High Temperature. Vol. 44, No. 3, 2006, pp. 389–395. Translated from Teplofizika Vysokikh Temperatur, Vol. 44, No. 3, 2006, pp. 393–400.

The Density of Alloys of Tin–Lead System in the Solid and Liquid States

S. V. Stankus and R. A. Khairulin

Kutateladze Institute of Thermophysics, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

Received June 9, 2005

Abstract—The method of gamma-raying the samples by a narrow beam of gamma radiation for cesium-137 isotope is used to investigate the density of five liquid alloys of a tin–lead system (17.64, 25.35, 25.61, 26.07, and 33.88 at.% Pb) in the temperature range from 293 to 1040 K with an error of 0.20–0.25%. Approximation dependences are obtained for the density of melts of investigated alloys, and our data are compared with the results of other authors. Procedural aspects of the investigation of the density of binary and multicomponent melts are treated, which are associated with the emergence of gradients of concentration of the components in the gravity field. Tables are compiled of the temperature dependences of the thermal properties of pure tin and lead from zero to 1600–1950 K. It is demonstrated that the density of the solid and liquid phases of tin–lead system in the investigated concentration range may be calculated in an additive approximation with an error of 0.1–0.3% or less.

INTRODUCTION

Because of the low liquidus temperature, availability and low price, and low pressure of vapors, as well as the relative inertness of melts, a tin–lead system may be treated as a reference system for the evaluation of experimental facilities for measuring the density ρ of multicomponent systems. One of the conditions for using this system as standard is the presence of high-accuracy and reliable experimental data. To the best of our knowledge, the first measurement of the density of liquid tin–lead alloys dates back to 1914 [1]. Since that time, different groups of researchers investigated this system. This interest in tin–lead alloys is associated both with their extensive applications in industry and with the unusual (in the opinion of a number of researchers) behavior of their properties in the liquid state. For example, Gavrilin *et al.* [2, 3] have found that homogeneous Sn–Pb melts separate in the case of exposure (15 to 240 min) in the vicinity of the liquidus temperature (T_L + (20–50 K)); experiments in internal friction [4] revealed an anomalous behavior of this property (890–1010 K), which was interpreted as a first-order liquid–liquid phase transition.

Analysis of the available data revealed that the reliability of the results of measurements of the properties of binary and multicomponent alloys is largely associated with the monitoring of homogeneity of samples. Several procedures are usually employed to provide for a homogeneous composition of melts. Samples are held for a long time (several hours) under significant superheat above the melting point. A mechanical agitation of melts is performed. The melts are prepared by melting highly homogeneous solid samples, etc. The achievement of equilibrium is monitored by the invariability of the parameter being measured in time. Unfortunately, in the absence of monitoring of the local distribution of components over the sample height, the use of the foregoing approaches does not guarantee the absence of concentration gradients. Following are several examples. In experiments performed to investigate the diffusion in a near-eutectic aluminum–germanium alloy (28.5 at.% Ge), the drop of concentration over the sample (35 mm high) decrease from 9 to 2 at.% after a four- or five-hour exposure of the melt at a temperature exceeding the liquidus temperature by 550 K (or by a factor of 1.8). Similar measurements for a Sn–Pb melt (50 at.% Pb) revealed a decrease in the concentration drop from 8 to 3 at.% after a five-hour exposure with a superheat by 520 K (or by a factor of two) [5]. Note that the presence of a vertical density gradient hampers the development of thermogravitational convection; therefore, the development of temperature gradients for agitation is not effective because of the low coefficient of volumetric expansion and high thermal conductivity of metal melts. The melting of homogeneous solid alloys almost always leads to the emergence of concentration gradients which are the higher, the more the composition differs from the composition of an alloy that melts at constant temperature. We observed no liquation effects in the melting of congruently melting intermediate compounds; however, during the melting of homogeneous eutectics, the melt was not always homogeneous [6]. Apparently, mechanical agitation (stirrers, bubbling, etc.) is the most reliable method of making a liquid sample homogeneous. Nevertheless, in this case as well, it is necessary to monitor the absence of concentration gradients. For methods of measuring the density of liquid such as pycnometric, dilatometric, indirect hydrostatic weighing, and drop methods, where the average density of the entire sample is determined, the time independence of readings is not an indication of equilibrium, especially in the cases of insignificant deviations of the values of density of alloys from the rule of additivity. The methods of direct hydrostatic weighing and of maximal pressure in a gas bubble are characterized by the possibility of performing direct measurements of the concentration gradient over the sample height; however, this calls for the introduction of a number of corrections which depend on the melt density. The problem of monitoring is solved most simply in the gamma-method by equipping the setup with a system of scanning the samples in height [7].

It is the objective of this study to experimentally investigate the density of alloys of tin–lead system in a wide temperature range of the solid and liquid states, compare the results with the available data, and compile reference tables for practical uses.

PROCEDURE AND EXPERIMENTAL EQUIPMENT

The measurements were performed by the method of gamma-raying the samples by a narrow beam of monochromatic gamma radiation in the temperature range from 293 to 1040 K in two different facilities GP-2 and P-3. The experimental equipment and the structure of GP-2 gamma densimeter were described in detail in [8]. The P-3 facility based on P-1 densimeter [9] is characterized by enhanced protection of NaJ(Tl) scintillation detector against scattered radiation and has a lead collimator of the detector, whose diameter may vary in a wide range without disturbing the overall adjustment of the gamma-raying system. The source of gamma quanta is provided by cesium-137 isotope with an activity of about 50 GBq. The initial radiation intensity recorded by the detector with an empty furnace is 4.5×10^4 pulse/s. The calculation results demonstrate that the difference of the build-up factor from unity for the employed geometry does not exceed 0.05%. A high-temperature electric furnace consists of water-cooled foundation, electric lead-ins, and a cap 340 mm in diameter and 340 mm high with flanges for the connection of vacuum and gas lines, as well as an equalizing block, heaters, and system of thermal-radiation shields. The equalizing block is made as a thick-walled copper sleeve (96 mm in diameter and 130 mm high) with a cover (20 mm thick) and a cavity (56 mm in diameter and 110 mm deep) which accommodates a crucible with the substance to be investigated. The block is mounted on a stainless steel support with a 150 W guard heater. The main heater with a resistance of 0.05 Ohm is made of 12Kh18N10T (chrome-nickel-titanium) steel 1 mm thick in the form of pipe with an outside diameter of 104 mm and 145 mm high provided with 12 vertical grooves for a zigzag flow of current. The working temperature range is 293–1100 K; the consumed power does not exceed 3 kW. The electric furnace may be moved vertically by 100 mm relative to the radiation beam by means of a hoisting gear. This enables one to investigate the density over the sample height. The position of the furnace is registered by a vertical displacement transducer. The measurements were performed at pressures from 10 μPa to 0.3 MPa. A control system enables one to vary the rate of variation of the sample temperature from 0.1 to 5 K/min and to maintain a constant temperature within 0.1 K or better. In this case, the temperature difference over the inner surface of the equalizing block does not exceed 0.5 K.

Measuring cells for samples included a cylindrical crucible of stainless steel or corundum (inside diameter of 25 mm, 60 mm high) and a cover with a thin-walled protective sleeve for a measuring thermocouple. The temperature was measured by Chromel–Alumel thermocouples. The thermocouples were calibrated against the solidification points of pure tin and antimony. The difference between the measured values of melting temperature and the reference values did not exceed 0.3–0.5 K. Prior to experiments, the gamma densimeter furnace was evacuated and filled with pure argon (99.992 vol.%) to a pressure of 0.1 MPa. The sample density was measured at the heating/cooling rate of 2 or 3 K/min (in single-phase regions) and 0.3 K/min or less in the melting–crystallization range. The mass factors of attenuation of radiation for tin and lead were measured directly in the facilities and amounted to 0.007549 and 0.01090 m^2/kg, respectively. The error of measurement of density at the maximal experimental temperature was estimated at 0.2–0.25% or less.

The investigated samples contained 17.64, 25.35, 25.61, 26.07, and 33.88 at.% Pb. The concentration of components was determined by the gravimetric method with an error of less than 0.01%. The purity of the starting components was higher than 99.99 mass %.

Table 1. Results of measurements of density and coefficients of volumetric thermal expansion of melts of Sn–Pb system at 600 K*

Concentration, at.% Pb	T_{max}, K	ρ, kg/m^3	$\beta\times10^{-5}$, K^{-1}
0.00	1936	6911.3±1.4	10.66±0.15
17.64	639	7670.5±1.5	11.08±0.34
25.35	753	7969.2±1.6	11.13±0.18
25.61	702	7971.2±1.6	11.04±0.28
26.07	1040	7993.2±1.6	10.86±0.22
33.88	638	8295.2±2.5	11.81±0.38

*T_{max} is the maximal temperature of measurements. The experimental data for pure tin are borrowed from [10]. Random error for confidence probability of 95% is given for density and CTE.

RESULTS AND DISCUSSION

Table 1 and Figs. 1 and 2 give typical results of measurements of the density of alloys of tin–lead system in the solid and liquid states. The experiments were performed as follows. The samples were heated somewhat above the liquidus temperature and agitated thoroughly by a mechanical stirrer. The homogeneity of the melt was checked by measuring the factor of attenuation of radiation at different heights. After that, the cell was heated to the maximal temperature and cooled to room temperature. No hysteretic effects and anomalous variation of density in the liquid state were observed in any of the experiments. The results of measurements in the heating/cooling cycle were reproduced within random errors. The temperature dependence of density of eutectic alloy

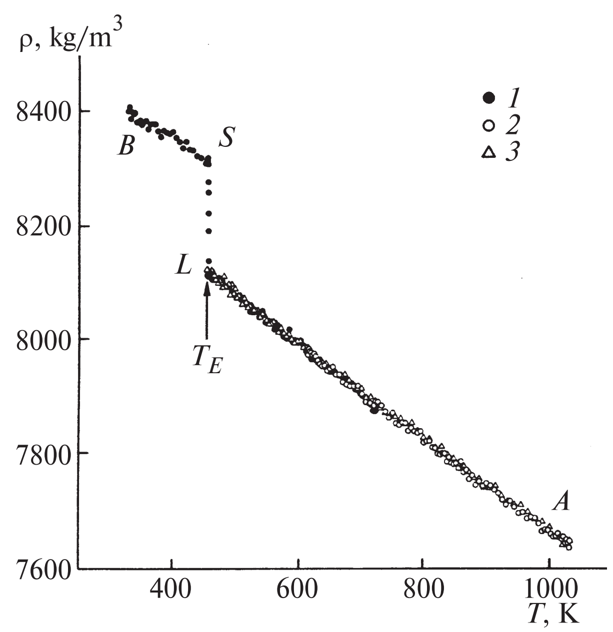

Fig. 1. The temperature dependence of the density of eutectic alloy (26.07 at.% Pb) in the solid (*BS*) and liquid (*LA*) states: (*1*) experimental data obtained in GP-2 facility in cooling the sample, (*2*, *3*) data obtained in P-3 facility in heating and cooling, respectively.

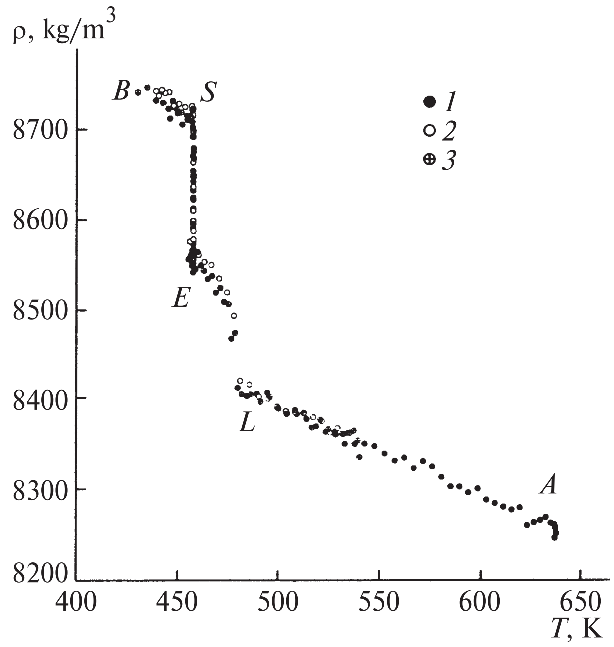

Fig. 2. Measured values of the density of alloy with 33.8 at.% Pb in the region of solid (*BS*)–liquid (*LA*) transition: (*1–3*) experimental data obtained in three successive coolings; *LE* and *ES* denote the crystallization of solid solution and eutectic, respectively.

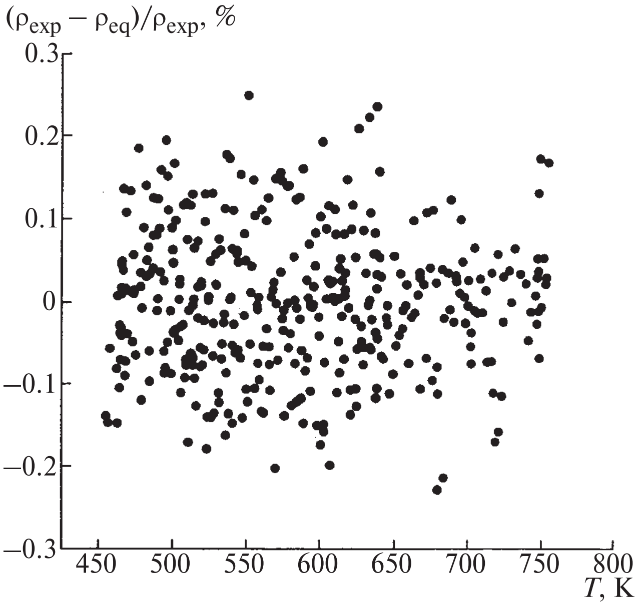

Fig. 3. Relative deviations of the measured values of the density of liquid alloys of Sn–Pb system from those calculated by approximating relation (2).

(26.07 at.% Pb) in the range of T_E from 456.6 to 1040 K is described by the equation

$$\rho = 8121.2 - 0.9176(T - 456.6) + 1.8691 \times 10^{-4} \times$$
$$\times (T - 456.6)^2 - 6.7890 \times 10^{-8}(T - 456.6)^3 \quad (1)$$

with the mean-square deviation of the experimental points of 0.07%. The coefficient of volumetric thermal expansion (CTE) of eutectic composition, calculated by Eq. (1), coincides with the CTE of pure tin [10] within random error of determination and, similar to the case of tin at $T < 1700$ K, decreases with increasing temperature. Such an anomalous behavior of the CTE of pure tin was explained in [10] by the destruction of residual directional bonds with increasing temperature.

The following experiment was performed in order to check the hypothesis of spontaneous separation of melts in the vicinity of the liquidus temperature [2, 3]. A sample of eutectic composition was heated to 617 K and thoroughly stirred by a mechanical stirrer. After that it was cooled to 459 K (3 K higher than the eutectic temperature) and held for six hours. The newly measured concentration profile demonstrated that no gradients of concentration of components arise in the sample under these conditions. Apparently, the initial melt was insufficiently homogenized in the experiments of [2, 3] or the distribution of components over the sample was disturbed during crystallization [6].

In order to obtain the dependence of density on temperature and concentration, all of the results of measurements in the ranges of T_L – 750 K and 0–33.88 at.% Pb were approximated by the equation

$$\rho = 7359.5 + 47.6554C - 0.10063C^2 -$$
$$- (0.74284 + 5.8927 \times 10^{-3}C)T, \quad (2)$$

where ρ is the density in kg/m^3, T is the temperature in K, and C is the atomic concentration of lead in the alloy in at.%. The mean-square relative deviations of the experimental data from the approximating equation (2) amounted to 0.09% (Fig. 3).

The density of alloys of tin–lead system was measured most accurately by the pycnometric method with an error of 0.05% in the entire range of concentrations with a step of 10% [11]. In this latter paper, previous investigations are reviewed. Comparison with [11] reveals that the density values obtained by us are systematically higher. The difference depends only slightly on temperature, increases almost linearly from 0.05–0.10% (pure tin) to 0.35–0.40% (eutectic alloy), and decreases again to 0.05–0.20% for an alloy with 33.88 at.% Pb. Although this difference in the data exceeds insignificantly the total errors of measurements, nevertheless its systematic pattern possibly points to insufficient homogenization of liquid samples in [11].

The temperature dependence of density of alloys in the solid state exhibits no special features and is linear for all concentrations. The calculated coefficients of thermal expansion coincide with the recommendations of Touloukian *et al.* [12] within the estimated errors of the latter (5–10%).

It is assumed that the excess volume of melts of tin–lead system has a low positive value [13]. In order to verify this statement, reliable data are required on the density of pure components in both condensed states. We will tabulate the recommended values of density of lead and tin using the recommendations of [12, 14] on the CTE and relative elongation of solid metals, as well as the data of [15] on the density jumps in melting and of [10, 16] on the CTE of melts. We will take 11 345±5.7 kg/m^3 and 7289.8±2.2 kg/m^3 as the reference values at 293.15 K for lead and tin, respectively. We obtained these values by the method of hydrostatic weighing of high-purity annealed sam-

Table 2. Temperature dependence of density, molar volume, and coefficient of volumetric thermal expansion of tin in the condensed state

Phase	T, K	ρ, kg/m^3	V, cm^3/mol	$\beta\times10^5$, K^{-1}	$\delta\rho$, %	$\delta\beta$, %
bct	0	7393.3	16.056	0	0.14	–
	5	7393.3	16.056	0.015	0.14	–
	25	7392.6	16.058	1.27	0.14	15
	50	7388.0	16.068	3.32	0.14	10
	75	7381.4	16.082	4.47	0.13	8
	100	7372.4	16.102	4.98	0.12	6
	150	7353.2	16.144	5.43	0.10	5
	200	7332.4	16.190	5.86	0.07	5
	273.15	7299.3	16.263	6.46	0.04	5
	293.15	7289.8	16.284	6.62	0.03	5
	298.15	7287.4	16.290	6.66	0.03	5
	400	7235.2	16.407	7.43	0.08	5
	500	7179.0	16.536	8.11	0.16	6
T_f^-	505.078	7176.1	16.542	8.15	0.16	6
T_f^+	505.078	6982.2	17.002	10.83	0.05	3.0
Melt	600	6911.3	17.176	10.66	0.06	2.5
	700	6838.7	17.359	10.49	0.07	2.0
	800	6767.9	17.540	10.33	0.08	1.7
	900	6698.9	17.721	10.18	0.09	1.5
	1000	6631.4	17.901	10.05	0.10	1.5
	1100	6565.5	18.081	9.93	0.11	1.5
	1200	6501.0	18.260	9.83	0.12	1.5
	1300	6437.7	18.440	9.75	0.13	1.7
	1400	6375.5	18.620	9.68	0.14	1.9
	1500	6314.2	18.800	9.63	0.15	2.1
	1600	6253.8	18.982	9.60	0.16	2.4
	1700	6194.1	19.165	9.59	0.17	2.8
	1800	6135.0	19.350	9.60	0.18	3.3
	1900	6076.3	19.537	9.63	0.19	3.8
	1950	6047.1	19.631	9.65	0.20	4.3

ples. The error was estimated from comparison with the X-ray density of metals calculated from the data of [17]. The errors of density and CTE in Tables 2 and 3 at other temperatures were borrowed from [10, 12, 14–16]. The notation in the tables is as follows: V is the volume per mole of matter, β is the coefficient of volumetric expansion, $\delta\rho$ is the error of density and molar volume, $\delta\beta$ is the error of coefficient of volumetric expansion, T_f is the melting temperature, the indexes + and – indicate phases below and above the melting temperature, bct indicates a body-centered tetragonal structure. Given below 286 K are data for the metastable state of bct tin. The density of solid (above 293 K) and liquid phases of lead and tin may be approximated by the following equations:

$$\rho_{\mathrm{sol}}^{\mathrm{Pb}} = 11345 - 0.959714(T - 293.15) - 3.715358 \times 10^{-4}(T - 293.15)^2, \tag{3}$$

$$\rho_{\mathrm{liq}}^{\mathrm{Pb}} = 10651 - 1.26276(T - 600.6) + 4.61964 \times 10^{-5}(T - 600.6)^2, \tag{4}$$

$$\rho_{\mathrm{sol}}^{\mathrm{Sn}} = 7289.8 - 0.4853(T - 293.15) - 2.41866 \times 10^{-4}(T - 293.15)^2, \tag{5}$$

$$\rho_{\mathrm{liq}}^{\mathrm{Sn}} = 6982.2 - 0.75643(T - 505) + 1.073 \times 10^{-4} \times (T - 505)^2 - 2.194 \times 10^{-8}(T - 505)^3. \tag{6}$$

Table 3. Temperature dependence of density, molar volume, and coefficient of volumetric thermal expansion of lead in the condensed state

Phase	T, K	ρ, kg/m^3	V, cm^3/mol	$\beta\times10^5$, K^{-1}	$\delta\rho$, %	$\delta\beta$, %
fcc	0	11589.4	17.878	0	0.08	–
	5	11589.4	17.878	0.076	0.08	10
	25	11584.5	17.886	4.35	0.08	4
	50	11568.1	17.911	6.52	0.08	3
	100	11525.9	17.977	7.72	0.07	1.5
	200	11434.3	18.121	8.27	0.06	1
	273.15	11363.8	18.233	8.60	0.05	1
	293.15	11345.0	18.264	8.67	0.05	1
	298.15	11340.0	18.272	8.68	0.05	1
	400	11237.8	18.438	9.15	0.06	1.5
	500	11130.6	18.615	9.93	0.08	3
	600	11015.3	18.810	10.90	0.10	5
T_f^-	600.6	11014.6	18.811	10.91	0.10	5
T_f^+	600.6	10651	19.454	11.86	0.10	5
Melt	700	10526	19.685	11.91	0.12	5
	800	10401	19.921	11.96	0.14	4
	900	10277	20.162	12.02	0.16	3
	1000	10154	20.406	12.07	0.18	2
	1100	10032	20.654	12.13	0.20	2
	1200	9911	20.906	12.18	0.22	2
	1300	9790	21.164	12.23	0.24	3
	1400	9671	21.425	12.29	0.26	4
	1500	9553	21.690	12.34	0.28	4
	1600	9435	21.961	12.40	0.30	5

The excess molar volume ΔV was calculated by the formulas [13]

$$\begin{aligned} \Delta V &= V_{\exp} - V_{\text{add}}, \\ V_{\exp} &= \frac{CM^{\text{Pb}} + (1-C)M^{\text{Sn}}}{\rho_{\text{all}}}, \qquad (7) \\ V_{\text{add}} &= \frac{CM^{\text{Pb}}}{\rho^{\text{Pb}}} + \frac{(1-C)M^{\text{Sn}}}{\rho^{\text{Sn}}}, \end{aligned}$$

where $V_{\exp}$ and V_{add} denote the measured value of molar volume and that calculated by the rule of additivity, respectively; M and ρ denote the molecular mass and the density of components, respectively; and ρ_{all} is the density of the alloy. Figures 4a and 4b give $V_{\exp}$ as a function of V_{add} for the solid and liquid states. It is shown that one can use formulas (3)–(6) and (7) to calculate fairly accurately the density of alloys of tin–lead system in both condensed states. According to our measurement results, the excess molar volume of the alloys is negative. However, its value (<0.25%) does not exceed the total errors of determination of the density of alloys and pure components. We can assume that the density of tin–lead system in the investigated range of temperatures and concentrations may be calculated in an additive approximation within 0.1–0.3% or better.

CONCLUSIONS

The experiments revealed that the results of measurements of the properties of alloys in the liquid state depend significantly on the homogeneity of the samples. No anomalous variation of density and hysteretic effects show up in homogeneous melts of tin–lead system, and no separation is observed in the vicinity of the liquidus temperature. The molar volume of Sn–Pb melts in the liquid state in the range of concentrations from zero to 34 at.% Pb obeys the rule of additivity with an error of 0.1–0.3% or less.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project no. 03-02-16120) and

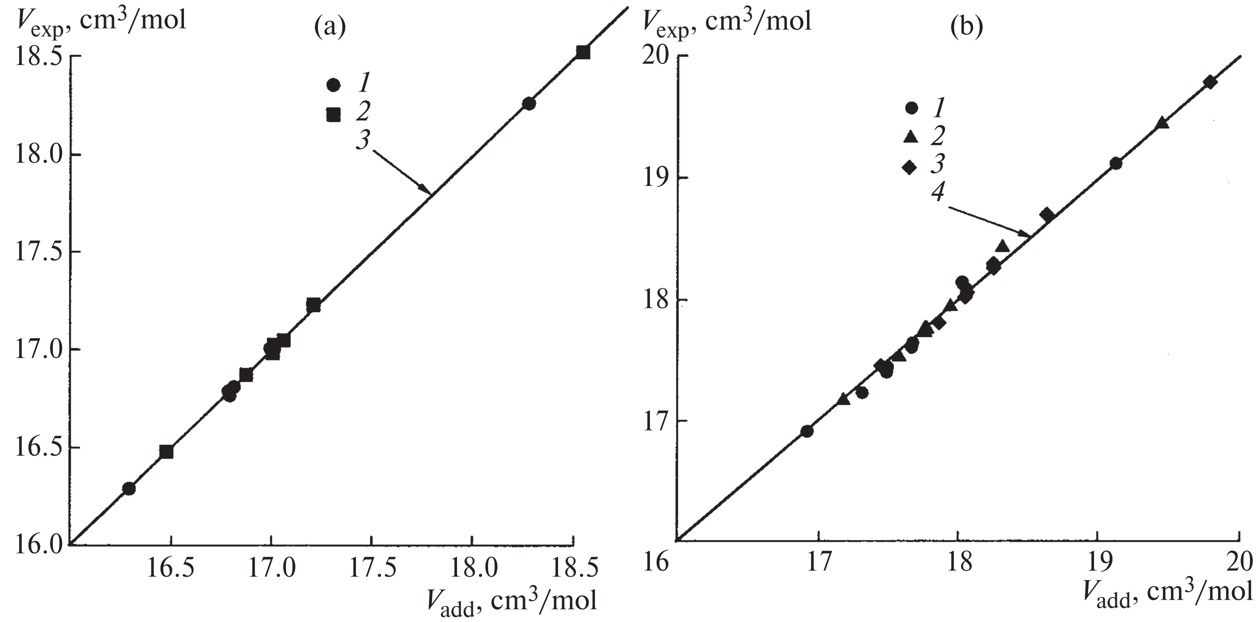

Fig. 4. The dependence of our experimental data on the molar volume of (a) solid and (b) liquid alloys of Sn–Pb system on those calculated by the additivity law; (a): (*1*) at a temperature of 293 K, (*2*) 456 K, (*3*) $V_{exp} = V_{add}$ line; (b): (*1*) at a temperature of 456 K, (*2*) 600 K, (*3*) 750 K, (*4*) $V_{exp} = V_{add}$ line.

by the Siberian Division of the Russian Academy of Sciences (project IG no. 171-03).

REFERENCES

1. Arpi, R., *Z. Metallk.*, 1914, vol. 5, p. 142.
2. Gavrilin, I.V., *Liteinoe Proizvod.*, 1982, no. 4, p. 2.
3. Gavrilin, I.V., Frolova, T.B., and Zakharov, V.P., *Izv. Akad. Nauk SSSR Met.*, 1984, no. 3, p. 191.
4. Zu, F.Q., Zhu, Z.G., Guo, L.J. *et al.*, *Phys. Rev.*, 2001, vol. 64b, p. 180203 (R).
5. Khairulin, R.A., Stankus, S.V., and Bezverkhy, P.P., *J. Alloys Compounds*, 2000, vol. 312, no. 1-2, p. 211.
6. Stankus, S.V. and Khairulin, R.A., Liquation in Liquid Alloys of Tin–Lead System, *Trudy XI Rossiiskoi konferentsii "Stroyenie i svoistva metallicheskikh i shlakovykh rasplavov* (Proc. XI Russian Conf. on the Structure and Properties of Metal and Slag Melts), Chelyabinsk: Izd. YuUrGU (South-Ural State Univ.), 2004, vol. 4, p. 37.
7. Khairulin, R.A. and Stankus, S.V., *J. Phase Equilibria*, 1999, vol. 20, no. 2, p. 148.
8. Stankus, S.V. and Khairulin, R.A., *Teplofiz. Vys. Temp.*, 1992, vol. 30, no. 3, p. 487.
9. Basin, A.S., Baginskii, A.V., Kolotov, Ya.L., and Stankus, S.V., High-Temperature Gamma Densimeter and Dilatometer, in *Gamma-metod v metallurgicheskom eksperimente* (Gamma Method in Metallurgical Experiment), Novosibirsk: Inst. of Thermophysics, Siberian Div., USSR Acad. Sci., 1981, p. 11.
10. Stankus, S.V. and Tyagel'skii, P.V., *Rasplavy*, 1991, no. 2, p. 14.
11. Thresh, H.R., Crawley, A.F., and White, W.G., *Trans. Metall. Soc. AIME*, 1968, vol. 242, p. 819.
12. Touloukian, Y.S., Kirby, R.K., Taylor, R.E., and Desai, P.D., Thermal Expansion. Metallic Elements and Alloys, in *Thermophysical Properties of Matter*, New York: Plenum, 1975, vol. 12, p. 1348.
13. Crawley, A.F., *Int. Metall. Rev.*, 1974, vol. 19, p. 32.
14. Novikova, S.I., *Teplovoye rashirenie tverdykh tel* (Thermal Expansion of Solids), Moscow: Nauka, 1974.
15. Stankus, S.V., The Variation of Density of Elements in Melting. Methods and Experimental Data, *Preprint of Inst. of Thermophysics, Siberian Div., Russian Acad. Sci.*, Novosibirsk, 1991, No. 247.
16. Khairulin, R.A. and Stankus, S.V., The Thermal Properties of Lead and Aluminum in the Solid and Liquid States, in *Teplofizicheskie svoistva rastvorov, rasplavov, i kompozitov*, Novosibirsk: Inst. of Thermophysics, Siberian Div., Russian Acad. Sci., 1992, p. 13.
17. Tonkov, E.Yu., *Fazovye diagrammy elementov pri vysokom davlenii* (Phase Diagrams of Elements at High Pressure), Moscow: Nauka, 1979.