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# Thermodynamic properties of MgO, Be, and W: a simplified computational approach

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**Abstract**

The recently developed classical mean-field potential (MFP) approach was employed to calculate the Helmholtz free energy for periclase (MgO), the Hugoniot equation of state for beryllium (Be) at pressures up to 2000 GPa, and the families of isentropic curves for tungsten (W). The excellent agreement between the theory and the experiment further demonstrated the high accuracy and applicability of the MFP approach.

## 1. Introduction

There are many areas, including high-velocity impact, the properties of materials in the mantle and the core of the Earth, controlled thermonuclear fusion of laser-compressed pellets (in another words, geophysics, astrophysics, particle accelerators, fission and fusion reactors), where we could have a better understanding if we had accurate acknowledge of the thermodynamic properties/equation of state (EOS) of condensed matter at high pressure and high temperature.

Experimentally, the thermodynamic properties of condensed matter at megabar pressures can now be probed in both static, low-temperature diamond-anvil-cell (DAC) experiments [1, 2] and in dynamic, high-temperature shock-wave experiments [3–8]. The DAC technique is suitable for the ordinary laboratory in which samples can be studied under controlled conditions. Using laser heating and refinements in instrumentation, temperatures of about 3000 K can be reached up to pressures of the order of 200–300 GPa. Even higher temperatures and pressures can be achieved by shock-wave methods. Accordingly, there is an urgent need to develop a theoretical method that can be used to facilitate the interpretation of the new data at extreme experimental conditions. With the tremendous technical advances in recent years, the DAC and the shock-wave techniques have been brought closer together; it is also highly desirable to compare and evaluate the measurements made by the two techniques.

  

Theoretically, for the temperature range above 300 K and towards 100 000 K, a realistic *ab initio* prediction of the thermodynamic properties of materials still remains an important challenge to the theory of condensed matter. In this regard, molecular dynamics simulation might in principle be the best tool, but the potential representing the interaction between the particles is somewhat too time-consuming to calculate in the *ab initio* framework. On the other hand, quasi-harmonic theory achieves great success for slightly lower temperatures. However, difficulties will be encountered when temperature becomes higher or the lattice potential deviates seriously from a harmonic one.

## 2. Calculational method

In a couple of papers [9], we have developed a classical mean-field potential (MFP) approach for calculating the various thermodynamic quantities of condensed matter without involving any adjustable parameter.

In this work, we use MgO, Be, and W to further test the MFP approach. To calculate the 0 K total energy, we employ the full-potential LAPW [10] method within the GGA [11]. In all the thermodynamic calculations, we do not make any attempts to analytically fit the LAPW calculated points, since the fitting might alter the original LAPW results. The raw LAPW numerical points are directly taken as the input, and more densely packed points with the lattice constant step of 0.005 au are derived by cubic spline interpolation for the convenience of one-dimensional numerical enumeration. From the lattice constant region of the LAPW calculations, extrapolations using the Lennard-Jones/Morse functions are invoked.

## 3. Results and discussion

*Periclase (MgO):*

An enormous theoretical and experimental effort has been devoted to obtaining the thermodynamic parameters of MgO. One major attraction is that MgO is one of the most important constituents of the Earth's lower mantle. Knowledge of its thermal properties at simultaneously high temperatures and pressures is the necessary input for a better understanding of many geophysical phenomena. Another attraction is that MgO has also been considered as a potential internal pressure standard, since no pressure-induced phase transition is observed at pressures up to 200 GPa. The Helmholtz free energy of MgO calculated here is compared with those from the empirical thermodynamic calculation by Anderson and Zou [12] in figure 1. Although there is excellent agreement, one may note a small deviation on the small-volume (high-pressure) side. At present, it is difficult to judge which is preferable between the present calculations and those of Anderson and Zou, because in the calculation of Anderson and Zou an extra empirical assumption regarding the Grüneisen parameter was used, while the present calculation can give a more accurate high-temperature EOS.

*Beryllium (Be):*

Beryllium is one of the key materials in reactors. The accurate determination of the high-pressure and high-temperature EOS of beryllium plays a critically important role in the field of inertial confinement fusion (ICF). The major motivations for taking Be as one of prototypes lie in the following facts:

(i) Very recently, Nellis *et al* [5] published EOS data on Be at shock pressures of 400–1000 GPa and Cauble *et al* [7] gave absolute EOS data for the TPa (1 TPa = 1000 GPa) regime.

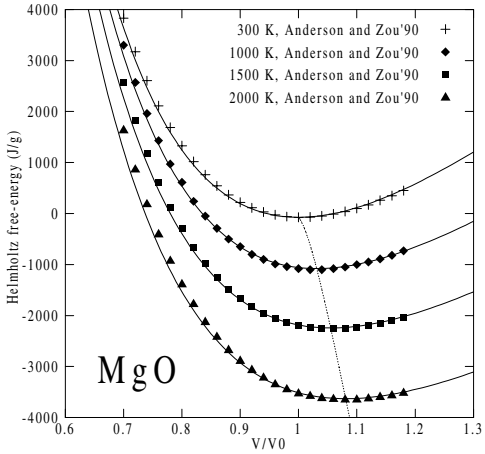


**Figure 1.** The Helmholtz free energy of MgO. The solid curves represent the results calculated here for $T = 300$, 1000, 1500, and 2000 K, the dotted curve marks the local minima of the calculated curves, and the plus signs, diamonds, squares, and triangles represent the results of empirical thermodynamic calculations by Anderson and Zou [12].

(ii) When shock-wave pressure is increased from 0.1 to 5 TPa, matter will undergo a continuous transition from condensed matter to dense plasma, and the theoretical understanding of this is a long-unresolved and interesting scientific issue.

(iii) The metal Be has been considered a 'representative substance': when it is shock compressed to $P$ above a few Mbar (1 Mbar = 100 GPa), it is strongly coupled, partially ionized, and warm condensed matter/fluid, with unusually strong electron–ion interaction, and is extremely difficult to model.

The Hugoniot EOS calculated here for pressures up to 2000 GPa is plotted in figure 2 using the $D$–$u$ (shock velocity against mass velocity) representation, together with the experimental data. Again, our calculated result falls well within the experimental uncertainties.

*Tungsten (W):*

For W, we have done two kinds of calculation:

(i) isentropic release from the principal Hugoniot; and
(ii) reduction of the measured shock-wave data to the room temperature isotherm.

The calculated $P$–$T$ curves for isentropic release and the principal Hugoniot for W are plotted in figure 3 together with those obtained from the empirically derived temperatures of McQueen *et al* [3]. Shown in figure 3 also are the high-pressure melting data for W measured very recently by Boehler and co-workers [2]. The agreement between our calculation and the empirical result of McQueen *et al* is very good except in the very high-pressure region, where the thermal electronic contribution has been neglected by McQueen *et al*.

One result that one cannot ignore in figure 3 is that the curves calculated here for isentropic release cross the DAC melting data given by Boehler and co-workers [2] in an abnormal way, i.e. when pressure decreases along the isentropic curve, the metal W will turn from a liquid to a solid. This is in contrast to the case for iron in the geophysical isentropic model, where the Earth's inner core is solid while the Earth's outer core is liquid.

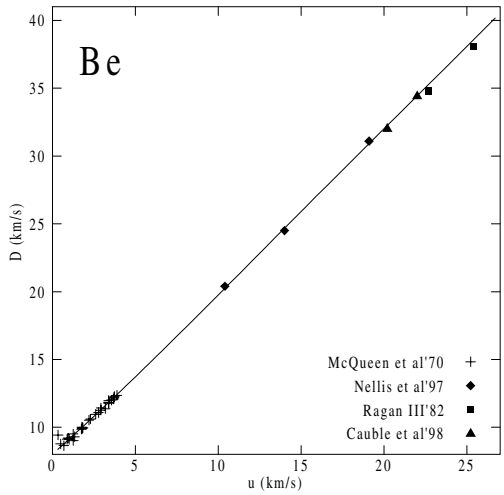


**Figure 2.** The principal Hugoniot of Be. The solid line represents the present calculations and the plus signs, diamonds, squares, and triangles represent the experiments of McQueen *et al* [3], Nellis *et al* [5], Ragan [6], and Cauble *et al* [7], respectively.

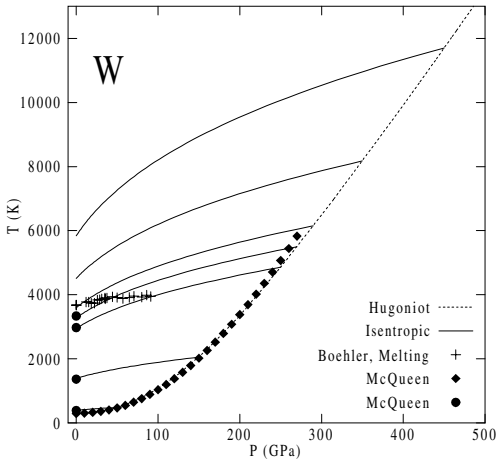


**Figure 3.** The $P$–$T$ EOS of W. The solid curves represent the curves calculated here for isentropic release at Hugoniot pressures of 450, 350, 290, 270, 250, 150, and 50 GPa from the top to the bottom, respectively. The dotted curve is the temperature calculated here along the principal Hugoniot. The diamonds show the empirically derived Hugoniot temperatures [3] and the solid circles the empirically derived temperatures [3] after isentropic release at the Hugoniot pressures of 270, 250, 150, and 50 GPa from top to bottom, respectively. The plus signs show the DAC melting data of Boehler and co-workers [2].

The traditional reductions of shock data to isothermal or isotropic states require specific heat and Grüneisen parameter values that are not well known. In the absence of experimental constraints, workers often make the plausible assumption that $\gamma/V = \text{constant}$. Since we have explicitly calculated the Helmholtz free energy $F(V, T)$ as functions of $V$ and $T$, all other thermodynamic parameters can be calculated.

The present reduction method is very simple. It just uses the MFP approach to calculate the thermal volume expansion of the principal Hugoniot relative to the 300 K isotherm. In figure 4

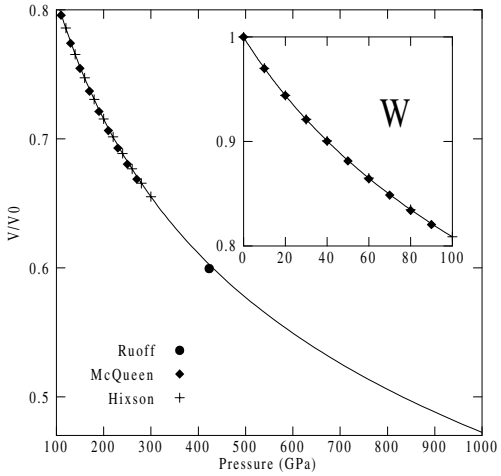


**Figure 4.** The 300 K EOS for W. Solid curve: the present reduction; solid circle: the DAC result of Ruoff *et al* [1]; diamonds: the empirical reduction of McQueen *et al* [3]; plus signs: the empirical reduction of Hixson and Fritz [8]. The inset shows the low-pressure regions.

we demonstrate the results of the present reductions of shock-wave data. For comparison, we also show the DAC experimental result Ruoff *et al* [1], the empirical reduction of McQueen *et al* [3], and the empirical reduction of Hixson and Fritz [8]. One notes that the present result and that of Hixson and Fritz are almost indistinguishable.

## 4. Summary

In summary, the thermodynamic properties of one oxide, MgO, one low-$Z$ metal, Be, and one heavy transition metal, W, have been calculated using the MFP approach. The excellent agreement between the theory and the experiment supports the MFP approach once again.

## Acknowledgments

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## References

[1] Ruoff A L, Xia H and Xia Q 1992 *Rev. Sci. Instrum.* **63** 4342
[2] Errandonea D, Schwager B, Ditz R, Gessmann C, Boehler R and Ross M 2001 *Phys. Rev.* B **63** 1321041–4
[3] McQueen R G, Marsh S P, Taylor J W, Fritz J N and Carter W J 1970 *High-Velocity Impact Phenomena* ed R Kinslow (New York: Academic) p 293, 530
[4] Kennedy G C and Keeler R N 1972 *American Institute of Physics Handbook* 3rd edn, ed D E Gray (New York: McGraw-Hill) pp 4–39
[5] Nellis W J, Moriarty J A, Mitchell A C and Holmes N C 1997 *J. Appl. Phys.* **82** 2225
[6] Ragan C E III 1982 *Phys. Rev.* A **25** 3360
[7] Cauble R *et al* 1998 *Phys. Rev. Lett.* **80** 1248
[8] Hixson R S and Fritz J N 1992 *J. Appl. Phys.* **71** 1721

[9] Wang Y 2000 *Phys. Rev.* B **61** R11 863
Wang Y, Chen D and Zhang X 2000 *Phys. Rev. Lett.* **84** 3220
[10] Blaha P, Schwarz K and Luitz J 1999 *WIEN97, a Full Potential Linearized Augmented Plane Wave Package for Calculating Crystal Properties* Technical University of Vienna (ISBN 3-9501031-0-4)
This is an improved and updated Unix version of the original copyrighted WIEN code, which was published by Blaha P, Schwarz K, Sorantin J and Trickey P 1990 *Comput. Phys. Commun.* **59** 399
[11] Perdew J P, Burke S and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[12] Anderson O L and Zou K 1990 *J. Phys. Chem. Ref. Data* **19** 69