

First principles calculation of the lattice specific heat of magnesium and beryllium

G.J. Vázquez and L.F. Magaña

Instituto de Física, Universidad Nacional Autónoma de México

Apartado postal 20-364, 01000 México, D.F., Mexico

e-mail: fernando@fenix.ifisicacu.unam.mx

Recibido el 21 de mayo de 1996; aceptado el 23 de octubre de 1997

We have used a local, first principles pseudopotential to calculate the interionic potential and, from it, the phonon dispersion curves, the phonon spectra and the lattice specific heat of beryllium and magnesium. This kind of pseudopotential has been used successfully for the prediction of properties of other materials. Our results are in good agreement with experiment. The pseudopotential is constructed from the electronic density induced around a nucleus in the metal electron gas. This electron density is previously calculated using density functional theory.

Keywords: Lattice specific heat

Utilizando un pseudopotencial local, obtenido a partir de primeros principios, calculamos el potencial interiónico y a partir de éste, las curvas de dispersión fonónicas, los espectros fonónicos y finalmente, los calores específicos de la red cristalina para berilio y magnesio como funciones de la temperatura. Este tipo de pseudopotencial ha sido utilizado anteriormente, con éxito, para la predicción de propiedades de otros materiales. Nuestros resultados están en buena concordancia con los resultados experimentales. El pseudopotencial se construye a partir de la densidad electrónica inducida alrededor de un núcleo en el gas de electrones del metal. Esta densidad electrónica se calcula previamente por medio de la teoría de funcionales de la densidad.

Descriptores: Calor específico de la red cristalina

PACS: 62.20; 63.20

1. Introduction

One of the main contributions to the specific of metals comes from the ion lattice. The first step in our present *ab-initio* calculation is to obtain the interionic potential. For simple metals this can be constructed using pseudopotential theory. Pseudopotentials may be phenomenological or may be obtained from first principles. It is clear at present that a pseudopotential determined in an empirical way can not be considered as weak always [1]. In this way its use in the calculation of the interionic potential, and from this, properties of the metal is not justified.

In this work we construct an *ab-initio*, local pseudopotential following the method proposed by Manninen *et al.* [2] who followed the work of Rasolt and Taylor [3]. From the pseudopotential we calculate the interionic potential. Then, using the harmonic approximation, we obtain the phonon dispersion curves and the phonon spectra and from these, the corresponding curves for the specific heat for each material.

In previous work we used this approach successfully to predict some properties of simple metals mainly with cubic symmetry. Among these properties are the lattice specific heat, elastic constants, phonon limited resistivity [4–9], the prediction of the critical temperature of superconducting metallic hydrogen and also the volume dependence of the critical temperature of superconducting aluminum [10, 11]. Recently it was applied to predict elastic constants of magnesium (which has hexagonal symmetry), successfully too [12].

In this report we apply the method to predict the lattice specific heat of two materials with hexagonal symmetry: Be and Mg.

The starting point is the calculation of the displaced electronic densities around a nucleus in an electron gas with an equilibrium density corresponding to each metal (Be and Mg respectively). This is done using the density functional formalism [13, 14] and the model of the nucleus embedded into a jellium vacancy [2]. Taking into account that in the pseudopotential formulation the pseudodensity must not contain wiggles near the ion, these wiggles in the calculated density had to be removed.

From this pseudodensity we define a local pseudopotential, as we explain below.

We have used atomic units (*i.e.*, magnitude of the electron charge = electron mass = $\hbar = 1$). The energy is given in double Rydbergs.

2. Interionic potential

The interionic interaction is given from pseudopotential theory and linear response theory [2] by

$$\Phi(r) = \left(\frac{z^2}{r}\right) \left[1 + \frac{2}{\pi z^2} \int \frac{dq \sin(qr) \epsilon(q) [\delta n(q)]^2}{q [1 - \epsilon(q)]}\right], \quad (1)$$

where r is the separation between the two ions, Z is the charge of the metal ion, $\varepsilon(q)$ is the dielectric response function of the electron gas, and $\delta n(q)$ is the Fourier transform of the induced charge pseudodensity.

For the model of the nucleus embedded in a jellium vacancy, the induced electronic density is calculated by taking the difference [2]

$$\delta n(r) = n(r) - n_\nu(r) - 2 \sum_b |\psi_b(r)|^2, \quad (2)$$

where $n(r)$ is calculated with the total charge density corresponding to a nucleus located at the center of a vacancy in jellium, and $\delta n(r)$ is the electron density around a jellium vacancy alone.

The bound states are given by $\psi_b(r)$. Charge neutrality of the metal is a necessary condition. We calculated $\delta n(q)$, the Fourier transform of the displaced electron pseudodensity, taking the Fourier transform of the density given by Eq. (2), after smoothing. In this smoothing, the conditions that the electronic charge is conserved and that $\delta n(r)$, and $(\partial \delta n(r)/\partial r)$ are continuous, are imposed [2]. It is convenient to mention that in the pseudopotential formulation, the pseudodensity must not contain wiggles near the ion, and the induced density calculated from density functional theory contains those wiggles in that region due to the orthogonalization of conduction states to core orbitals. The unscreened pseudopotential form factor, $\nu(q)$, is related to $\delta n(q)$ by

$$\nu(q) = \frac{4\pi \delta n(q) \varepsilon(q)}{q^2 [1 - \varepsilon(q)]}. \quad (3)$$

Equation (3) is used to obtain an effective local pseudopotential, which in linear response will give the exact induced displaced electronic density outside the region of smoothing. In this way some of the non linear screening effects are included into the pair potential calculated from this pseudopotential. The dielectric function we used satisfies by construction, the compressibility theorem which is important in connection with the interionic potential [15, 16]. It is given by [15, 16]

$$\varepsilon(q) = 1 + \left(\frac{4\pi}{q^2} \right) G(q) \quad (4)$$

where

$$G(q) = \frac{G_o(q)}{1 - \left(\frac{4\pi}{k_{tf}^2} \right) G_o(q)(1 - L)} \quad (5)$$

and $G_o(q)$ is the usual Lindhard polarizability, k_{tf} is the Fermi-Thomas screening constant, and L is the ratio

$$L = \frac{\partial \mu / \partial r_s}{\partial E_F / \partial r_s}, \quad (6)$$

where μ is the chemical potential, E_F is the Fermi energy and $\mu(r_s) = E_F(r_s) + \mu_{xc}(r_s)$. Here, $\mu_{xc}(r_s)$ is the exchange-correlation contribution to the chemical potential. Using the

expression of Gunnarson and Lundquist [17], for exchange-correlation (which we used in the calculation of the induced electronic density) the value of L is:

$$L = 1 - \left(\frac{4}{9\pi^4} \right)^{\frac{1}{3}} r_s \left(1 + \frac{0.6213}{r_s + 11.4} r_s \right). \quad (7)$$

With the induced charge pseudodensity and the dielectric function already given, we used Eq. (1) to calculate the interionic potential.

3. Phonons and specific heat

From the interionic potential we calculated the phonons and associated force constants, using the harmonic approximation. Magnesium and Beryllium have an hexagonal close packed structure (HCP). For this structure, we had a good convergence with four neighbor shells. From the interionic potentials we can find the force constants and, from these, the corresponding phonon dispersion curves. To calculate the phonon frequency distribution, $F(\nu)$, from the force constants obtained in the phonon dispersion curve, we followed the method of Gilat and Raubenheimer [18].

From $F(\nu)$, the specific heat is calculated numerically by the integral

$$C_\nu = \frac{\partial \langle E \rangle}{\partial T} = k_B \int_0^{\nu_m} d\nu \left(\frac{\beta h \nu}{2} \right) \frac{F(\nu)}{\sinh(\beta h \nu / 2)}, \quad (8)$$

where $\langle E \rangle$ is the average of the internal energy, T is the temperature and ν_m is the maximum phonon frequency.

The resulting phonon dispersion curve for beryllium is in Fig. 1, where we compare with experimental values. Although pseudopotential nonlocality can be especially important for Be, our calculated phonon frequencies are in good agreement (10%) with experiment. This agreement is also satisfactory for Mg (20%), Fig. 2. In Figs. 3 and 4 we show our calculated lattice specific heats and compare with experimental results. We can see a good agreement. This is specially true for temperatures where the harmonic approximation applies [it is well known that the harmonic approximation is valid for temperatures below $\Theta_D/50$, with Θ_D the Debye temperature (for Be, $\Theta_D = 1000\text{K}$ and for Mg, $\Theta_D = 400\text{K}$). See, for example, Ref. 19. For larger temperatures a deviation starts to occur. For high temperatures the anharmonic effects become more important, as it happens with the specific heat [20–22]. Finally, it is important to notice that even when this method was applied very successfully to metals with cubic symmetry, its extension to metals with hexagonal symmetry had to be explored. This extension is not obvious. This is because in the calculation of the electronic pseudodensity, by solving the density functional formalism equations, a spherical symmetry is taken. However, results are satisfactory for the specific heat for these two hexagonal symmetry materials too.

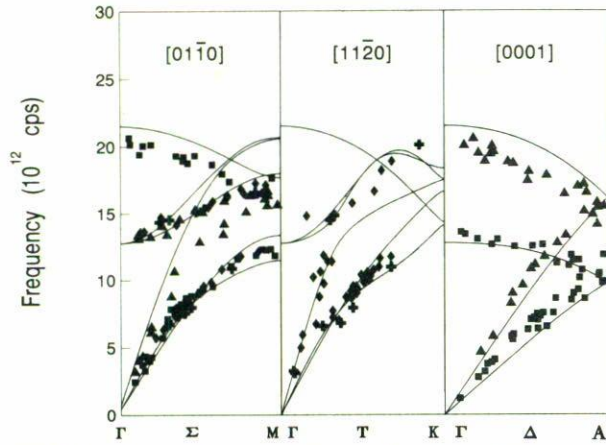


FIGURE 1. Phonon dispersion curve for beryllium. Experimental results: ■ ▲ ◆ ✕ (Ref. 23). We are using $r_s = 1.87 a_0$, where a_0 is the Bohr radius. Results from this work: —.

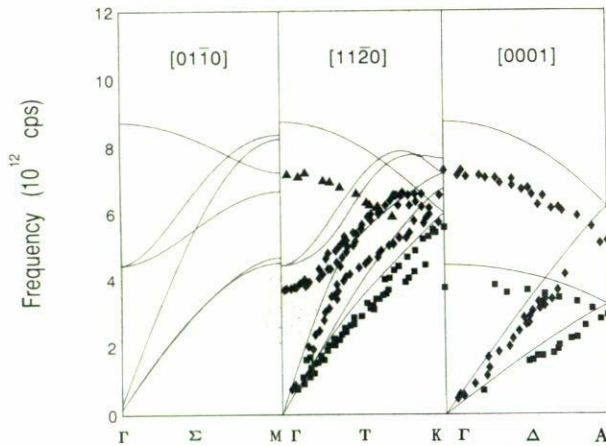


FIGURE 2. Phonon dispersion curve for magnesium. Experimental results: ■ ▲ ◆ ✕ (Ref. 24). We are using $r_s = 2.66 a_0$, where a_0 is the Bohr radius. Results from this work: —.

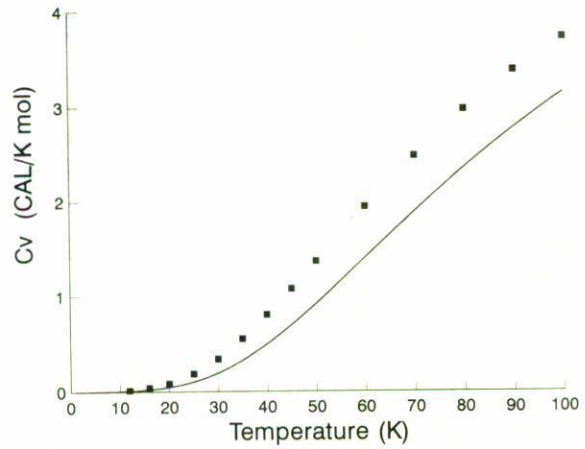


FIGURE 3. Lattice specific heat for beryllium. Results from this work: —; experimental results: ■ (Ref. 25). For this material, $\Theta_D = 1000\text{K}$.

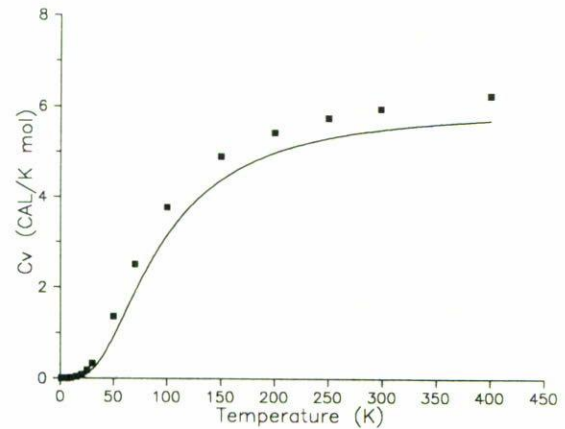


FIGURE 4. Lattice specific heat for magnesium. Results from this work: —; experimental results: ■ (Ref. 26). We are using $r_s = 2.66 a_0$. For this material, $\Theta_D = 318\text{K}$.

1. A.K. Gupta, P. Jena, and K.S. Singwi, *Phys. Rev. B* **18** (1978) 2712.
2. Manninen, P. Jena, R.M. Nieminen, and J.K. Lee, *Phys. Rev. B* **24** (1981) 7057.
3. R. Rasolt and R. Taylor, *Phys. Rev. B* **11** (1975) 2717.
4. L.F. Magaña and G.J. Vázquez, *Phys. Rev. B* **36** (1987) 4700.
5. G.J. Vázquez and L.F. Magaña, *Phys. Lett. A* **122** (1987) 267.
6. L.F. Magaña and G.J. Vázquez, *J. Phys. F* **17** (1987) L237.
7. G.J. Vázquez and L.F. Magaña, *J. Phys. France* **49** (1988) 497.
8. G.J. Vázquez and L.F. Magaña, *J. Phys. CM* **2** (1990) 623.
9. E.A. Mendoza, G.J. Vázquez, and L.F. Magaña, *J. Phys. France* **50** (1989) 3489.
10. L.F. Magaña and G.J. Vázquez, *Phys. Rev. B* **38** (1988) 9495.
11. J.S. Arellano and L.F. Magaña, *Rev. Mex. Fís.* **36** (1990) 596.
12. L.F. Magaña and G.J. Vázquez, *J. Phys.: Condensed Matter* **7** (1995) L393.
13. H. Hohenberg and W. Kohn, *Phys. Rev.* **136** (1964) B964.
14. W. Kohn and L.J. Sham, *Phys. Rev.* **140** (1965) A1133.
15. M.S. Duesbery and R. Taylor, *Phys. Rev. B* **7** (1970) 2870.
16. R. Taylor, *J. Phys. F* **8** (1978) 1699.
17. O. Gunnarson and B.I. Lundqvist, *Phys. Rev. B* **13** (1976) 4274.
18. G. Gilat and L.J. Raubenheimer, *Phys. Rev.* **144** (1966) 390.
19. *American Institute of Physics Handbook* (1957) p. 4.
20. S.H. Taole, H.R. Glude, and R. Taylor, *Phys. Rev. B* **18** (1978) 2643.
21. C.A. Krier, R.S. Craig, and W.E. Wallace, *J. Phys. Chem.* **61** (1957) 522.
22. D.L. Martin, in *Proc. Phys. Soc., London, Sec. A* **254** (1960) 433.
23. R.E. Schmunk, R.M. Brugger, P.D. Randolph, and K.A. Strong, *Phys. Rev.* **128** (1962) 562.
24. A.J. Pindor and R. Pynn, *J. Phys. C* **2** (1969) 1037.
25. R.W. Hill and P.L. Smith, *Philos. Mag.* **44** (1953) 636.
26. R.S. Craig *et al.* *J. Am. Chem. Soc.* **76** (1954) 238.