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Ab initio thermodynamics of metals: Al and W

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We present an *ab initio* pseudopotential calculation of thermodynamic properties of aluminum and tungsten. The difference of almost one order of magnitude of the experimental linear thermal expansion coefficients of these materials is well reproduced by our calculations and explained in terms of microscopic quantities. The specific heat is reported and compared with available experimental data. Mode-Grüneisen parameters, Debye temperature, and temperature dependence of isothermal and adiabatic bulk modulus as well as the pressure dependence of compressibility complete the work.

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I. INTRODUCTION

The implementation of perturbation theory into a density functional framework has permitted, in the last decade, the *ab initio* calculation of the phonon dispersion of semiconductors[1,2] and metals.[3] The success of these calculations has also driven increasing interest into lattice properties that cannot be described by the harmonic approximation as, e.g., the thermal expansion of a solid,[4] the phonon lifetime,[5] or the shift[6] of phonon frequencies when the temperature is changed. These calculations, in good agreement with experimental data, are performed using norm-conserving pseudopotentials, that improves the description of electronic bonds in different environment compared to semiempirical pseudopotentials used in previous calculation of dynamical properties (for a review see, e.g., Ref. 7).

While in principle the temperature dependence of the phonon frequency depends on phonon anharmonic contributions as well as electronic ones,[6,7] the thermodynamic properties of solids are commonly studied within the quasiharmonic approximation.[8] The change of phonon frequencies due to thermal expansion of the lattice was studied in Ref. 4 within the quasi-harmonic approximation to compute the Grüneisen parameter and the linear thermal expansion coefficient of semiconductors. The same approximation was used to calculate the dependence of the lattice parameter on the isotopic composition of simple[9] and compound semiconductors[10] with good agreement with experimental data.[11] In these works the phonon frequencies and their derivatives were computed at zero temperature and the thermal expansion coefficient is calculated by varying only the temperature of the thermal occupation number in the corresponding formula. This approach can provide accurate results compared to the experimental data up to above the room temperature.[4,6,10] Recently the thermodynamic properties of silver[12] were computed solving the equation of state at different temperatures to find the equilibrium volume; the various ingredients necessary to evaluate the thermal properties were obtained performing *ab initio* calculations at different volumes. In the present work we computed only dynamical quantities at the zero temperature volume, as done in Refs. 6 and 10; however, the procedure adopted here describes satisfactorily the thermodynamic properties far above room temperature where the simplest approximation of Refs. 6 and 10 fails.

The procedure we used takes into account in a simple self-consistent way the thermal expansion of the lattice. We derived expressions that are based on zero-temperature quantities and that permit an accurate computation of the thermal expansion as well as other thermodynamic properties up to very high temperature (roughly about four times the Debye temperature).

In this work we present an *ab initio* calculation of the thermodynamical properties of aluminum, one of the most commonly used metals, and of tungsten, which is largely employed in high-technology devices.[13] The latter presents at room temperature one of the smallest thermal expansion coefficients among metallic elements,[14] whereas, at the same temperature, the value for aluminum is more than five times larger.

The paper is organized as follows. In Sec. II we give a brief description of the theory to state the approximations we have used and to introduce notations and formulas for further discussion; in Sec. III we give an account of the technicalities used to compute the dynamical matrix, within the density functional framework introduced by Baroni, Giannozzi, and Testa[1] and used in successive developments (see, for example, Ref. 2). Finally, in Sec. IV we present the results we have obtained by implementing the perturbation theory of Sec. II for aluminum and tungsten and compare them with available experimental data.

II. THEORY

In the quasiharmonic approximation the Helmholtz free energy at a given volume V and temperature T is given by

$$F(V,T) = U_0(V) + F_{vib}(V,T), \tag{1}$$

where $U_0(V)$ is the zero-temperature classical energy, while

$$F_{vib}(V,T) = \frac{1}{2}\sum_{n,\mathbf{q}} \hbar\omega(n,\mathbf{q}) + k_B T \sum_{n,\mathbf{q}} \ln(1 - e^{-\hbar\omega(n,\mathbf{q})/k_B T}) \tag{2}$$

represents the vibrational contribution to F. The frequency of the nth mode, $\omega(n,\mathbf{q})$, depends on the unit-cell volume and the masses of the constituent atoms. From the definition of pressure[15] we obtain the equation of state

$$P=-\left(\frac{\partial F}{\partial V}\right)_T, \tag{3}$$

which, for a given temperature and pressure, produces an implicit expression for the equilibrium volume. In order to obtain a simple expression for the temperature dependence of volume (since we are interested only in the case where $P=0$, in the following we will drop the pressure index) we introduce the linear thermal expansion coefficient

$$\alpha(T)=\frac{1}{3V}\frac{\partial V}{\partial T}. \tag{4}$$

By differentiating Eq. (3) with respect to the temperature it is easy to obtain the expression for the linear thermal expansion coefficient at constant pressure:

$$\alpha(T)=-\frac{1}{6B_T(T)V(T)T}\sum_{n,\mathbf{q}}\hbar\omega(n,\mathbf{q})\gamma(n,\mathbf{q})\frac{\xi}{1-\cosh\xi}, \tag{5}$$

where we have defined

$$\xi=\frac{\hbar\omega(n,\mathbf{q})}{k_BT},$$

and the Grüneisen parameter of mode $n,\mathbf{q}$ is

$$\gamma(n,\mathbf{q})=-\frac{V}{\omega(n,\mathbf{q})}\frac{\partial\omega(n,\mathbf{q})}{\partial V}, \tag{6}$$

where V is the unit-cell volume at temperature T and the isothermal bulk modulus $B_T\equiv V(\partial^2F/\partial V^2)|_T$ is given by

$$B_T=V\frac{\partial^2U_0}{\partial V^2}-\frac{1}{2V}\sum_{n,\mathbf{q}}\frac{\hbar\omega(n,\mathbf{q})}{\cosh\xi-1}[\xi\gamma^2(n,\mathbf{q})+\beta(n,\mathbf{q})\sinh\xi], \tag{7}$$

where we have introduced the concavity parameter

$$\beta(n,\mathbf{q})\equiv-\frac{V^2}{\omega(n,\mathbf{q})}\frac{\partial^2\omega(n,\mathbf{q})}{\partial V^2}, \tag{8}$$

which is proportional to the second derivative of the phonon frequencies and which describes the deviation from the linear behavior of the volume dependence of the frequency $\omega(n,\mathbf{q})$. At $T=0$ K the second term in the square brackets of Eq. (7) gives the zero-point energy contribution to the bulk modulus (while the first is vanishing).

In the quasiharmonic approximation the phonon frequencies are functions of the temperature only through their volume dependence. From the definition [Eq. 4] of the linear thermal expansion coefficient the unit-cell volume at temperature T can be written as

$$V=V_0\exp\left[3\int_0^T\alpha(T')dT'\right], \tag{9}$$

where V_0 indicates the zero-temperature unit-cell volume. From Eq. (5) $\alpha(T)$ depends only on the volume and on the phonon frequencies (and their derivatives); since in the quasiharmonic approximation the latter are assumed to depend only on the volume, we obtain two coupled equations that can be easily solved.

In the present computation we assume that the phonon frequencies, in the range of the temperature we are interested, can be well approximated by a Taylor expansion up to the second order on the volume:

$$\omega(n,\mathbf{q})=\omega_0(n,\mathbf{q})\left[1-\gamma_0(n,\mathbf{q})\left(\frac{V-V_0}{V_0}\right)-\frac{1}{2}\beta_0(n,\mathbf{q})\times\left(\frac{V-V_0}{V_0}\right)^2\right]. \tag{10}$$

where the subscript 0 denotes the quantities at $T=0$. With this approximation the Grüneisen parameter becomes

$$\gamma(n,\mathbf{q})=\frac{V\omega_0(n,\mathbf{q})}{V_0\omega(n,\mathbf{q})}\left[\gamma_0(n,\mathbf{q})+\beta_0(n,\mathbf{q})\left(\frac{V-V_0}{V_0}\right)\right]. \tag{11}$$

These expressions are functions only of zero-temperature quantities that can be computed once and for all. The only other ingredient is the linear thermal expansion coefficient that can be calculated through Eqs. (5) and (9).

As a by-product we can easily obtain the specific heat at constant volume (pressure) defined as $C_V=-T(\partial^2F/\partial T^2)|_V$ $[C_P=-T(\partial^2F/\partial T^2)|_P]$. From Eq. (1) we obtain

$$C_V=-k_B\frac{1}{2}\sum_{n,\mathbf{q}}\frac{\hbar\xi^2}{1-\cosh\xi}, \tag{12}$$

while the specific heat at constant pressure can be obtained using the relation[15]

$$C_P=C_V+9\alpha^2B_TVT. \tag{13}$$

In order to compute correctly the specific heat at low temperature we have to take into account that, approaching to the absolute zero, only the acoustic phonons close to the Brillouin-zone center contribute to C_V. In this region the acoustic branches are linear with respect the wave vector, $\omega(n,\mathbf{q})=c(n,\hat{\mathbf{q}})q$ (where $\hat{\mathbf{q}}\equiv\mathbf{q}/|\mathbf{q}|$). We define the average of the inverse third power of the long-wavelength phase velocities of the three acoustic modes over the solid angle Ω:

$$\frac{1}{c^3}\equiv\frac{1}{3}\sum_{n=1}^{3}\int\frac{d\mathbf{\Omega}}{4\pi}\frac{1}{c(n,\hat{\mathbf{q}})}. \tag{14}$$

To the lowest order in temperature the expression for the specific heat per unit volume is[8]

$$\frac{C_V}{V}=\frac{2\pi^2}{5}k_B\left(\frac{k_BT}{\hbar c}\right)^3, \tag{15}$$

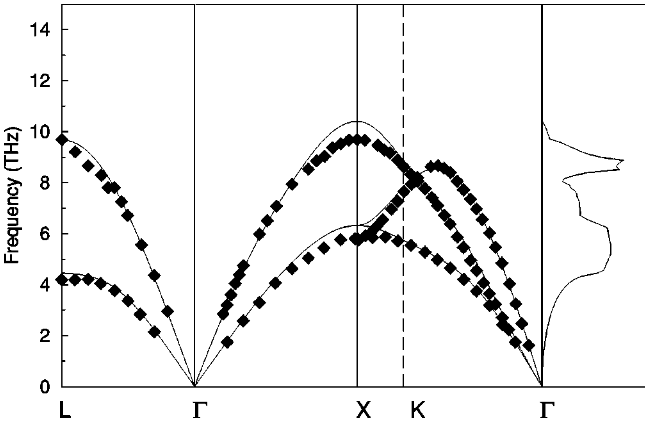

FIG. 1. One phonon density of states and phonon dispersion relation of aluminum along some high-symmetry directions of the Brillouin zone at absolute zero. Diamonds denote experimental data at $T=80$ K (from Ref. 24).

which gives the correct power behavior for vanishing temperature. The Debye temperature can be obtained through the relation

$$\Theta=\frac{\hbar c}{k_B}(6\pi\rho)^{1/3}, \tag{16}$$

where ρ is the inverse of the unit cell volume.

Finally, since the bulk modulus is often obtained from the measure of the elastic constants, it is useful to introduce the adiabatic bulk modulus that can be obtained from the formula

$$B_S=B_T\frac{C_P}{C_V}. \tag{17}$$

Once the quantities are computed at $T=0$ K, the temperature as well as the pressure dependence of the above quantities at a given temperature[16] can be obtained. In the latter case one has to consider the volume as the independent variable. At a given volume the pressure is obtained from Eq. (3).

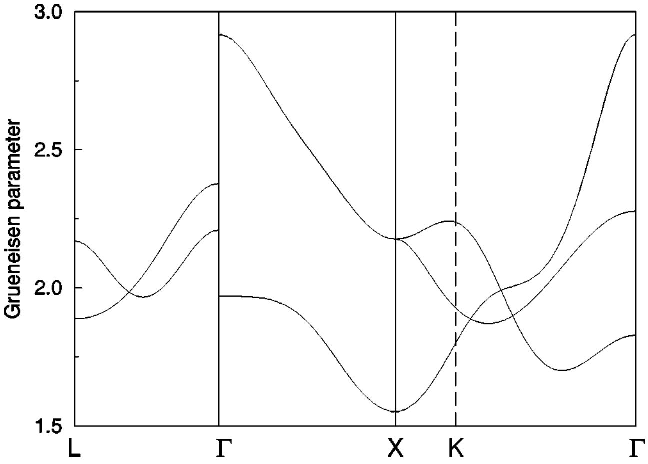

FIG. 2. Mode-Grüneisen parameter of aluminum along some high-symmetry directions of the Brillouin zone. Note the the discontinuity at the Γ point.

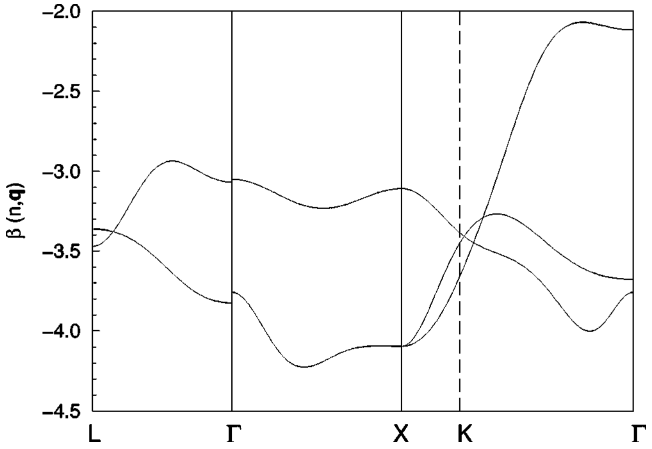

FIG. 3. Concavity parameter $\beta(n,\mathbf{q})$ of aluminum along some high-symmetry directions of the Brillouin zone. Note the the discontinuity at the Γ point.

III. COMPUTATIONAL DETAILS

We have performed our first-principles calculation by using the adiabatic approximation within a plane-wave pseudopotential scheme. The phonon-dispersion curves are obtained by finding the eigenvalues of the dynamical matrix that is computed from the linear response to a phonon displacement employing the density functional perturbation theory.[1,2] The first and second derivatives of the phonon frequencies with respect to the volume are computed by using perturbation theory according to the scheme proposed in Ref. 10.

We used separable norm-conserving pseudopotentials[17,18] generated in a similar way as those of Ref. 3 and 19 to calculate phonon frequencies of aluminum and tungsten, respectively. In our calculations we have used the local-density approximation for the exchange and correlation energy calculated by Monte Carlo techniques by Ceperley and Alder,[20]

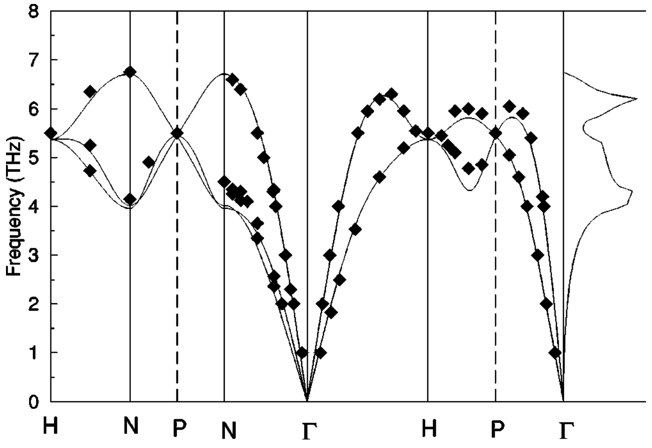

FIG. 4. Same as Fig. 1 but for tungsten with experimental data at $T=296$ K from Ref. 25.

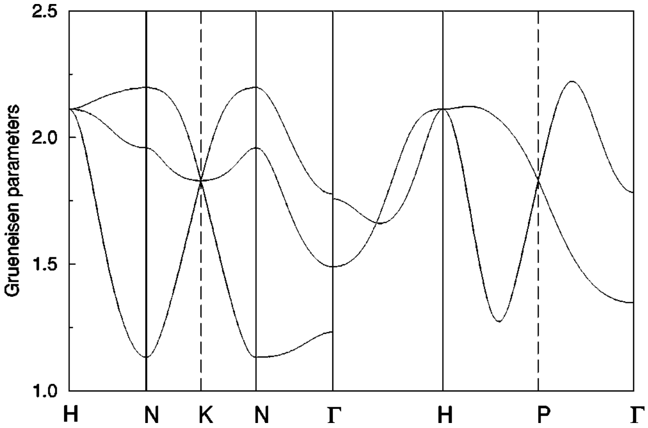

FIG. 5. Same as Fig. 2 but for tungsten.

as interpolated by Perdew and Zunger.[21] Our basis set was truncated to a kinetic energy cutoff of 16 Ry for aluminum and to 28 Ry for tungsten. The Brillouin-zone integration over electronic states necessary to compute the dynamical matrix was performed using the special-point and smearing techniques.[3,22,23] We used 146 special points for aluminum and 55 for tungsten in the irreducible wedge of the Brillouin zone, to ensure the convergence of the dynamic properties.[3,19] The reciprocal space integration over phonon states [the **q** points appearing in Eqs. (5), (7), and (12)] was performed by using 408 special points for aluminum and 240 for tungsten. The volume dependence of the total energy U_0 appearing in Eq. (7) is obtained by fitting the first-principles results by the Murnagan equation of state.

IV. RESULTS

Aluminum and tungsten are metals that crystallize in a face-centered cubic structure and a body-centered cubic structure, respectively. We have computed their thermodynamic properties according to the scheme exposed in Sec. II.

Figures 1, 2, and 3 display, respectively, the phonon dispersion relation, the mode Grüneisen parameters, and the beta parameters at zero temperature of aluminum along some high-symmetry directions in the Brillouin zone. Figures 4, 5, and 6 show the corresponding quantities for tungsten. The parameters γ and β of aluminum are generally larger in magnitude than those of tungsten. Approaching the Brillouin zone center the acoustic branches vanish linearly with a slope that depends on the direction. As a consequence the Grüneisen parameter γ as well as the concavity parameter β are discontinuous at the Γ point. The phonon branches reproduce those in Refs. 3 and 19 obtained by the same method. Our results for the Grüneisen parameter of aluminum differ in a significant way from those obtained using an empirical pseudopotential.[26] This difference can be attributed by the fact we use norm-conserving pseudopotential that provides a better description of the valence states.

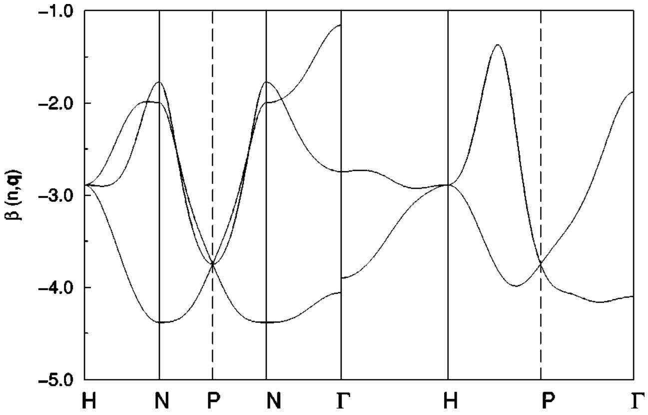

FIG. 6. Same as Fig. 3 but for tungsten.

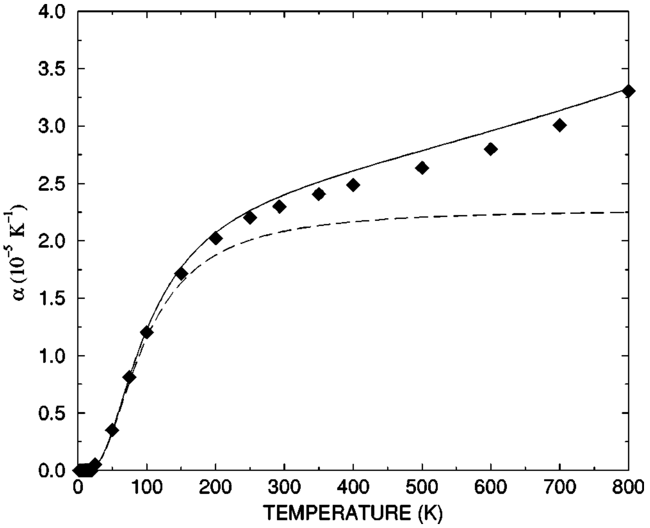

FIG. 7. Linear thermal expansion coefficient in aluminum. The results obtained with (without) the thermal expansion of the unit-cell volume are denoted by a solid (dashed) line. Diamonds indicate experimental data from Ref. 14.

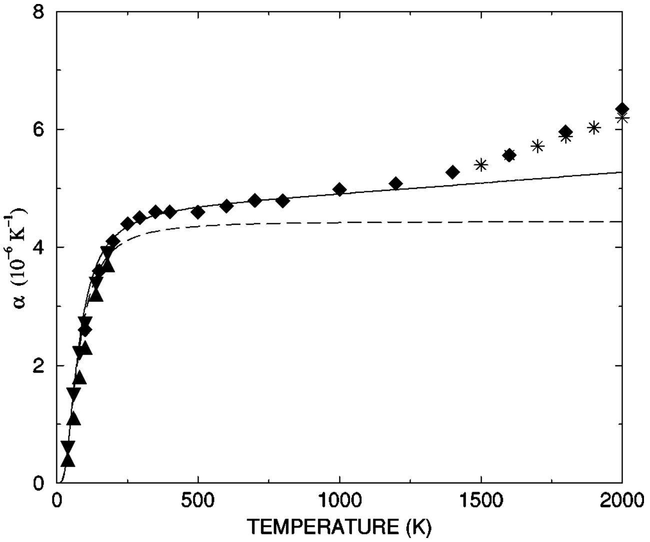

FIG. 8. Same as Fig. 7 but for tungsten. Diamonds, stars, triangles up and down indicate experimental data from Ref. 14, Ref. 27, Ref. 28, and Ref. 29, respectively.

Our results for the linear thermal expansion coefficient of

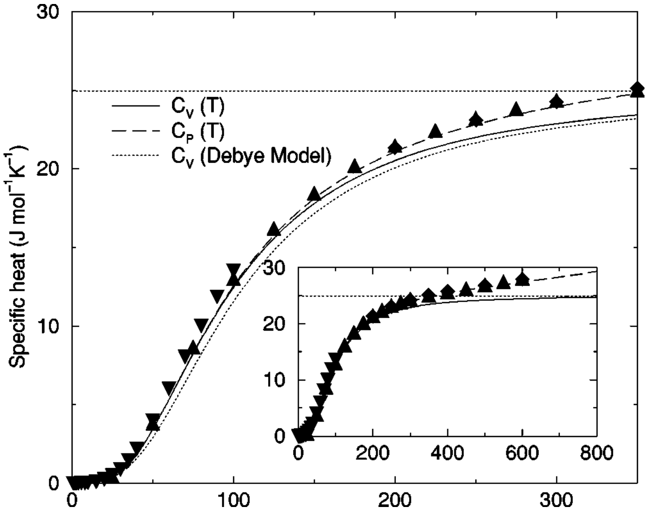

FIG. 9. Temperature dependence of specific heat of aluminum. The specific heat at constant volume is denoted by a solid line; the specific heat at constant pressure is denoted by a dashed line. The result of the Debye model is denoted by a dotted line. Triangles up and down denote experimental data of C_P (respectively from Ref. 7 and Ref. 30). The horizontal line is the C_V classical value.

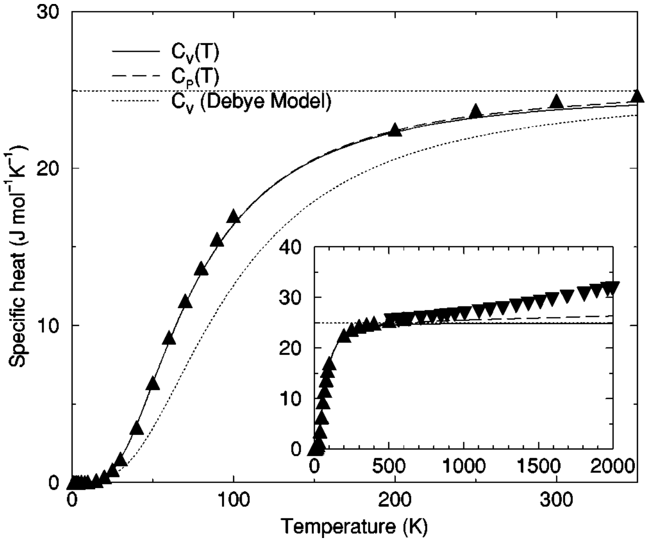

FIG. 10. Same as Fig. 9 but for tungsten. Triangles up and down denote experimental data (respectively from Ref. 31 and Ref. 30).

aluminum and tungsten are displayed in Figs. 7 and 8. The solid line is our theoretical result obtained according to the procedure exposed in Sec. II and compared with the experimental data from Ref. 14 denoted by diamonds. Our results describe the thermal expansion coefficient up to high temperature. For aluminum there is no appreciable difference between theory and experiment over the whole range of temperatures where the experimental data are available; for tungsten a deviation of the experimental data can be noticed only above 1500 K, when higher-order terms in the expansions (10) and (11) and other anharmonic processes are expected to become important.

To show the contribution of the self-consistent procedure we have performed a calculation using the same zero-temperature quantities but with the temperature dependence given only by the Bose-Einstein factor, as done in Ref. 10, to compute the linear thermal expansion coefficient up to room temperature. The results are displayed in Figs. 7 and 8 as dashed lines. While this approximation is accurate up to 300 K, it gives an underestimation of the linear thermal expansion coefficient at high temperature.

The difference in the magnitude of the linear thermal expansion coefficient of aluminum and tungsten can be attributed to two different mechanisms according to the results exposed above. One is the contribution due to microscopic dynamical quantities (phonon frequencies, Grüneisen, and concavity parameters), i.e., the contribution of the terms in the sum in Eq. (5). The magnitude of the Grüneisen parameters of aluminum is larger than that of tungsten. Further the phonon energies of aluminum are, on average, smaller than those of tungsten. At finite temperature this fact favors the thermal occupation of phonons in aluminum with respect to tungsten. As a consequence the microscopic contribution is larger in aluminum than tungsten. The other mechanism responsible for the difference of the linear thermal expansion coefficient is related to the product between bulk modulus and unit-cell volume by which the right-hand side of Eq. (5) is divided. At zero temperature the product $B(T)V(T)$ of tungsten is about three times that of aluminum. The combination of these two contributions is responsible for the different magnitude of the linear thermal expansion coefficient of the two materials.

TABLE I. Calculated bulk modulus, lattice constant, and Debye temperature at $T=0$ K, and elastic constants at room temperature. Values in parentheses denote experimental data from Ref. 30 unless explicitly stated. Here da_0/dM is the derivative of the lattice parameter with respect to the atomic mass.

Compound	B(0)	a_0	Θ	$\frac{da_0}{dM}$	C_{11}	C_{12}	C_{44}
	(Kbar)	(a.u.)	(K)	(10^{-9} amu^{-1})	(10^{11} N/m^2)	(10^{11} N/m^2)	(10^{11} N/m^2)
Al	794 (783)	7.50 (7.63)	462 (428) [a]		1.15 (1.07)	0.52 (0.60)	0.32 (0.28)
W	3200 (3142) [b]	6.05 (5.97)	387 (400) [a]	−1.56	4.68 (5.22)	2.18 (2.04)	2.04 (1.61)

[a] From Reference 14.

[b] From Reference 32.

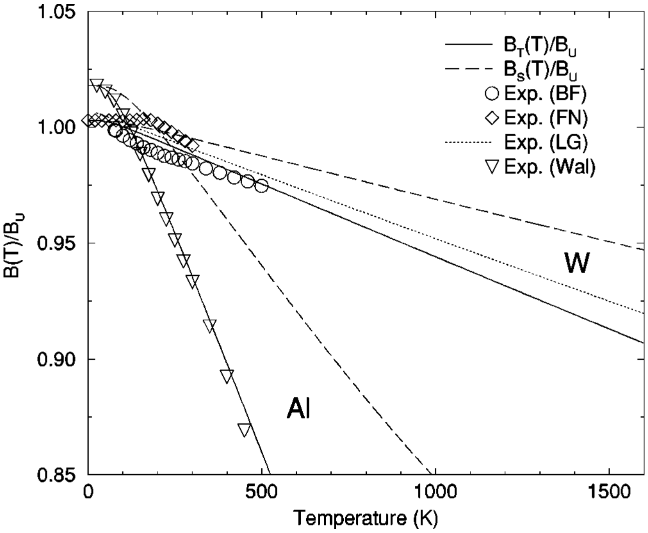

FIG. 11. Temperature dependence of isothermal (solid line) and adiabatic (dashed line) bulk modulus of aluminum and tungsten. $B_U \equiv V(\partial^2 U/\partial V^2)$ is the contribution of the zero-temperature classical energy to the bulk modulus. The deviation from unity at $T=0$ is the contribution due to zero-point motion. Circles, diamonds, and dotted line denote tungsten experimental data (from Refs. 33, 32, and 34 respectively). Triangles denote aluminum experimental data (from Ref. 7).

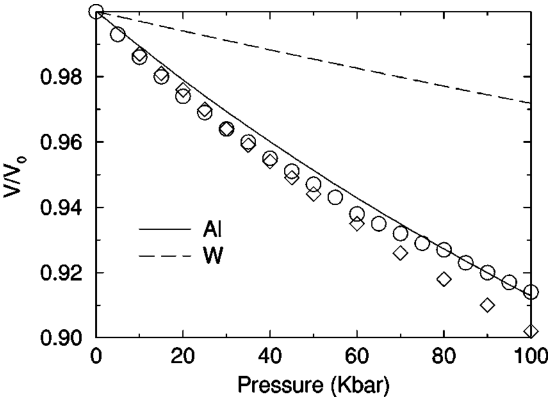

FIG. 12. Pressure dependence of unit-cell volume of aluminum (solid line) and tungsten (dashed line) at room temperature (V_0 denote the volume at zero pressure). Circles and diamonds denote aluminum experimental data (from Ref. 14).

In Figs. 9 and 10 we display the specific heat of aluminum and tungsten, respectively. The solid (dashed) line is our result for the specific heat at constant volume (pressure), while triangles denote experimental data of C_P.[7,30] The horizontal line is the classical value of $C_V = 24.9$ J mol^{-1} K^{-1}. We have also performed a calculation of the specific heat using a Debye model and the experimental data of Table I; the results underestimate the experimental data and this discrepancy is significant for tungsten. In contrast, our first-principles results agree well with experiment for aluminum, while for tungsten the agreement is less satisfactory at high temperature, where the quasiharmonic approximation is expected to fail.

The Debye temperature, computed according to Eq. (16) is reported in Table I. Due to the larger Debye temperature of aluminum, the specific heat of this material vanishes faster than that of tungsten when approaching the absolute zero.

The computed bulk modulus at zero temperature is displayed in Table I for both materials. The bulk modulus includes the zero point motion contribution that is found to be of a few percent for aluminum (1.8%) but negligible for tungsten (0.3%). Figure 11 displays the temperature dependence of the isothermal (solid line) and adiabatic (dashed line) bulk modulus of aluminum and tungsten. The experimental data of the adiabatic bulk modulus of tungsten are also reported. The percentage variation of the bulk modulus with respect the zero-temperature value is bigger in aluminum than expected since this material presents a larger thermal expansion coefficient than tungsten.

Since, to the best of our knowledge, the dependence of the lattice parameter on atomic mass is known only for few semiconductors, we have investigated this effect in the metals we have considered. While aluminum does not have stable isotopes, natural tungsten is a mixture of five different isotopes, ^{180}W (isotopic abundance 0.13%), ^{182}W (26.3%), ^{183}W (14.3%), ^{184}W (30.67%), and ^{186}W (28.6%). We have computed the derivative of the lattice constant with respect to the atomic mass. The result is reported in Table I and is about three orders of magnitude smaller than in zinc-blende semiconductors.[9,10] This is due to the presence in the latter materials of optical branches that give the largest contribution to the change of the lattice constant.[10]

It is well known that the elastic constants of a material are related to the slope of the acoustic phonon modes near the zone center;[8] so we can obtain the former quantities and their temperature dependence from our database. However, at the Γ point the acoustic frequencies are vanishing, so they are expected to be more sensitive to the convergence and to numerical errors than the phonon branches far from the Brillouin-zone center. For this reason this procedure is less accurate for the computation of the elastic constants by straining the unit cell, as done, e.g., in Ref. 35. The elastic constants at room temperature are displayed in Table. I with experimental data. The deviations from the experiment are, in this case, about two to three times the ones reported in Ref. 35.

To test the capability of the theory to predict the change of volume under pressure we have computed the compressibility, i.e., the inverse of the bulk modulus, at different pressure. Our results are displayed in Fig. 12; as usual,[14] they are reported as the relative variation of the unit-cell volume to compare with experimental data.

V. CONCLUSIONS

In this paper we have seen how, performing only first-principles calculation at $T=0$, it is possible to compute the temperature dependence of several thermodynamic quantities within the quasiharmonic approximation requiring a small amount of extra computations. Our results agree with available experimental data up to very high temperature and provide useful predictions where the experimental data are lacking. This scheme can be also applied to compute the high-pressure thermodynamic behaviors. We have given a realistic prediction of the effect of isotopic substitution in metals with one atom per unit cell.

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