# Entropy of bcc → L, fcc → L, and fcc → bcc phase transitions of elemental substances as function of transition temperature

1 author:

Alexander L'vovich Udovsky

Russian Academy of Sciences, Baikov Institute of Metallurgy and Materials Science; National Research Nuc…

**86** PUBLICATIONS   **127** CITATIONS

Some of the authors of this publication are also working on these related projects:

Development of theoretical bases of creation of stable nano-technology gradient ferritic steels, hardened by disperse oxide particles View project

Federal target program "Integration" for the project N K0573. View project

=== **PHYSICS** ===

# Entropy of bcc → L, fcc → L, and fcc → bcc Phase Transitions of Elemental Substances as Function of Transition Temperature

## A. L. Udovskiĭ

Presented by Academician I.I. Novikov October 20, 1999

Received October 20, 1999

In the last two-three decades, the thermodynamic calculations of phase diagrams for both binary and multicomponent systems have been in general use (see, e.g., [1–3]). For most systems, a thermodynamic description of virtual phase transitions for pure components entering a system is necessary for performing these calculations. Thus, e.g., for calculating the Ni–Cr phase diagram, it is necessary to know the enthalpies and entropies of phase transitions for Ni and Cr both in the case of the actual phase transitions [fcc ⟶ liquid melt (L) for Ni and bcc ⟶ L for Cr] and virtual phase transitions of metastable phases of pure Ni (bcc phase) and Cr (fcc phase) to the liquid phase.

Studies on the relative stability of various phases for pure components have a rather long history. Trawton, and then Nernst and other researchers (see [4]), assumed the entropy of evaporation to be constant under atmospheric pressure for thermodynamically similar substances. Later on, this hypothesis was generalized by Krompton [4], who assumed the melting entropy jumps to be equal for all chemical elements with similar crystal structures (the "generalized Trawton rule") [5]. Later, Kaufman [5] calculated the differences in enthalpy and entropy between hcp and bcc phases, as well as between hcp and fcc phases of transition metals, as the functions on the number of the group in the Mendeleev periodic table of elements. They suggested that the elements of the same group in the periodic table have similar values for the phase transition entropy if the transition occurs between phases of the same type. In particular, the entropy of melting for bcc phases of elemental Zr, Hf, Nb, Ta, Mo, and W has the same value of 2 cal/(g atom K). Comparison of these values with recent thermodynamic experimental data [6] shows that both the generalized Trawton rule and the assumptions of [5] do not agree well with experiment.

*Baĭkov Institute of Metallurgy and Materials Science,*
*Russian Academy of Sciences, Leninskiĭ pr. 49,*
*Moscow, 117334 Russia*

In [7], plots of the melting entropy for bcc, fcc, and hcp phases of metals as functions of melting temperature are presented. However, an attempt to graphically extrapolate experimental data on the entropies of phase transitions to zero temperature results in a finite value of the entropy difference between the various phases. This contradicts the third law of thermodynamics (the vanishing of the entropy at zero temperature).

The goal of this paper is using physical models for phases to construct the dependence of melting entropies on the phase-transition temperature for both bcc and fcc phases of most chemical elements of the periodic table, which could be free of the contradictions mentioned above.

The temperature dependence of the Gibbs free energy for any phase of a pure component can be described by the following formula (see, e.g., [8]):

$$G(T) = H(0) - \int_0^T S(T)dT, \qquad (1)$$

where $H(0)$ is the enthalpy at 0 K; $S(T)$ is the temperature dependence for the entropy. Then, the difference in the Gibbs free energies between α- and β-phases of the component as a function of $T$ has the form

$$\Delta G^{\alpha \rightarrow \beta}(T) \equiv G^{\beta}(T) - G^{\alpha}(T)$$
$$= \Delta H^{\alpha \rightarrow \beta}(0) - \int_0^T \Delta S^{\alpha \rightarrow \beta}(T)dT. \qquad (2)$$

Since, at the temperature of the phase transitions α ⟶ β, the Gibbs free energies for α- and β-phases are equal, we find from (2)

$$\Delta H^{\alpha \rightarrow \beta}(0) = \int_0^{T^{\alpha \rightarrow \beta}} \Delta S^{\alpha \rightarrow \beta}(T)dT; \qquad (3)$$

i.e., the difference between the enthalpies of α- and β-phases of the pure component at zero temperature is

equal to the area bounded by the $\Delta S^{\alpha \rightarrow \beta}(T)$ curve at temperatures ranging from zero to the temperature $\alpha \rightarrow \beta$-phase transition point $T^{\alpha \rightarrow \beta}$. Dividing the integration range in the right-hand side of (2) into two parts, from zero to $T^{\alpha \rightarrow \beta}$ and $T^{\alpha \rightarrow \beta}$ to $T$, and then substituting (3) into (2), we find

$$\Delta G^{\alpha \rightarrow \beta}(T) = \int\limits_{T}^{T^{\alpha \rightarrow \beta}} \Delta S^{\alpha \rightarrow \beta}(T)dT. \tag{4}$$

Using the definition of specific heat, relationship (4) can be presented in the form

$$\Delta G^{\alpha \rightarrow \beta}(T) = \int\limits_{T}^{T^{\alpha \rightarrow \beta}} dT' \int\limits_{0}^{T} \Delta C_P^{\alpha \rightarrow \beta}(T'')dT''/T''. \tag{5}$$

All relationships (1)–(5) are exact. Then, we use conventional models to describe the temperature dependence of the specific heat for the phases under study, e.g., for the $\alpha$-phase,

$$C_P^{\alpha}(T) = C_V^{\alpha}(T)(1 + \alpha_V^{\alpha}(T)\gamma_G^{\alpha}(T)T) + \gamma^{\alpha}(T)T. \tag{6}$$

In (6), the specific heat is considered as a sum of the lattice contribution (with the anharmonism taken into account) and the electronic contribution (with the renormalized electron–phonon coupling constant), $\alpha_V^{\alpha}$ is the temperature-dependent volume coefficient of the thermal expansion for the $\alpha$-phase, and $\gamma_G^{\alpha}(T)$ is the temperature-dependent Grüneisen parameter of the $\alpha$-phase, which can be written in the form [9]

$$\gamma_G^{\alpha}(T) = \gamma_G^{\alpha}(T)_{LT} - \frac{2\exp(-\theta_D^{\alpha}/3T)}{3[1 + \exp(-\theta_D^{\alpha}/3T)]}, \tag{7}$$

where $\gamma_G^{\alpha}(T)_{LT}$ is the Grüneisen parameter at low temperatures and $\theta_D^{\alpha}$ is the Debye temperature for the $\alpha$-phase. For solid phases, $C_V^{\alpha}(T)$ is described by the Debye model.

We consider the temperature range in which $T > \max(\theta_D^{\alpha}, \theta_D^{\beta})$. The anharmonism will be described within the framework of the quasi-harmonic theory; i.e., we describe the lattice contribution of the specific heat by the Debye temperature depending on the volume. The latter, in its turn, depends on temperature as well {see formulas (67.5) and (67.6) in [10]}. It is well known that the difference $C_P - C_V$ at high temperatures is proportional to the first power in $T$, and we have $C_P - C_V \ll C$ [10, p. 226] for each phase. However, when we analyze the difference between specific heats of $\alpha$- and $\beta$-phases of the pure component as a function of temperature, the value of $C_P - C_V$ at the temperature of the phase transition can be comparable with the entropy jump at this temperature. For example, according to the experimental data [6], we have for the fcc $\longrightarrow$ bcc phase transition in Ca that $\mathrm{mod}(C_P^{bcc} - C_P^{fcc})/\Delta S^{fcc \rightarrow bcc} = \mathrm{mod}(-1.2332/1.2973) = 0.95$; in the case of Hf, $\mathrm{mod}(C_P^{bcc} - C_P^{fcc})/\Delta S^{fcc \rightarrow bcc} = \mathrm{mod}(-6.6207/2.9069) = 2.28$; for the fcc $\longrightarrow$ bcc phase transition in Th, this ratio is equal to 2.63. The characteristics considered here are presented in the table for fcc $\longrightarrow$ bcc and hcp $\longrightarrow$ bcc phase transitions for 19 elements, among which the ratio of the difference of the specific heats in various phases to the entropy of the phase transition is on the order of unity for 17 elements. These facts confirm our previous statement. Thus, to describe the differences between thermodynamic functions of different phases in a sufficiently wide temperature range around the phase transition, we should take into account the difference in the specific heats of the various phases of the elements themselves. In this case, the entropy of the $\alpha$-phase as function of temperature at $T > \theta_D^{\alpha}$ has the following form:

$$S^{\alpha}(T) = 3(R\ln(T/\theta_D^{\alpha}(T))) + 4R + \gamma^{\alpha}T, \tag{8}$$

where

$$\theta_D^{\alpha}(T) \simeq \theta_D^{\alpha}(0)(1 - \bar{\alpha}_V^{\alpha}\gamma_G^{\alpha}T), \tag{9}$$

$$\bar{\alpha}_V^{\alpha} = 1/T^{\alpha \rightarrow \beta} \int\limits_{0}^{T^{\alpha \rightarrow \beta}} \alpha_V^{\alpha}(T)dT, \tag{10}$$

$\bar{\alpha}_V^{\alpha}$ is the mean volume coefficient of thermal expansion and

$$\gamma_G^{\alpha} = (\gamma_G^{\alpha})_{LT} + 1/3 \tag{11}$$

is the Grüneisen parameter in the high-temperature limit, which is obtained from relationship (7) under condition $\theta_D^{\alpha}/3T \ll 1$. In this case, the difference between entropies of the $\alpha$- and $\beta$-phases for the pure component as a function of temperature takes the form

$$\Delta S^{\alpha \rightarrow \beta}(T) = 3R\ln(\theta_D^{\alpha}(0)/\theta_D^{\beta}(0))$$
$$+ \{3R(\bar{\alpha}_V^{\alpha}\gamma_G^{\alpha} - \bar{\alpha}_V^{\beta}\gamma_G^{\beta}) + (\gamma^{\beta} - \gamma^{\alpha})\}T. \tag{12}$$

Thus, for the temperature range, whose lower limit exceeds the maximum Debye temperature of $\alpha$- and $\beta$-phases of the pure component, the temperature dependence of the entropy difference between $\alpha$- and $\beta$-phases of the pure component has a linear form. Since only nine elements have the fcc $\longrightarrow$ bcc phase transition (at atmospheric pressure), the sampling for finding the entropy jump at the fcc $\longrightarrow$ bcc phase transition is not sufficiently representative. However, the following approach can be used. We can also take into consideration two phase transitions bcc $\longrightarrow$ L and

Parameter of nonlinearity entering into the temperature dependence for the difference in the Gibbs free energy between fcc (hcp) and bcc phases for pure elements

| Element | Phase transition | $T^{\alpha \rightarrow \beta}$, K [6] | $\Delta S^{\alpha \rightarrow \beta}(T^{\alpha \rightarrow \beta})$, J/(mol K) [6] | $[C_P^{\alpha \rightarrow \beta}]_{T^{\alpha \rightarrow \beta}}$, J/(mol K) [6] | $[C_P^{\alpha \rightarrow \beta}]_{T^{\alpha \rightarrow \beta}}/\Delta S^{\alpha \rightarrow \beta}$ |
|---|---|---|---|---|---|
| Am | fcc $\longrightarrow$ bcc | 1350 | 4.3422 | 1.2898 | 0.297 |
| Be | hcp $\longrightarrow$ bcc | 1527 | 4.4853 | −1.852 | −0.413 |
| Ca | fcc $\longrightarrow$ bcc | 716 | 1.2973 | −1.2332 | −0.951 |
| Ce | fcc $\longrightarrow$ bcc | 1000 | 2.9916 | −0.1165 | 0.039 |
| Fe | fcc $\longrightarrow$ bcc | 1667.5 | 0.4953 | 2.1830 | 4.407 |
| Gd | hcp $\longrightarrow$ bcc | 1535 | 2.3959 | −1.0745 | −0.448 |
| Hf | hcp $\longrightarrow$ bcc | 2016 | 2.9069 | −6.6207 | −2.278 |
| Ho | hcp $\longrightarrow$ bcc | 1703 | 2.5084 | −4.0963 | −1.633 |
| La | fcc $\longrightarrow$ bcc | 1134 | 2.7524 | 4.515 | 1.640 |
| Mn | fcc $\longrightarrow$ bcc | 1411 | 1.3525 | 3.2561 | 2.407 |
| Sc | hcp $\longrightarrow$ bcc | 1608 | 2.4927 | 4.1361 | 1.659 |
| Sr | fcc $\longrightarrow$ bcc | 820 | 1.0207 | −2.361 | −2.313 |
| Tb | hcp $\longrightarrow$ bcc | 1562 | 2.8045 | −0.3401 | −0.1213 |
| Th | fcc $\longrightarrow$ bcc | 1633.2 | 2.2034 | −5.7949 | −2.630 |
| Ti | hcp $\longrightarrow$ bcc | 1155 | 3.6104 | −5.0272 | −1.392 |
| Tl | hcp $\longrightarrow$ bcc | 507 | 0.7097 | 2.0997 | 2.959 |
| Y | hcp $\longrightarrow$ bcc | 1752 | 2.8490 | −2.453 | −0.861 |
| Yb | fcc $\longrightarrow$ bcc | 1033 | 1.693 | 4.059 | 2.398 |
| Zr | hcp $\longrightarrow$ bcc | 1139.45 | 3.6011 | −6.3138 | −1.753 |

fcc $\longrightarrow$ L for pure elements, since the bcc $\longrightarrow$ L phase transition occurs for 39 elements, and the fcc $\longrightarrow$ L phase transition is observed for 13 elements. Then, on the one hand, according to (7), the difference in enthalpies at 0 K between fcc and bcc phases is expressed in the form

$$\Delta H^{fcc \rightarrow bcc}(0) = \int_0^{T^{fcc \rightarrow bcc}} \Delta S^{fcc \rightarrow bcc}(T)dT, \quad (13)$$

and, on the other hand, it can be expressed as the combination bcc $\longrightarrow$ L and fcc $\longrightarrow$ L phase transition

$$\Delta H^{fcc \rightarrow bcc}(0) = \Delta H^{fcc \rightarrow L}(0) - \Delta H^{bcc \rightarrow L}(0)$$
$$= \int_0^{T^{fcc \rightarrow L}} \Delta S^{fcc \rightarrow L}(T)dT - \int_0^{T^{bcc \rightarrow L}} \Delta S^{bcc \rightarrow L}(T)dT. \quad (14)$$

Thus, on one hand, the difference of enthalpies at 0 K between fcc and bcc phases of the pure component can be expressed through the integral of the difference of entropies for the corresponding phases, which is defined within the range from zero temperature up to the fcc $\longrightarrow$ bcc phase transition, whereas the difference of enthalpies at 0 K between the fcc and bcc phases of the pure component can be expressed through the difference of two integrals. The first one is defined through the entropy difference between the liquid and fcc phases of the component, and the second integral is calculated through the difference of entropies between the liquid and bcc phases of the pure component within the range from 0 K to the melting temperature for the bcc phase of this component.

For describing the vibration contribution to the entropy of the liquid phase for the pure component, we can use the Einstein model. The anharmonism can be introduced with the help of the Grüneisen parameter for a liquid phase, similarly to the quasi-harmonic
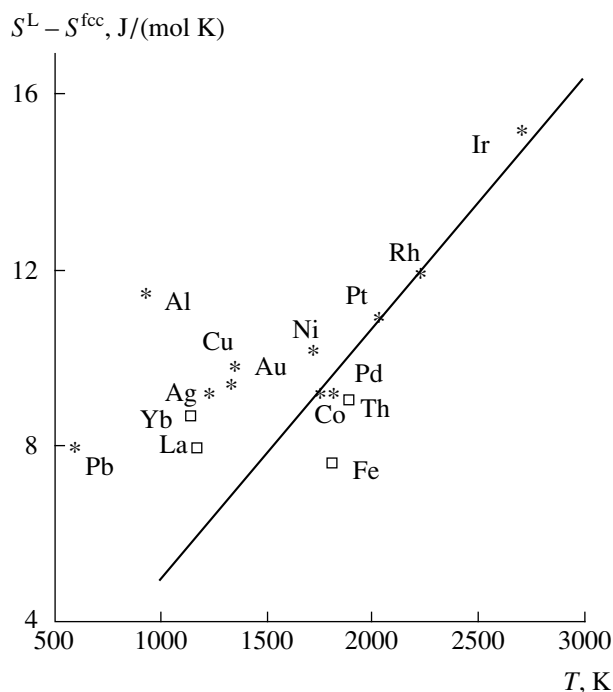
**Fig. 1.** Comparison of the melting entropy jump for pure components with the fcc structure as a function of melting temperature [relationship (20)] with the corresponding experimental data [6].
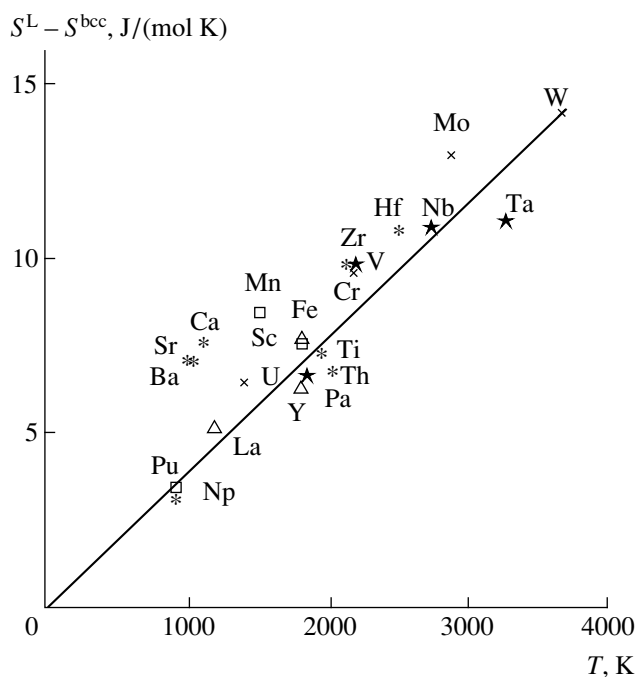


**Fig. 2.** Comparison of the calculating melting-entropy jump for pure components with bcc structure as a function of melting temperature [relationship (21)] and the relevant experimental data [6].

approach for solids. The Grüneisen parameter can be defined as

$$\gamma_{GE}^L = -\frac{\partial \ln \theta_E^L}{\partial \ln V}.$$

In this case, the entropy of the liquid phase for the component depends on temperature (for the case $T > \theta_E^L$) and can be presented in the form

$$S^L(T) = 3R\ln(T/\theta_E^L(T)) + 3R + \gamma^L T, \qquad (15)$$

where the temperature dependence of the Einstein temperature has the form

$$\theta_E^L(T) = \theta_E^L(0)(1 - \bar{\alpha}_V^L \gamma_{GE}^L T), \qquad (16)$$

and $\bar{\alpha}_V^L$ and $\gamma^L$ are, respectively, the mean volume coefficient of thermal expansion and the coefficient characterizing the electron specific heat for the liquid phase of the pure component. In this case, the difference between the entropies of solid, e.g., α-phase, and the liquid phase of the pure component as a function of temperature is written as:

$$\Delta S^{\alpha \to L}(T) = 3R\ln(\theta_D^\alpha(0)/\theta_E^L(0))$$
$$+ \{3R(\bar{\alpha}_V^\alpha \gamma_G^\alpha - \bar{\alpha}_V^L \gamma_{GE}^L) - R + (\gamma^L - \gamma^\alpha)\}T. \qquad (17)$$

Thus, according to relationship (17), the temperature dependence for the difference between the entropies of liquid and solid phases, e.g., of the bcc phase, also has a linear form, however, with a different free term and a temperature slope compared to the temperature dependence of the entropy difference between solid phases. As a rule, the Einstein temperature, the Grüneisen parameter, and the coefficient of the electronic specific heat for the liquid phase of pure components are unknown. We present dependence (17) for bcc $\longrightarrow$ L and fcc $\longrightarrow$ L phase transitions only in a functional form as relationships (18) and (19) with unknown coefficients, which we determine based on the experimental data:

$$\Delta S^{\text{bcc} \to L}(T) = a^{\text{bcc} \to L} + b^{\text{bcc} \to L}T, \qquad (18)$$

$$\Delta S^{\text{fcc} \to L}(T) = a^{\text{fcc} \to L} + b^{\text{fcc} \to L}T. \qquad (19)$$

Using the available reference data on the thermal properties for all bcc metals undergoing the bcc $\longrightarrow$ L phase transitions [6], we calculate the coefficients in dependence (19), employing the $\chi^2$ criterion (the generalized least-squares method) [11]. As a result, we get

$$\Delta S^{\text{fcc} \to L}(T)$$
$$= -0.685 + (5.655 \times 10^{-3})T, \quad \text{J/(mol K)}. \qquad (20)$$

The calculated dependence (20) is compared in Fig. 1 with the experimental data for bcc $\longrightarrow$ L phase transi-

tions in 13 pure elements. Using a similar procedure, we processed the experimental data on fcc ⟶ L phase transitions in all 39 elements [6]. The results are presented in the form of the following relationship,

$$\Delta S^{bcc \longrightarrow L}(T)$$
$$= -0.03 + (3.8403 \times 10^{-3})T, \quad J/(mol\ K), \tag{21}$$

and are compared with the experimental data in Fig. 2. The accuracy of relationships (20) and (21) can be verified by comparing the calculated difference of the entropies for phase transitions between bcc and fcc phases as a function of the bcc ⟶ fcc phase-transition temperature of the elements,

$$\Delta S^{fcc \longrightarrow bcc}(T) = S^{L}(T) - S^{fcc}(T)$$
$$- (S^{L}(T) - S^{bcc}(T)) \equiv \Delta S^{fcc \longrightarrow L}(T) - \Delta S^{bcc \longrightarrow L}(T) \tag{22}$$

with the corresponding experimental data.

Substituting the derived relationships (20) and (21) into (22), we obtain

$$\Delta S^{fcc \longrightarrow bcc}(T) \equiv S^{bcc}(T) - S^{fcc}(T)$$
$$= a^{fcc \longrightarrow bcc} + b^{fcc \longrightarrow bcc}T \tag{23}$$
$$= -0.682 + (1.8147 \times 10^{-3})T.$$

In Fig. 3, the results of calculation based on (23) are compared with the experimental data of [6] for the fcc ⟶ bcc phase transition in pure elements Ca, Ce, La, Mn, Sr, Th, and Yb. The phase transition in Fe is not included since the bcc ⟶ fcc transition here occurs twice due to the effect of ferromagnetism on the bcc phase. Figure 3 demonstrates satisfactory agreement of the experimental data with a fit made according to (23). When the temperature tends to zero, the entropy difference between the solid phases below the Debye temperature also tends to zero as

$$S^{bcc} - S^{fcc} = 3R\{(T/\theta^{bcc})^3 - (T/\theta^{fcc})^3\}$$
$$= 18R(T/\theta_{av})^3(\Delta\theta/\theta_{av}), \tag{24}$$

where $\theta_{av} = (\theta^{bcc} + \theta^{fcc})/2$ is the mean Debye temperature and $\Delta\theta = (\theta^{fcc} - \theta^{bcc})/2$. Therefore, in the first approximation the temperature dependence of the entropy difference between the bcc and fcc phases can be written as

$$\Delta S^{fcc \longrightarrow bcc}(T) = S^{bcc}(T) - S^{fcc}(T)$$
$$= \begin{cases} 0, & 0 < T < \theta_{av} \\ const \times (T - \theta_{av}), & T > \theta_{av}, \end{cases} \tag{25}$$

i.e., within the temperature range from zero up to the mean Debye temperature, this difference $\Delta S^{fcc \longrightarrow bcc}(T)$ is approximately taken to be zero [see (24)], and above $\theta_{av}$, it is taken in the form of a linear dependence according to relationship (12). It follows from (23) and

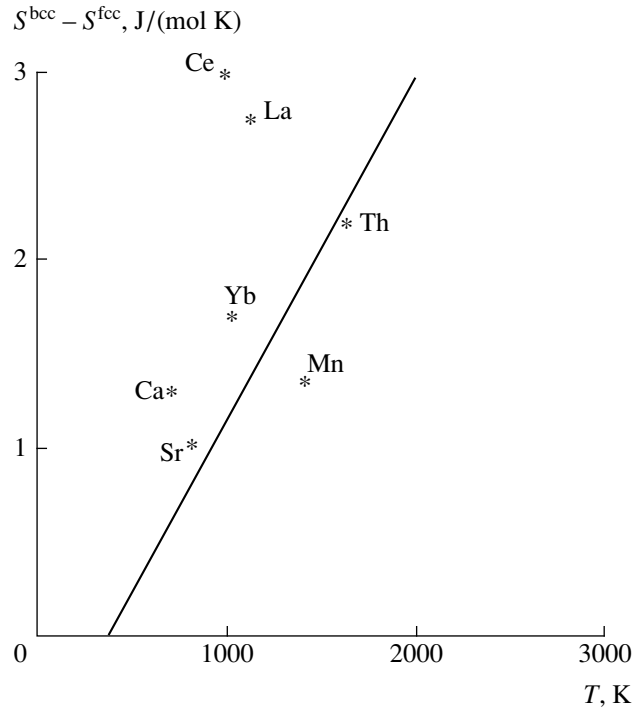**Fig. 3.** Comparison of the calculated entropy jump at fcc ⟶ bcc phase transition for pure components with the fcc structure as a function of phase transition temperature [relationship (23)] and the relevant experimental data [6].

(25) that the ratio $a^{fcc \longrightarrow bcc}/b^{fcc \longrightarrow bcc} = \theta_{av}$. Thus, as it follows from (25), $\Delta S^{fcc \longrightarrow bcc}(T) = 0$ at $T = \theta_{av}$. Using the values of coefficients in (23), we find that $\theta_{av} = 375.8$ K. Relationships (14), (20), and (21) obtained in this paper allow us, in particular, to evaluate the melting entropy for the metastable bcc phase of Ni [it equals 5.032 J/(mol K)] and the energy difference at 0 K between the fcc and bcc phases of Ni (3200 J/mol), if we take into account that, according to [6], $T_{Ni}^{bcc \longrightarrow L} = 1318$ K. These results agree well with *ab initio* calculations [12], according to which $\Delta H_{Ni}^{bcc \longrightarrow fcc}(0\ K) = 3$ kJ/mol, and also with the value of 3536 J/mol reported in [6] without details of the estimation method.

## REFERENCES

1. L. Kaufman and H. Bernstein, *Computer Calculation of Phase Diagrams* (Academic, New York, 1970; Mir, Moscow, 1972).

2. G. Cacciamani, Y. A. Chang, G. Grimvall, *et al.*, CALPHAD: Comput. Coupling Phase Diagrams Thermochem. **21**, 220 (1997).

3. P. Liang, H. L. Lukas, H. J. Seifert, and F. Aldinger, in *Proceedings of the Final Workshop "COST 507, Definition of Thermochemical and Thermophysical Properties to Provide a Database for the Development of New Light Alloys," Vaals, 1997* (Office Official Publ. Eur. Communities, Luxembourg, 1998), Vol. 1, pp. 114–127.

4. K. A. Putilov, *Thermodynamics* (Nauka, Moscow, 1971), pp. 278-292.

5. L. Kaufman, in *Phase Stability in Metals and Alloys*, Ed. by A. Rudman, J. Stringer, *et al.* (New York, 1967; Mir, Moscow, 1970).

6. A. Dinsdale, CALPHAD: Comput. Coupling Phase Diagrams Thermochem. **15**, 317 (1991).

7. N. Saunders, P. Miodovnik, and A. Dinsdale, CALPHAD: Comput. Coupling Phase Diagrams Thermochem. **12**, 351 (1988).

8. A. L. Udovskiĭ, in *Alloys for Nucleonics* (Nauka, Moscow, 1979), pp. 56–70.

9. V. L. Moruzzi, J. F. Janak, and K. Schwartz, Phys. Rev. B: Condens. Matter. **37**, 790 (1988).

10. L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Nauka, Moscow, 1976; Pergamon, Oxford, 1980), Part 1.

11. D. Hudson, *Statistics. Lectures on Elementary Statistics and Probability* (Geneva, 1964; Mir, Moscow, 1970).

12. H. L. Skriver, Phys. Rev. B: Condens. Matter. **31**, 1309 (1985).

*Translated by T. Galkina*