Optimization of the Heat Capacities of Diamond-Like Compounds

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Abstract: The fourth group of pure diamond-like elements is, in addition to diamond, silicon, germanium, alpha tin, and diamond-like lead. Flerovium (^{114}Fl) closes this group. There should be no other elements in this group according to the fine structure constant or the Sommerfeld constant $\alpha = e^2 / \hbar c$. The parameter α is a dimensionless quantity, and its numerical value is close to 1/137. The fine structure constant determines the limit of the maximum number of protons in the nucleus, at which electrons can still have stable orbits. In other words, this constant allows us to determine that with the highest probability, the last neutral atom of the periodic table will be element 137. In the case of diamond-like phases with a sphalerite structure, the limiting value of the heat capacity C_p falls on 114 elements (^{114}Fl) and has 30.5065 J mol-at^{-1} K^{-1} = 3.67 R or Ln (C_p/R) = 1.3.

Keywords: Heat capacity, diamond like phases, similarity method.

1. Introduction

The accumulated numerous experimental data and theoretical studies of the heat capacity of solid phases make it possible to carry out a generalizing thermodynamic analysis of diamond-like isostructural phases of 4-th group elements and their structural analogs of fluorite phases $A^{III}B^V$ and $A^{II}B^{VI}$.

The fourth group of pure diamond-like elements is, in addition to diamond, silicon, germanium, alpha tin, and diamond-like lead. Flerovium (^{114}Fl) closes this group. There should be no other elements in this group according to the fine structure constant or the Sommerfeld constant:

$$\alpha = e^2/\hbar c \qquad [1]$$

In this expression, e is the electron charge, c is the speed of light, $\hbar$ is the reduced Planck's constant, or Dirac's constant ($\hbar = h/2\pi$), which connects the amount of energy of electromagnetic radiation with its frequency. The parameter α is a dimensionless quantity, and its numerical value is close to 1/137. The fine structure constant determines the limit of the maximum number of protons in the nucleus, at which electrons can still have stable orbits. In other words, this constant allows us to determine that with the highest probability, the last neutral atom of the periodic table will be element 137. Researchers [2] share the same opinion.

The second important point of this work is the search for the limiting value of C_p for diamond-like structures.

2. Materials and Methods

In this work, the Similarity Method is applied to the critical analysis of heat capacities in the solid state of the diamond-like phases. The relationship of the heat capacities of $A^{III}B^V$ isostructural phases vs. the logarithm of the sum of atomic numbers of elements of the $A^{III}B^V$ phases were used to estimate the continuum above 298 K [3]. This method helps identify the reasonable values of heat capacities for the temperature region 0-T_mK.

The heat capacity at constant pressure C_p can be expressed as $C_p = C_v + (\alpha_{t\cdot\text{ex}})^2 \, BVT + cT$, where the first term is the lattice contribution; the second term is

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the contribution due to volume change, with B being the bulk modulus, V being the molar volume, and $\alpha_{t.ex}$ being the volume thermal expansion; the third term is the electron contribution with c known as the electronic constant [4]. The unknown parameters can be measured experimentally or calculated. For example, the calculated coefficients of linear thermal expansion for wurtzite AlN phase ($\alpha_{t.ex}$) were obtained in Ref. [5]. The difference between C_p and C_v increases for AlN with the increasing of temperature and compounds about 6% at 1,200 K. At a temperature close to $T_m = 4,840 \pm 50$ K, this value can be in the range of 3.7R-3.8R Jmol-at^{-1}K^{-1} [5]. It can be assumed that the maximum C_p of any solid at a temperature close to T_m does not exceed 4R =33.256 J mol-at^{-1}K^{-1}. In the case of diamond-like phases with a sphalerite structure, the limiting value of the heat capacity C_p falls on 114 elements (^{114}Fl) and has 30.5065 Jmol-at^{-1}K^{-1} = 3.67 R or Ln (C_p/R) = 1.3.

3. Results and Discussions

This quantity arises when plotting the isotherms C_p vs. Ln (N) or Ln (C_p/R) vs. Ln (N). The Maier-Kellye equation is quite suitable for describing the heat capacity of the high-temperature region. The heat capacities below this region should be considered as the heat capacities belonging to the low-temperature region. All isotherms of the heat capacities C_p can be described from a linear equation to a polynomial of the third degree. The obtained fan-shaped isotherms are localized at the point C_p = 30.5065 Jmol-at^{-1}K^{-1}=

3.67R or Ln (C_p/R) = 1.3 for Ln (^{114}Fl) = 4.7362. The heat capacities of Si, Ge, HgTe compound and the virtual point of flerovium, which is the only one for the entire series of isotherms, were used as the main reference points of the isotherms [6]. The C_p(T) of HgTe phase was calculated with help of our results [7] and literature data [8, 9]. The values of the heat capacities of the sphalerite's phases were found from the corresponding equations of the isotherms. The optimized heat capacity of α-Sn is relatively a little below the accepted one in Ref. [6]. This model gives the possibility to calculate the C_p of diamond-like Pb [10] (See Figs 1-3).

4. Conclusion

In this work, the proposed method made possible to describe the heat capacity of solid phases with a sphalerite structure from 0 K to the melting temperature T_m rigorously. The calculation of the heat capacities at low temperatures from 0 to 50 K was carried out using the reference values [6] of the heat capacities for silicon, germanium, mercury telluride and the ultimate value of the heat capacity of the fourth group which corresponds to flerovium. In this case it is convenient the dependence Ln C_p/R vs. Ln (N). For temperatures above 100K, it is advisable to use the C_p vs. Ln (N). The description of the heat capacity for HgS, HgSe, and Pb from 0 to T_mK was obtained for the first time. Correction of the heat capacities of sphalerite phases at low temperatures is carried out within the framework of the chosen model.
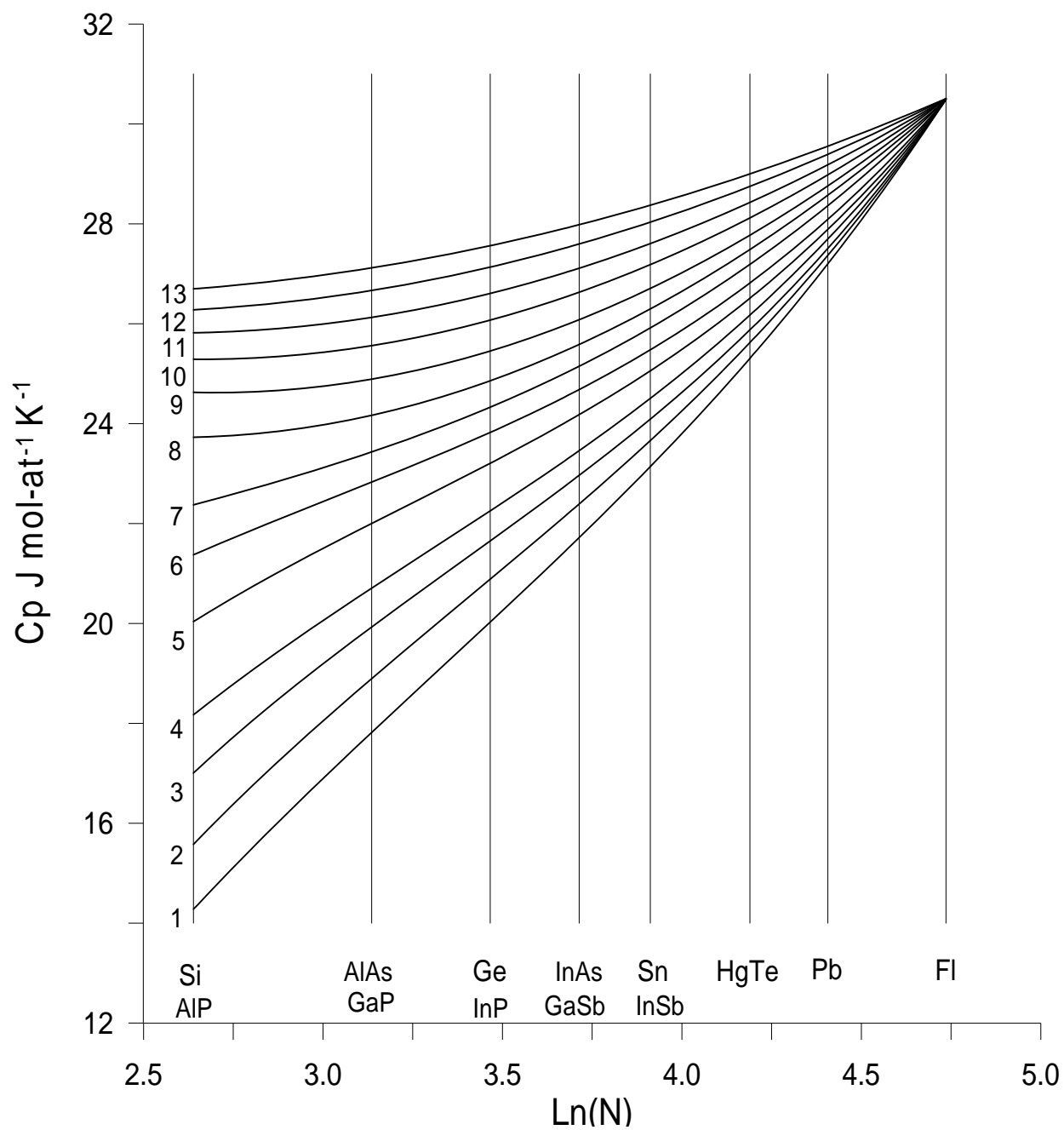
Fig. 1   Isotherms of the like-diamond phases. 1: 180 K; 2: 200 K; 3: 225 K; 4: 250 K; 5: 300 K; 6: 350 K; 7: 400 K; 8: 500 K; 9: 600 K; 10: 700 K; 11: 800 K; 12: 900 K; 13: 1,000 K.
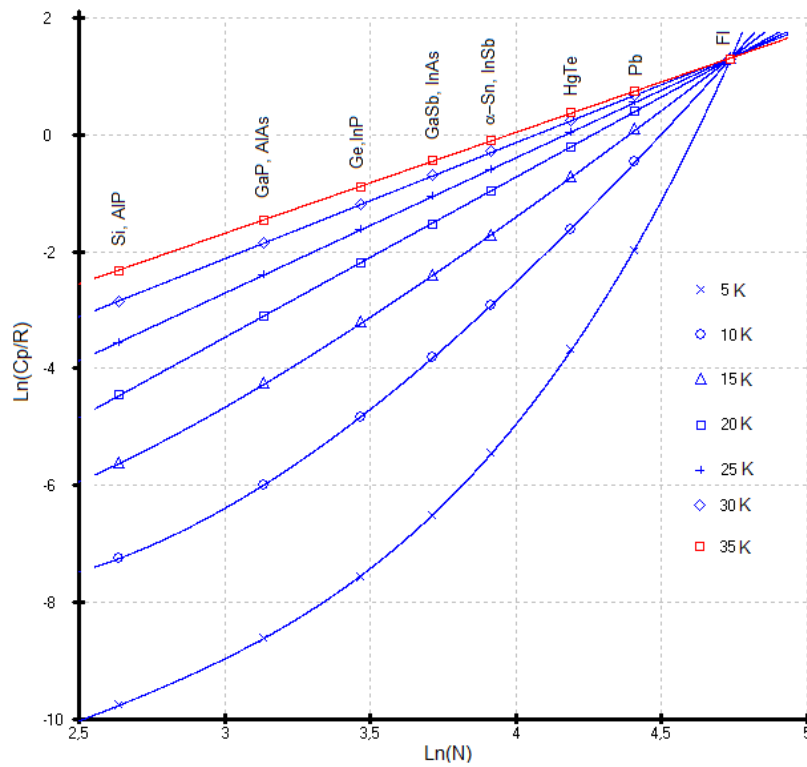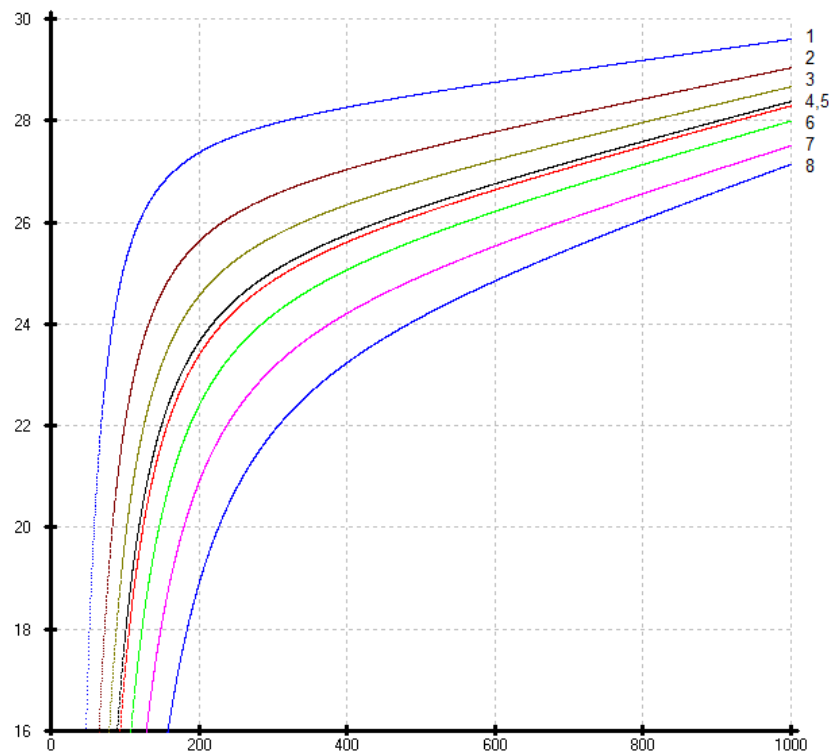
Fig. 2   Isotherms at low temperature 5-35 K.

Fig. 3   The heat capacities of diamond-like phases in the region of temperature 50-1,000 K. 1: Pb, 2: HgTe, 3: HgSe, 4: α-Sn (black), 5: HgS (red), 6: GaSb, 7: Ge, 8: GaP; The C_p of the diamond-like phases is localized at the point C_p = 30.5065 Jmol-at^{-1}K^{-1}= 3.67R or Ln (C_p/R) = 1.3 for Ln (^{114}Fl) = 4.7362.

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