A CALPHAD Helmholtz Energy Approach to Assess the Thermodynamic and Thermophysical Properties of Fcc Ag

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Abstract. In this paper, the CALPHAD Helmholtz energy approach, based on the Debye-Grüneisen model, has been used to calculate the thermodynamic and thermophysical properties of fcc Ag (Silver). Through this approach, thermodynamic properties, e.g. heat capacity and Gibbs energy, and thermophysical properties, e.g. volume, thermal expansion, bulk modulus are connected each other. The values of these properties can be simultaneously reproduced by several model parameters of the approach. Besides, the parameters have more physical significance, which ensures a high accuracy of the thermodynamic and thermophysical properties not only at normal pressure and temperature but also at extremely high pressures and low temperatures.

Introduction

CALPHAD[1-3]has nowadays become a mature and powerful technique for the study of thermodynamic properties of complex systems. The traditionalCALPHADGibbs energy approach requires many fitting parameters with polynomials. Therefore, the obtained parameters may have no physical and the internal relations among these properties are completely lost. As a consequence, abnormal behavior such as negative entropy may appear in temperature or pressure extrapolation.

In this work, we use the CALPHAD Helmholtz energy approach, which is mainly composed of Morse function, Debye-Grüneisen model and free electron Fermi gas model. And its applicability for fcc Ag is based on a previous work of Lu[4].By using this approach, both thermodynamic properties and thermophysical propertiescan be accurately reproduced in a wide range of temperature (from 0 K to melting point) and pressure (from ambient pressure to hundreds of GPa).

Method

For a system, with a constant temperature and volume, the Helmholtz energy F can be approximated comprises the total energy from ab initio electronic total energy calculations at T=0K,E_{tot}, the free energy of the vibrating lattice F_D and the contribution due to the thermal excitations of electrons,F_{el}:

$$\begin{aligned}F(T,V) &= E_{tot}(V) + F_D(T,V) + F_{el}(T,V)\\ &= E_{tot}(V) + E_D(T,V) - TS_D(T,V) + E_{el}(T,V) - TS_{el}(T,V) \quad (1)\end{aligned}$$

Where T is temperature and V is volume. $E_D$andS_D are the vibrational energy and entropy, respectively. E_{el}andS_{el} are the counterparts due to electronic excitations.

The total energy can be calculated from ab initio. In this work, it is represented by a Morse function (for example, [5]):

$$E(x) = -E_c\left(2e^{-\varphi(x-x_0)} - e^{-2\varphi(x-x_0)}\right) + E_{ref}(2)$$

In the present work， we use the Debye–Grüneisen model[6] to describe the contribution of

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vibrating lattices F_D.

$$E_D(T,V) = \frac{9}{8}N_a k_B \theta_D + 3N_a k_B T D\left(\frac{\theta_D}{T}\right) \quad (3)$$

$$S_D(T,V) = 3N_a k_B \left[\frac{4}{3}D\left(\frac{\theta_D}{T}\right) - \ln\left(1 - e^{-\theta_D/T}\right)\right] (4)$$

There are three well-known approximate ways to account for the Grüneisenparameterγ,and they can be combined using the following expression[7-9]:

$$\gamma(V) = \frac{1}{3}(\lambda - 1) - \frac{V}{2}\frac{\partial^2\left[PV^{(2/3)(\lambda+1)}\right]/\partial V^2}{\partial\left[PV^{(2/3)(\lambda+1)}\right]/\partial V} (5)$$

The Debye temperature $\theta_D$can be described as follow:

$$\theta_D(V) = DV^{2/3}\left[-\frac{\partial P(V)}{\partial V} - \frac{2(\lambda+1)}{3}\frac{P(V)}{V}\right]^{1/2} \quad (6)$$

The thermal excitations of electrons are not negligible for many materials, especially at cryogenic temperatures and at high temperatures near melting points. The simplest way to model the electronic excitations is the free electron Fermi gas model, which treats the conduction electrons as a freely moving electron gas and applies Pauli exclusion principle and Fermi–Dirac distribution.

In the free electron Fermi gas model, the heat capacity of the electron gas can be described as follows in order to account for data both at low and high temperatures:

$$C_V^{el} = \gamma_{el}T + a \cdot T^b \quad (7)$$

$\gamma_{el}$is treated as a function of volume, but temperature-independent,i.e.

$$\gamma_{el}(V) = \gamma_{el}^0\left(\frac{V}{V_0}\right)^{\alpha} \quad (8)$$

Where γ_{el}^0 is the Sommerfeld parameter at V_0, the equilibrium volume at 0 K and 1 bar. The parameter ‘α’ is a constant. Both parameters can be evaluated from the measured heat capacity at cryogenic temperatures and 1 bar, and the parameter ‘α’ is further adjustable to fit high temperature data.

Results and Discussions

With many experimental and theoretical data collected by literatures, we can undertake a comprehensive study. In the present work, the model parameters of fcc Ag are optimizedand listed in Table 1. Comparisons between the present calculations and experimental data of all kinds of properties for fcc Ag are shown in Figs 1–7.

Heat Capacity at 1 Bar, Cp

Lots of experimental data for heat capacity of fcc Ag can be collected in the literature. Data from AIP[10],Chatenier and Nobel[11], Bronson et al.[12,13]and Meads et al.[14] are adopted for the present assessment. Fig.1 shows good agreement among various experimental data with the calculation result. In Figure 1, both heat capacity with electronic contribution and without electronic contribution of Ag have been calculated in the present work and plotted as solid and dotted lines respectively.

Table 1: Model parameters that can be assessed or input and the values for fccAg.

Parameter	Unit	For fcc Ag
x_0	m	4.064717×10^{-10}
E_c	J/mol	2.460677×10^{5}
φ	—	1.758539
E_{ref}	J/mol	3.33258×10^{5}
ν	—	0.37
λ	—	0
γ_{el}^{0}	J/mol/K^2	6.090×10^{-4}
α	—	0.2

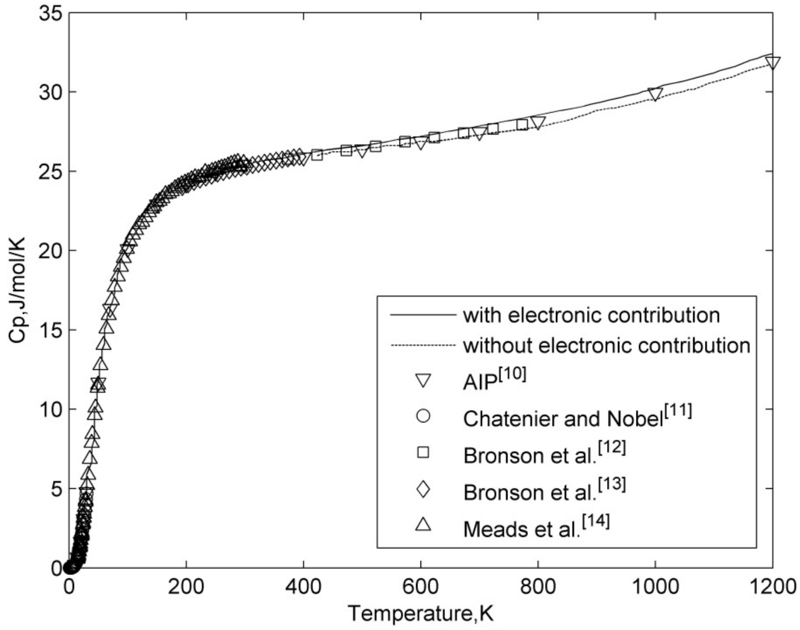

Fig. 1Heat capacity at atmospheric pressure compared with the experimental data for fcc Ag.

Electronic Contribution to Heat Capacity

The total heat capacity can be approximately expressed as:

$$C_P \cong C_v = \gamma_{el} T + AT^3 \quad (9)$$

On both sides of Eq. (9) divided by T:

$$\frac{C_p}{T} \cong \frac{C_v}{T} = \gamma_{el} + AT^2.(10)$$

In order toidentify the electronic contribution, we plot C_p/T as a function of T^2 and then fit a straight line on the graph, the intercept at $T^2 = 0$ provides the electronic coefficient of heat capacityγ_{el} at 0 K and constant A is given from the slope of the line.

The selected values for heat capacity at extremely low temperature between 0 K and 4 K come from Isaacs[15], Corak et al.[16], Green and Culbert[17]and Shinozakiet and Arrott[18] and the graph of C_p/T versus T^2 is plotted in Fig. 2.

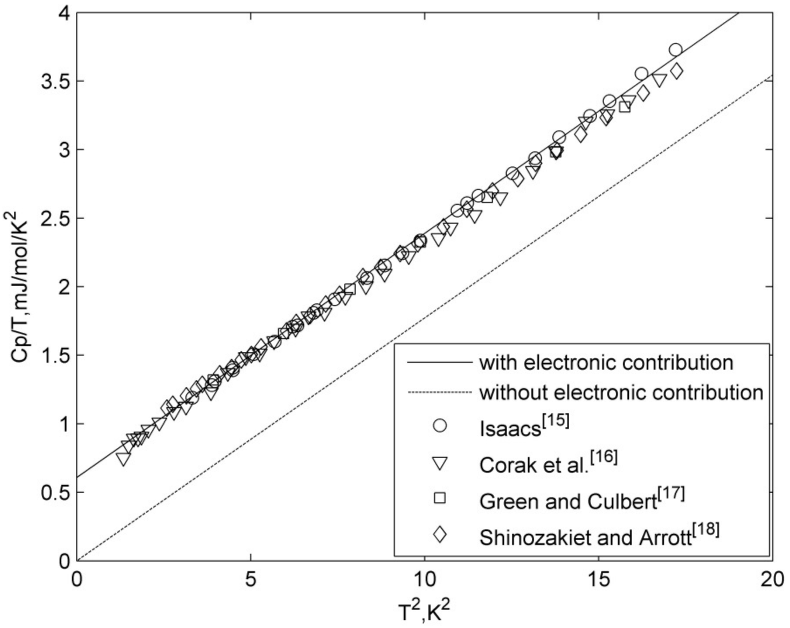

Fig.2 Calculated heat capacity of fcc Ag at cryogenic temperatures.

Molar Volume and the Coefficient of Linear Thermal Expansion (CTE) at 1 Bar

Literature data of thermal expansion coefficients (CTE) used for the assessent in the present work come from two manuals which are TPRC[19]and AIP[10]. Besides, other experimental data from literature are only used for comparison. The temperature dependence of the present calculated CTE at 1 bar along with the experimental data is shown in Fig. 3. The calculated results are somewhat lower than the experimental data from 200 K to 500 K. However, the agreement is acceptable.

Fig. 4 demonstrated the molar volumeat different temperatures with a representative selection of experimental data for molar volume for comparison. Obviously the present calculation matches the experimental data perfectly.

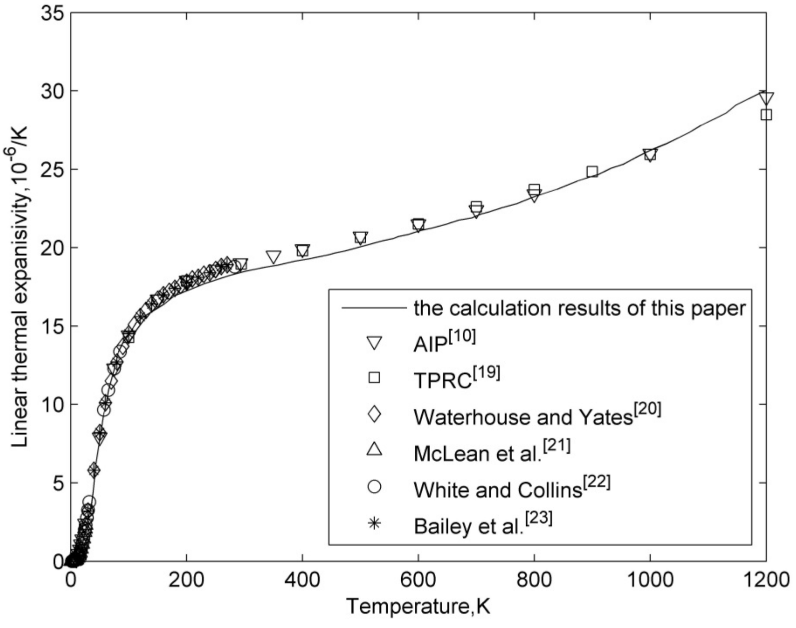

Fig. 3. Calculated coefficient of linear thermal expansion (CTE) at atmospheric pressure compared with the experimental data for fcc Ag.

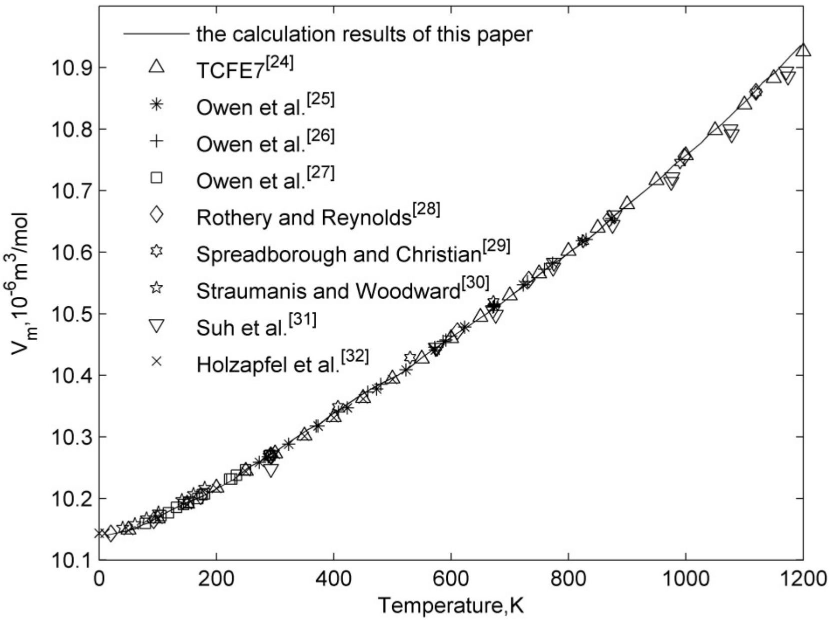

Fig. 4. Calculated molar volume of fcc Ag at atmospheric pressure compared with the experimental data.

Bulk Modulus at 1 Bar

Most experiment data[32-35]of bulk modulus in Fig. 5 obtained by measuring the adiabatic elastic constant c_{44},$\frac{1}{2}(c_{11}-c_{12})$,and $\frac{1}{2}(c_{11}+c_{12}+2c_{44})$. On the other hand, calculated results of bulk modulus by interatomic potential energy function and the Boltzmann distribution function can be gained in Mohazzabi[36] paper. The calculated result of the present work is plotted in Figure 5 along with the data from the literature. Our calculated result agrees well with most of these literature data and lower than Mohazzabi[36]and Biswas[35] data.

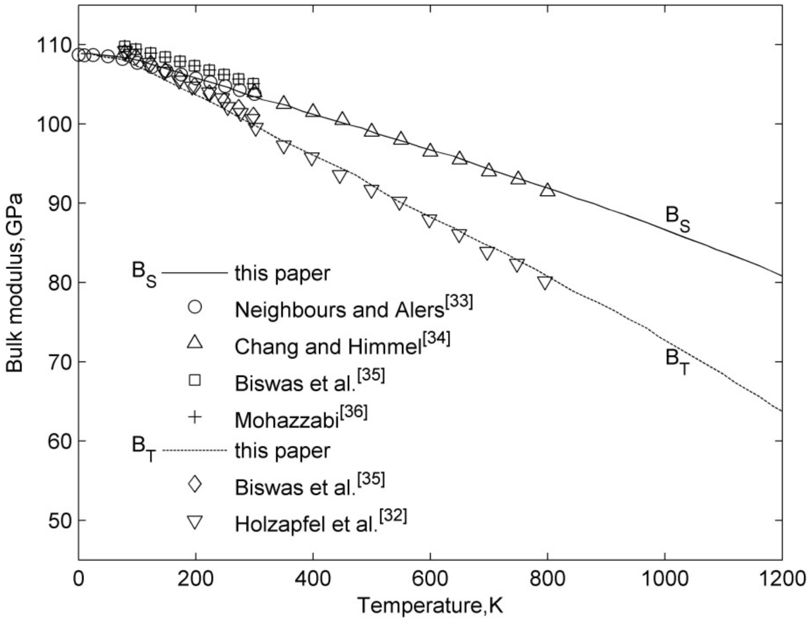

Fig. 5. Calculated adiabatic (B_S) and isothermal (B_T) bulk modulus at atmospheric pressure compared with the experimental data for fcc Ag.

Properties at High Pressures

Fig.6 demonstrates the pressure dependence of the molar volume of fcc Ag. The consistency between the present calculation and experimental data of Akahamaet al.[37]is quite excellent. Akahama et al. measured the atomic volume of Ag up to 155GPa. This was performed by powder x-ray diffraction experiments.

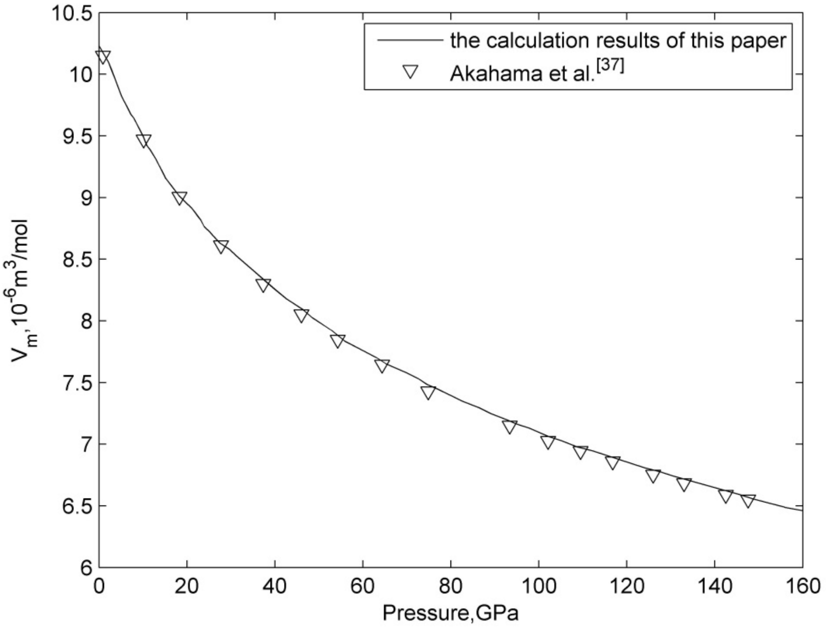

Fig. 6. Calculated molar volume of fcc Ag at 298 K and high pressures.

Conclusions

In summary, we have successfully assessed and calculated the thermodynamic and thermophysical properties of fcc Ag simultaneously through the present CALPHAD approach, which is superior to the traditional CALPHAD modeling. A set of model parameters with physical significance has been obtained through assessments. The thermodynamic and thermophysical properties were calculated by these parameterswith high accuracy. The present approach is adequate to describe the properties not only at normal pressure and temperature but also at extremely high pressure and low temperatures with high accuracy and without any abnormal behavior.

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