several hundred grams. The resolidified samples were characterized by melting points (eutectic temperature), chemical analysis and metallography. Using differential thermal analysis the heats of fusion were determined and the behaviour of the intermetallic phase LiPb in vacuum and high purified He was studied. The results from these investigations were applied to characterize Li(17)Pb(83) prepared in high amounts for technical application as a potential liquid breeder material.

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1. Introduction

The decision of several governments some years ago to start the work in the technical application of nuclear fusion, includes the discussion of materials being able to breed Tritium by the nuclear reaction of Li with neutrons. From the very beginning of this discussion it was clear that solid (Li-ceramics) as well as liquid breeder materials were possible: the pure metal Lithium and the eutectic alloy Li(17)Pb(83) [1,2]. This paper will discuss only the preparation and characterization of Li(17)Pb(83) and LiPb with a special view to prepare samples for thermophysical property measurements and to the quality control in technical production processes. Within the frame of this work the preparation of LiPb is not only a matter of basic interest. With respect to some discussions in using Li_7Pb_2 as solid breeder material, the knowledge of the behaviour in different atmospheres of Li-compounds having much higher Li-concentrations than Li(17)Pb(83) is of interest for the handling of these compounds as well as for the measurements of their thermophysical properties.

2. Preparation of Li(17)Pb(83) and LiPb

A basis for the preparation of binary alloys is the phase diagram of the constituent elements (Fig. 1) [3]. As can be seen, the eutectic Li(17)Pb(83) is formed by the components LiPb and Pb in the quasibinary system LiPb-Pb and shows the lowest melting temperature (508 K) in the system Li-Pb, except the melting temperature of the pure Li (452 K). The theoretical compositions of the two alloys mentioned corresponds to the following concentration: 83 at% Pb (99.32 wt%) 17 at% Li (0.68wt%) for Li(17)Pb(83) and 50 at% Pb (96.76 wt% Pb), 50 at% Li (3.24 wt%) for LiPb, using an atomic weight of 6.941 g for Li and 207.2 for Pb. Some details of the preparation methods are given below (Table 1).

Table 1: Conditions for preparing Li(17)Pb(83) and LiPb.

Elements		T (K)	melting process	
			atmosphere [4]	crucible
Li(17)Pb(83)	Li*(99.4)Pb**(99.99)	623	<1 vpm O ₂ , N ₂ , H ₂ O	SS
LiPb	Li*(99.4)Pb(99.999)	825	" " " " " additionally purified by Ti-chips at 895 K	Al ₂ O ₃

* Metallgesellschaft Frankfurt/Main (0.5 Na, 0.01 K, 0.03 Ca, <0.01 Al, <0.03 Si)

** Firma Ventron

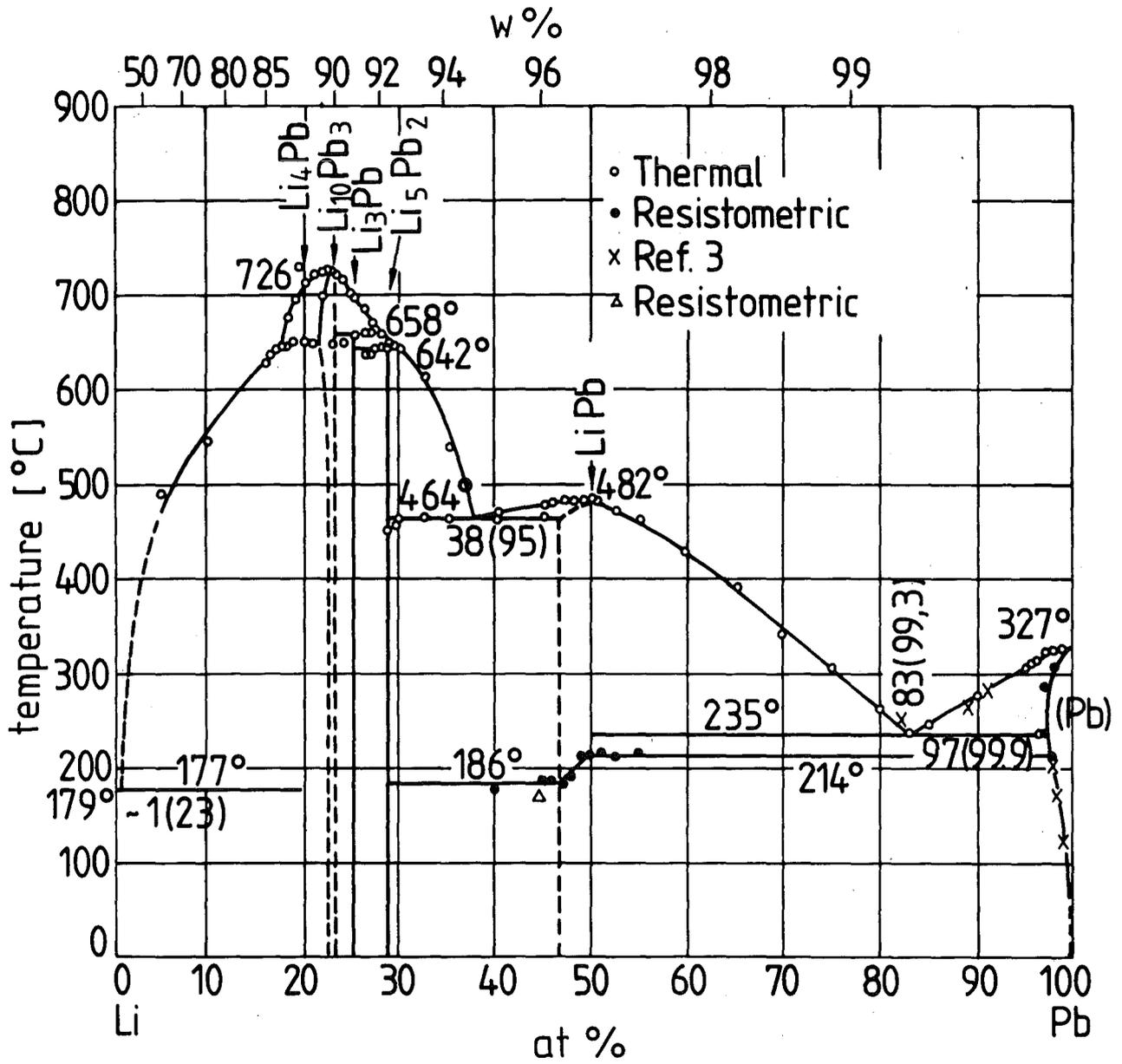


Fig. 1: Phase diagrams of the Li-Pb system [3].

To correct for possible higher evaporation losses of Li (vapour pressure of Li at 825 K $\sim 1.7 \cdot 10^{-2}$ mmHg compared to $\sim 10^{-4}$ mmHg for lead [5]) the Li-concentration was slightly higher than the nominal value.

The curves of the thermal analysis of Li(17)Pb(83) and of LiPb are shown in Fig. 2. The measured temperatures $T_E = 508$ K and T_M (LiPb) = 759 K agree well with the respective temperatures in Fig. 1. The temperatures were measured with sheated thermocouples calibrated against the ice- and boiling point of distilled pure water for the preparation of Li(17)Pb(83). LiPb was synthesized in a special box with installed thermocouples non-calibrated (for allowed tolerances see [7]).

3. Characterization of Li(17)Pb(83) and LiPb

No X-ray studies were performed. The identification of the LiPb-structure [6] needs exposure times up to 8 hours, times for which the integrity of the very small X-ray-samples could not be guaranteed. Apart from this one has to realize that for the eutectic composition the Pb-reflexes will blacken the X-ray film at these long times.

3.1 Chemical analysis

With the method of atomic absorption spectroscopy the Lithium concentration was determined (Table 2), oxygen impurities were below the detection limit of the method (hot extraction method, 0.01 %). There was no possibility for chemical analysis with respect to nitrogen impurities.

Table 2: Li-concentrations in Li(17)Pb(83), LiPb*

	Li (w%)	Li (mol%)
Li(17)Pb(83)	0.67 ± 0.01	16.8 ± 0.2
LiPb	3.82 ± 0.01	54.2 ± 0.1

The paper of Gruber and Kleiber [8], which is a basic work for the phase diagram confirmed a homogeneity range of the LiPb to the Li-rich side up to 54 mol% Li. They found the beginning of the two phase region at a Li-concentration of 55 mol%. There we found in all cooling curves of LiPb (Fig. 2) a horizontal solidification line, we think that the intermetallic phase LiPb is homogeneous and at the Li-rich side of the range of homogeneity of this phase.

* The chemical analysis were carried out by the chemical analysis group at IMF I-KfK

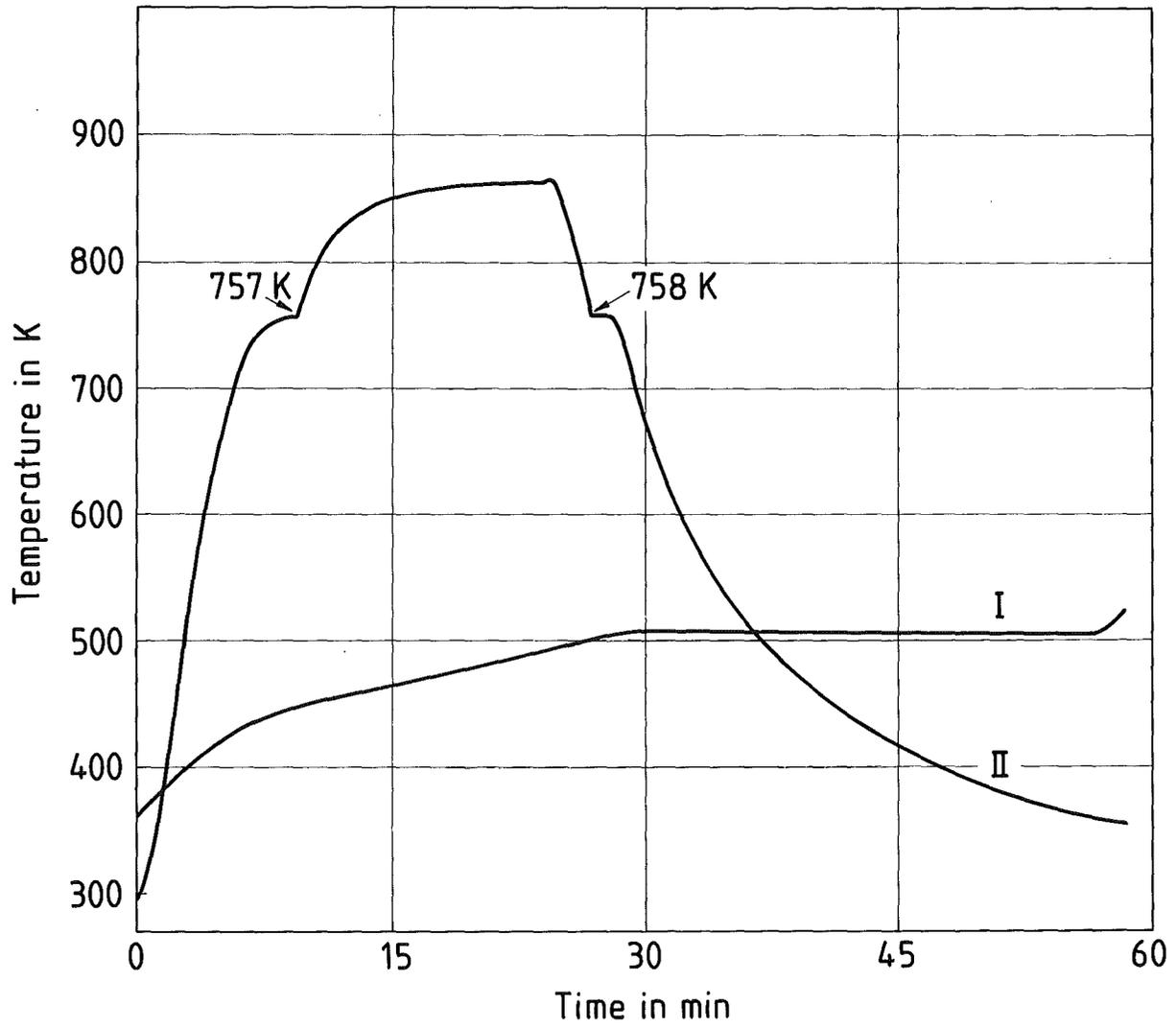


Fig. 2: Thermal analysis of Li(17)Pb(83) and LiPb.

3.2 Metallographic Investigations

All preparations were carried out in normal atmosphere. Samples of both materials were embedded in vacuum (EpoFix). Li(17)Pb(83) was grinded on SiC-paper with Decalin, then diamond polished (3 - 0.25 μm), followed by etchpolishing with Al_2O_3 (1 μm). Because of the very rapid reaction with N_2 (Li) and O_2 (Pb) at the surface, this has to be cleaned with Ammonium tartrate solved in aqua dest several times during the whole procedure. The homogeneity of the microstructure is shown in Fig. 3, the eutectic structure in Fig. 4. The preparation of the microstructure of LiPb was much more difficult, because of the great affinity of Li to nitrogen as well as to oxygen. All the steps of preparation: grinding (SiC), polishing (diamond down to 0.25 μm) and cleaning of the surface were undertaken with absolute waterfree ethanol. Immediately after preparation the surface was protected against oxygen and nitrogen with immersion oil. Fig. 5 shows the microstructure of LiPb with grain boundaries.

3.3 Differential Thermal Analysis

The experiments were carried out with a Netzsch DTA on samples of about 500 mg in crucibles of Al_2O_3 . The atmosphere was high purified (99.999 %) He (stagnant). The heating rates were always 2 K/min. The sensitivity S ($\frac{\mu\text{Vs}}{\text{mJ}}$) was evaluated in melting metals of high purity. Between 5 - 11 independent measurements for one metal were performed to get the sensitivity, the data of heat of fusion and the melting points were taken from [9].

Fig. 6 shows the sensitivity as function of temperature. The standard deviation for S for each metal is about 7 %. This does not allow to calculate a temperature dependent sensitivity S , although the typical maximum at about 470 K seems to exist. Nevertheless we calculated the heat of fusion for Li(17)Pb(83) and LiPb with a mean sensitivity of $0.140 \frac{\mu\text{Vs}}{\text{mJ}}$. Fig. 7 shows the typical DTA-curves for both substances. Table 3 gives the results.

Table 3: Results of DTA-experiments with Li(17)Pb(83) and LiPb

	extrapol. onset temperature T_{eo} (K)*	latent heat of fusion (J/g)
Li(17)Pb(83)	504 ± 0.5	$33.9 \pm 10 \%$
LiPb	747 ± 0.5	$51.9 \pm 10 \%$
for comparison		
Pb	596	23.03 [9]

*For definition show JACTA-tables. T_{eo} is always about 3 to 5 K lower than melting points determined by direct observation.

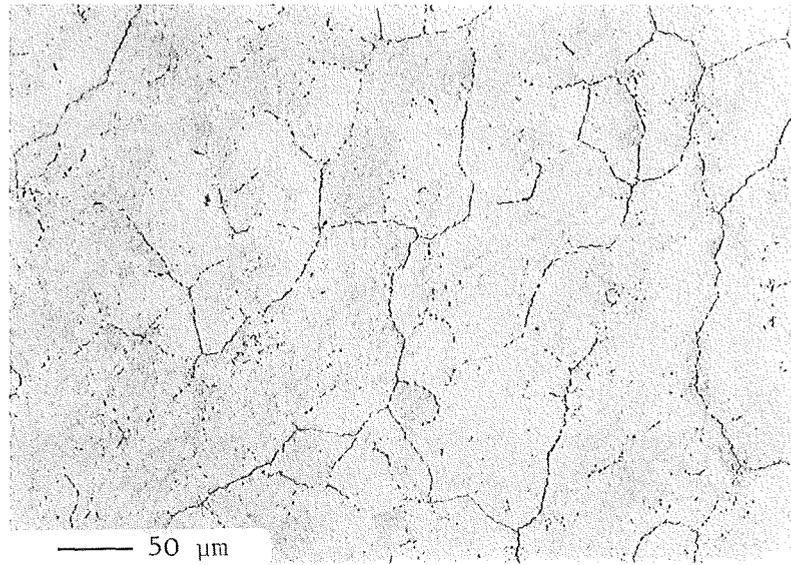


Fig. 3: Microstructure of Li(17)Pb(83).

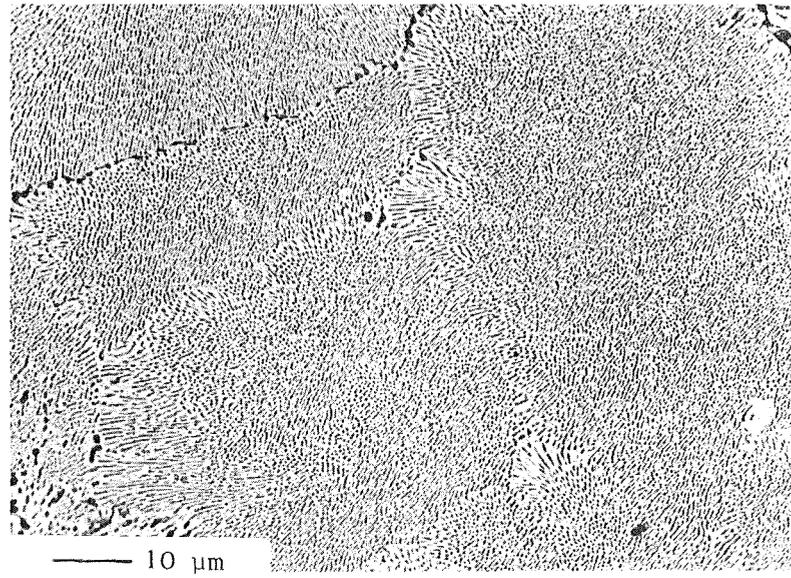


Fig. 4: Microstructure of Li(17)Pb(83).

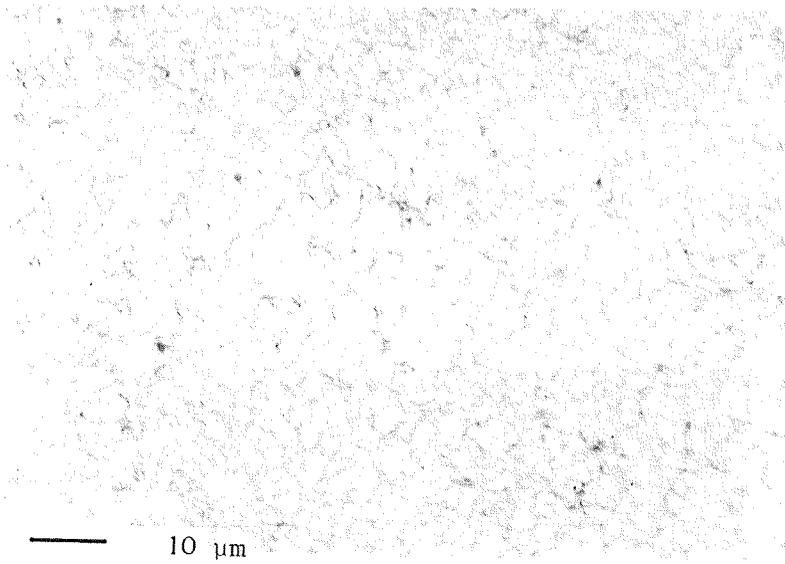


Fig. 5: Microstructure of LiPb.

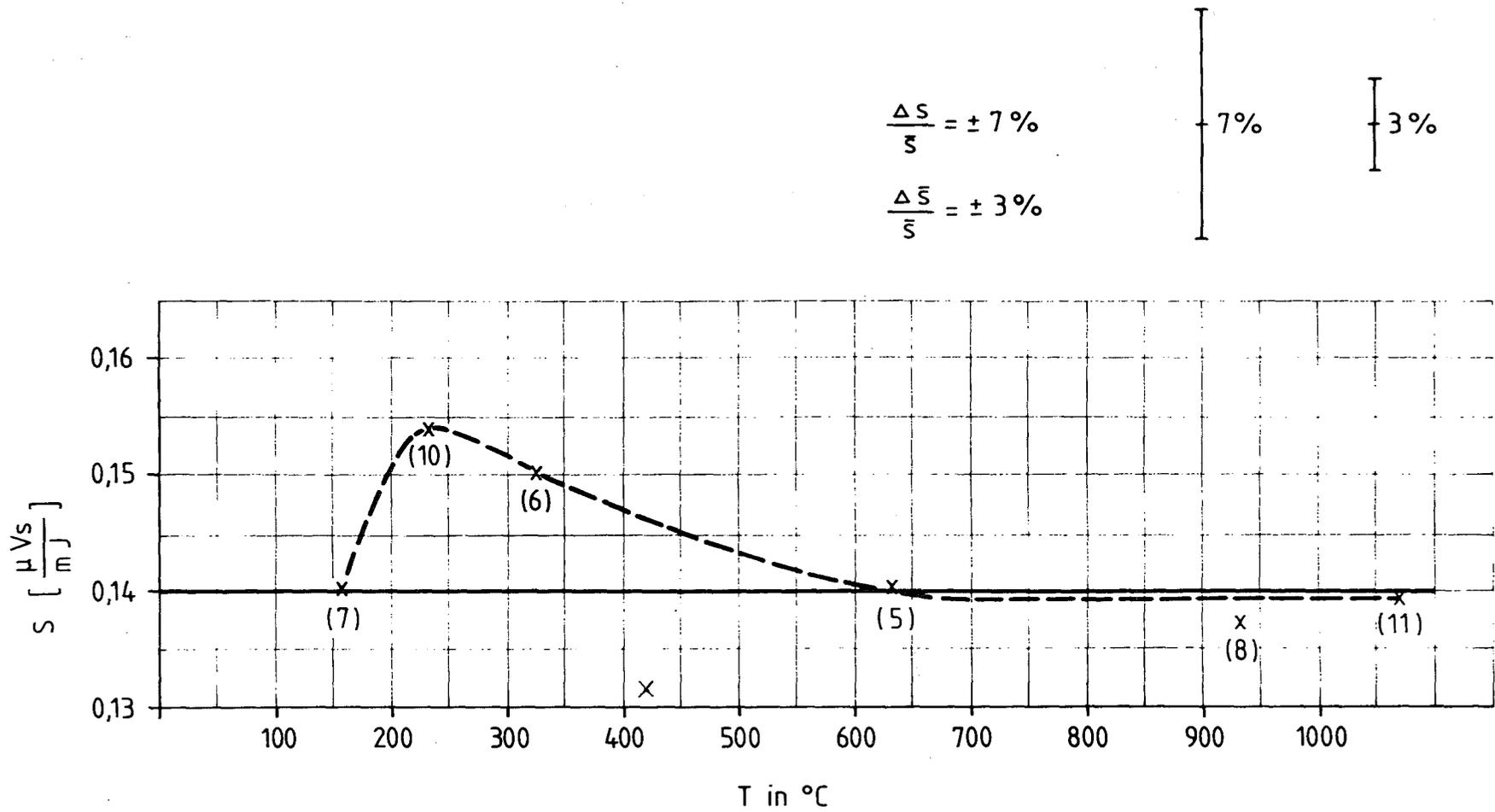
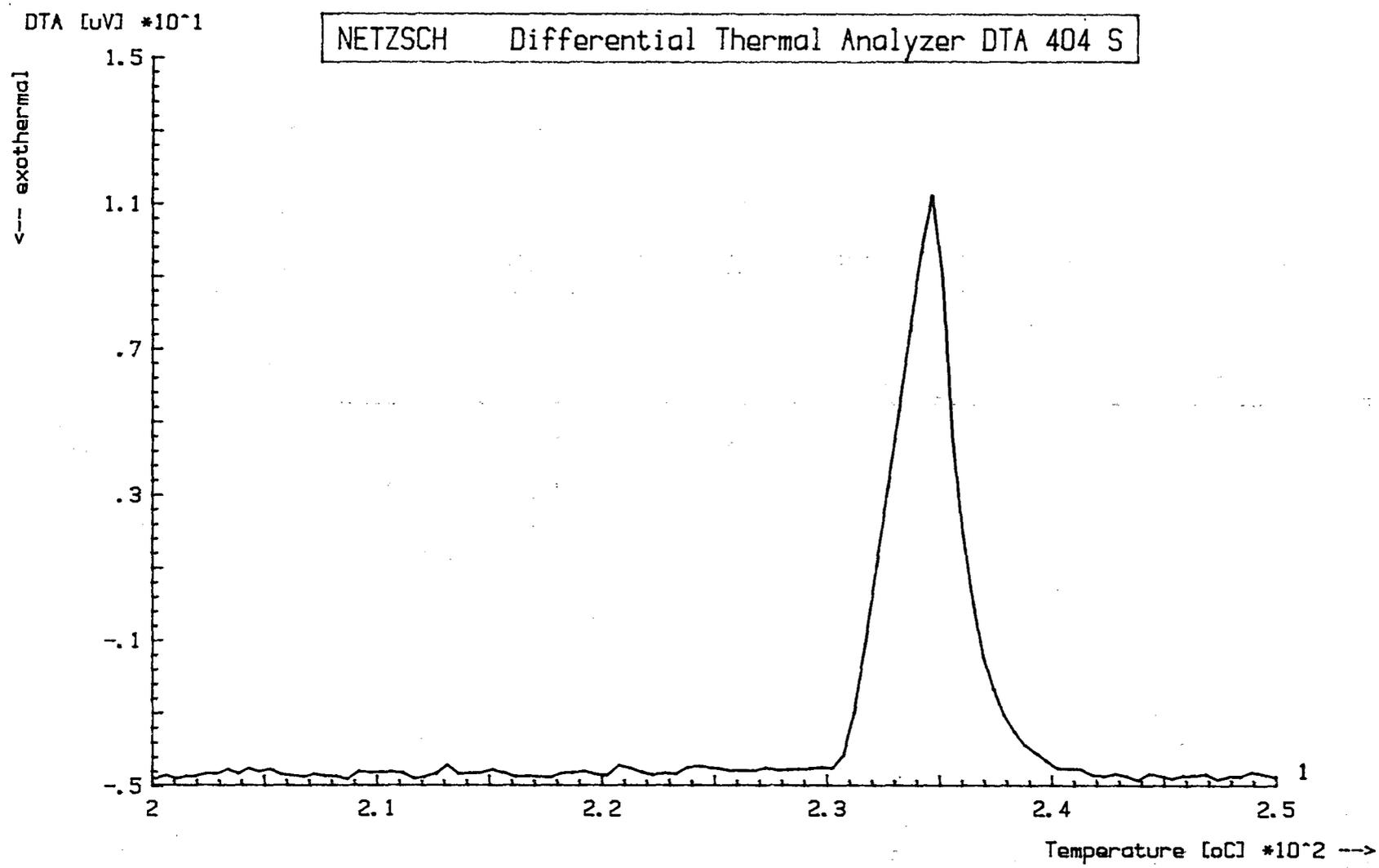
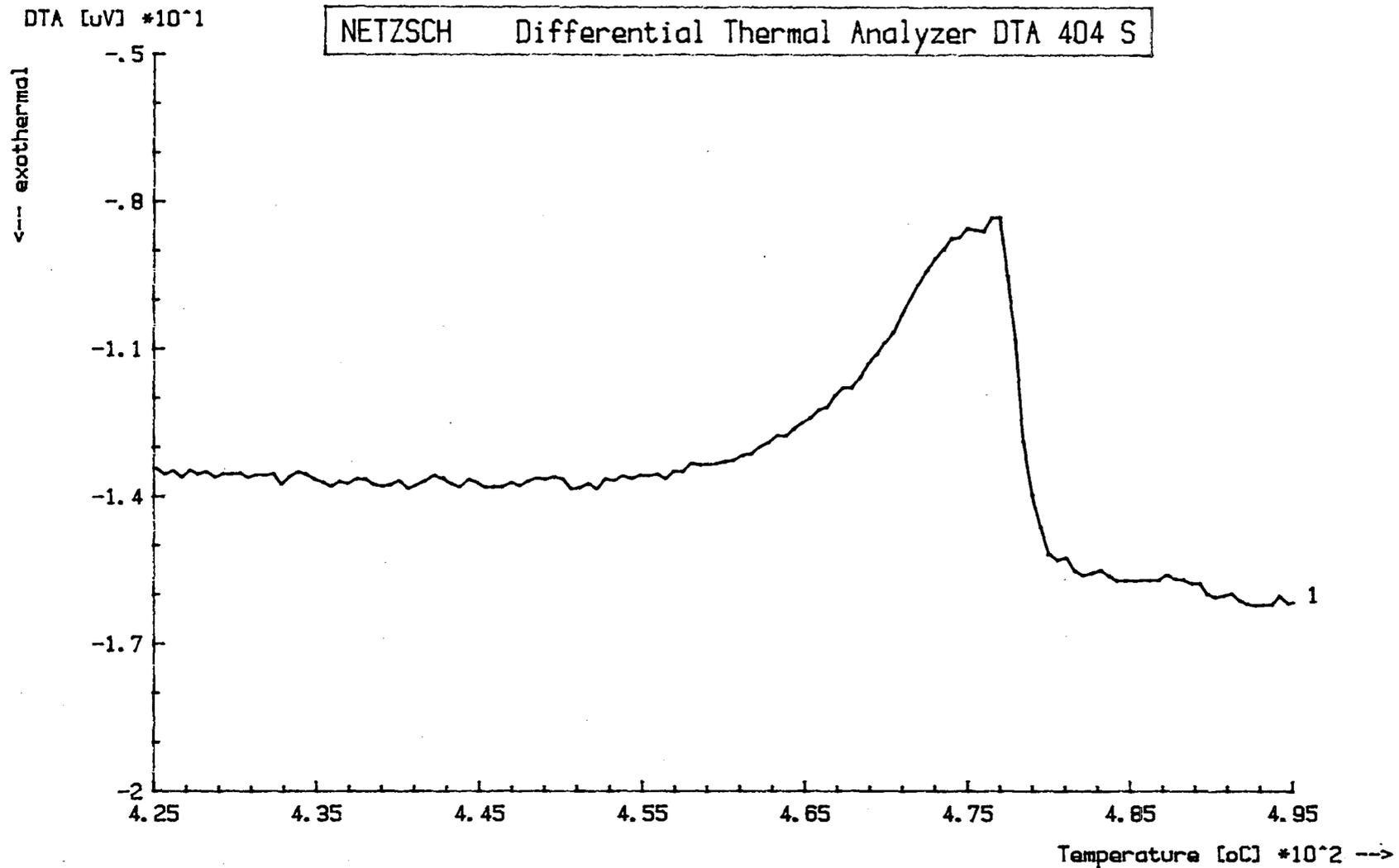


Fig. 6: Sensivity S of the DTA-equipment.



SAMPLE:	LI17PB83	No. 1	IDENTITY No.:	DTA 889	SAMPLE WEIGHT:	275.3 mg
ATMOSPHERE:	HE				Nr. 683 (IMFI/Sc)	
CRUCIBLE:	AL203					
RATE:	2.0 K/min (b)					

Fig. 7a: Typical DTA-curves of Li(17)Pb(83).



SAMPLE:	LIPB	No. 1	IDENTITY No.:	821.7	SAMPLE WEIGHT:	311.7 mg
ATMOSPHERE:	HE				Nr.684 (IMFI/Sc)	
CRUCIBLE:	AL203					
RATE:	2.0 K/min (0)					

Fig. 7b: Typical DTA for LiPb.

Kühlbörsch and Reiter measured the heat of fusion of Li(17)Pb(83) in a Calvet calorimeter [10] as 29.59 J/g. Within the margin of error both values agree with each other. Kühlbörsch and Reiter did not give a precision for their data.

All methods used for the characterization show uniform results: the pure eutectic alloy and the intermetallic compound LiPb could be synthesized in amounts (~ 1000 g for Li(17)Pb(83) and 50 - 100 g LiPb) which are sufficient for the sample preparation necessary for physical property measurements.

4. The behaviour of LiPb in different atmospheres

The fact that only the production of the LiPb alloys could be done in boxes constructed for the handling of liquid alkali metals, while the adjustment of the samples for property measurements has to be carried out in normal atmosphere and the measurements either in high pure He (see above) or in vacuum ($p \sim 10^{-6}$ mbar) created the problem of the behaviour of LiPb alloys in atmospheres with even small amounts of O_2 and N_2 . The first kind of investigations were done by means of differential thermal analysis.

The masses of LiPb used for the DTA were about 450 mg prepared in the special box and weighed in waterfree ethanol. As reference for the temperature high pure Aluminum was used. The samples were heated several runs up to 975 K. Fig. 8 shows in a typical graph the appearance of Li(17)Pb(83) and its increase in the peak height, while the peak height and melting temperature of "LiPb" decreases. The following mechanism for this phenomenon is supposed: The very high affinity of Li to nitrogen leads to the formation of Li_3N , thus enriching the alloy with Pb. Obviously the heating rate in the experiments (2 K/min) was small enough to show the lowering of the solidification temperature of the Pb-rich alloy as well as the melting temperature of the eutectic alloy. We estimated from the DTA-curve the amount of eutectic alloy in the following way: Using the known sensitivity of the DTA-equipment, the heat of fusion for the eutectic alloy, the mass of the eutectic formed can be estimated directly from the peaks of Li(17)Pb(83). The temperature of melting or solidification of the "LiPb" and the phase diagram were used to estimate the amount of Li(17)Pb(83) at the respective times in the DTA-graphs. The results are presented in Fig. 9 showing the mass percentage of Li(17)Pb(83) formed through the reaction of Li with nitrogen as function of the square root of time. This function is well represented by a linear dependence up to times of more than

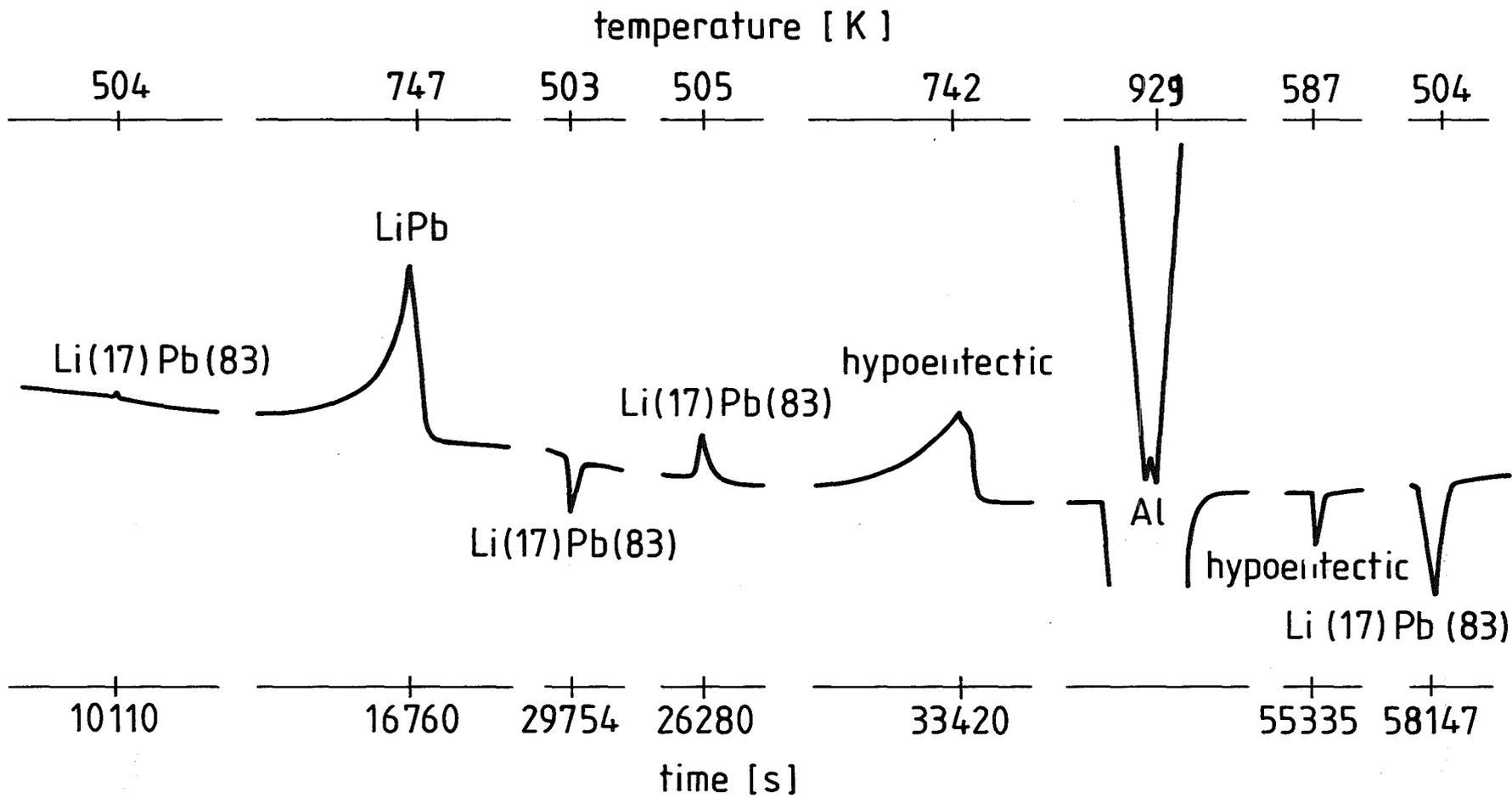


Fig. 8: Longtime behaviour of LiPb in He (DTA).

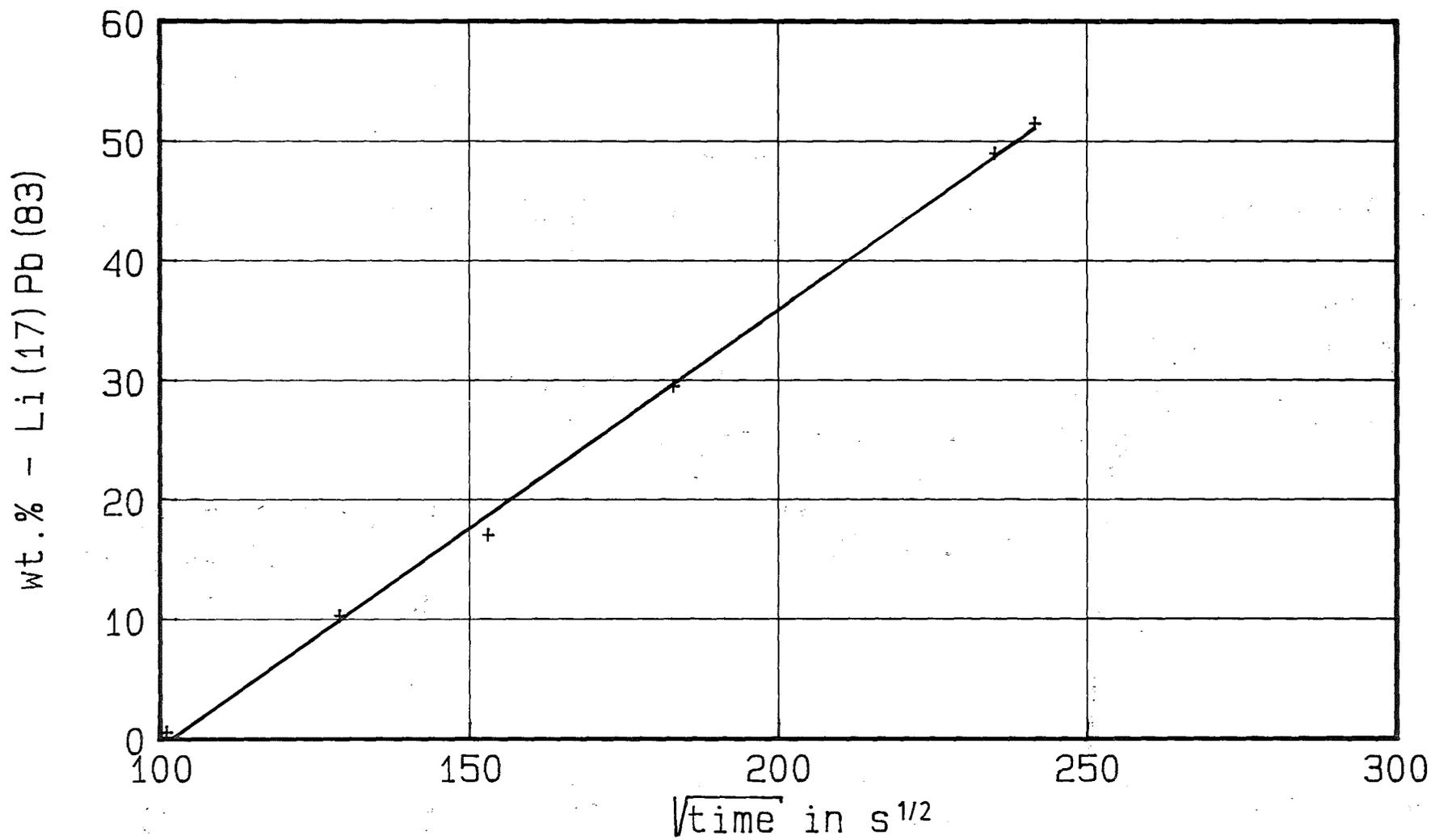


Fig. 9: Mass percentage of Li(17)Pb(83) formed through the reaction of Li with nitrogen.

15 hours. We will not conclude that this function represents the true kinetic of the mentioned reaction, because temperature and time changed during the experiments. But this is accurately what happens in measuring thermophysical properties as a function of temperature.

The influence of nitrogen impurities in vacuum (10^{-6} mbar) was investigated in preparing samples of LiPb in the special box for thermal diffusivity measurements with the laser flash technique. The sample had a weight of about 5 g, cylindrical shape with 1.0 cm diameter and up to 0.4 - 0.5 mm in thickness.

The measurements were carried out in vacuum, with point welded thermocouples as temperature sensors.* Mounting and adjustment of the sample were carried out in normal atmosphere. The thermal diffusivity of the eutectic alloy was measured before. The value at room temperature (293 K) is $0.178 \text{ cm}^2/\text{sec}$. The intermetallic sample was heated in several runs up to 470 - 550 K. The thermal diffusivity α was measured in this experiment only at 293 K. The results are given in Fig. 10, showing α as a function of time. In the beginning we have a linear dependence between both parameters, where the prolongation leads directly to the correct value of the diffusivity of the eutectic alloy at a time of about 100000 sec, which is 50 % earlier than in He-atmosphere. Although the reaction stops at times of ~ 20000 sec, the change in the diffusivity at this point is about 50 %. From this the conclusion is drawn, that property measurements should be carried out either in He-atmosphere or with samples encapsulated in protective materials.

5. Characterization of eutectic alloys prepared under technical conditions

Two producers (European Research Center in Gel, in the following material (I) and Metallgesellschaft in the following material (II)) prepared of the elements Li and Pb the eutectic alloy in amounts of several hundred kg up to 1000 kg. From these ingots samples for characterization in the same manner as with the materials described above (in the following material (III)) were taken. The samples were remolten in the special box and after solidification under the same conditions as before the different samples were taken for chemical analysis, metallographic preparation and differential thermal analysis (Table 4).

* For details see Part II of the paper.

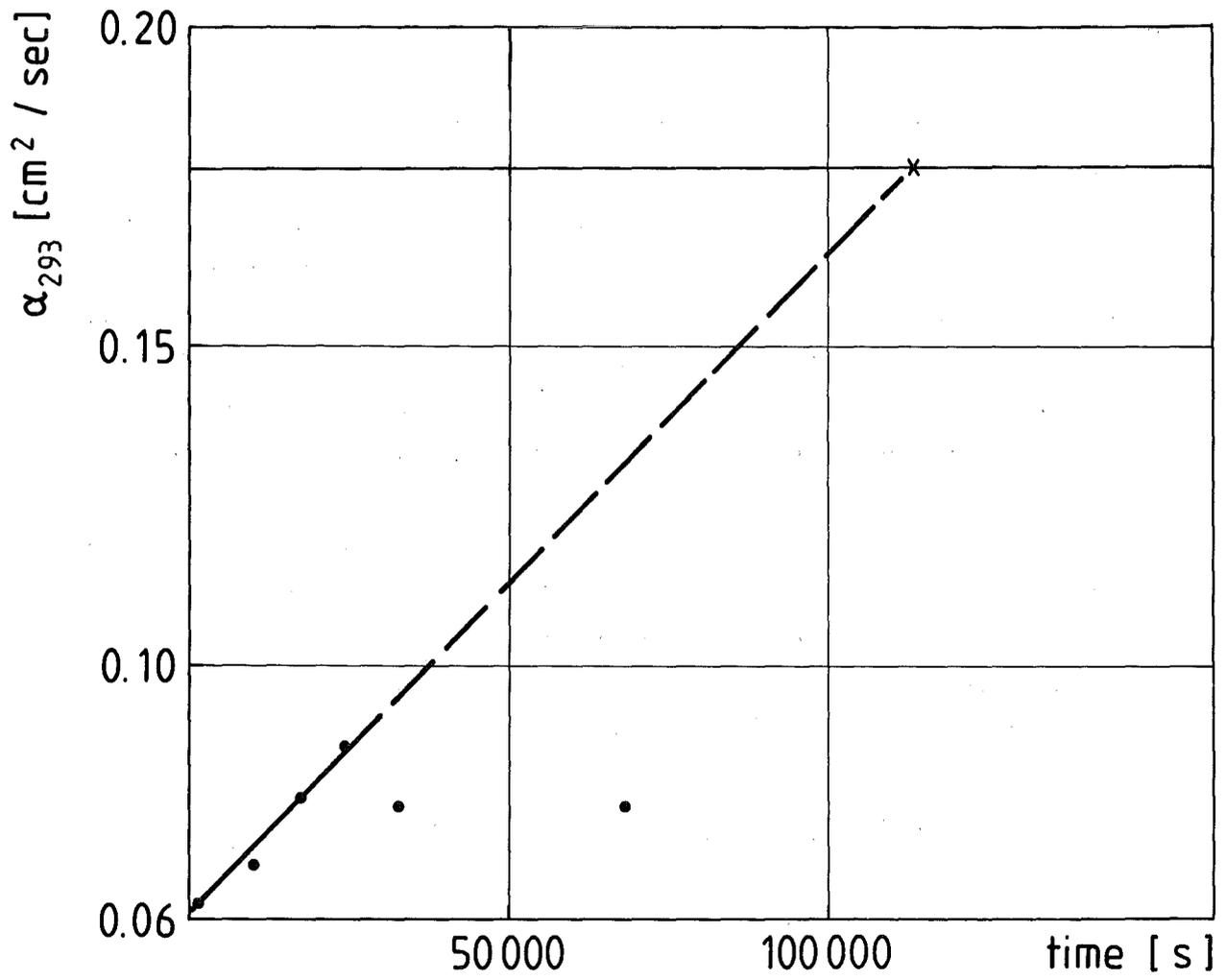


Fig. 10: Longtime behaviour of LiPb in vacuum (thermal diffusivity α at 293 K)

Table 4: Results of chemical analysis and DTA of Li(17)Pb(83) of different origin.

	Mat. I	Mat II	Mat. III
Li	0.68 ± 0.02 0.64*± 0.01	0.66 ± 0.01	0.67 ± 0.01
extrapol. onset temp.			
T _{eo} in K	505 ± 0.5	504 ± 0.5	504 ± 0.5

*Analysis after a run of about 500 hours in a loop on 695 K

The chemical analysis as well as the DTA give within the margin of error no information of a possible difference between the three materials. In opposite to this the metallography gives another image. In one sample of Mat. I the eutectic microstructure is as perfect (Fig. 11) as it is in all samples of Mat. III (Fig. 3 and 4), while another one (Fig. 12) shows precipitations of Pb within the eutectic. This means a certain inhomogeneity of chemical composition in this material. Mat. II is well described by Fig. 13 showing in all samples a relative high amount of spherical Pb precipitations besides the eutectic alloy.

6. Conclusion

The eutectic alloy Li(17)Pb(83) and the intermetallic compound LiPb were prepared for thermophysical property measurement. The characterization shows a homogeneous product. Investigations of the reaction behaviour of LiPb with elements of the atmosphere resulted in higher corrosion in vacuum with the elements N₂ and/or O₂ than in high purified He. The characterization of Li(17)Pb(83) products of two different producers leads to the conclusion that neither the chemical analysis nor the DTA has up to now the precision to differentiate between the different alloys in the same way as it is possible by microstructural analysis.

The authors wish to thank Dr. Borgstedt and his group at the Institute of Materials and Solid State Research at the Nuclear Research Center in Karlsruhe for their interest and help in using their special boxes for the preparation of the materials.

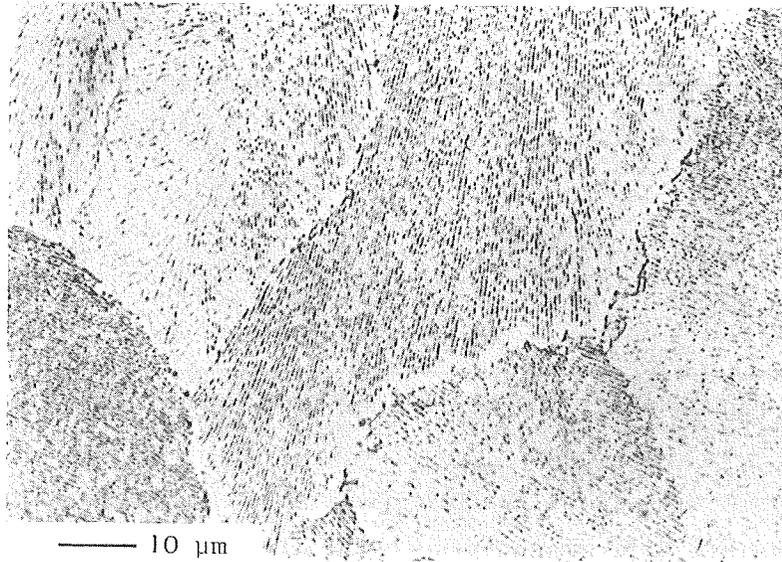


Fig. 11: Microstructure of Li(17)Pb(83) (Mat. I).

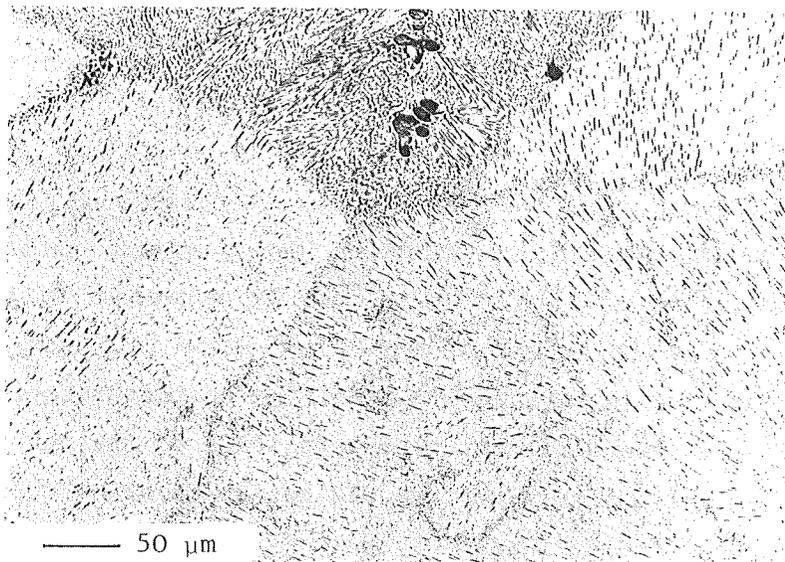


Fig. 12: Microstructure of Li(17)Pb(83) (Mat. I).

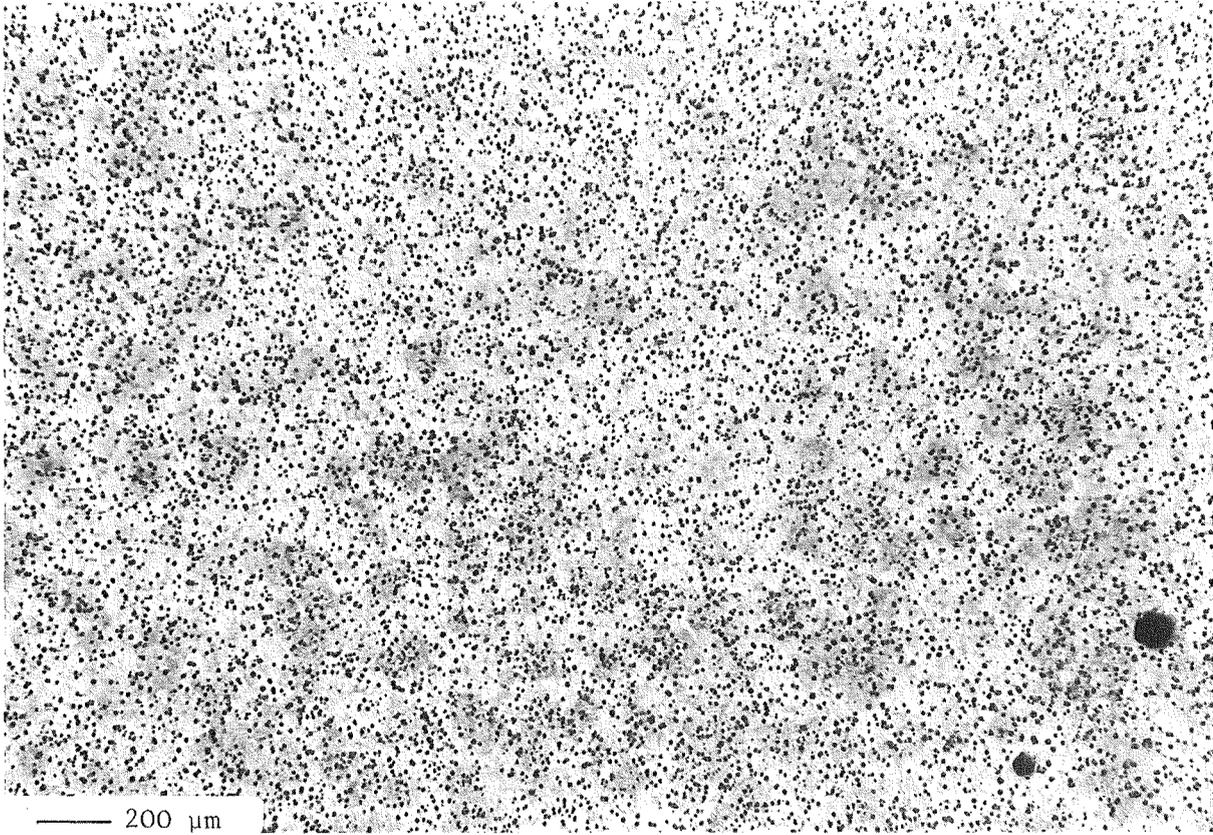


Fig. 13: Microstructure of Li(17)Pb(83) (Mat. II).

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THERMOPHYSICAL PROPERTIES IN THE SYSTEM Li-Pb

Part II: Thermophysical properties of the Li(17)Pb(83)
eutectic alloy

U. Jauch, G. Haase, B. Schulz

Abstract

Methods of measurements and results for the following properties of Li(17)Pb(83) are presented: density, specific heat, latent heat of fusion, surface energy, thermal conductivity and diffusivity, electrical conductivity and viscosity. The range of the temperature for extrapolation of the physical properties is discussed.

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1. Introduction

The correct description of the thermohydraulic behaviour of a liquid interacting with a strong magnetic field requires also the knowledge of the thermophysical properties of the respective material.

In this - second - part of the paper the measurements and methods used for this purpose are described as applied to the eutectic alloy Li(17)Pb(83). If possible the data will be discussed considering the work published previously.

We distinguish in the following between thermodynamic and transport properties, a somewhat artificial differentiation, but it separates additive properties like heat of fusion, surface energy, density, specific heat from structure dependent properties like for example thermal and electrical conductivity. This is done in view of the third part of this paper, in which the estimation of some of the physical properties in the whole system Li-Pb is described.

2. Sample Preparation

All samples used were prepared and characterized as published in [1], that is melting the pure elements lithium and lead in a highly purified argon-atmosphere.

The measurements of the physical properties were performed either in highly pure He or Ar or in vacuum. In the latter case the samples were encapsulated either in Al_2O_3 , BN or CaF_2 crucibles. There was no sign of chemical interaction between the alloy and the crucible material in the temperature range investigated during the time of measurement. Directly before adjustment of the sample in the respective apparatus the surface of the sample was cleaned by etching in a mixture of $\text{CH}_3\text{COOH} + \text{H}_2\text{O}_2$.

3. Thermodynamic Properties of the Li(17)Pb(83) alloy

According to definition we will treat here the measurements of specific heat, latent heat of fusion, density thermal expansion and surface energy.

3.1 Specific Heat and Latent Heat of Fusion

The specific heat c_p was measured using a Perkin Elmer differential scanning calorimeter, which works up to 1000 K. The calorimeter was calibrated against sapphire (National Bureau of Standards). The results are shown in Fig. 1a and 1b for the solid and liquid state respectively. The standard deviation of the solid state measurements resulting from data of four samples is $\pm 2\%$. In the liquid state only two samples have been measured and the spread of data of the molten alloy indicates a standard deviation of $\pm 3\%$. The data can be fitted by the equations:

$$RT \leq T \leq 508 \text{ K} \quad c_p = -0.02417 + 3.927 \cdot 10^{-4} T + \frac{4986.7}{T^2}$$

$$508 \leq T \leq 800 \text{ K} \quad c_p = 0.195 - 9.116 \cdot 10^{-6} T$$

$$[c_p] = \text{J/gK}; [T] = \text{K}$$

The shape of the curve of the specific heat in the solid state cannot be discussed in detail, because it results from the addition of the specific heat functions of Pb and LiPb, the latter of which is not known. The value at the melting point in the liquid state of $0.1904 \text{ J/gK} \approx 33.0 \text{ J/gatom}\cdot\text{K}$ is in good agreement with the expected one given as $35.6 \text{ J/gatom}\cdot\text{K}$ for pure metallic melts and $32.2 \text{ J/g}\cdot\text{atom}\cdot\text{K}$ for molten intermetallic phases at their melting points [2]. Furthermore the very slight decrease with temperature of the specific heat in the liquid state corresponds to the behaviour of the specific heat of other well known metallic melts [3]. The only available data on the specific heat of Li(17)Pb(83) were published by Kühlbörsch and Reiter [4]. They performed their measurements with a calorimeter of the Calvet-type and got comparable data for the solid state, but a strong increase of c_p ($0.1953 \rightarrow 0.2254 \text{ J/gK}$) upon melting and a strong decrease of about 23 % from 508 to 573 K. This strong decrease would result in $c_p \approx 0$ at 800 K (300 K above melting) a somewhat improbable result.

The measurement of the latent heat of fusion ΔH_f of Li(17)Pb(83) was described in detail in part I of this work, therefore the values will just be repeated:

Melting temperature 508 K, $\Delta H_f = (33.9 \pm 0.34) \text{ J/g}$.

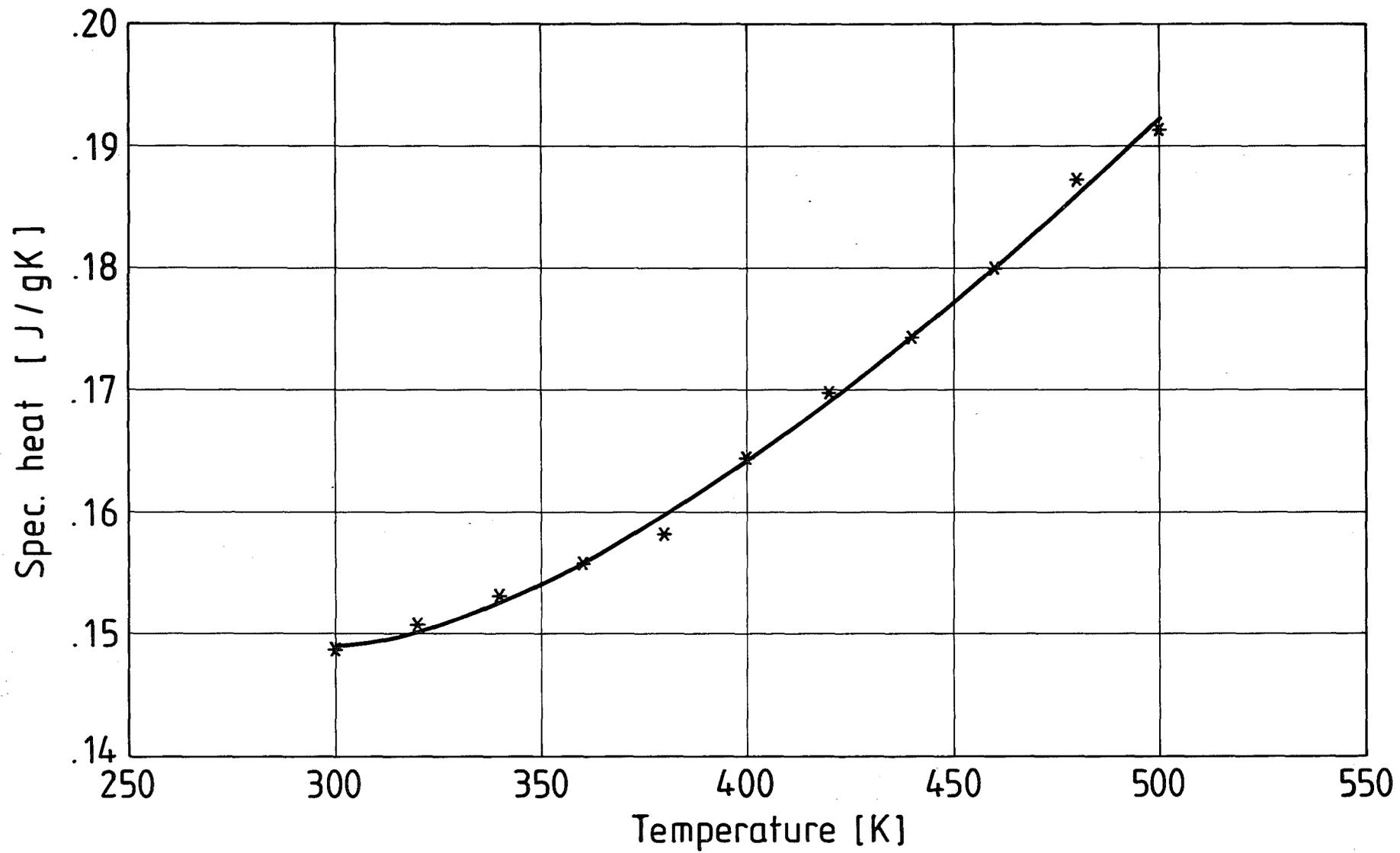


Fig. 1a: Specific heat at constant pressure of solid Li(17)Pb(83).

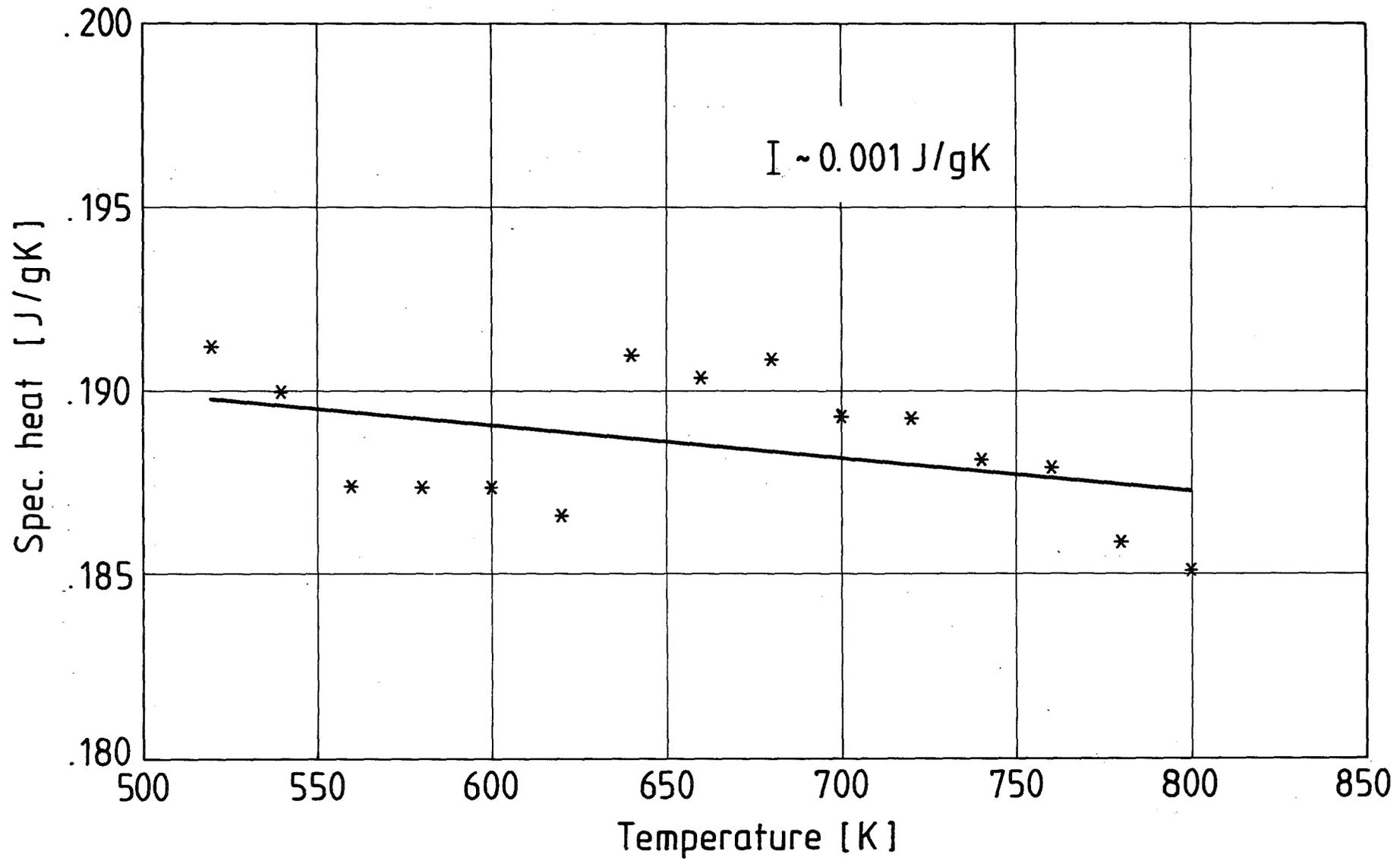


Fig. 1b: Specific heat at constant pressure of liquid Li(17)Pb(83).

3.2 Density, Thermal Expansion and Surface Energy

The room temperature density of Li(17)Pb(83) was determined as $(10.22 \pm 0,08) \text{ g/cm}^3$. With a difference dilatometer using copper (NBS-standard-reference-material 736) as reference the relative thermal expansion of Li(17)Pb(83) was measured dynamically (2 K/min) and stepwise. In the range $RT < T < 450 \text{ K}$ the relative thermal expansion is a linear function of the temperature. The linear thermal expansion coefficient is $\alpha_{th} = (41 \pm 4) \cdot 10^{-6} \text{ K}^{-1}$. Thus one gets for the density in solid state:

$$\rho_s = 10.25 (1 - 126 \cdot 10^{-6} t) \quad [t] = ^\circ\text{C},$$

or

$$\rho_s = 10.60 (1 - 122 \cdot 10^{-6} T) \quad [T] = \text{K}.$$

For $T = T_m = 508 \text{ K}$ we have $\rho_{TS} = 9.94 \text{ g/cm}^3$.

The evaluation of the density of the liquid eutectic was performed using the sessile drop method as described earlier [5]. We obtained:

$$\rho_l = 9.99 (1 - 168 \cdot 10^{-6} t) \quad [t] = ^\circ\text{C},$$

$$\rho_l = 10.45 (1 - 161 \cdot 10^{-6} T) \quad [T] = \text{K}$$

for the temperature range $508 < T < 625 \text{ K}$ with $\Delta\rho/\rho = \pm 5\%$

For $T = T_m = 508 \text{ K}$ we have $\rho_l = 9.60 \text{ g/cm}^3$.

The volume increase upon melting is given by:

$$\text{for } T = T_m, \quad \frac{V_l - V_s}{V_s} = 0.035 \hat{=} 3.5 \%$$

A view on the volume change upon melting of pure metals [6] shows for Pb a value of 3.5 %, which is in good agreement with our data. The influence of Li ($\Delta V/V = 1.6 \%$) should be negligible. The density of the liquid eutectic corresponds by chance completely to the value interpolated from the liquid density data of Ruppertsberger and Speicher [7] measured in the whole Li-Pb system. Their density functions for an alloy with 80 at.% Li and for pure Pb follow the equations:

For 80 at.% Pb ($T_m = 533$ K) $\rho_l = 9.70 (1 - 72.1 \cdot 10^{-6} T)$, $[T] = K$

For 100 at.% Pb ($T_m = 600$ K) $\rho_l = 11.47 (1 - 118 \cdot 10^{-6} T)$

The fact that the volume thermal expansion coefficient of Li(17)Pb(83) is remarkably higher than that of Pb (in the liquid and in the solid state) is pointed out without explanation at the moment.

With the sessile drop technique the surface energy γ_{LV} of Li(17)Pb(83) was determined. We obtained at the melting point $\gamma_{LV} = 0.48 \text{ J/m}^2$ ($T = 508$ K) and a temperature dependance $d\gamma_{LV}/dT \approx -0.5 \cdot 10^{-3} \text{ J/m}^2\text{K}$. The wetting angle θ of Li(17)Pb(83) against SS 316L drops from 120° at 513 K to 115° at 540 K, to values $\theta < 90^\circ$ (87°) at 625 K. It should be mentioned that these experiments were particularly difficult. A completely new set-up of the used technique was built into a special box for protection of the samples against nitrogen and oxygen. Even then, it occurred sometimes during heating that a solid surface coating on the molten droplet was formed, which yielded a higher wetting angle at the respective temperature. This phenomenon increased the number of runs to obtain the few data which we think describe the wetting behaviour of the eutectic alloy against SS 316L correctly.

4. Transport Properties of Li(17)Pb(83)

While the measurement technique of the thermodynamic properties of molten metals is well established, the evaluation of data for transport properties is much more difficult taking into account the atmospheric conditions i.e. the high affinity of the alloy against nitrogen and oxygen. Therefore the thermal and electrical conductivity measurements were performed in thermodynamically closed systems (capsules plus samples) which themselves were adjusted either in vacuum or in Ar. The experimental technique was always checked with liquid lead.

4.1 Thermal Diffusivity and Conductivity

The capsules for the samples for diffusivity measurements of the alloy consists of an alumina-tube having the same thickness as the cylindrical shaped sample. The sample was then covered with CaF_2 -discs on both sides to allow the absorption of the laser flash (wavelength $1.06 \mu\text{m}$) only in the surface

of the sample and the registration of the temperature rise at the rear face of the sample with an In-Sb-infrared detector. We measured for lead (99.99 metallic purity) at 298 K for samples with and without capsules a thermal diffusivity of $\alpha = 0.229 \text{ cm}^2/\text{sec}$ compared to 0.231, 0.27 and 0.228 at 318 K as reviewed by Touloukian et al. [8]. At 571 K we obtained $\alpha = 0.182 \text{ cm}^2/\text{sec}$ compared to $0.191 \text{ cm}^2/\text{sec}$ at 562 K, 0.200 at 571 K and 0.220 at 568 K [8]. The authors [8] quoted by Touloukian reported as errors for the data $\pm 1.6/\pm 6.1$ up to $\pm 5 \%$. The standard deviation of our measurements taking all samples together is $\pm 3 \%$ at 298 K, which increases up to $\pm 5 \%$ at 570 K. As a mean value in the liquid state α equals $(0.134 \pm 0.010) \text{ cm}^2/\text{sec}$ at 623 K, which is the value nearest to the melting point and is to compare with a value of $(0.109 \pm 0.004) \text{ cm}^2/\text{sec}$ at 669 K [8]. Although the data in the liquid state are higher than other reported values, the data in the solid state agree well with the literature data. Thus we decided to use the above mentioned type of capsules to determine the thermal diffusivity of Li(17)Pb(83) in the solid and the liquid state. The results are presented in table 1 and fig. 2. Both include also the thermal conductivity data using the specific heat- and density functions given above.

Table 1: Thermal diffusivity and conductivity of Li(17)Pb(83).

T [K]	α [cm^2/sec]	c_p [J/gK]	ρ [g/cm^3]	λ [W/cmK]
298	0.178 ± 0.006	0.149	10.21	0.271
353	0.180	0.154	10.14	0.281
433	0.170	0.172	18.04	0.294
473	0.177 ± 0.006	0.184	9.98	0.325
513	0.0667	0.190_3	9.59	0.122
533	0.0668	0.190_1	9.55	0.121
553	0.0687	0.189_9	9.52	0.124
573	0.0764	0.189_8	9.49	0.138
583	0.0748	0.189_7	9.47	0.134
623	0.0789 ± 0.006	0.189_3	9.40	0.140

The following equations represent the results in the solid state:

$$\text{For } 300 < T < 508 \text{ K we have } \alpha_S = 0.190_5 - 3.5 \cdot 10^{-5} T \text{ W/cmK} \quad [T] = \text{K}$$

$$\text{and } \lambda_S = 0.177 + 2.94 \cdot 10^{-4} T \text{ " "}$$

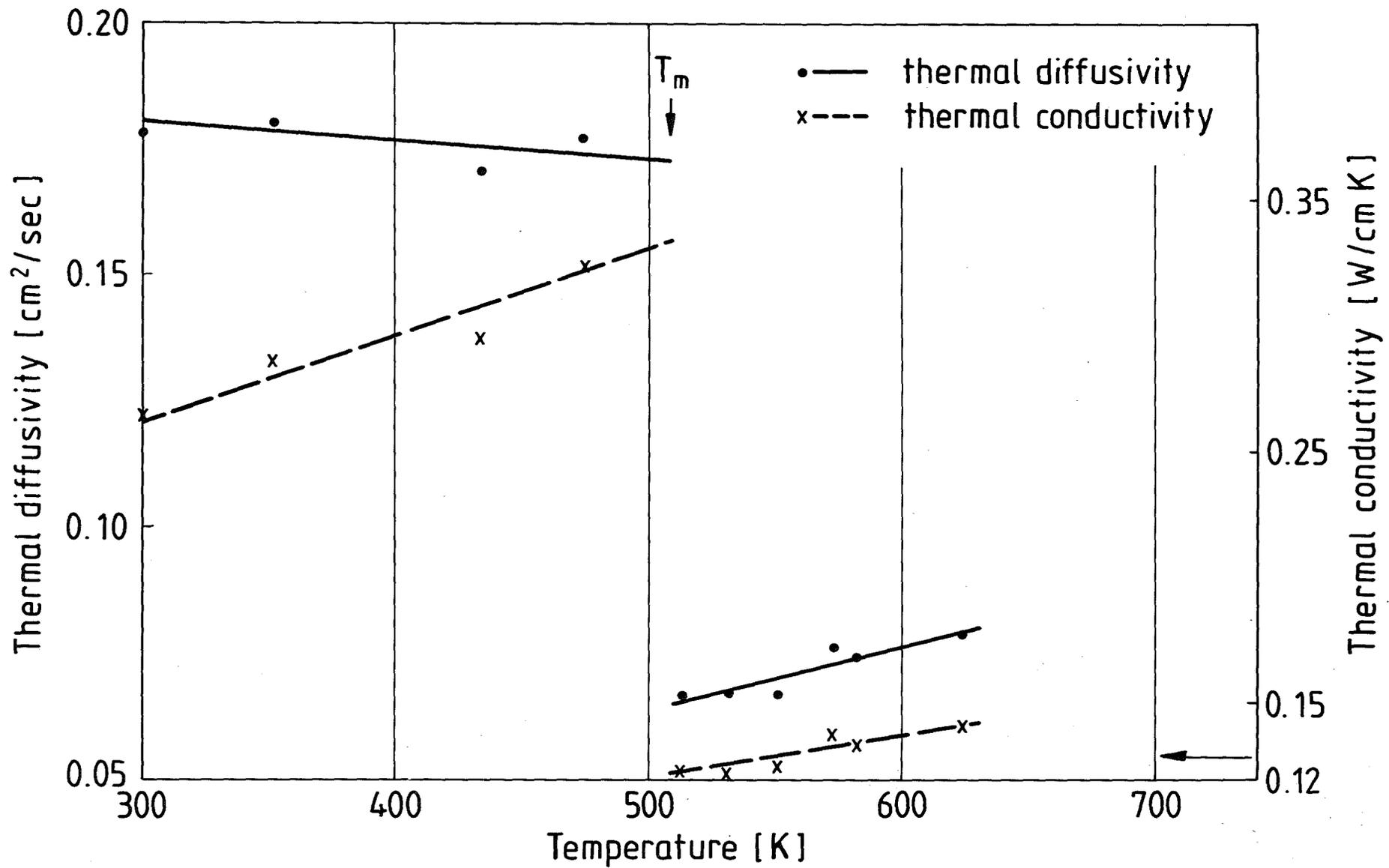


Fig. 2: Thermal diffusivity and conductivity of Li(17)Pb(83).

For the liquid state we have

$$\text{for } 508 < T < 625 \text{ K } \alpha_L = 1.3 \cdot 10^{-3} + 13.0 \cdot 10^{-5} T \quad \text{W/cmK} \quad [T] = \text{K}$$

$$\text{and } \lambda_L = 1.95 \cdot 10^{-2} + 19.6 \cdot 10^{-5} T \quad \text{"} \quad \text{"}$$

The standard deviation of the thermal conductivity follows from $\lambda = \alpha \cdot c_p \cdot \rho$ with $\Delta\lambda/\lambda = \pm \sqrt{(\Delta\alpha/\alpha)^2 + (\Delta c_p/c_p)^2 + (\Delta\rho/\rho)^2} \approx 10\%$. The character of the temperature function of the thermal diffusivity and conductivity is mainly determined by the specific heat function in the solid and liquid state as can be seen in combining the data in fig. 1 with the originally measured data of the thermal diffusivity in fig. 2.

4.2 Electrical Resistivity

The four point Thompson bridge was used to measure the electrical resistivity ρ_{el} . The samples were mounted in capsules of boronnitride. The size of the samples were 5 x 0.7 x 0.5 mm. The length of the potential drop in the sample was 38.0 mm. Silver coated copper wires were used to implement the electrical connections. The temperature was measured with a NiCr-Ni thermocouple. The capsules were mounted in a graphite furnace. The measurements were carried out in vacuum. The size of the sample was corrected for thermal expansion taking into consideration the density function of Li(17)Pb(83) given above. We obtained for pure lead (99.99) at the melting point in solid state $\rho_{el s} = 54.7 \cdot 10^{-6} \Omega\text{cm}$ and an increase to $100 \cdot 10^{-6} \Omega\text{cm}$ at 600 K upon melting. Thus the ratio $\rho_{el l}/\rho_{el s}$ is 1.83, which is lower than the values quoted in [9], which are between 1.90 and 1.94 (measured). At 840 K we measured $108 \cdot 10^{-6} \Omega\text{cm}$ compared to 103.8 to $109.2 \cdot 10^{-6} \Omega\text{cm}$ [9]. The method has a relatively low accuracy of about $\pm 5\%$.

The results for the eutectic alloy are presented in fig. 3. They follow the equations:

$$\rho_{el s} = 0.74 \cdot 10^{-6} + 10.54 \cdot 10^{-8} T \text{ for } RT < T \leq 508 \text{ K,}$$

$$\rho_{el l} = 102.3 \cdot 10^{-6} + 0.0426 \cdot 10^{-6} T \text{ in the range } 508 < T < 933 \text{ K,}$$

$$[\rho] = \Omega\text{cm}, [T] = \text{K with } \Delta\rho_{el}/\rho_{el} = \pm 5\%$$

$$\frac{\rho_{el l}}{\rho_{el s}} = \frac{123.9}{54.3} = 2.28$$

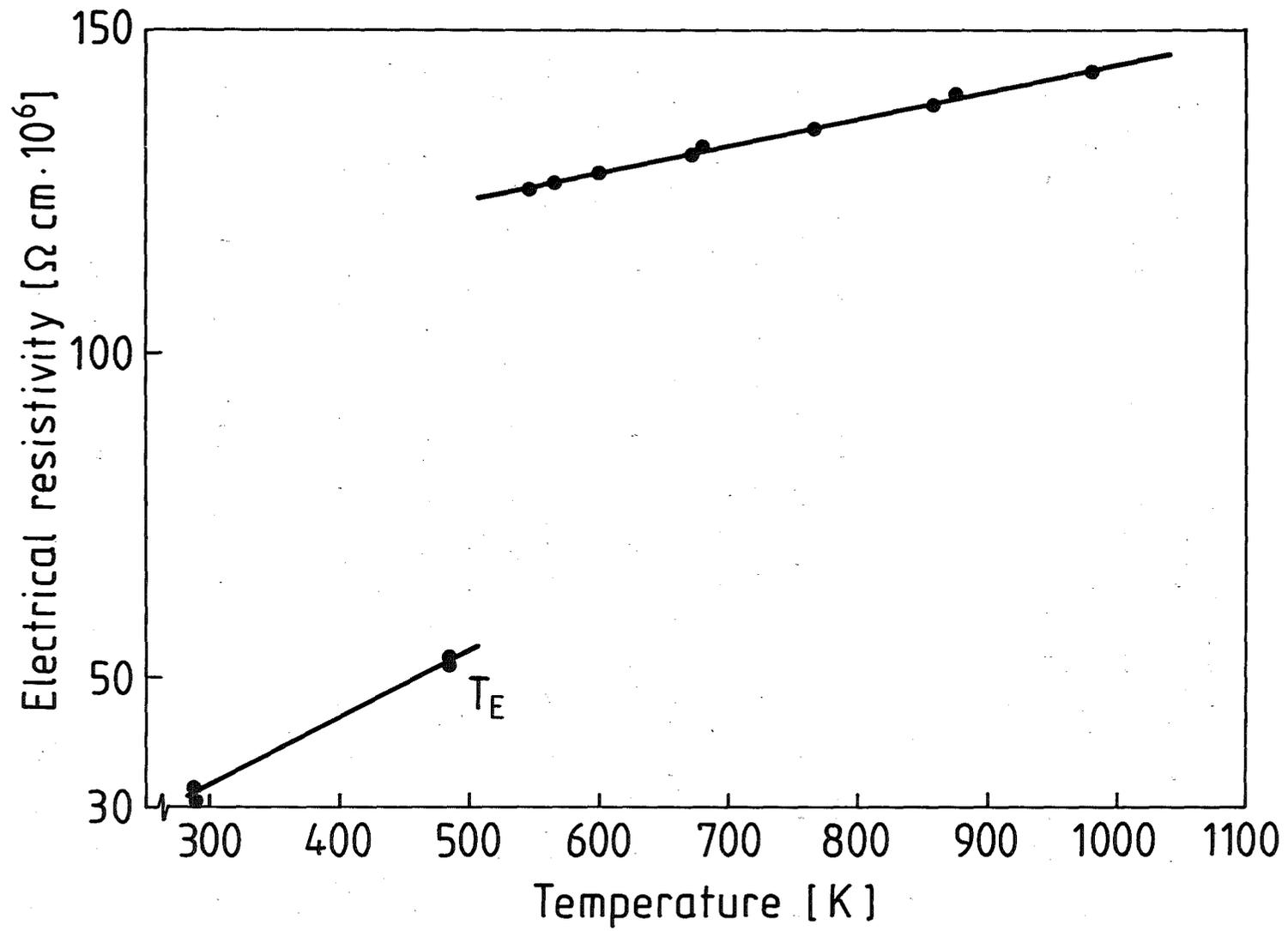


Fig. 3: Electrical resistivity of Li(17)Pb(83).

4.3 Viscosity

The viscosity of the eutectic alloy was measured with a viscosimeter of the Searle-type, specially developed for measurements of metallic melts [10,11]. The measuring system consists of alumina. The measurements were carried out in Ar-atmosphere. The calibration was performed with standard-oils of the Physikalisch-Technische Bundesanstalt.

The results for pure lead (99.99) given in the Arrhenius type of equation is:

$$\eta = \eta_0 e^{\frac{Q}{RT}} \quad \text{with } \eta_0 = 0.491 \text{ mPas}$$
$$\frac{\Delta\eta}{\eta} = \pm 7 \% \quad \text{and} \quad Q = 8490 \text{ J/molK}$$
$$[T] = \text{K}$$

The data compilation of Gmelin [9] shows for η_0 values of 0.408 and 0.422 mPas. The activation energy for viscous flow Q is given by 9607 and 9712 J/molK. A combination of all known data leads to 8414 J/molK [9], which is very close to the measured activation energy Q .

Measuring the viscosity of Li(17)Pb(83) one has to take into account that a significant solution of O_2 and N_2 in the liquid alloy will result in the formation of solid lithium nitride and lead oxide, i.e. a formation of a suspension which will increase the viscosity [10,11]. During a run of measurements this could be detected in deviations of the measured data from the Arrhenius plot as shown as an example in fig. 4. Thus many measurements had to be undertaken with fresh material to ensure the viscosity data in the higher temperature range. Finally for Li(17)Pb(83):

$$\eta = 0.187 e^{\frac{11640}{RT}} \text{ mPas} \quad \text{and} \quad [Q] = \text{J/molK}$$

Fig. 5 shows the Arrhenius plot of the data.

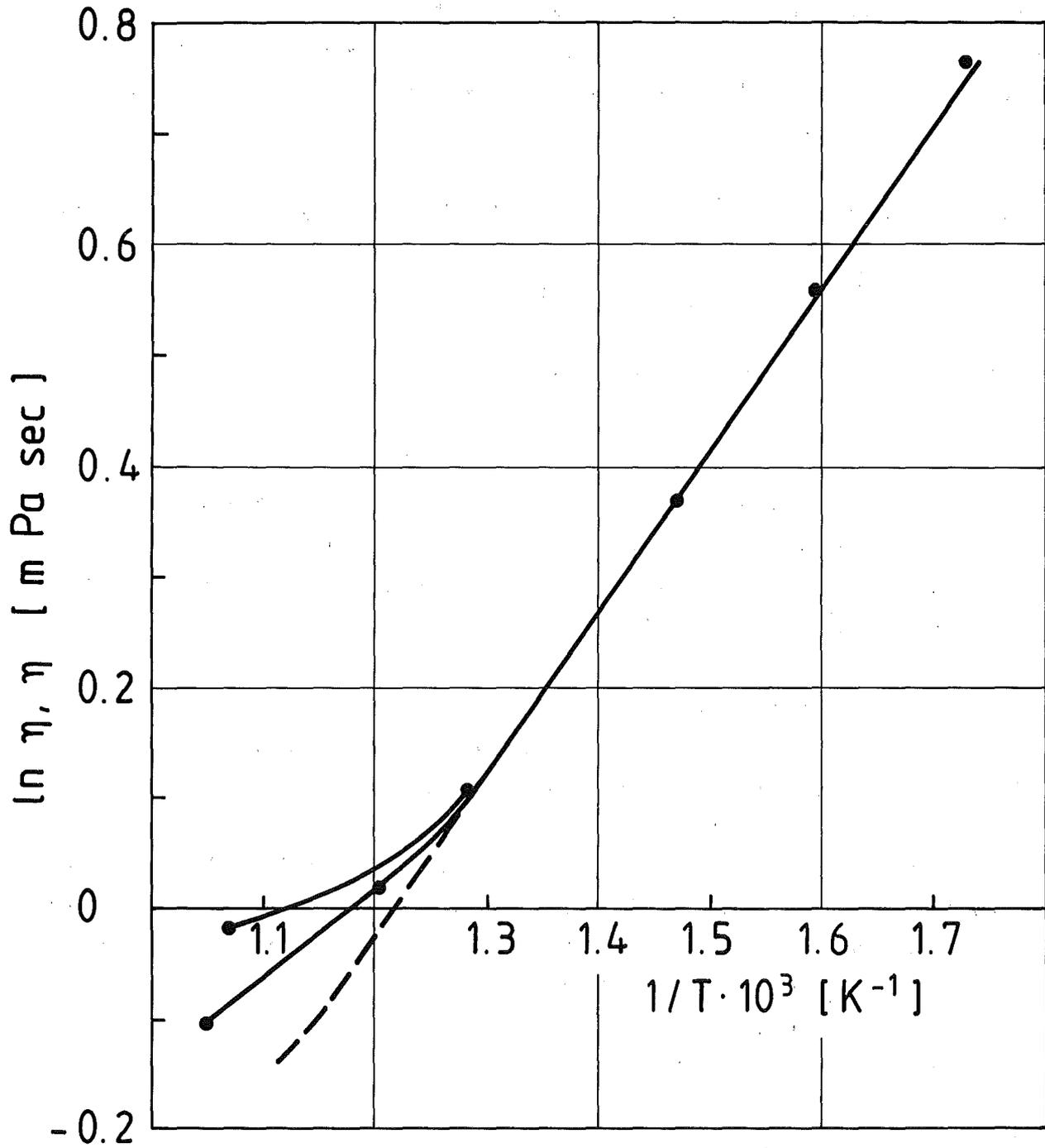


Fig. 4: Deviation of the viscosity of Li(17)Pb(83) from the Arrhenius function.

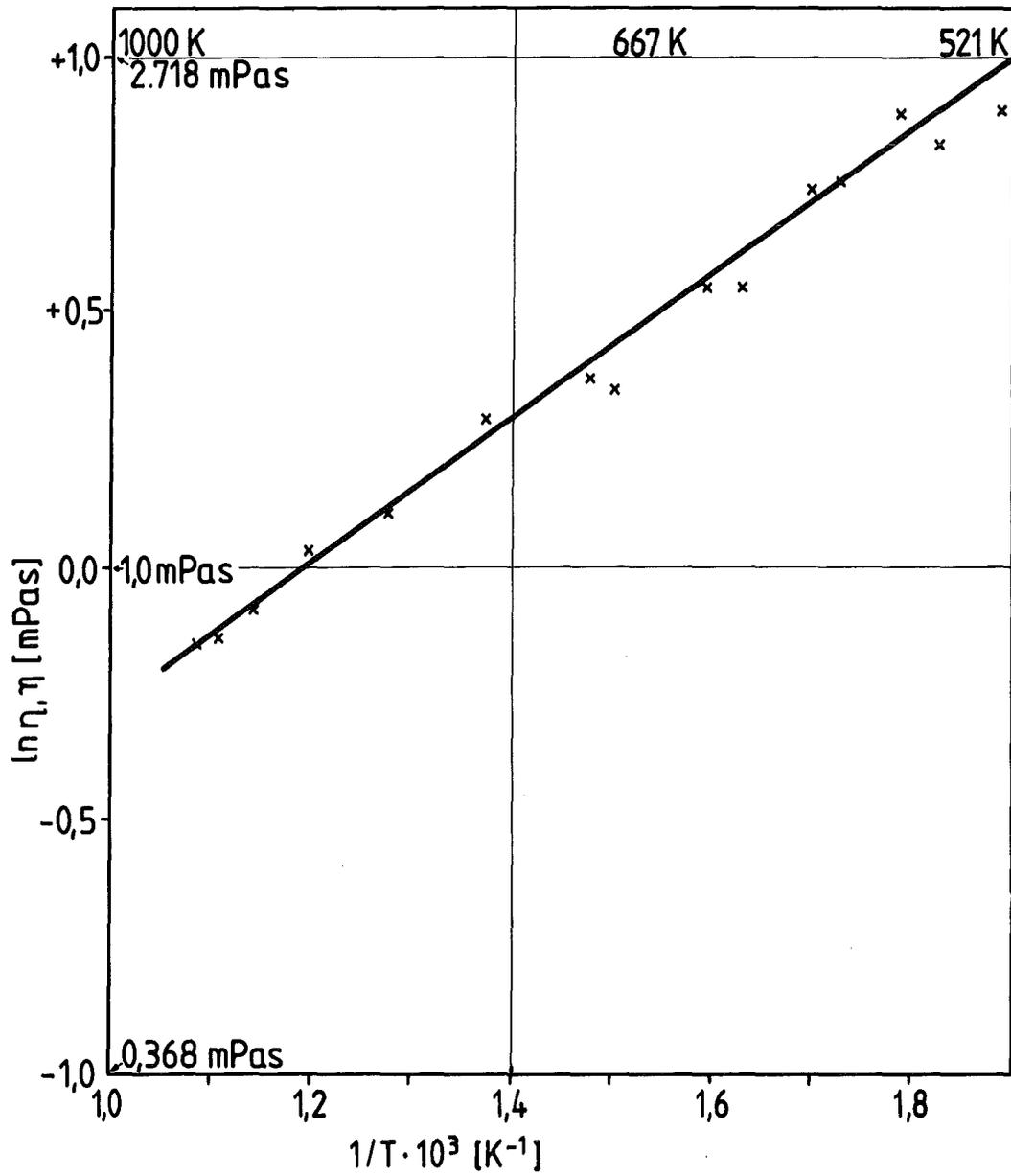


Fig. 5: Viscosity of Li(17)Pb(83).

5. Extension of the Validity Range of the Data of the Measured Properties

As can be seen, the experimental evaluation of thermophysical properties was undertaken in different temperature ranges (the highest temperature reached was 933 K). It is an important question to consider the possibility of extrapolating property data to higher temperatures not covered by the experiments. An answer can be tried based on the knowledge of the viscosity isotherms in binary alloys [12]. It was shown that the simple Andrade equation correlates (in very good agreement with experimental data for many metals and alloys [2]) the viscosity at the melting point with solid state quantities at the same temperature. Furthermore the most structure dependent property, which is the viscosity, shows in the isotherms the significant features of the liquidus of the phase diagram sometimes up to a factor of 2.5 of the melting point (fig. 6). Thus an extrapolation of the data should be possible up to 1250 K.

6. Concluding Remarks

The thermophysical property measurements described in this second part of the paper "Thermophysical Properties in the System Li-Pb", were undertaken partially with equipment originally not constructed for experiments in the liquid state. Thus the accuracy is sometimes relatively low. For example in the case of the electrical resistivity, whose standard deviation with $\pm 5\%$ is not comparable with other well known methods for measuring this property in the liquid state. Nevertheless the authors think that the data describing the thermophysical behaviour of the liquid Li(17)Pb(83) eutectic alloy is of adequate accuracy to design a liquid metal blanket for controlled nuclear fusion.

The authors wish to thank R. Brandt, University of Stuttgart, for the determination of the specific heat.

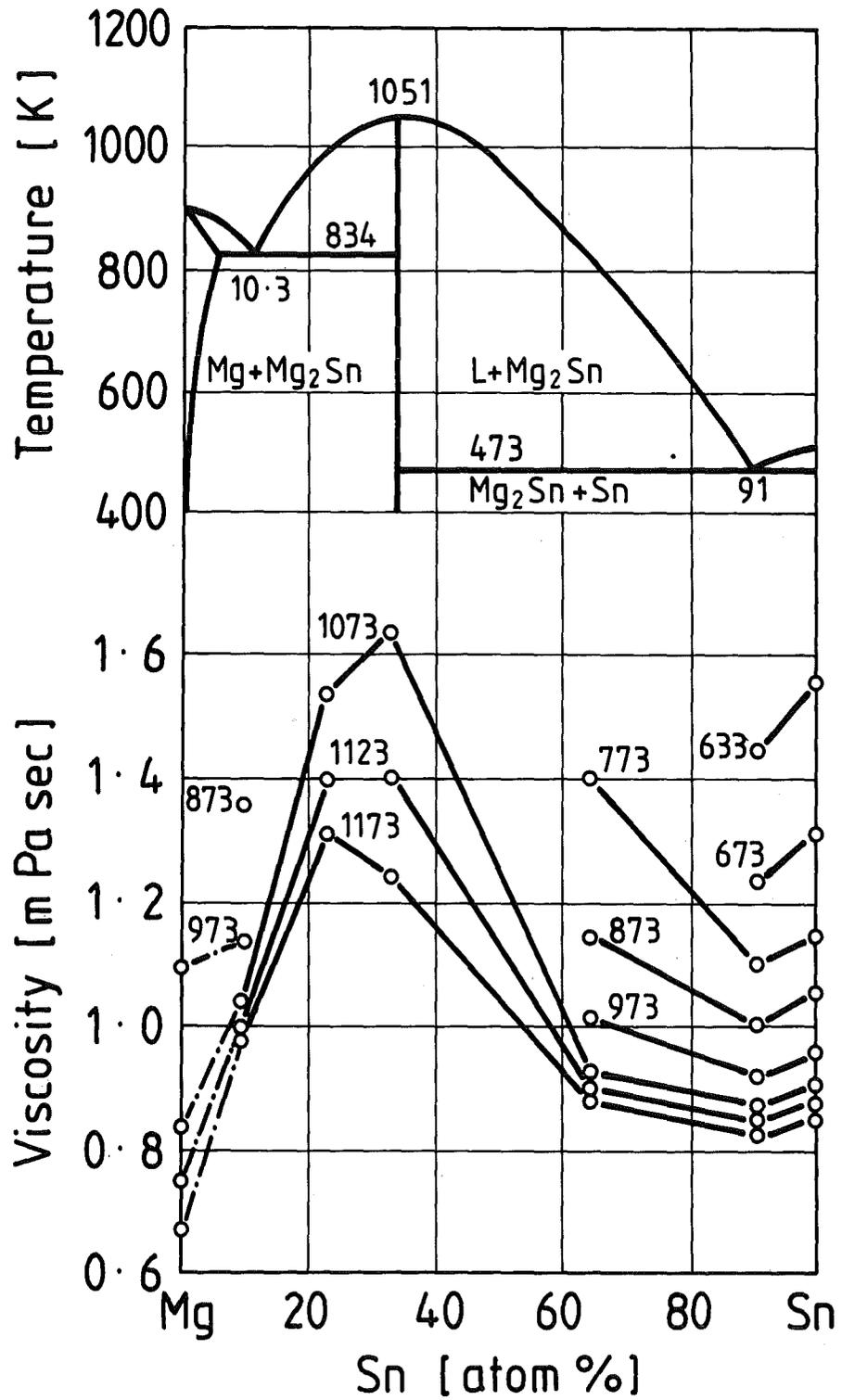


Fig. 6: Viscosity isotherms and phase diagram. of Sn-Mg (after Richardson [12])

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Part III

Estimation of Thermophysical Properties in the system Li-Pb

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Abstract

Based on the phase diagram and the knowledge of thermophysical properties data of alloys and intermetallic compounds in the Li-Pb system, quantitative relationships between several properties and between the properties in solid and liquid state are used:

- to interpret the results on thermophysical properties in the quasibinary system LiPb-Pb and
- to estimate unknown properties in the concentration range $100 > \text{Li (at.\%)} > 50$.

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10. Estimated thermal conductivity of the intermetallics LiPb, Li_8Pb_3 , Li_3Pb , Li_7Pb_2 , $\text{Li}_{22}\text{Pb}_5$ at solidus temperature (electron and phonon conductivity).

1. Introduction

In parts I and II of this paper the work was concentrated on the preparation and experimental determination of the thermophysical behaviour of the eutectic alloy Li(17)Pb(83) especially in the liquid state. As a possible liquid breeder material in nuclear fusion technology it is evident that among others the alloy with lowest melting point in the whole system (except pure Li) was chosen for this purpose. On the other hand it may be possible that a Li-Pb alloy with a high melting point can act as solid breeder material. From this point of view thermophysical properties of the intermetallic compound Li_7Pb_2 are of some interest, because this alloy has a much higher Li-content than the eutectic mentioned above. Based on our experience in handling Li-Pb alloys, it is nearly sure that measurements of the thermophysical properties of these compounds can only be carried out in boxes in a very pure atmosphere, regarding O_2 and N_2 contamination. Thus it is worthwhile to try an estimation of some of the important physical properties in the Li-Pb system in using the knowledge we have up to now.

2. Phase relationships in the system Li-Pb

In 1958 Hansen, Anderko [1] recommended the phase diagram for the Li-Pb system as shown in fig. 1. It is still valid in the range of Li-concentrations ≤ 50 at.%, whereas the higher Li-concentrations were investigated in the late fifties and reviewed by Elliot [2] resulting especially in a change of the composition of the intermetallic compounds.

2.1 Solubility of Li in Pb and of Pb in Li

Hansen, Anderko [1] recommended the solubility of Li in solid lead to be 3 at.% (0.1 wt.%) at the eutectic temperature of 508 K. Data down to 300 K are extrapolated and result in 0.35 at.% (0.01 wt.%) Li. No data could be found for the solubility of lead in solid Li.

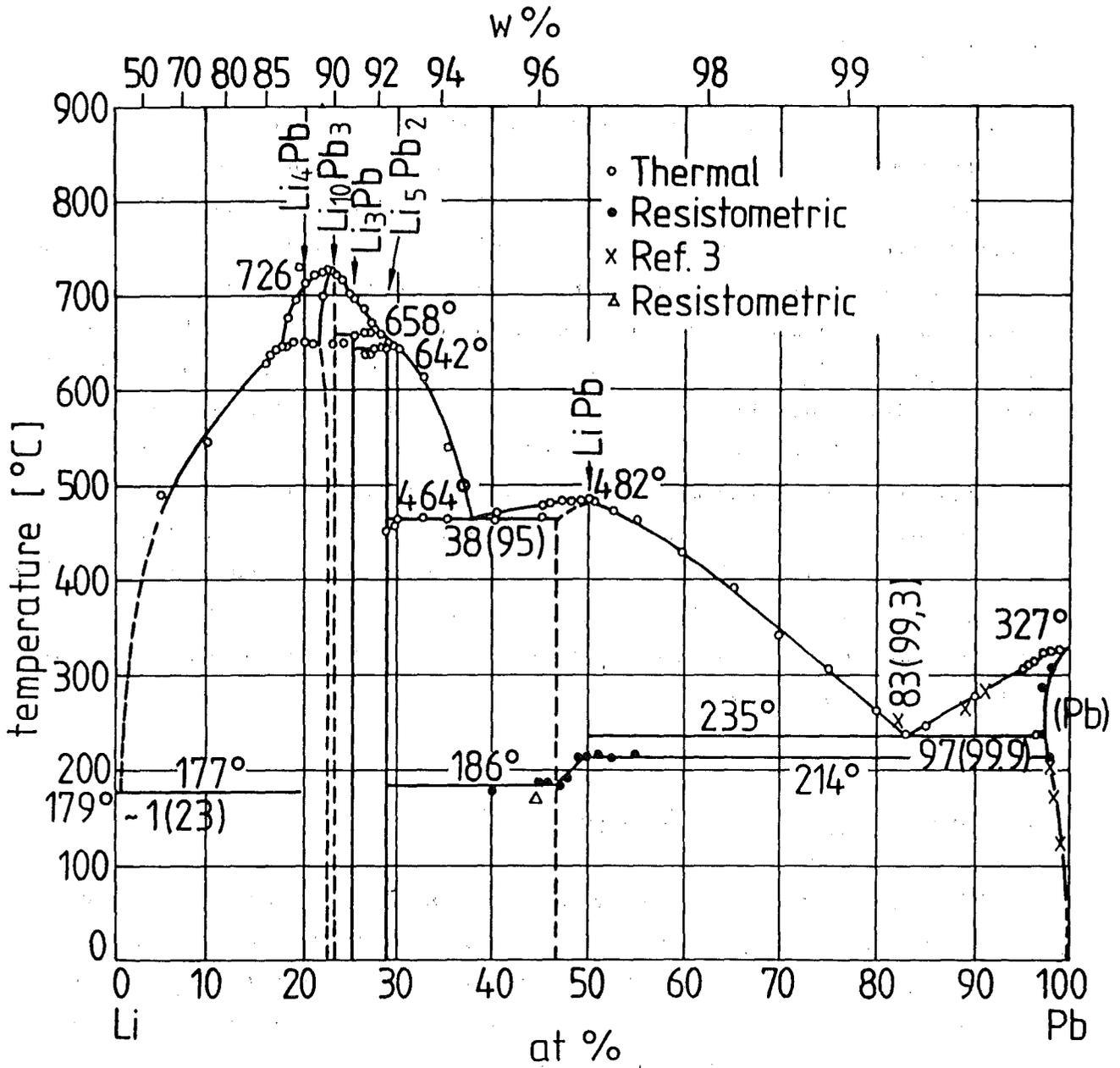


Fig. 1: Phase diagram of the binary system Li-Pb (according to [1]).

Table 1: Intermetallic phases and structure properties in the system Li-Pb [5,1], compositions in brackets refer to [1].

compound	molecular weight (g)	mole % (Li)	wt.% (Li)	melting point (K) [1]	Cell type	Cell constants (Å)	X-ray density (g/cm ³)
Li	6.941	100	100	453.7	b.c.c.*	3.508	0.53 at 298 K
Li ₂₂ Pb ₅ (Li ₄ Pb)	1188.7	81.5	12.8	peritectic reaction ~ 923 K	b.c.c. subcell b.c.c.	20.08 3.34 ₇	3.86 "
Li ₇ Pb ₂ (not in [1])	463.0	77.8	10.5	1005	hexag.	a = 4.751 c = 8.589	4.59 "
Li ₃ Pb	228.0	75.0	9.1	peritectic reaction ~ 933 K	b.c.c.	a = 6.687	5.06 "
Li ₈ Pb ₃ (Li ₅ Pb ₂)	677.1	72.7	8.2	peritectic reaction ~ 918 K	monoclin	a = 8.24 b = 4.757 c = 11.03 β = 104.5 ^o	5.37 "
βLiPb	214.1	50	3.2	755 K	simple cubic T > 493 K	a = 3.563	7.86 at T > 493 K
β'LiPb					rhomboedral	a = 3.542 α = 89.5 ^o	8.00 at 298 K
Pb	207.2	0	0	600 K	f.c.c.*	a = 4.950	11.35 "

* b.c.c. = body-centred cubic

f.c.c. = face-centred cubic

2.2 Intermetallic phases

Elliot [2] referred for his recommendation to the papers of Zalkin and Ramsey [3,4,5], and from [5] the information is taken, which is presented in table 1 as the state of the knowledge on intermetallic phases in the Li-Pb system. Included in this table too are the pure components Li and Pb.

It was worthwhile to note that Zalkin and Ramsey supposed the compound $\text{Li}_{10}\text{Pb}_3$ (mentioned in [1]) to be a mixture of the compounds Li_3Pb and Li_7Pb_2 . They described generally the type of structure of the intermetallic compounds as the basic Li-body-centred cell, in which the Pb atoms occupy regular sites of Li-atoms.

The intermetallic phase LiPb was reported [5,13] to have a homogeneity range to the Li-rich side ($\text{Li}_{0.53}\text{Pb}_{0.47}$) and a phase transformation at $T = 487$ K [13] for LiPb which decreases to $T = 457$ for $\text{Li}_{0.53}\text{Pb}_{0.47}$, below this temperature a highest Li-concentration for the LiPb-phase is supposed to be 52 at.% [13].

2.3 Eutectic alloys

Three eutectic alloys can be found in [1]. Their typical data are given in table 2.

Table 2: Eutectic alloys and structure properties in the system Li-Pb [5,1].

eutectic alloys	eutectic temp. (K)	eutectic composition (at.% Li)	eutectic composition (wt.% Li)	present phases	amount of present phases (wt.%)
Li, $\text{Li}_{22}\text{Pb}_5$ (tentative)	450	99	77	Li + $\text{Li}_{22}\text{Pb}_5$	74 Li
Li_8Pb_3 , $\text{Li}_{0.53}\text{Pb}_{0.47}$	473	62	5	LiPb + Li_8Pb_3	~ 50 Li_8Pb_3
LiPb, Pb	508	17	0.68	LiPb + Pb	21 LiPb

2.4 Other two phase regions in the solid state

All areas between the peritectic intermetallics $\text{Li}_{22}\text{Pb}_5$ - Li_7Pb_2 , Li_7Pb_2 - Li_8Pb_3 are two phase regions in the solid state. The peritectic decomposition of these phases results in a mixture of one solid and one liquid phase above the peritectic temperature.

2.5 Two phase regions in the liquid state

In liquid state both components Li and Pb are completely miscible.

3. Knowledge of the thermophysical properties in the binary system Li-Pb

3.1 The pure components Li and Pb

The thermophysical properties data for Pb are taken mainly from Gmelin [6], they were compiled in 1972. For the thermal conductivity we refer to the recommended curve in [7]. For the Li-properties the basis is the IUPAC Handbook of Thermodynamic and Transport Properties of Alkali Metals (1985) [8] for properties especially in the liquid state, for the solid state it is once more referred to Gmelin [9] and the Touloukian series [3,10,12]. To the new edition of Ullmann's Encyclopedie [12] and original contributions in the literature. The specific heat data of liquid lead are very contradictory in the values themselves as well as in the temperature dependence. Thus this property was experimentally determined in the solid and liquid state in using once more the Perkin-Elmer DSC. The data are shown in table 3 for the solid, in table 4 for the liquid state.

Table 3: Thermophysical properties of solid Li and Pb.

Property	T (K)	Li	T (K)	Pb
Molecular weight (g)		6,941		207.2
Density ρ (g/cm ³)	293	0.534 [2]	293	11.341 [6]
rel. lin. therm. expansion $\Delta l/l_0$	293	0	293	0
	400	$53 \cdot 10^{-4}$ [11]	400	$31.7 \cdot 10^{-4}$ [11]
	650	$80.4 \cdot 10^{-4}$	500	63.8
			600	98.8
lin. therm. expansion coefficient α_{th}/K^{-1}	293	$46 \cdot 10^{-6}$ [11]	293	$28.9 \cdot 10^{-6}$ [11]
	400	$53 \cdot 10^{-6}$	400	30.6
	650	$56 \cdot 10^{-6}$	500	33.3
			600	36.7
Specific heat c_p (J/gK)	300	3.559 [10]	298	0.128 [6]
	340	3.695 [10]		↓ linear
	400	3.981 [10]	580	0.141 [6]
	453	4.232 [10]	300-600	$0.119 + 3.67 \cdot 10^{-5} T$

Table 3: contd.

Properties	T (K)	Li	T (K)	Pb
compressibility	-		600	$\kappa_{ad} = 2.92$ [6]
κ (10^{-7} cm ² /N)	-	7.2 [9]	600	$\kappa_{is} = 3.5$ [6]
thermal conductivity	300	0.768 [7]	300	0.352 [7]
			400	0.338 [7]
λ (W/cmK)	350	0.738 [7]	350	0.348 [7]
	400	0.721 [7]	500	0.325 [7]
	453.7	0.712 [7]	600	0.312 [7]
electrical resistivity	273	8.55 [12]	273	19.3 [6] *
ρ_{el} ($\mu\Omega$ cm)	453.7	16 [13]	373	28.6 [6]
			473	40.0 [6]
			573	51.0 [6]
			600	49.0 [6]

*different original authors, quoted after [6].

Table 4: Thermophysical properties of liquid Li and Pb

Properties	T (K)	Li	T (K)	Pb
melting point		453.7 [8]		600 [6]
T_m (K)				
latent heat of fusion ΔH_s (J/g)		431.4 [12]		23.03 [6]
Density at T_M ρ_{TM} (g/cm ³)	453.7	0.5147 [8]	600	10.665 [6]
Volume expansion γ_{th} coefficient (K^{-1})	460	$58.65 \cdot 10^{-5}$ [8]	630-800	$124 \cdot 10^{-6}$ [6]
	500	54.63		
	600	50.94		
	800	57.51		
	1000	66.99		
Volume increase upon melting		1.5 [12]		3.56 [6]
$\frac{V_{1TM} - V_{STM}}{V_{STM}}$ (%)				
surface energy γ_{LV} (10^3 J/m ²)	$T_M - 1673$	$398.3 - 0.147 T$ [8]	$T > 600$	$458 - 0.113 (T - T_m)$ [6]
specific heat C_p (J/moleK)	453.7	30.49 [8]	600	30.46
	700	29.49	700	30.05
	1000	28.59	800	29.42
Compressibility				
κ_{is} (isotherm) (10^{-7} cm ² /N)	453.7	$0.95259 \cdot 10^{-4}$ [8]	600	3.5 [6]
κ_{ad} (adiabatic) (10^{-7} cm ² /N)		$1.0149 \cdot 10^{-4}$	1073	5.3 [6]

Table 4: contd.

Properties	T (K)	Li	T (K)	Pb
Viscosity (mPas)	460	0.58875 [8]	T > 600	$\lg \eta = 0.4401 \cdot 10^3 / T - 0.3134$ [6] $\eta = 0.486 \cdot e^{\frac{8419}{8.31 T}}$ [6]
	500	0.53062		
	600	0.42857		
	700	0.36236		
thermal conductivity λ (W/cmK)	453.7	0.428 [8]	600	0.155 [7]
	500	0.442	700	0.174
	800	0.541	800	0.190
	1000	0.600	1000	0.215
electrical resistivity ρ_{el} ($\mu\Omega\text{cm}$)	453.7	24.8 [8]	600	95-96 [6]
	500	26.33	↓	↓ linear
	800	34.71	↓	↓
	900	37.22	1273	126.3 [6]
	1000	39.69		

3.2 The eutectic alloy Li(17)Pb(83) and the intermetallic compound LiPb

While the measurements of the thermophysical properties of the eutectic are described in detail in the second part of this paper, they will only be repeated in the following. The preparation of the intermetallic compound LiPb was presented in the first part. We measured some of the thermophysical properties (density, thermal expansion, latent heat of fusion, thermal diffusivity and electrical resistivity) of the intermetallic compound; because of the high affinity of the compound to oxygen and nitrogen it was not possible to determine the specific heat, the surface energy or the viscosity. The data are once more divided into solid and liquid state properties in tables 5 and 6.

Table 5: Thermophysical properties of Li(17)Pb(83) and LiPb in the solid state.

Property	T (K)	Li(17)Pb(83)	T (K)	LiPb
molecular weight (g)		173.16		214.1
Density ρ (g/cm ³)	298	10.22		8.15
X-ray-calculation				8.00 [5]
rel. lin. therm. expansion coefficient α_{th} (K ⁻¹)	298-450	$41 \cdot 10^{-6}$	382 423 448 567	$25.6 \cdot 10^{-6}$ 30.9 30.9 30.6
estimation from crystallographic data			168-343 403-628	$30 \cdot 10^{-6}$ [5] $45 \cdot 10^{-6}$ [5]
Specific heat (J/gK)	298-508	$-0.02417 + 3.927 \cdot 10^{-4} T + 4986.7/T^2$		-
thermal conductivity λ (W/cmK)	300-508	$0.177 + 2.94 \cdot 10^{-4} T$		-
thermal diffusivity α (cm ² /sec)	300-508	$0.190_5 - 3.5 \cdot 10^{-5} T$	293 368 475 573 673	0.0482 0.0562 0.0853 0.0839 0.0951
electrical resistivity ρ_{e1} ($\mu\Omega m$)	300-508	$0.74 + 10.54 \cdot 10^{-2} T$	635 694 721 323 373 423 493 533	60.5 67.1 68.8 86.7 [13] 81.4 [13] 73.0 [13] 52.7 [13] 61.7 [13]
phase transformation at 487.K				

Table 6: Thermophysical properties of Li(17)Pb(83) and LiPb in the liquid state.

Property	T (K)	Li(17)Pb(83)	T (K)	LiPb
melting point T_m (K)		508		755
latent heat of fusion ΔH_m (J/g)		33.9		51.1
Density at T_M ρ_{TML} (g/cm ³)	508	9.6	755	6.97 ± 0.03 [14]
Volume expansion coefficient γ_{th} (K ⁻¹)		~ 161·10 ⁻⁶	770-965	90.4
Volume increase upon melting (%)		3.5		9.9; 8.2*
surface energy γ_{LV} (10 ³ J/m ²)	508	0.48		-
ad. compressibility κ_{ad} (cm ² /N)			755	4.58·10 ⁻⁷ [14]
Specific heat (J/moleK)	508-800	33.77 - 1.58·10 ⁻³ T		-
Viscosity η (mPas)	T > 508	$\eta = 0.187 e^{11640/8.314 T}$		-
thermal conductivity λ (W/cmK)	508-625	1,95·10 ⁻² + 19.6·10 ⁻⁵ T		-
thermal diffusivity α (cm ² /sec)			777	0.0436
electrical resistivity $\rho_{el 1}$ ($\mu\Omega$ cm)	508-933	102.3 + 0.0426·T	755-1000	90.32 + 0.0889·T

* For the first value 8.00 was used as room temperature density and 30.6·10⁻⁶ for α_{th} , while for the second value the data of Zalkin and Ramsey [5] were taken.

3.3 Investigations covering the whole concentration range between Li and Pb

Here we have to discuss the work of Zalkin and Ramsey for evaluating the room temperature density and thermal expansion [5], the paper of Ruppertsberger and Speicher [14] on the density, thermal expansion of the molten alloys and their compressibility, the experiments described by Grube and Kleiber [13] for the electrical resistivity in solid state and for the liquid state results of Nguyen and Enderby [15], Mejer et al. [16] and Hubberstey et al. [17] for dilute solutions of Pb in liquid lithium.

The results are presented in figs. 2 - 5, showing the property as function of the atomic concentration of lead. The figures include the pure components and the data for Li(17)Pb(83) and LiPb shown in tables 3 - 6. They represent no property isotherms (except the room temperature density in fig. 2), but refer all to the solidus or to the liquidus temperature. More than one value for one concentration is caused from different results of different authors. There is nearly no contradiction in the interpretation of the physical meaning of the results for the electrical conductivity in the system Li-Pb in the literature. Regarding especially the derivation of the electrical resistivity vs. concentration fig. 6 [15,16] it is to be seen that in liquid state in the range from 15 to 30 at.% Pb, this derivation has a negative sign for the resistivity of the liquid alloy. The resistivity of the intermetallic compound LiPb changes this sign in solid state (fig. 7). It is negative up to the transformation temperature (487 K), and shows normal metallic behaviour up to the melting point and in liquid state (see tables 3, 4). From results of the excess volume in liquid state [14], the Knight shifts and Seebeck coefficients the following conclusions are drawn in literature [15,16]: In the system Li-Pb, the alloys show a metallic-like behaviour for Pb concentrations higher 50 at.%. It is discussed [15,16] that the behaviour of the electrical resistivity in liquid state at this concentration demonstrates clearly the end of this behaviour. At lower lead concentrations, especially for the intermetallic compounds (table 1), a nonmetallic behaviour is expected. Mejer et al. suppose for the "Li₄Pb" (Li₂₂Pb₅) compound a filled p-band of lead and a depleted s-band of Li. A bonding character being intermediate between ionic and metallic, where the tendency to metallic bonding should be higher in liquid than in solid state is attributed to the intermetallics. On the other hand the absolute values of the electrical resistivity are comparable to typical alloys showing metallic conduction. Typical ionic melts have electrical resistivities in the range of 1 - 10 Ωcm, i.e. by 4 orders of magnitude higher than

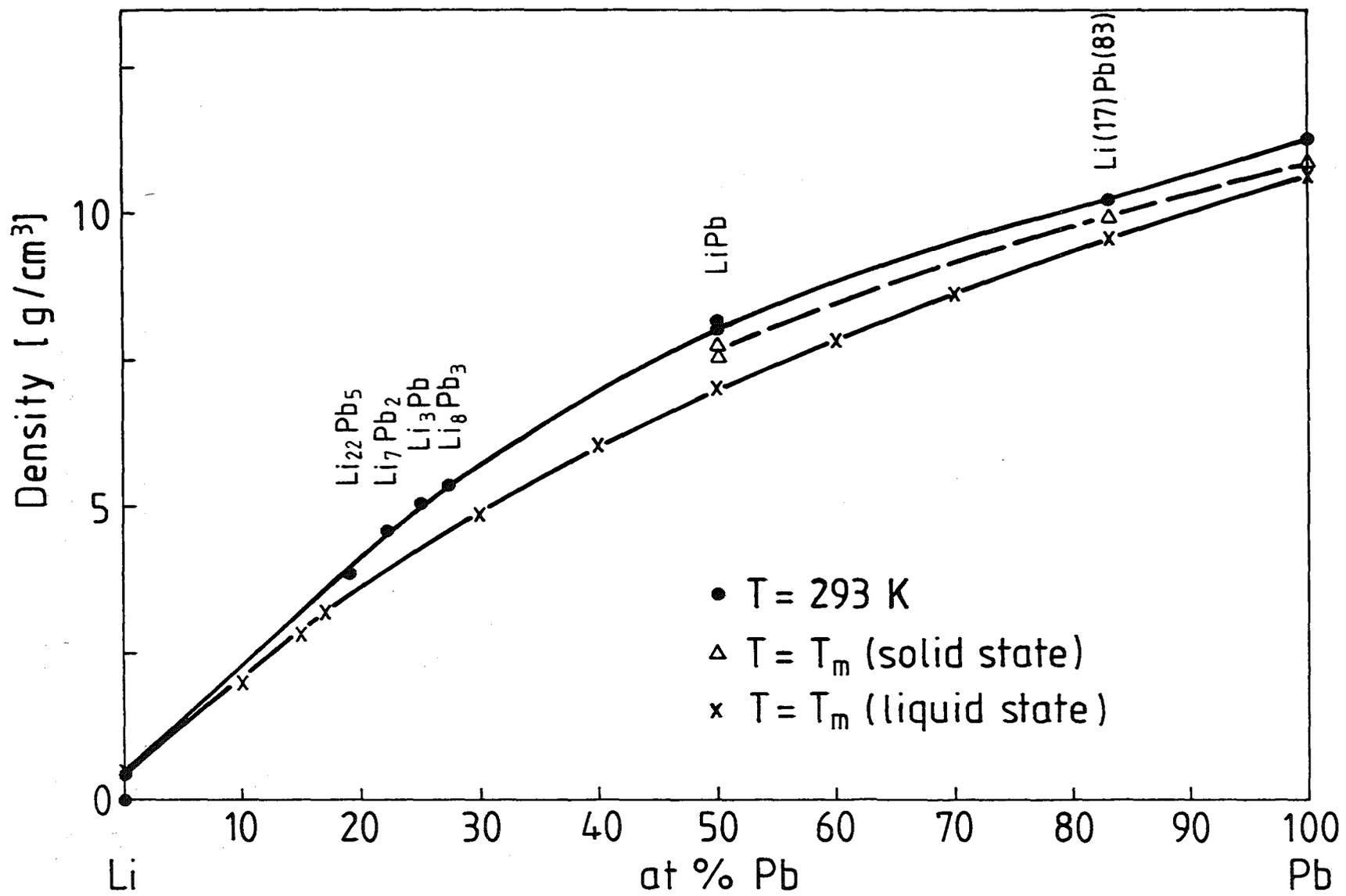


Fig. 2: Density of Li-Pb-alloys (Literature and own data).

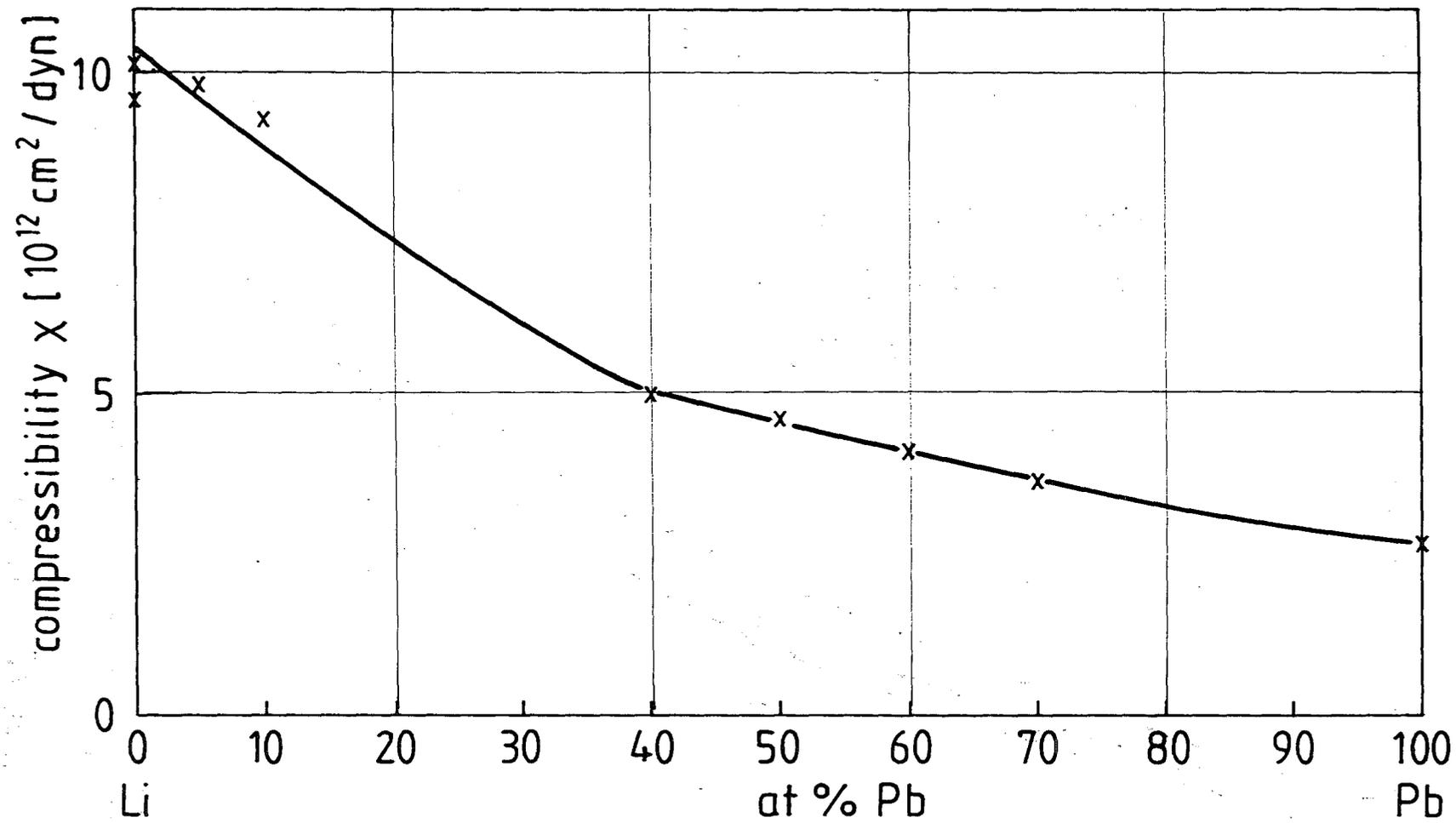


Fig. 3: Compressibility (adiabatic) of Li-Pb alloys at liquidus temperatures (literature).

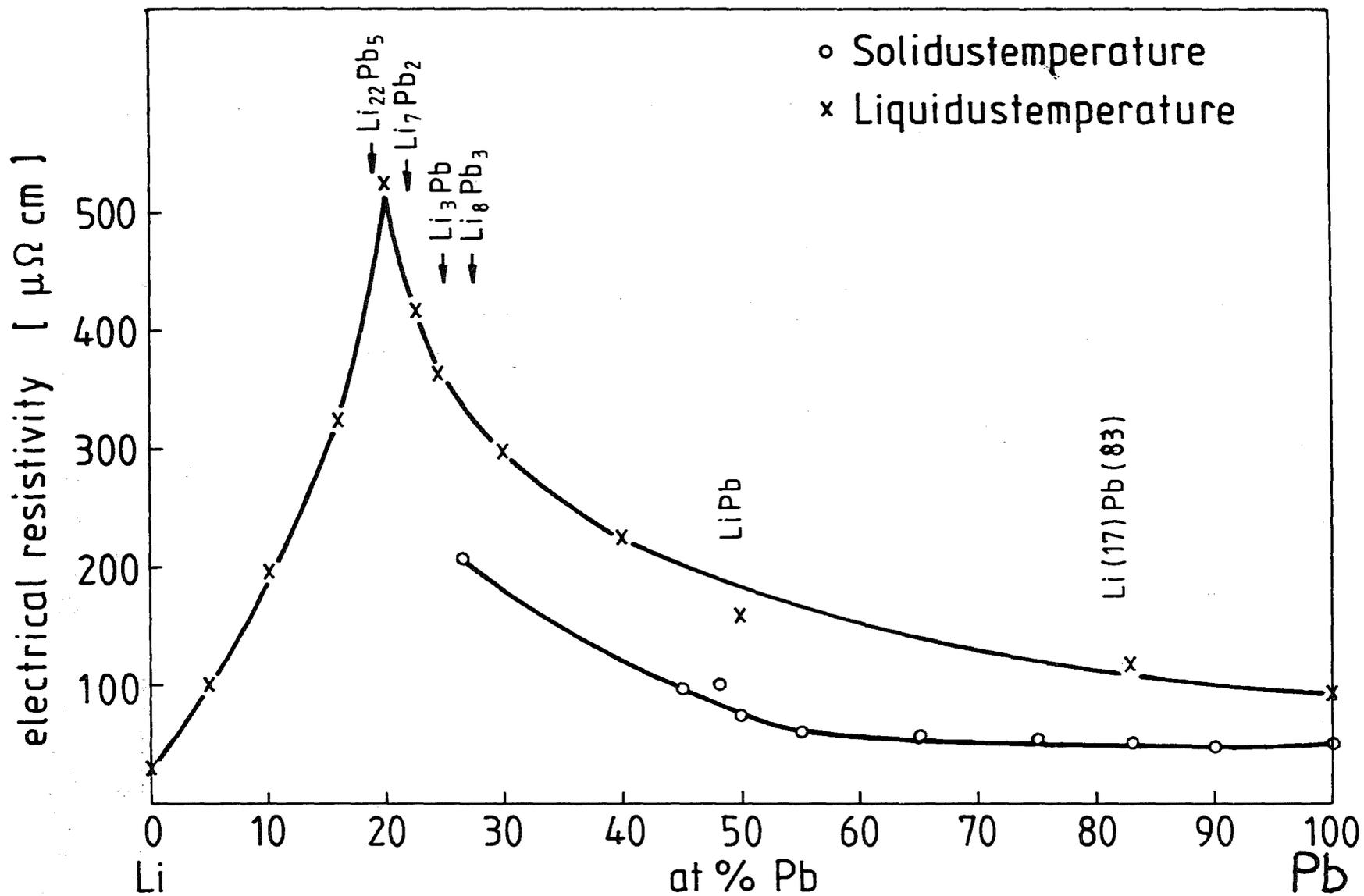


Fig. 4: Electrical resistivity of Li-Pb alloys (Literature and own data).

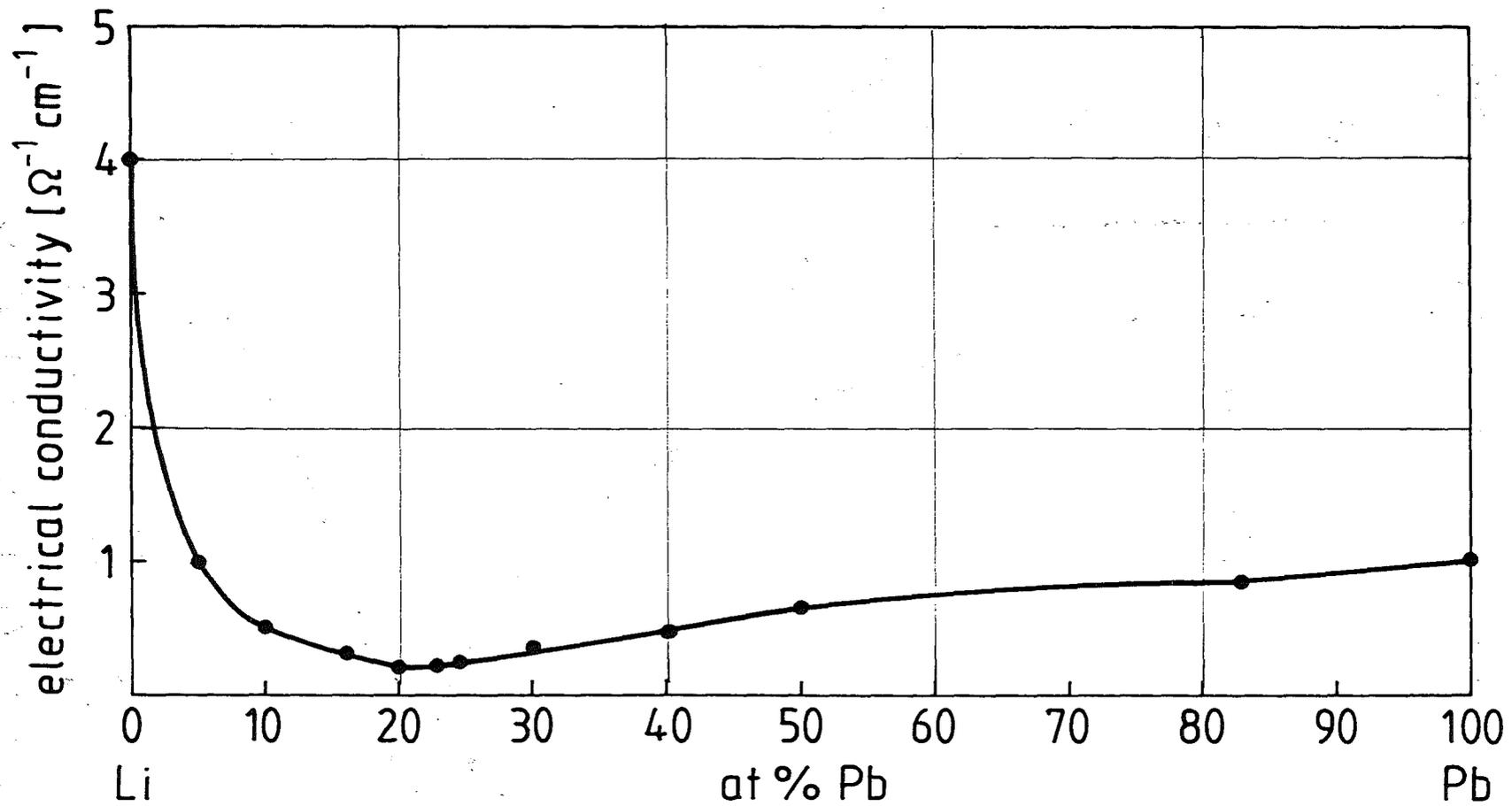


Fig. 5: Electrical conductivity at liquidus temperature of Li-Pb alloys.

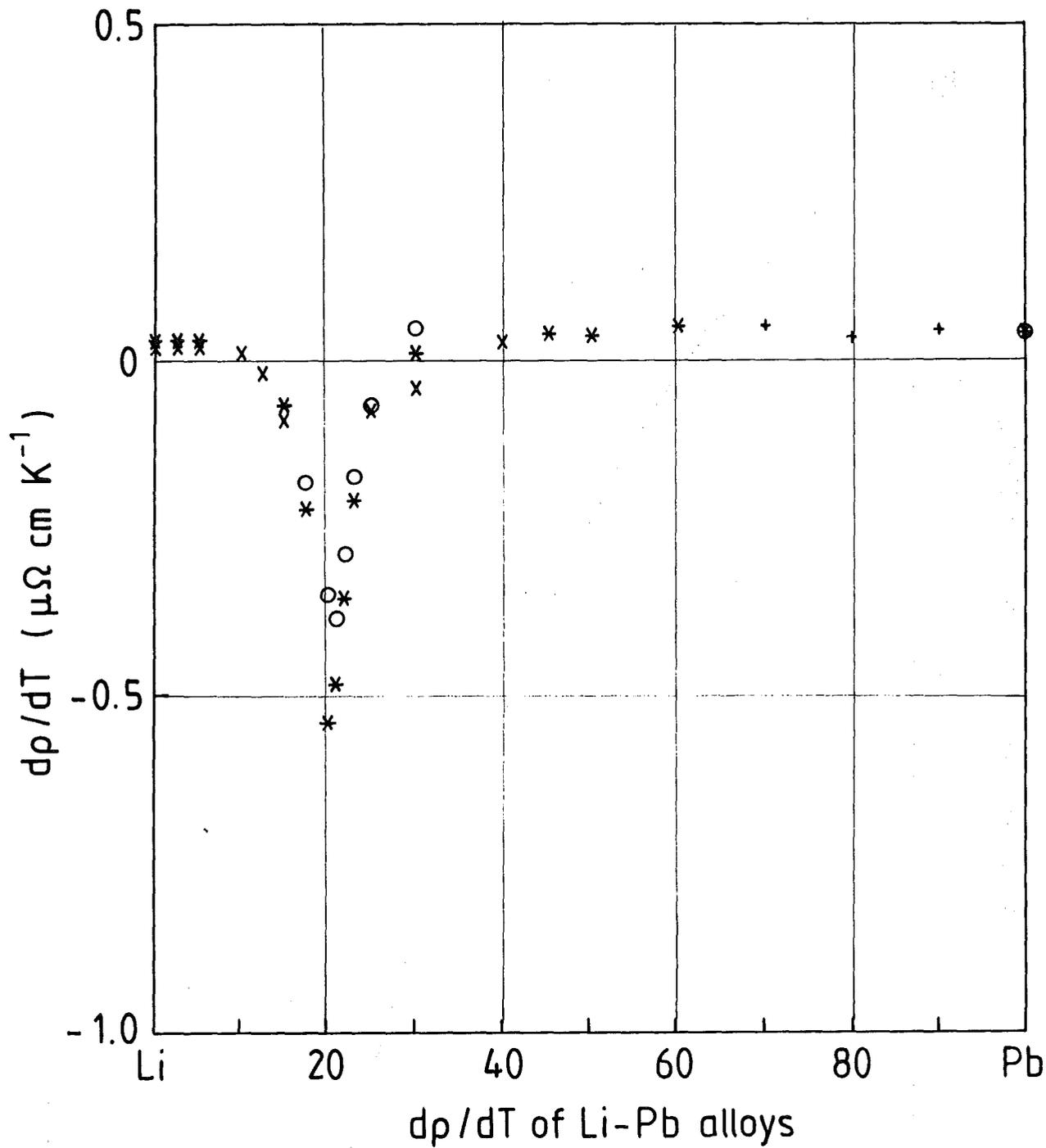


Fig. 6: Derivation ρ_{e1} of Li-Pb alloys (after 16).

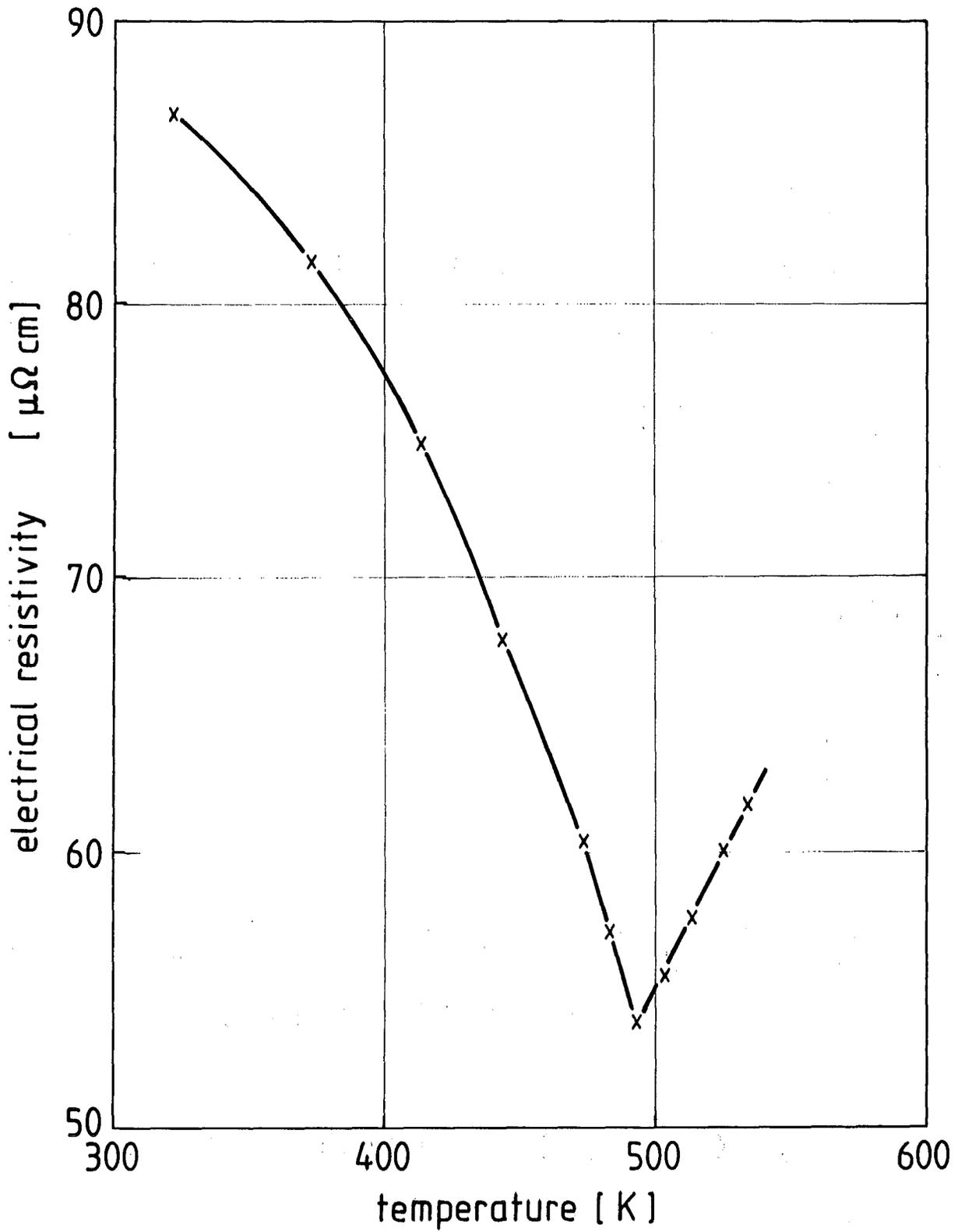


Fig. 7: Electrical resistivity of the Li-Pb intermetallic compound vs. temperature [13].

the electrical resistivity of Li-Pb-alloy melts over the whole concentration range.

Based on the data of Gruber and Kleiber [13] it is now possible to calculate from the measured data of the 55 and 60 at.% Li-alloys in the solid state the electrical resistivity of the pure intermetallic phase Li_8Pb_3 (see fig. 1 and table 2). In these two phase regions the resistivity of the mixture of the two phases depends on the volume concentration of the phases, the resistivities of the phases and their structural arrangement in a representative volume [18,19]. It is reasonable to take for the eutectic structure the normal lamellae-solidification (see the Li(17)Pb(83) microstructure in part I of this paper). For this type of structure and because the resistivities of both phases Li_8Pb_3 and LiPb are comparable, an approximation for the resistivity of the alloys results in using the so-called first order bound, i.e. the mixing rule for the resistivities

$$\rho_{\text{alloy}} = \rho_{\text{Li}_8\text{Pb}_3} \cdot c_{\text{vLi}_8\text{Pb}_3} + \rho_{\text{LiPb}} \cdot c_{\text{vLiPb}}$$

c_{v} - volume concentration of the respective phases

A better approximation is given in taking the phase Li_8Pb_3 as lamellae-shaped inclusions ($F = 0$ [18]) which are oriented statistically in a matrix of $\text{Li}_{0.53}\text{Pb}_{0.47}$. Then one gets [18]:

$$1 - c_{\text{vLi}_8\text{Pb}_3} = \frac{\kappa_{\text{Li}_8\text{Pb}_3} - \kappa_{\text{alloy}}}{\kappa_{\text{Li}_8\text{Pb}_3} - \kappa_{\text{Li}_{0.53}\text{Pb}_{0.47}}} \cdot \left(\frac{\kappa_{\text{alloy}} + 2\kappa_{\text{Li}_8\text{Pb}_3}}{\kappa_{\text{Li}_{0.53}\text{Pb}_{0.47}} + 2\kappa_{\text{Li}_8\text{Pb}_3}} \right)^{-1}$$

From the phase diagram the weight and volume fraction of the $\text{Li}_{0.53}\text{Pb}_{0.47}$ -phase in equilibrium with the eutectic alloy, as well as the total weight and volume fraction of the intermetallics being present in the 55 and 60 at.% Li-alloys were calculated and are given in table 7. The stoichiometry of the LiPb-phase remained constant. The calculation of the volume fraction was performed with the density data presented in fig. 2. The electrical conductivity for the 53, 55, 60 at.% Li-Pb-alloy were taken from Grube, Kleiber [13, tab.4].

Table 7: Special data for the composition of the 55 and 60 at.% LiPb-alloys.

Li-concentration			
at.%			
present phases	$\text{Li}_{0.53}\text{Pb}_{0.47}$ + Li_8Pb_3	microstructure	eutectic alloy + Li_8Pb_3
55 at.% Li	6.5 wt.% Li_8Pb_3 △ 9 vol.% Li_8Pb_3		21 wt.% eutectic △ 23.5 vol.% eutectic
60 at.% Li	26 wt.% Li_8Pb_3 △ 29 vol.% Li_8Pb_3		86 wt.% eutectic △ 87 vol.% eutectic

The data of the 55 at.% alloy were not used. They would lead to a ρ -T-function showing a maximum between 323 and 473 K which does not seem to be probable.

The results of the evaluation of the Grube, Kleiber data are shown in fig. 8 represented

$$\rho_{\text{Li}_8\text{Pb}_3} = -39 + 28 \cdot 10^{-2} T \text{ } \mu\Omega\text{cm}, [T] = \text{K}$$

at the temperature of the peritectic decomposition ($T_p = 915 \text{ K}$) one gets

$$\rho_{\text{TP}} = 217 \text{ } \mu\Omega\text{cm}$$

this value is also shown in fig. 4 and follows quite well the line of the behaviour of alloys with lower Li-concentrations.

Thus we decided to treat all intermetallic compounds in the Li-Pb system especially with respect to the transport of charge and heat as being dominated by metallic-like behaviour. It is tried too, to estimate the order of magnitude for phonon conductivity at the melting point of the intermetallics.

4. Relationships for the estimation of thermophysical properties

These relationships do not mean a theoretical calculation of properties in a physical sense. Experimental data and empirical rules on the behaviour of metals and alloys are used as much as possible. This is done with the view,

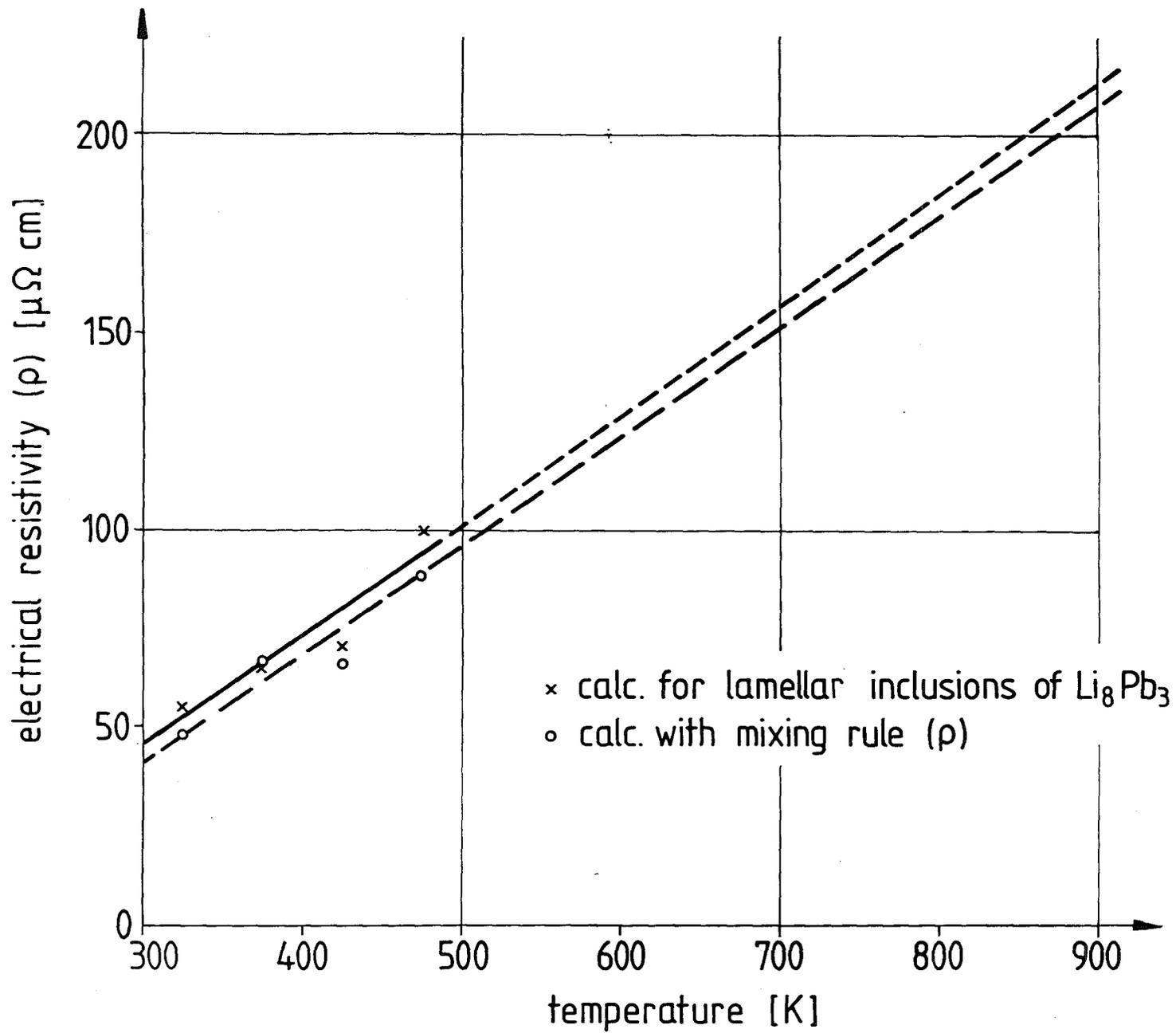


Fig. 8: Electrical resistivity of the Li_8Pb_3 intermetallic compound calculated from data in [13].

that for designing a solid metallic breeder blanket, it is the physical properties in the solid state of the high melting intermetallics that are of interest and where we have the greatest lack of knowledge in the whole system.

4.1. Thermodynamic properties

We use for the latent heat of fusion ΔH_m of the congruent melting intermetallics

$$1) \Delta H_m = \Delta S_m \cdot T_m$$

T_m - melting point
 ΔS_m - entropie of fusion

according to Kubaschewski [20] for ordered intermetallics $A_x B_y$

$$2) \Delta S_m = \Delta S_A n_A + \Delta S_B n_B - R(n_A \ln n_A + n_B \ln n_B)$$

n_A, n_B - mole fractions

$$n_A = \frac{x}{x+y} \quad n_B = \frac{y}{x+y}$$

The heat of fusion for the eutectics should obey the mixing rule for the heat of fusion of the phases of which the eutectic consists. Alloys which are melting non-congruently (peritectic alloys) are not treated here.

For the specific heat at constant pressure, we use the empirical value presented in [20,21], i.e. in the liquid state the specific heat per g atoms:

$$3) C_{pA} = 32.2 \text{ J/g} \cdot \text{atom} \cdot \text{K}$$

For the solid state, the heat capacity obeys in the two phase regions the mixing rule with respect to the pure phases. For the one phase intermetallics there is of course the possibility of the mixing rule for the pure elements and using the atomic concentrations in the respective phase. This is only a real estimation, not a calculation as compared to the application of the mixing rule for the heat capacity of a mixture of two phases.

The density can be estimated either from the solid into the liquid state or vice versa.

For metals with coordination number ~ 8 the volume change on melting is:

$$4) \frac{V_{TS1} - V_{TSS}}{V_{TSS}} = 2.5 \% \quad [22]$$

$V_{TS1,S}$ - molar volume of solid and liquid compound at T_S

while for metals with coordination number ~ 12 we have

$$5) \frac{\Delta V_{TS}}{V_{TSS}} = 5.5 \% \quad [22]$$

Since we know the liquid densities and the room temperature densities of the intermetallic compounds a first estimation of their thermal expansion in solid state should be a good approximation.

An estimation of the specific surface energy γ_{LV} is possible in using the empirical dependence between γ_{LV} (fig. 9) and melting point, and for the temperature dependence in using the Eötvös-Regel.

$$6) \frac{d\gamma_{LV}}{dT} = - \frac{0.64}{3 \sqrt{(M/\rho_L)^2}}$$

M - Molecular weight

ρ_L - density of the liquidus at T_S [21]

4.2 Transport properties

The electrical resistivity in solid state at T_S , $\rho_{el S}$ can be calculated from the electrical resistivity in the liquid state $\rho_{el l}$ in using the well known ratios between both values for metals of the coordination number ~ 8 and metals of the coordination number 12.

$$7) \frac{\rho_{el l}}{\rho_{el S}} = 1.58 \text{ and } 2.08 \text{ resp.}$$

The thermal conductivity λ will be estimated from the Lorentz law i.e.

$$8) \lambda \cdot \rho_{el} = L_0 \cdot T$$

$$L_0 = 2.443 \cdot 10^{-8} \text{ V}^2 \cdot \text{K}^{-2}$$

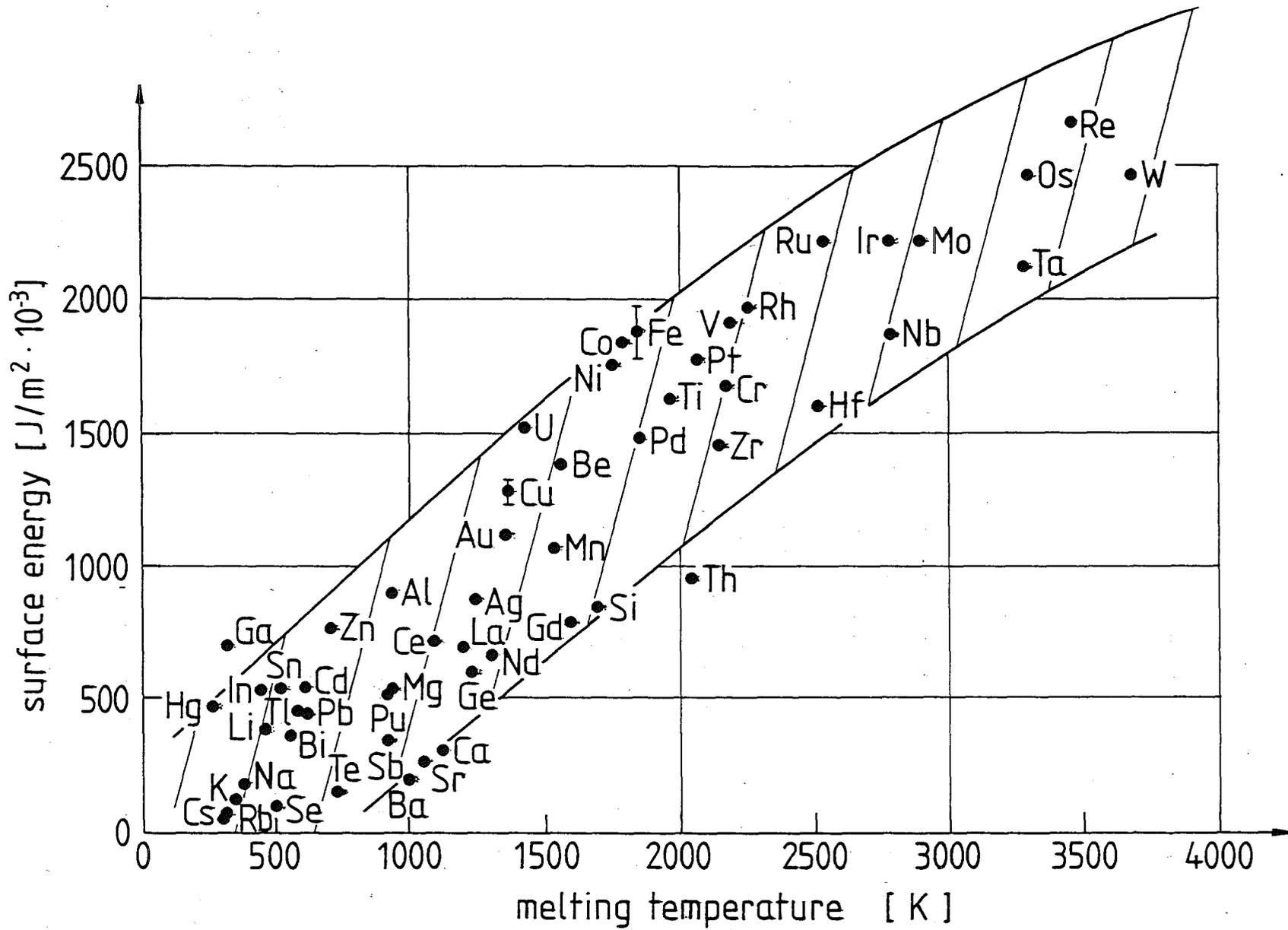


Fig. 9: Specific surface energy of metals vs. their melting points [23].

This relationship in the solid state was shown to be valid even for metallic glasses [24], in the liquid state there might be deviations to higher values of L_0 , because contributions to the thermal conductivity due to convections cannot be excluded during measurements of λ [25].

An imagination of the range of order for the phonon part of the thermal conductivity, which is the main mechanism in solid state in ionic crystals is given by:

$$9) \lambda \sim 1/3 c_v \cdot \rho \cdot \bar{v} \cdot \bar{l}$$

c_v - specific heat at constant volume

\bar{v} - phonon velocity (sound velocity)

\bar{l} - mean free path of phonons

The viscosity is estimated with the Andrade-equation

$$10) \eta_{TS} = 6.12 \cdot 10^{-2} \sqrt{T_S \cdot M} \cdot (V_M)^{-2/3}$$

V_M - molar volume

M - molecular weight

η_{TS} - viscosity in mPas at the melting point T_S

It was already shown in detail [21] that this equation covers pure metals, eutectic alloy, normal solutions and ionic melts.

For the activation energy Q_η a first approximation is possible with the empirical relationships [26]:

$$11) Q_\eta = 1.804 \cdot T_S^{1.348} \quad [Q_\eta] = \text{J/g} \cdot \text{atom}$$

The general equation for the temperature dependence of the viscosity is taken as

$$\eta = \eta_0 \cdot e^{Q/RT} \quad R = 8.314 \text{ J/mol} \cdot \text{K}$$

$$[\eta] = \text{mPas}$$

5. Comparison between measured and calculated properties in the quasibinary system LiPb-Pb and for Li

In this part of the paper, a proof is tried for the validity of the equations 1) - 11) for this quasibinary system. The physical data used are given in table 1 - 6.

5.1 Thermodynamic properties

Latent heat of fusion

We use the data for pure Li and Pb for the calculation of ΔH_S of LiPb (equ. 1, 2) and the mixing rule for ΔH_S of Li(17)Pb(83).

$$\begin{aligned} \Delta H_S(\text{Li}) &= 2994 \text{ J/mole} & \Delta H_S(\text{Pb}) &= 4772 \text{ J/mole} \\ \Delta S_S(\text{Li}) &= 6.599 \text{ J/moleK} & \Delta S_S(\text{Pb}) &= 7.953 \text{ J/mol K} \\ \Delta S_S(\text{LiPb}) &= 13.04 \text{ J/moleK} \\ \Delta H_S(\text{LiPb}) &= 9844 \text{ J/moleK} & \Delta H_S(\text{meas.}) &= 1094 \text{ J/mol} \\ \Delta H_S(\text{Li(17)Pb(83)}) & \quad (21 \text{ wt.\% LiPb} + 7.0 \text{ wt.\% Pb}) &= 28.9 \text{ J/g} \hat{=} 5000 \text{ J/mole} \\ \Delta H_S(\text{Li(17)Pb(83)measured}) &= 33.9 \text{ J/g} = 5867 \text{ J/mole} \end{aligned}$$

The difference between measured and estimated values for LiPb is only 5 %; for Li(17)Pb(83) the difference is much higher about 17 %.

Specific heat

First the specific heat of the LiPb intermetallic must be calculated with the mixing rule:

$$c_p(\text{LiPb}) = \frac{c_p(\text{Li(17)Pb(83)}) - c_p(\text{Pb}) \text{ wt.\% Pb}}{\text{wt.\% LiPb}}$$

$$c_p(\text{LiPb}) = \frac{c_p(\text{Li(17)Pb(83)}) - 0.791 c_p(\text{Pb})}{0,21}$$

T (K)	c_p (Li(17)Pb(83)) (J/g·K)	c_p (Pb) (J/g·K)	c_p (LiPb) (J/g·K)	C_p (LiPb) (J/moleK)
300	0.1490	0,129	0,224	48.0
340	0.1545	0,130	0.244	52.2
400	0.1641	0,133	0,281	60.1
450	0.176	0,135	0,330	70,7
500	0.1921	0,137	0.399	85.4

This possibility of calculation only exists up to the lowest liquidus temperature. For extrapolation to higher temperatures we use as first approximation a linear fit:

$$C_p(\text{LiPb}) = -0.040 + 8.5 \cdot 10^{-4} \cdot T \quad \text{J/g} \cdot \text{K}$$

300 < T < 755 K

The estimation of the molar heat capacities from the heat capacities of the elements can only be carried out up to the melting temperature of Li (453 K).

T (K)	C_p (Li) (J/moleK)	C_p (Pb) (J/moleK)	C_p (LiPb) (J/moleK)
300	24.7	26.7	51.4
340	25.6	26.9	52.5
400	27.6	27.6	55.2
450	29.4	28.0	57.4

The estimation of the heat capacity in solid state from the pure elements holds for low temperatures (400 K) with deviations up to 10 %. For higher temperatures one has to take into account systematic errors up to 20 % of the value. For the liquid state the empirical value for intermetallics cannot be proved.

Density and thermal expansion

The volume changes upon melting are listed below:

	$\Delta V_{TS}/V_{TS}$ (%)	
	measured	empirical rule
Li	1,5	2.5
LiPb	9.0 (mean of values in table 6)	
Li(17)Pb(83)	3,5	
Pb	3.5	5

Apart from the deviations in the volume increase upon melting for the pure elements, which are not too surprizing for an empirical rule, the most important measured value is that for the intermetallic compound, showing clearly that for the thermal expansion the assumed ionic part of the bonding in the intermetallics of Li-Pb compounds is dominating. These high values of the volume increase upon melting are very typical for ionic compounds (see for example [26]). Thus 9 % will be used for the other intermetallics.

Surface energy

	γ_{LV} (10^3 J/m ²)		$d\gamma_{LV}/dT$ (10^3 J/m ² ·K)	
	measured	empirical	measured	empirical
Li	0.332	0.40	- 0.147	- 0.10
Li(17)Pb(83)	0.48	0.27	- 0.5	- 0.09
Pb	0.458	0.46	- 0.113	- 0.09

The deviation between measured and estimated surface energies is in the allowed range (see fig. 9), while the temperature dependence differs by a factor of 5 for the eutectic alloy. We think that the uncertainty in the measured $d\gamma/dT$ is the reason for that.

5.2 Transport properties

The electrical resistivity ratio of ρ_{el} in solid and liquid state at liquidus and solidus temperatures, respectively, gives as a mean value (fig. 4) for the concentrations $0 < \text{Pb} < 48.1$ at.% a value of 2.05. In fig. 4 the resistivity at solidus temperature for the LiPb compound is given for the stoichiometric composition (our data) and for the $\text{Li}_{0.519}\text{Pb}_{0.481}$ (Grube and Kleiber). As described in detail by Zalkin and Ramsay the number of the next neighbours in the unit cell of the intermetallic compounds is definitely higher than 8 and Nguyem and Enderby discussed 10 for this value in the liquid state of $\text{Li}_{22}\text{Pb}_5$, therefore we will use 2.05 for all intermetallic compounds to calculate $\rho_{el s}$, which is the electrical resistivity at solidus temperature in solid state.

For the thermal conductivity there is first to calculate this property for LiPb from the thermal diffusivity, specific heat and density. We get

$$\lambda = \alpha \cdot \rho \cdot c_p$$

T (K)	α (cm ² /sec)	c_p (J/g·K)	ρ (g·cm ³)	$\bar{\rho}$	λ (W/cm·K)	
300	0.0490	0.22	8.00*	8.00**	8.00	0.0862
400	0.0615	0.30 ₅	7.92	7.92	7.92	0.149
500	0.0740	0.39	7.85	7.82	7.84	0.226
600	0.0815	0.47 ₅	7.77	7.71	7.74	0.300
755 ($\equiv T_m$)	0.1065	0.61	7.66	7.54	7.60	0.493
777	0.0436	0.301			6.97	0.0915

* with $\bar{\alpha}_{th} = 30.8 \cdot 10^{-6} \text{ K}^{-1}$

** data of Zalkin and Ramsay

Calculation of the Lorentz number L.

$$\frac{\lambda \cdot \rho_{el}}{T} = L$$

Substance		T (K)	λ (W/cm K)	ρ_{el} ($\mu\Omega$ cm)	L (V^2/K^2)	\bar{L} (V^2/K^2)
Li	s.s.	273	0.781	8.55	$2.446 \cdot 10^{-8}$	
		453.7	0.712	16	2.511	
	l.s.	453.7	0.428	24.8	2.34	solid state (s.s)
LiPb	s.s.	323	0.0876	86.7 [13]	2.35	$2.481 \cdot 10^{-8}$
	β - β'	487	0.215	53.7 [13]	2.37	
	l.s.	755	0.493	70.5	4.60	
		755	0.0915	157.4	1.91	
Pb	s.s.	300	0.352	23.1	2.71	liquid state
		600	0.312	49.0	2.54	(l.s.)
	l.s.	600	0.155	95	2.45	$2.56 \cdot 10^{-8}$
Li(17)Pb(83)	l.s.	508	0.119	123.9	2.90	

The results for L are satisfactory. Seen from the calculation of the thermal conductivity from the thermal diffusivity with estimated specific heat data and the Lorentz number for LiPb at T_m it results, that the estimation of the specific heat of the intermetallics both in liquid as in solid state seems to be the most difficult property, discussing extrapolations to the melting point. We have no reasons for doubts on the original measured data, which are the electrical resistivity and thermal diffusivity. As a result we will use the theoretical value L_0 for the calculation of the thermal conductivity from electrical resistivity data.

Calculation of the viscosity

	Viscosity at T_s, T_e		Q (J/moleK)	
	measured	calculated	measured	calculated
Li	0.598	0.606	5508	6880
Li(17)Pb(83)	2.94	2.64	11640	8010
Pb	2.63	2.99	8419	10030

Differences of about 10 % must be taken into account for the viscosity at the melting point as was discussed earlier [21]. The deviation becomes higher in extrapolating to higher temperatures because of the deviation in calculating Q.

6. Estimation of thermophysical properties of intermetallics of Li-concentrations higher than 50 at.%

This part will only consist of the application of the knowledge worked out in the chapters above. The results are presented in two tables (8,9).

6.1 Thermodynamic properties

Table 8: Estimated thermodynamic properties of the intermetallics Li_8Pb_3 , Li_3Pb , Li_7Pb_2 , $\text{Li}_{22}\text{Pb}_5$

Inter-metallic	ΔS_f (J/moleK)	T_S (K)	ΔH_f (J/mole)	C_p (300 K) (J/g·K)	C_p (liqu.) (J/g·K)	ρ_{TS} S_3 (g/cm ³)	$\gamma_{th} \cdot 10^{+6}$ (K ⁻¹)	γ_{LV} (J/m ²)	$d\gamma_{LV}/dT$ (J/m ² ·K)
Li_8Pb_3	-	dec.915	-	0.41	0.52	5.01	110	-	-
Li_3Pb	-	" 933	-	0.44	0.57	4.63	130	-	-
Li_7Pb_2	11.3	1005	11360	0.49	0.63	4.31	86	0.70	- 0.03
$\text{Li}_{22}\text{Pb}_5$	-	dec.923	-	0.57	0.73	3.82	16	-	-

Data from table 1, fig. 2,9 and equations 1),2),3), $\frac{\Delta V_{TS}}{V_{TS}} = 9\%$, are used.

6.2 Transport properties

Because of the knowledge of the electrical resistivity of Li_8Pb_3 (see above) fig. 4 could be completed (fig. 10) in that way, that the electrical resistivity at solidus temperature ρ_{elT_S} of intermetallics beyond Li_8Pb_3 was estimated using 2.05 as mean ratio for the resistivities in liquid and solid state at liquidus and solidus temperature. From that the thermal conductivities at the solidus temperature λ_S were calculated with $L_0 = 2.443 \cdot 10^{-8} \text{ V}^2/\text{K}^2$. For the viscosity equations 10) and 11) were used.

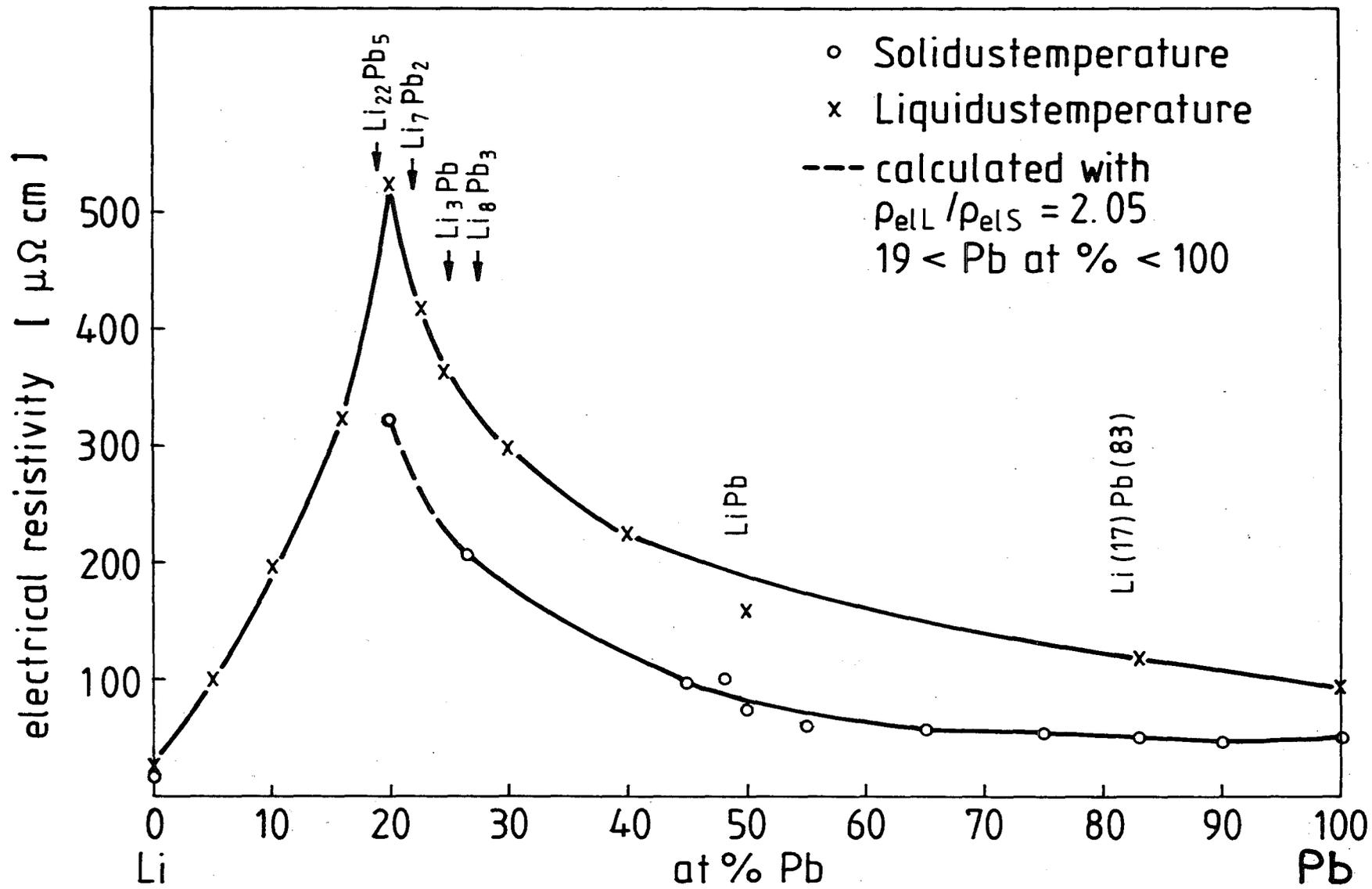


Fig. 10: Electrical resistivity of Li-Pb alloys (extrapolated to 85 at.% Li).

Table 9: Estimated transport properties of the intermetallics LiPb, Li₈Pb₃, Li₃Pb, Li₇Pb₂, Li₂₂Pb₅.

Intermetallic compound	T _{sol.} (K)	ρ _{e1 TS} (μΩcm)	λ _{TS} (W/cm·K)	T _{liqu.} (K)	η _{TS} (mPas)	Q (J/mole)
LiPb	755	85	0.22	755	2.50	27.3·10 ³
Li ₈ Pb ₃	915	217	0.11	931	1.74	199·10 ³
Li ₃ Pb	933	230	0.099	973	2.03	77·10 ³
Li ₇ Pb ₂	1005	260	0.094	1005	1.74	181·10 ³
Li ₂₂ Pb ₅	923	320	0.070	1000	1.37	540·10 ³

An estimation of the temperature dependence of the electrical resistivity or conductivity is not possible. Generally an increase with temperature in the thermal conductivity is expected.

To give an imagination of the contribution of the phonon part at the melting point of the thermal conductivity we have to know for application of:

$$\lambda = 1/3 \cdot c_v \cdot \rho \cdot \bar{v} \cdot \bar{l}$$

the specific heat at constant volume which is taken as 3R from classical theory. The density at melting point was estimated (see above), the velocity \bar{v} is derived as sound velocity from the compressibilities in liquid state (fig. 3), this value is slightly higher than the value at solidus in solid state. For the mean free parts of phonons we take the lowest possible value which is the distance between next neighbours in the cell. Thus we estimate a minor contribution of the phonon part in thermal conduction, but it is reasonable to take this value at the highest possible temperature in solid state, whenever it is reached then at this temperature (for $T > \Theta$ (Debye temperature) $\bar{l} \sim \frac{1}{a+bT}$). The results are presented in table 10 together with the sum of the electron and phonon part of the thermal conductivity.

Table 10: Estimated thermal conductivity of the intermetallics LiPb, Li₈Pb₃, Li₂₂Pb₅ at solidus temperature (electron and phonon conductivity).

Intermetallic compound	c_v (J/g·K)	ρ (g/cm ³)	\bar{v} (cm ² /sec)	\bar{l} (cm)[5]	λ_{ph} (W/cm·K)	λ_{el} (W/cm·K)	$\lambda = \lambda_{ph} + \lambda_{el}$ (W/cm·K)
LiPb	0.116	6.97	$0.18 \cdot 10^{+6}$	$3.5 \cdot 10^{-8}$	0.005	0.22	0.22
Li ₈ Pb ₃	0.0367	5.01	0.21	2.91	0.003	0.11	0.11
Li ₃ Pb	0.109	4.63	0.19	~ 3.0	0.001	0.099	0.10
Li ₇ Pb ₂	0.054	4.31	0.18	~ 3.0	0.005	0.094	0.10
Li ₂₂ Pb ₅	0.021	3.82	0.17	3.0	0.003	0.070	0.073

In all cases the electron part is much higher than the phonon part (~ a factor of 5 - 20). There the phonon part will strongly increase with decreasing temperature, while the electron part will decrease there might result a relatively low temperature dependence of the total thermal conductivity of the intermetallics in the Li-Pb system.

7. Final remarks

The aim of this paper was to give an idea of the thermophysical behaviour of the intermetallic compounds in the system Li-Pb, which may act as a potential solid breeder material in nuclear fusion technology. Therefore it was necessary to summarize the experimental knowledge on this subject we have up to now, including sometimes its critical review. We had to make assumptions for the estimation of the physical properties from which we think that they are consistent with the experimental results as well as with our general knowledge of the thermophysical behaviour of solids and liquids in binary metallic systems at high temperatures. If these assumptions are wrong our estimations will be wrong and not inaccurate. The accuracy of the individual physical properties estimated is only partly discussed. This question has to be answered in a dialogue between experimentalists and blanket designers.

If a higher precision and more security is necessary the experimental determination of the physical properties will be the consequence. This requires as was shown in part I and part II of this work, not only a careful determination of the properties. The control of the material by metallography and analytical chemistry, especially with view to nitrogen and oxygen contamination has the same importance, seen from our point of view.

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