THERMODYNAMIC PROPERTIES OF LIQUID METALS AND ALLOYS

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A modified cellular model of liquids is used to develop a method for calculating thermodynamic properties of liquid metals and their alloys, which are widely used in compact modern heat exchange equipment operating at high thermal flux densities. The approach presented herein permits calculation of the properties of metals from various groups by a single consistent technique. Good agreement was found with experimental data for a significant number of liquid metals and their alloys.

A knowledge of thermodynamic properties of liquid metals is necessary for project design in the field of energy generation, metallurgy, and high temperature technology. It is desirable that data on liquid metal properties be presented in the form of compact equations of state, convenient for use in computers and atomated data systems.

It should be noted that the significant disparity in the character of interparticle interaction in normal and metallic liquids does not lead to qualitative differences in their thermodynamic surfaces. In connection with this fact, in the present study for description of the thermodynamic properties of liquid metals and alloys we will use the equation of state of [1, 2], obtained on the basis of a cellular model, in which the intermolecular interaction is approximated by an effective potential function (12, 6) with temperature-dependent parameters.

The equation of state has the form

$$z = 1 - 1{,}744\,\frac{\varepsilon_\ell}{kT}\,[(b_{0\ell}\rho)^2 - 0{,}4654\,(b_{0\ell}\rho)^4], \tag{1}$$

where the temperature functions ε_ℓ and $b_{0\ell} = 2\pi N\sigma^3_\ell/3$ are expressed by functions [3]

$$\varepsilon_\ell/k = 0{,}795T_c \exp[c(1 - T/T_c)]; \quad \sigma_\ell^{-3} = a - bT. \tag{2}$$

Equation of state (1) has a theoretical basis, conveys all the principles of the thermodynamic behavior of liquids, has good extrapolation capabilities, and describes the thermodynamic properties of the condensed phase of materials with high accuracy [2, 3]. It is valid for the density range $\rho \geq 1.8\ \rho_c$ and temperatures $T_{tr} \leq T \leq T_c$ and contains three (aside from T_c) constants, a, b, c, the values of which can be determined from experimental pvT data by the method of [4].

Equation (1) will be used below to describe the thermodynamic properties of 18 liquid metals, 26 binary liquid alloys, and one three-component liquid metal system.

Among the most widely studied metallic liquids are the alkali metals Li, Na, K, Rb, and Cs. Detailed experimental data on pvT properties at high pressure are available only for sodium [5, 6], rubidium [5], and cesium [5, 7]. The density of liquid alkali metals on the liquid boundary curve has been the object of thorough experimental study [8, 9] and was generalized in the monograph [10]. In addition, corresponding data were published in the handbook [11]. Information on the thermal properties of liquid lithium and potassium at high pressure are lacking, there being only data on the liquid boundary curve in [10] and [11]. Comparative analysis of these two sets of data shows that for lithium up to T = 1500 K the density values agree within 0.5%, while at higher temperatures the deviation increases to ±3%. Considering that the authors of [10] recommend an uncertainity value for their data in this interval of 2-5%, we chose the data of [11] for reference thermal properties of lithium on the liquid boundary curve. Regarding analogous pvT data for potassium, the agreement be-

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TABLE 1. Constants of Eq. (1), Defined from pvT Data for Dense Liquids

Metal	$a \cdot 10^2$	$b \cdot 10^6$	c	$\overline{\delta\rho}$, %
Na	3,761669	5,7556	—0,0406	0,14
Cs	1,294970	2,5758	0,0065	0,25

TABLE 2. Calculated Valus of Liquid Na Density Using Constants a, b, c (Table 1) Determined from pvT Data of [6]

T, K	p, MPa	ρ_{calc}, kg/m³	$\delta\rho$, %
373,15	67,4	935,9	—0,26
393,15	95,2	937,1	—0,13
	213,9	958,8	0,09
	345,6	979,5	0,12
413,15	15,1	915,8	—0,41
	122,5	938,1	—0,03
	241,6	959,2	0,14
	373,6	979,5	0,12
	520,3	999,3	—0,03
433,15	41,7	917,3	—0,25
	149,4	938,9	0,06
	268,8	959,5	0,17
	401,3	979,4	0,11
	548,3	998,8	—0,07
453,15	67,9	918,5	—0,12
	175,9	939,5	0,12
	295,7	959,7	0,18
	428,4	979,2	0,09
	575,8	998,3	—0,13
473,15	93,6	919,5	—0,01
	202,0	940,0	0,17
	322,0	959,6	0,18
	455,2	978,8	0,05
	602,9	997,6	—0,19
493,15	20,6	899,2	—0,26
	118,8	920,3	0,07
	227,6	940,3	0,20
	348,0	959,5	0,17
	481,5	978,3	0,00
	629,6	996,9	—0,27

tween [10] and [11] for that case is within ±0.5% for density ρ'. When we consider that [10] predicts an accuracy of 0.5% on the liquid boundary line for potassium density, we may consider the two sets of data to be of equal value.

The constants of Eq. (1) for Na and Cs as obtained by the method of [4] from the experimental data of [5-7] are presented in Table 1, with the metal critical temperatures being taken from bandbook [12]. With these constants Eq. (1) describes the experimental data on the metals studied on the liquid boundary curve and at high pressures to an accuracy $\overline{\delta\rho}$ = 0.2-0.5%. Table 2, for example, presents results of a comparison of calculated density values with experimental data of [6] for Na. Analysis of this and similar tables shows that Eq. (1) for metallic liquids can be simplified considerably, relying on the following considerations.

It is known from the theory of liquid metals that the character of the ion subsystem, and thus, many properties of the metallic liquid, are determined mainly by repulsive forces, while change in attractive forces has little effect on close order, which latter can in the first approximation be described successfully in terms of a system of rigid spheres [13]. On the other hand, in accordance with Eq. (2) the concrete form of the temperature dependence of ε_ℓ/k will be determined by the constant c. As evident from Table 1, the values of this constant for sodium and cesium are close to zero, and if we consider that a marked absolute change in ε_ℓ/k defined by this constant does not affect the calculated values of the thermal properties strongly [4], we may take c = 0. In fact, as calculations have shown, definition of the constants a and b with a zero value of c (i.e., $\varepsilon_\ell/k = 0.795\ T_c$) leads to good results (Table 3).

TABLE 3. Constants of Eq. (1), Defined from pvT Data of Dense Liquid at c = 0

Metal	$a \cdot 10^2$	$b \cdot 10^6$	$\overline{\delta\rho}$, %
Na	3,789597	6,3731	0,06
Cs	1,295000	2,5737	0,15

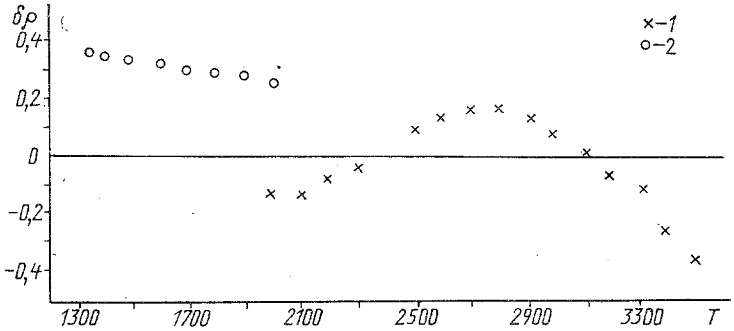

Fig. 1. Quality of description of basic thermal properties of liquid copper and deviation of calculated density values from data of [17]: 1) data of [16], p = 300 MPa; 2) [17], p = 0.034 MPa. δρ, %; T, K.

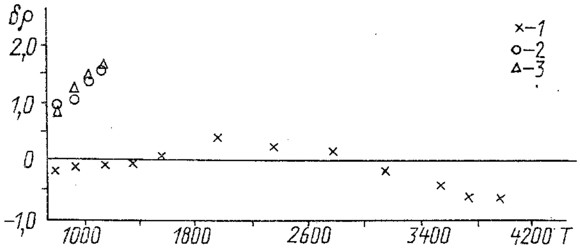

Fig. 2. Quality of description of basic thermal properties of liquid aluminum and deviation of calculated density values from data of [18, 19]: 1) data of [16], p = 300 MPa; 2) [19], p = 0.034 MPa; 3) [18], p = 0.1 MPa.

Equality to zero of the constant c eases the problem of finding the values of the constants a and b in the equation of state appearing in temperature function (2), for the determination of which it is sufficient to use any nonisothermal set of experimental data points. For this purpose we may take pvT data on the liquid boundary curve of the liquid metal studied, or data on the isobar p = 1 atm, which are the most accessible values. A method of determining a and b for a known value of c using similar data was described in [4].

Using constants a and b obtained in this manner (for c = 0) Eq. (1) describes experimental data on both the liquid boundary curve and the single phase region of liquid Na, Rb, and Cs (Table 4). Values of the equation of state obtained for liquid Li and K were used to calculate thermodynamic properties at high pressure.

Equation (1) can also serve as a reliable basis for calculating the caloric properties of metallic liquids in the presence of corresponding functions (specific heat, enthalpy) on their liquid boundary curves, for which known thermodynamic relationships can be used. Thus, data available in the literature on liquid bismuth density values at atmospheric pressure [14] were used to determine the constants a and b. Table 5 is a selective presentation of calculations of density, enthalpy, and isobaric specific heat for high pressure together with a comparison to reference data from [15]. The starting point of the calculations was enthalpy data from [15] at p = 0.1 MPa.

The deviation of calculated density values for liquid copper and aluminum at high and low pressure from the experimental data of [6] is shown in Figs. 1, 2. For these metals the constants a and b were determined from experimental data of [16] at p = 300 MPa, since they were presented there over a wider temperature range than at p = 0.034 MPa.

TABLE 4. Parameters of Equation of State of Liquid Metals and Quality of Thermal Property Description

Metal	Initial data				$a\cdot10^2$	$b\cdot10^6$	Calculation range			$\overline{\delta\rho}_{\text{ref}}$, %	$\overline{\delta\rho}_{\text{calc}}$, %
	T_c, K	p_{ref}, MPa	ΔT, K	reference			p_{calc}, MPa	ΔT, K	$p_{\max}$, MPa		
1	2	3	4	5	6	7	8	9	10	11	12
Li	3680	LBC	450—2000	[11]	7,0005	9,4489		450—2000	100	0,15	
Na	2503	LBC	500—1500	[5, 6]	3,7815	5,9654	40—629	500—1500	630	0,15	0,25
K	2280	LBC	336—1400	[10, 11]	1,9907	3,5732		336—1400	100	0,09	
Rb	2106	LBC	420—1300	[10, 11]	1,6196	3,1704	1,08—73	420—1300	75	0,23	0,23
Cs	2050	LBC	500—1200	[7, 10]	1,2980	2,5551	5,0—60	500—1200	60	0,12	0,35
Ca	4280	LBC	1114—2000	[10]	3,4937	3,4355		1115—2000	50	0,03	
Sr	4000	LBC	1041—2000	[10]	2,5685	1,3871		1040—2000	50	0,07	
Ba	4400	LBC	1000—2000	[10]	2,2529	0,7181		1000—2000	50	0,06	
Cu	8390	300	2000—3500	[16]	12,090	7,6772	0,034	2000—4000	300	0,12	0,31
Ag	7040	0,1	1234—2450	[18]	8,3399	5,1868		1240—2500	50	0,07	
Hg	1763	LBC	273—1073	[11]	6,0260	1,9677		273—1100	50	0,18	
Al	8000	300	933—4000	[16]	8,2866	5,3039	0,034	950—4000	300	0,25	1,35
Tl	4470	0,1	577—760	[18]	5,0906	3,4696		580—2000	50	0,01	
Pb	4960	0,1	610—970	[18]	4,7315	3,2114		610—2000	50	0,01	
Bi	4200	0,1	540—1730	[14]	4,3911	2,9641	1,0—100	540—2000	100	0,08	0,19
Fe	9600	0,034	1811—2300	[17—20]	12,611	7,5083	0,1	1820—3000	50	0,01	0,23
Co	10460	0,034	1767—2370	[17]	13,134	8,3677	0,1	1770—3000	50	0,01	1,11
Ni	10330	0,034	1728—2370	[17]	13,388	8,8147	0,1	1730—3000	50	0,01	1,38

TABLE 5. Comparison of Calculated and Reference [15] Values of Bismuth Thermodynamic Properties

p, MPa	ρ_{lit}, kg/m^3	ρ_{calc}, kg/m^3	$\delta\rho$, %	H_{lit}, kJ/kg	H_{calc}, kJ/kg	$c_{p\,lit}$, $\frac{kJ}{kg \cdot deg}$	$c_{p\,calc}$, $\frac{kJ}{kg \cdot deg}$
$T = 510$ K							
0,1	10095,4	10061,7	—0,33	—5,09	—5,10	0,1487	0,1500
10	10099,6	10073,1	—0,26	—4,17	—4,20	0,1488	0,1500
20	10103,9	10084,4	—0,19	—3,25	—3,20	0,1488	0,1500
30	10108,2	10095,6	—0,12	—2,33	—2,30	0,1488	0,1500
40	10112,4	10106,8	—0,06	—1,41	—1,40	0,1488	0,1500
50	10116,7	10117,8	0,01	—0,49	—0,40	0,1488	0,1500
100	10137,7	10171,9	0,34	4,12	4,20	0,1489	0,1500
150	10158,6	10224,0	0,64	8,71	8,80	0,1490	0,1500
200	10179,1	10274,4	0,94	13,30	13,40	0,1491	0,1500
$T = 900$ K							
0,1	9610,3	9599,6	—0,11	48,87	48,90	0,1334	0,1330
10	9615,1	9617,4	—0,03	49,79	49,80	0,1334	0,1330
20	9620,0	9625,1	0,05	50,72	50,70	0,1334	0,1330
30	9624,9	9637,7	0,13	51,64	51,60	0,1334	0,1330
40	9629,7	9650,2	0,21	52,57	52,60	0,1333	0,1330
50	9634,6	9662,5	0,29	53,50	53,50	0,1333	0,1330
100	9658,6	9722,7	0,66	58,12	58,10	0,1333	0,1330
150	9682,2	9780,3	1,01	62,75	62,60	0,1333	0,1330
200	9705,5	9835,6	1,34	67,36	67,20	0,1333	0,1330

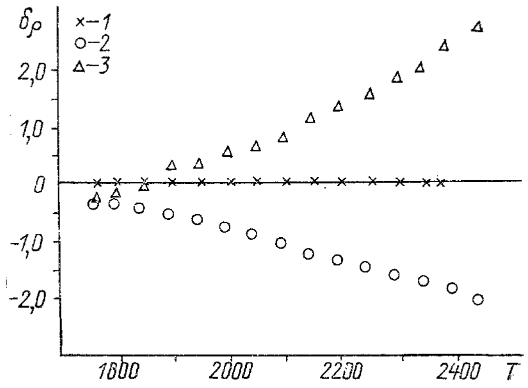

Fig. 3. Deviation of calculated density values of liquid cobalt from data of [17-19]: 1) data of [17], p = 0.034 MPa; 2) [19], p = 0.034 MPa; 3) [18], p = 0.1 MPa.

The results obtained permit the conclusion that the equality c = 0 is valid for liquid metals belonging to various groups. In the study of alloys below we will make an additional assumption that opens great possibilities for studying properties of metallic liquids, since the method described herein can be used to construct equations of state.

Table 4 presents values of the constants a, b and T_c, temperature and pressure ranges over which the constants of Eq. (1) were determined and calculations performed, reference sources for pvT data, the mean errors of their reproduction and description of other authors' data.

On the basis of the results obtained it can be said that for Fe the calculated liquid density values are in good agreement with the data of [17-20]. The maximum deviation is 0.5% of the density.

For liquid cobalt (Fig. 3) there are large deviations between the data of [18] and [19], reaching maximum values of $\delta\rho \sim 5\%$ at high temperature. A similar pattern can be seen for liquid nickel. The calculated density values of these metals agree well with the data of [17], which lie between the values of [18] and [19]. Apparently the data of [18, 19] are in need of refinement.

Thus, equation of state (1) with constants c = 0 and a and b defined from values on the liquid boundary curve or at p = 1 atm provides a quantitatively and qualitatively correct

TABLE 6. Parameters of Equation of State of Liquid Alkali Metals Satisfying Thermodynamic Similarity Conditions

Metal	T_c, K		$a\cdot10^2$	$b\cdot10^6$	bT_c/a
	[12]	corrected value			
Na	2503±50	2540	3,7844	6,0568	0,4065
K	2280±50	2272	1,9903	3,5595	0,4063
Rb	2106±15	2091	1,6188	3,1453	0,4063
Cs	2043±15	2054	1,2979	2,5678	0,4064

TABLE 7. Quality of Description of Thermal Properties of Alloys (p = 0.1 MPa) by Equation of State (3)

Alloy	Number of states	Δx	ΔT, K	$\overline{\delta\rho}$, %	Literature source
Na+K	9	0—1	350—1300	0,17	[10]
Cs+K	9	0—1	350—1300	0,71	[10]
Na+K+Cs	1	—	300—1300	0,21	[10]
Pb+Bi	1	—	403—973	0,35	[11]
Hg+Tl	7	0—1	300—600	0,90	[23]

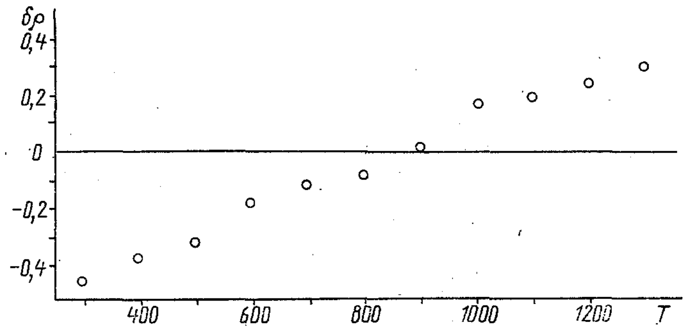

Fig. 4. Deviation of calculated densities of three-component liquid system Na + K + Cs from experimental data of [10]: x, molar fraction; $x_{Na} = 0.139$, $x_K = 0.435$, $x_{Cs} = 0.426$.

description of thermodynamic properties of liquid metals in the single phase state region, and in that case has the form

$$z = 1 - 1{,}38648\frac{T_c}{T}\left[(b_0\ell\rho)^2 - 0{,}4654\,(b_0\ell\rho)^4\right] \tag{3}$$

and contains three constants — a, b, and T_c: $z = z(T, \rho, T_c, a, b)$.

In the dimensionless coordinates $\tau = T/T_c$ and $\omega = \rho/a$ the equation of state takes on the form

$$z = z(\tau, \omega, \xi),$$

where ξ is some dimensionless complex, in the given case equal to

$$\xi = bT_c/a. \tag{4}$$

Consequently, for liquid metals a three-parameter law of corresponding states is valid, in which the parameter ξ acts as the thermodynamic similarity criterion. Analysis of data on liquid alkali metals (see Table 6) shows that for Na, K, Rb, and Cs the identical value of criterion (4) is characteristic. Thus, in this current study we have definitely established the fact of thermodynamic similarity of the indicated liquid metals, i.e., we have confirmed the proposition set forth previously in [21].

This fact is additional evidence of the justification of Eq. (1), and on the other hand, speaks of the reliability of calculated values of thermal properties of liquid potassium at high pressure, i.e., in the state region not studied experimentally.

Equation (1) was recommended in [1] for study of liquid solutions and prediction of their properties using only data on the pure components involved. To do this it is necessary to make use of the theory of conformal solutions, since the form of the effective potential for all liquid components is taken identical. Of all the approximations of this theory the best is the single-liquid one, in accordance with which the solution is considered as a pure liquid, whose parameters ε and σ are defined by the mixing laws [22]:

$$\varepsilon\sigma^3 = \sum_i\sum_j x_i x_j \varepsilon_{ij}\sigma_{ij}^3; \quad \sigma^3 = \sum_i\sum_j x_i x_j \sigma_{ij}^3. \tag{5}$$

In addition to Eq. (5), [1] proposed mixing laws of the type

$$\varepsilon\sigma^3 = \sum_i\sum_j x_i x_j \varepsilon_{ij}\sigma_{ij}^3; \quad \varepsilon = \sum_i\sum_j x_i x_j \varepsilon_{ij}, \tag{6}$$

where the parameters of the inhomogeneous interaction ε_{ij} and σ_{ij} are defined in terms of mean geometric and mean arithmetic combination rules, while the choice between Eqs. (5) and (6) is made by the criterion established in [1].

In the present study the method of [1] was used to calculate density of a number of liquid metallic alloys. Comparison with reference data shows that use of equation of state (3) with mixing rules (5) or (6) allows prediction of properties of liquid alloys including those of the three-component system Na + K + Cs, with a mean density error of $\overline{\delta\rho}$ = 0.2-0.9% (see Table 7).

Figure 4 illustrates the satisfactory description of the density of the ternary liquid system Na + K + Cs using only data on the pure components.

Summarizing the above, we may conclude that equation of state (1) has good predictive properties. For determining thermodynamic properties in the high pressure range it is sufficient to have available initial experimental data on the liquid boiling line (or at p = 1 atm). In Table 4, columns 9 and 10 indicate the T and p range in which use of Eq. (3) can be recommended for practical calculations. We will also note that the simplicity of the form of Eq. (3), its compactness, and the presence of only two (not counting T_c) constants makes possible its effective use in automated design systems.

NOTATION

a, b, c, constants of liquid equation of state; c_p, isobaric specific heat; H, enthalpy; k, Boltzmann's constant; N, Avogadro's number; p, pressure; R, universal gas constant; T, temperature; T_c, critical temperature; T_{tr}, triple point temperature; v, specific volume; x_i, molar fraction of component i; z, compressibility factor; δA, relative uncertainty in calculation of quantity A; ΔA, range of variation of A; ε_ℓ, liquid equation of state parameter; ρ, density; σ_ℓ, liquid equation of state parameter.

LITERATURE CITED

1. P. M. Kessel'man and I. V. Onufriev, Inzh.-Fiz. Zh., 37, No. 2, 316-323 (1979).
2. P. M. Kessel'man, Inzh.-Fiz. Zh., 54, No. 1, 65-72 (1988).
3. P. M. Kessel'man and S. A. Inshakov, Inzh.-Fiz. Zh., 46, No. 6, 959-964 (1984).
4. P. M. Kessel'man, S. A. Inshakov, and I. V. Onufriev, Inzh.-Fiz. Zh., 52, Mo. 3, 409-414 (1987).
5. N. B. Vargaftik, V. F. Kozhevenikov, V. G. Stepanov, et al., Inzh.-Fiz. Zh., 35, No. 5, 901-905 (1978).
6. I. N. Makarenko, A. M. Nikolaenko, V. A. Ivanov, and S. M. Stishov, Zh. Eksp. Teor. Fiz., 69, No. 5 (11), 1723-1733 (1975).
7. P. N. Ermilov, "Experimental study of density and calculation of tables of thermodynamic properties of cesium in the liquid phase at high temperature and pressure", Candidate's Dissertation [in Russian] Moscow (1983).

8. V. A. Kirillin, ed., Thermophysical Properties of Alkali Metals. A Handbook [in Russian], Moscow (1970).
9. E. E. Shpil'rain, K. A. Yakimovich, S. N. Skovorod'ko, and A. G. Mozgovoi, "Density and thermal expansion of liquid alkali metals", in: Reviews of Thermophysical Properties of Materials, No. 6 (44) [in Russian], Moscow (1983).
10. P. I. Bystrov, D. N. Kagan, G. A. Krechetova, and E. E. Shpil'rain, Liquid Metal Heat Transport Agents for Heat Pipes and Energy Equipment [in Russian], Moscow (1988).
11. N. B. Vargaftik, Handbook of Thermophysical Properties of Gases and Liquids [in Russian], Moscow (1972).
12. V. P. Glushko, ed., Thermal Constants of Materials, Issue 10 [in Rusian], Moscow (1982).
13. E. I. Khar'kov, V. I. Lysov, and V. E. Fedorov, Thermodynamics of Metals [in Russian], Kiev (1982).
14. A. A. Aleksandrov, V. S. Okhotin, Z. I. Panina, and Z. A. Ershova, Thermophysical Properties of Substances and Materials, Issue 14 [in Russian], Moscow (1980), pp. 74-79.
15. V. S. Okhotin, "Experimental and theoretical study of technically important liquids in order to create high precision equations and tables of thermophysical properties", Doctoral Dissertation [in Russian], Moscow (1987).
16. G. R. Gathers, Int. J. Thermophys., 4, No. 3, 209-226 (1983).
17. W. D. Drothing, High Temp. High Pressures, 13, No. 4, 441-458 (1981).
18. A. R. Regel' and V. M. Glazov, Physical Properties of Electronic Alloys [in Russian], Moscow (1980).
19. V. V. Tekuchev and V. I. Stremousov, Zh. Fiz. Khim., 59, No. 9, 2258-2260 (1985).
20. A. S. Basin and S. V. Stankus, Scientific Reports of the II All-Union Conference on Properties of Fused Metals and Slags. Part II. Study of Fused Metals [in Russian], Sverdlovsk (1976), pp. 63-64.
21. Yu. P. Krasnyi and V. P. Onishchenko, Ukr. Fiz. Zh., 17, 1704-1713 (1972).
22. T. W. Leland, J. S. Rowlinson, and G. A. Sather, J. Chem. Soc. Faraday Trans., 64, No. 6, 1447-1452 (1968).
23. T. Sato, T. Stami, and M. Shimoji, J. Phys. Soc. Japan, 51, No. 8, 2493-2500 (1982).