The density and thermal expansion of eutectic alloys of lead with bismuth and lithium in condensed state

2008 J. Phys.: Conf. Ser. 98 062017

(http://iopscience.iop.org/1742-6596/98/6/062017)

Journal of Physics: Conference Series **98** (2008) 062017 doi:10.1088/1742-6596/98/6/062017

The density and thermal expansion of eutectic alloys of lead with bismuth and lithium in condensed state

S V Stankus[1,3], R A Khairulin[1], A G Mozgovoy[2], V V Roshchupkin[2] and M A Pokrasin[2]

[1] Kutateladze Institute of Thermophysics, Siberian Division of the Russian Academy of Sciences, Novosibirsk–90, 630090 Russia
[2] Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, Moscow, 119991 Russia

E-mail: stankus@itp.nsc.ru

Abstract. The method of penetrating gamma-radiation is used to measure the density of lead-bismuth and lead-lithium eutectics in the condensed state in the range from room temperature to ~1250 K. The chemical composition of investigated eutectic alloys of Pb-Bi and Pb-Li systems is determined within ±0.2% by mass, and the lead content in these alloys turns out to be 44.6 and 99.3% by mass, respectively. The confidence error of the experimental results, which combines the systematic and random components, does not exceed 0.3% and 0.2% for the solid and liquid phases, respectively. The investigation results are compared with the available literature data on the density of eutectic alloys of lead with bismuth and lithium in the condensed state.

1. Introduction

The lead-bismuth eutectic is an advanced liquid-metal heat-transfer agent for transport and spaceborne fast-neutron power reactors, in particular, in strategic submarines [1], and the lead-lithium eutectic is regarded as one of the basic tritium-breeding materials of the blanket of ITER fusion reactor [2]. State diagrams of these metal systems have been studied quite well [3, 4]. The melting temperature (T_m) of eutectic alloys of Pb–Bi and Pb–Li systems and the lead content in these systems are 398.1 and 508.1 K in accordance with the 1990 International Temperature Scale (ITS–90) [5] and 44.1 and 83.0 at.%, respectively.

In designing and developing such power plants, which operate under extreme thermal conditions, the knowledge of the thermophysical properties of their structural materials and heat-transfer agents is of great practical importance. Given in this paper are the results of experimental investigation of the density of eutectic alloys of lead with bismuth and lithium at temperatures from 293 to 1225 K; these results are used to calculate the coefficient of volumetric thermal expansion of investigated alloys in the same temperature range.

2. Current status of the problem

The experimental data available from the literature on the density of lead–bismuth and lead–lithium eutectics are given in table 1. Their confidence error was determined as a result of detailed analysis, as was done in [16], and amounted to approximately 0.5%. However, differences are observed between the literature data, which extend beyond the limits of this error. This disagreement appears to be largely due to the difference between the chemical compositions of investigated eutectic alloys, especially in the case of the Pb–Li system, whose components are characterized by greatly differing values of density or specific volume. Therefore, the recommended reference data on the density of

[3] To whom any correspondence should be addressed.

lead-bismuth and lead-lithium eutectics [17], which are based on the investigation results of different researchers given in table 1, need to be refined. For this purpose, we performed new measurements of the density of Pb–Bi and Pb–Li eutectic alloys in the condensed phase at technically important temperatures.

3. Material and method of measurements

The investigated alloys of eutectic composition were prepared by mixing from starting components under high vacuum or under low pressure of inert gas. Lead, bismuth, and lithium were 99.995, 99.985, and 99.95% by mass pure, respectively.

The method of penetrating gamma-radiation, described in detail in [18], was used for measuring the density of eutectic alloys of Pb–Bi and Pb–Li systems in the condensed state. In brief, this method consists in the following. The alloy under investigation was placed in a sealed steel ampoule and heated by an electric resistance furnace. At steady-state temperature, the alloy was irradiated by a narrow beam of γ-quanta, the source of which was provided by ^{137}Cs isotope with an activity of 240 GBq. The density of the flux of gamma-radiation at the experimental temperature was determined by monitoring its intensity before and after its passage through the eutectic alloy in the ampoule.

Table 1. Literature data on the density of eutectic and near-eutectic alloys of Pb–Bi and Pb–Li systems in the condensed state.

Authors, reference no., year of publication	Method of investigation	Pb content in the alloy, at.%	Temperature range of investigation, K	Number of experimental points
		Lead-bismuth eutectic		
S A Been et al., [6], 1950	Method of maximal pressure in gas bubble	43.7	480–1271	9
N A Nikol'skiy et al., [7, 8], 1959	Method of hydrostatic weighing	44.7	423–858	17
I V Kazakova et al., [9], 1984	Method of sessile drop	43.3	T_m–1073	–
B B Alchagirov et al., [10], 2003	Pycnometric method	44.8	410–727	84
		Lead-lithium eutectic		
H Ruppersberg and W Speicher, [11], 1976	Method of maximal pressure in gas bubble	80.0	491–653	5
B Schulz et al., [12, 13], 1986–1991	Dilatometric method	83.2	293–450	–
	Method of sessile drop		T_m–625	–
J Saar and H Ruppersberg, [14], 1987	Method of maximal pressure in gas bubble	80.0	617–1083	10
G M Kalinin et al., [15], 1991	Method of penetrating gamma-radiation	83.0	293–900	–
B B Alchagirov et al., [16], 2005	Pycnometric method	83.0	580–770	115

4. Measurement results and their analysis

The basic conditions of measurements of the density of lead-bismuth and lead-lithium eutectics in the condensed state are given in table 2, and the measurement results are given in figure 1. The confidence error of these experiments, which combines the systematic and random components, was 0.3% for the solid phase and 0.2% for the liquid phase.

Table 2. Basic conditions of investigation of the density of eutectic alloys of Pb–Bi and Pb–Li systems.

Investigated alloy	Aggregate state	Thermal condition	Temperature range, K	Number of experimental points
Pb–Bi eutectic	Solid phase	Heating	293–T_m	2
	Liquid phase	Cooling	1225–401	202
		Heating	404–1224	153
Pb–Li eutectic	Solid phase	Cooling	506–360	29
		Heating	506–508	6
	Liquid phase	Cooling	877–524	47
		Heating	522–880	44

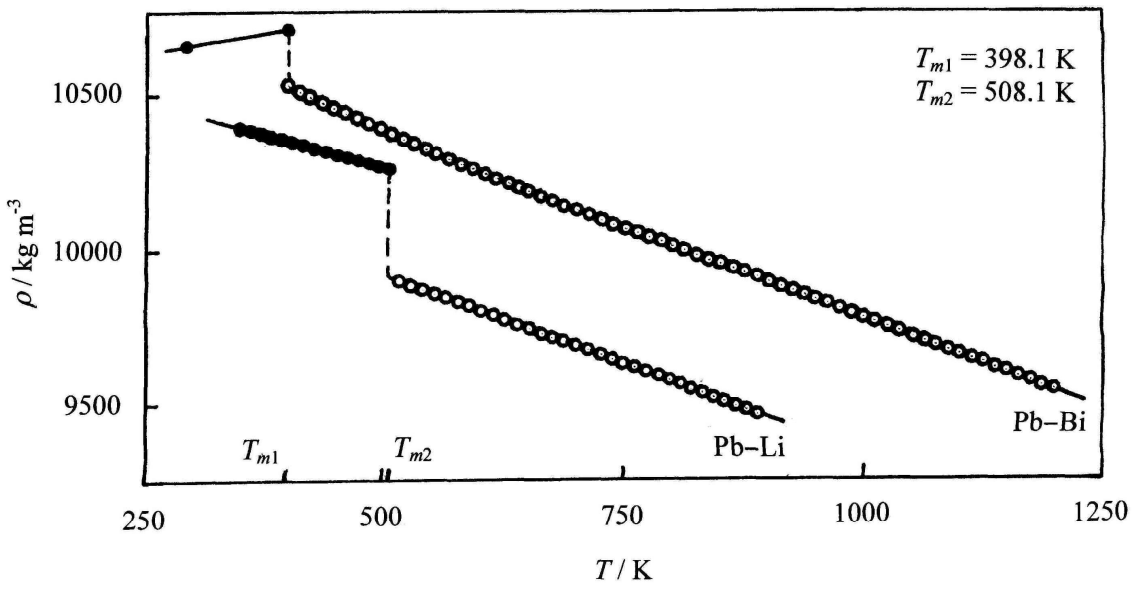

Figure 1. The temperature dependence of density of investigated eutectic alloys in the solid (●) and liquid (○) phases.

The least squares method was used for processing the experimental data obtained for the density of each one of the investigated alloys in the solid and liquid phases. A polynomial in integral powers of temperature of the form

$$\rho = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + \ldots \quad (1)$$

was used as the approximating equation, where ρ is in kg m^{-3} and T is in K in accordance with ITS–90.

The optimal power of approximating equation (1) was determined by regression-statistical analysis of the results of mathematical treatment using Fisher's ratio test [19]. The coefficients of this equation are given in table 3.

Table 3. Coefficients of approximating equation (1).

Investigated alloy	Aggregate state	a_0, kg m^{-1}	a_1, kg m^{-3} K^{-1}	$a_2 \cdot 10^3$, kg m^{-3} K^{-2}	$a_3 \cdot 10^6$, kg m^{-3} K^{-3}
Pb–Bi eutectic	Solid phase	10521.75	0.46030	–	–
	Liquid phase	11136.77	–1.69728	0.45496	0.12290
Pb–Li eutectic	Solid phase	10681.51	–0.82551	–	–
	Liquid phase	10520.42	–1.19064	–	–

The deviation of the results of our measurements of the density of lead-bismuth and lead-lithium eutectics (ρ_{exp}) from the data calculated by approximating equation (1) (ρ_{eq}) is given in figures 2 and 3. The mean square value of this deviation did not exceed 0.1% for the solid phase and 0.15% for the liquid phase.

Figures 4 and 5 illustrate the deviation of the experimental data of other researchers (ρ_{lit}) on the density of lead-bismuth and lead-lithium eutectics in the solid and liquid phases from those calculated by approximating equation (1). One can see that the results of measurements of the density of liquid eutectic alloy of Pb–Bi system, available in the literature [6, 9, 10], agree with one another and with the experimental data of the present investigation within their error of ±0.5%; it is only the relatively old data [7, 8] that differ from them to a much greater degree. The situation is somewhat different in the case of eutectic alloy of Pb–Li system (see figure 5). A discrepancy reaching 3% in the vicinity of the melting temperature is observed between the experimental data of the present study and of Kalinin et al. [15], on the one hand, and the experimental results of [12, 13, 16], on the other hand. This discrepancy is apparently caused by the differences in the chemical composition of investigated alloys. Indeed, the difference in the lead (or lithium) content in the lead-lithium eutectic within the error of its determination (±0.2% by mass) causes the variation of the density of this alloy of about 2%.

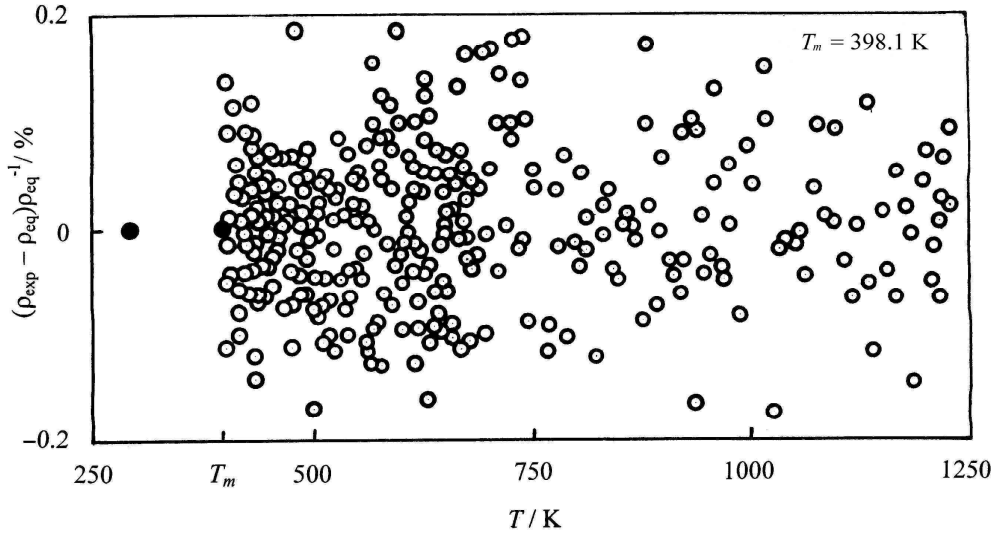

Figure 2. The deviation of the experimental data of the present study on the density of eutectic alloy of Pb–Bi system in the solid (●) and liquid (○) phases from approximating equation (1).

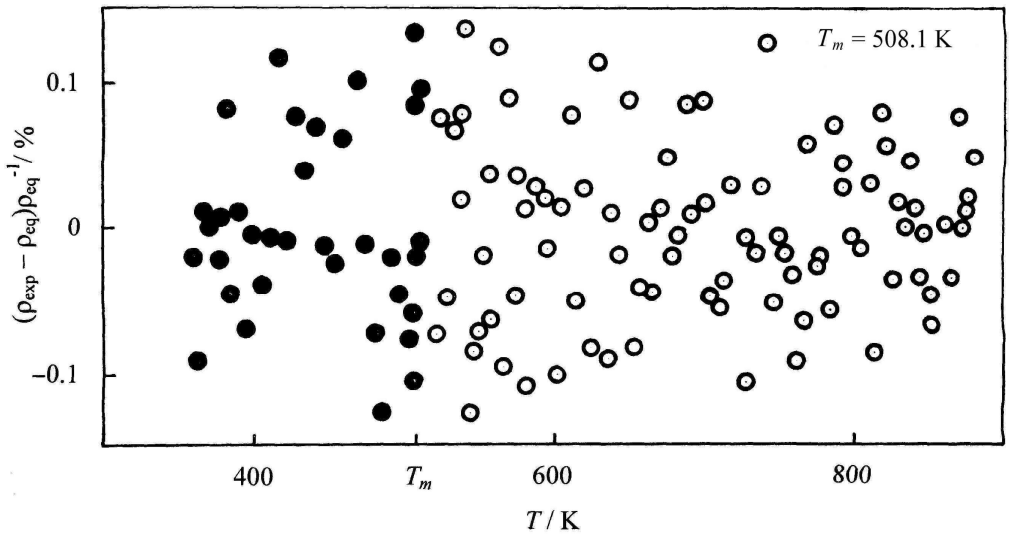

Figure 3. The deviation of the experimental data of the present study on the density of eutectic alloy of Pb–Li system in the solid (●) and liquid (○) phases from approximating equation (1).

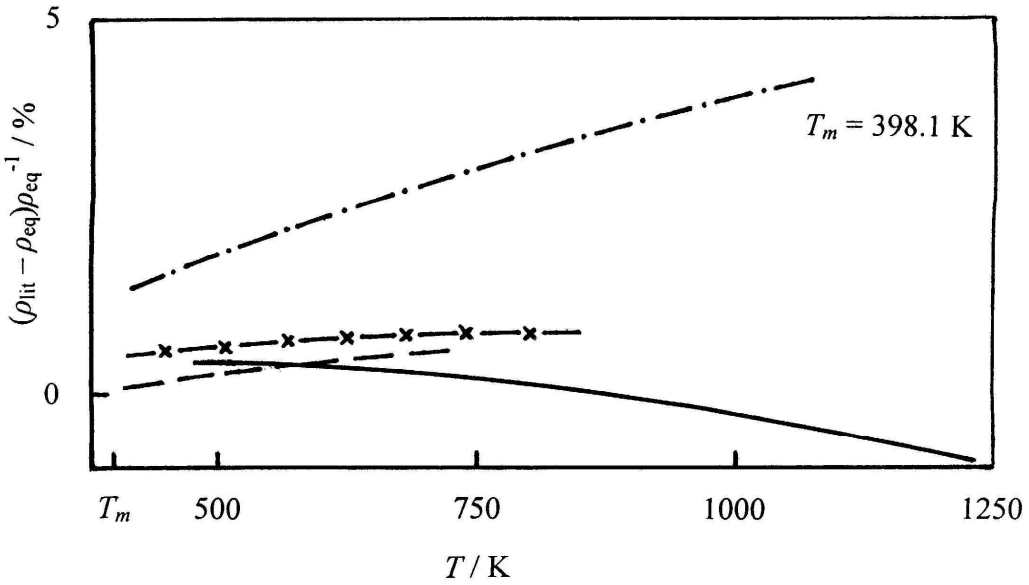

Figure 4. The deviation of the experimental data of other researchers on the density of lead-bismuth eutectic in the liquid phase from approximating equation (1): (—) Been et al., (– **x** –) Nikol'skiy et al., (– · –) Kazakov et al., (– –) Alchagirov et al.

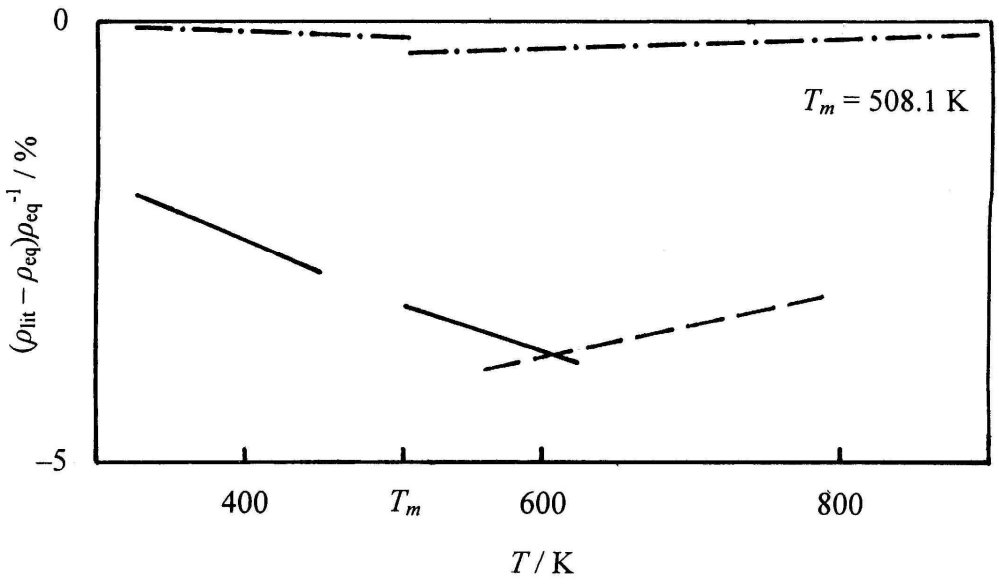

Figure 5. The deviation of the experimental data of other researchers on the density of lead-lithium eutectic in the condensed phase from approximating equation (1): (—) Schulz et al., (– · –) Kalinin et al., (– –) Alchagirov et al.

The coefficient of volumetric thermal expansion (CVTE) of eutectic alloys of Pb–Bi and Pb–Li systems was calculated by the formula

$$\beta = (\mathrm{d}\rho/\mathrm{d}T)\rho^{-1}, \tag{2}$$

where $\mathrm{d}\rho/\mathrm{d}T$ is the first derivative of density with respect to absolute temperature, which is determined from approximating equation (1).
The values of β, calculated by formula (2) for each one of the phases of eutectic alloys in the investigated temperature ranges with a step of 10 K, were processed by the least squares method using the approximating equation

$$\beta\, 10^5 = b_0 + b_1 T + b_2 T^2 + \dots , \tag{3}$$

where β is in K^{-1} and T is in K in accordance with ITS–90.
The optimal number of terms of approximating equation (3) was likewise found using Fisher's ratio test [19]. The coefficients of this equation are given in table 4.

Table 4. Coefficients of approximating equation (3).

Investigated alloy	Aggregate state	b_0, K^{-1}	$b_1\, 10^3$, K^{-2}	$b_2\, 10^6$, K^{-3}
Pb–Bi eutectic	Solid state	4.372	–0.186	–
	Liquid state	13.338	–1.108	0.417
Pb–Li eutectic	Solid state	7.721	0.635	–
	Liquid state	11.221	1.531	–

The error of calculated values of CVTE of lead-bismuth and lead-lithium eutectics in the condensed state was estimated by the errors of terms appearing in formula (2) and amounted to 5% and 3% for the solid and liquid phases, respectively.

The values of CVTE of Pb–Bi eutectic alloy were obtained by us for the first time; those of Pb–Li eutectic alloy agree within their error with the data of Kalinin et al. [15] and differ significantly from the data of [12, 13, 16], as was previously observed for the density of this alloy.

The values of density and CVTE of lead-bismuth and lead-lithium eutectics, calculated by approximating equations (1) and (3) in the range from room temperature to 1000 K with a step of 50 K, are given in table 5. In so doing, the density jump during melting $\delta\rho = (\rho_{sol} - \rho_{liq})\rho_{sol}^{-1}$ for eutectic alloys of Pb–Bi and Pb–Li systems turned out to be 1.68% and 3.38%, respectively. For example, according to the data of [20], the density jump during melting of pure lead is 3.20%.

Table 5. The density and coefficient of volumetric thermal expansion of lead-bismuth and lead-lithium eutectics in the condensed state.

T, K	Pb–Bi eutectic		Pb–Li eutectic	
	ρ, kg m^{-3}	$\beta\ 10^5$, K^{-1}	ρ, kg m^{-3}	$\beta\ 10^5$, K^{-1}
293.15	10656.7	4.317	10439.5	7.907
300	10659.8	4.316	10433.9	7.912
350	10682.9	4.307	10392.6	7.943
398.1 (solid)	10705.0	4.298	–	–
398.1 (liquid)	10525.4	12.83	–	–
400	10522.8	12.83	10351.3	7.975
450	10453.9	12.76	10310.0	8.007
500	10386.5	12.68	10268.8	8.039
508.1 (solid)	–	–	10262.1	8.044
508.1 (liquid)	–	–	9915.5	12.00
550	10320.4	12.60	9865.6	12.06
600	10255.6	12.52	9806.0	12.14
650	10192.0	12.44	9746.5	12.22
700	10129.4	12.36	9687.0	12.29
750	10067.9	12.27	9627.4	12.37
800	10007.2	12.18	9567.9	12.45
850	9947.3	12.09	9508.4	12.52
900	9888.1	12.00	9448.8	12.60
950	9829.6	11.91	9389.3	12.68
1000	9771.6	11.81	9329.8	12.75

4. Conclusions

High-precision measurements were performed of the density of eutectic alloys of Pb–Bi and Pb–Li systems in the condensed phase; the measurements results were used to develop tables of recommended reference data on density and CVTE of investigated alloys at technically important temperatures, which refine the tables employed heretofore in nuclear and fusion power engineering [17].

Acknowledgments

We acknowledge financial support of this study by the Russian Foundation for Basic Research (projects nos. 07-08-00071 and 07-08-00589).

References

[1] Askhadulin R Sh et al. 2001 *50 Let Osvoyeniya Tekhnologii Tyazhelykh Teplonositelei (Svinets-Vismut, Svinets, Gallii)* [*Fifty Years of Mastering the Technology of Heavy Coolants* (*Lead-Bismuth, Lead, Gallium*)] (Obninsk, Kaluga Region, Russia: Leipunskiy Physics and Power Engeneering Institute) (in Russian)
[2] Mikhailov V N, Evtikhin V A, Lyublinskiy I E, Vertkov A V, and Gumanov A N 1999 *Litii v Termoyadernoi i Kosmicheskoi Energetike XXI veka* (*Lithium in Fusion and Space Power Engineering in XXI Century*) (Moscow, Russia: Energoatomizdat) (in Russian)
[3] Hansen M and Anderko K 1958 *Constitution of Binary Alloys* (New York: McGraw–Hill)
[4] *Binary Alloy Phase Diagrams* 1986 (vols. 1 and 2) ed T B Massalski (Metals Park, OH: American Society for Metals)
[5] Preston-Thomas H 1990 *Metrologia* **27** 3
[6] Been S A, Edwards H S, Teeter C E, and Calkins V P 1950 *The Densities of Liquids at Elevated Temperatures. I. The Densities of Lead, Bismuth, Lead-Bismuth Eutectic, and Lithium in the Range from Melting Point to 1000 ˚C* (*1832 F*) NEPA Report 1585 (Oak Ridge, TN: Fairchild Engine and Airplane Corp.)
[7] Nikol'skiy N A, Kalakutskaya N A, Pchelkin I M, Klassen T V, and Vel'mishcheva V A 1959 *Teploenergetika* (*Power Engeneering*) **2** 92 (in Russian)
[8] Nikol'skiy N A, Kalakutskaya N A, Pchelkin I M, Klassen T V, and Vel'mishcheva V A 1959 *Voprosy Teploobmena* (*Problems of Heat Transfer*) (Moscow, Russia: USSR Academy Sciences) p 36 (in Russian)
[9] Kazakova I V, Lyamkin S A, and Lepinskikh B M 1984 *Zhurnal Fizicheskoy Khimii* (*J. Phys. Chem.*) **58** 1534 (in Russian)
[10] Alchagirov B B, Shamparov T M, and Mozgovoy A G 2003 *High Temp.* **41** 210
[11] Ruppersberg H and Speicher W 1976 *Z. Naturforsch.* **13A** 47
[12] Jauch U, Haase G, and Schulz B 1986 *Thermophysical Properties in the System Li-Pb. Part II: Thermophysical Properties of Li(17)Pb(83) Eutectic Alloy* (Karlsruhe: Kernforschungszentrum Karlsruhe GmbH) p 25
[13] Schulz B 1991 *Fusion Eng. Des.* **14** 199
[14] Saar J and Ruppersberg H 1987 *J. Phys. F*: *Met. Phys.* **17** 305
[15] Kalinin G M et al. 1991 *Study of Li17-Pb83 Eutectic Properties* (*USSR Contribution to ITER*) Preprint ET–91/01 (Moscow, Russia: Research and Development Institute of Power Engineering)
[16] Alchagirov B B, Mozgovoy A G, Taova T M, and Sizhahzhev T A 2005 *Perspektivnye Materialy* (*Advanced Materials*) **6** 35 (in Russian)
[17] Kirillov P L and Deniskina N B 2000 *Teplophizicheskie Svoystva Metallicheskikh Teplonositeley: Spravochnye Tablitsy i Sootnosheniya* (*The Thermal Properties of Liquid-Metal Coolants*: *Reference Tables and Relations*) Preprint FEI–0291 (Moscow, Russia: TsNIIAtominform) (in Russian)
[18] Stankus S V, Khairulin R A, Mozgovoy A G, Roshchupkin V V, and Pokrasin M A 2005 *High Temp.* **43** 368
[19] Hudson D J 1970 *Statistics*. *Lectures on Elementary Statistics and Probability* (Geneva: CERN Report)
[20] Stankus S V 1991 *Izmenenie Plotnosti Elementov pri Plavlenii: Metody i Experimentalnye Dannye* (*Variation of the Density of Elements in Melting. Methods and Experimental Data*) Preprint 247–91 (Novosibirsk: Institute of Thermophysics, Siberian Division of the USSR Academy Science)