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# The lattice specific heat and elastic constants of sodium and potassium from first principles

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Received 1 August 1989, in final form 8 November 1989

**Abstract.** We have calculated the constant volume lattice specific heat and the elastic constants of sodium and potassium using local, first-principles pseudopotentials. This kind of pseudopotential has been useful in the calculation of properties of aluminium and lithium and in the calculation of the phonon limited resistivity of sodium and potassium. It is obtained from the induced electron density around an ion in the corresponding electron gas. From each pseudopotential we obtained the interionic potential, the phonons (which are calculated by the harmonic approximation) and finally the lattice specific heat and the elastic constants for sodium and potassium. The results are in good agreement with experimental results.

## 1. Introduction

In order to calculate the lattice contribution to the specific heat and elastic constants of sodium and potassium, we started by calculating the interionic potential for each one of these metals, from first principles.

It is clear, at present, that a pseudopotential determined in an empirical way cannot be always considered as weak [1], and therefore its use in the calculation of the interionic potential and from this, the phonons to calculate the specific heat, elastic constants and other properties of metals, is not justified.

For simple metals the interionic potential can be constructed from first principles using pseudopotential theory. We constructed a first principles pseudopotential following a method proposed by Manninen *et al* [2] who had followed the spirit of the work of Rasolt and Taylor [3] and of Dagens *et al* [4], with some differences.

In the approach of Rasolt and Taylor [3] the displaced electronic density around an impurity in an electron gas is calculated by non-linear screening theory. Then a non-local pseudopotential is defined in order to reproduce, as closely as possible, the non-linear displaced electronic density by linear response theory, except in a region close to the ion. In this way, the non-linear effects are partially included.

In the method we have used, the starting point is also the displaced electronic density around an impurity in an electron gas, which has an equilibrium density equal to that of the corresponding metal. This calculation is also made by non-linear screening theory, considering the screening of the ion within the model of the nucleus embedded in a jellium vacancy [2]. The pseudodensity is obtained by smoothing the non-linear density in a small region close to the nucleus. The smoothing of the electronic density is done in

order to remove all the ‘wiggles’ near the nucleus. This modelled density is taken as the pseudodensity. The unscreened pseudopotential form factor is given in terms of the Fourier transform of the pseudodensity and the dielectric function. With this definition of the pseudopotential, some of the non-linear screening effects are also included in the pair potential obtained from the pseudopotential.

In previous work we employed the same kind of pseudopotential we use in this work. We successfully used the pseudopotential with the model of the nucleus embedded in a jellium vacancy, in the calculation of the lattice specific heat of lithium [5], and aluminium [6], and in determining the pressure dependence of the lattice specific heat of lithium [7], and aluminium [7], and also in the calculation of the pressure dependence of the elastic constants of aluminium and lithium [8]. More recently we also explored, with good results, the application of the pseudopotential in the calculation of the phonon limited resistivity of aluminium [9], and of sodium and potassium [10].

In this work we construct the local, first principles pseudopotentials for sodium and potassium in order to calculate the lattice contribution to the specific heat and the elastic constants for each of these metals.

In the second section we describe briefly the method used to construct the pseudopotential from the displaced electron density. We also exhibit the dielectric function we have used in this work, which satisfies by construction, the compressibility theorem which is important in connection with the interionic potential [2, 11].

In the third section we describe the calculation of phonons and elastic constants. Section 4 is for the results and conclusions.

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

## 2. The pseudopotentials and interionic potentials

We started by calculating the displaced electron densities around a nucleus in an electron gas for sodium (Na) and potassium (K) respectively. This was done using the density functional formalism [12, 13], and the model of the nucleus embedded in a jellium vacancy. 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, as we explain below.

From pseudopotential theory and linear response theory [14], the interionic potential is given by:

$$\Phi(r) = \frac{Z^2}{r} \left( 1 + \frac{2}{\pi Z^2} \int_0^\infty \frac{dq \sin(qr) \varepsilon(q) (\delta n(q))^2}{q(1 - \varepsilon(q))} \right) \quad (1)$$

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]

$$\delta n(r) = n(r) - n_v(r) - 2 \sum_{\substack{\text{bound} \\ \text{states}}} |\psi_b(r)|^2 \quad (2)$$

where  $n(r)$  is calculated with the total charge density corresponding to a nucleus located

at the centre of a vacancy in jellium, and  $n_v(r)$  is the electron density around a jellium vacancy alone. Charge neutrality of the metal is a necessary condition. The bound states are represented by  $\psi_b(r)$ .

We calculated  $\delta n(q)$ , the Fourier transform of the displaced electron pseudodensity, taking the Fourier transform of the density given by (2) after smoothing. In this smoothing, the conditions that the electronic charge is conserved and that  $\delta n(r)$ , and  $(\partial/\partial r)(\delta n(r))$  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 orthogonalisation of conduction states to the core orbitals.

The unscreened pseudopotential form factor,  $v(q)$ , is related to  $\delta n(q)$  by

$$v(q) = \frac{4\pi \delta n(q) \epsilon(q)}{q^2(1 - \epsilon(q))}. \quad (3)$$

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 in 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 [2, 11]. It is given by [2, 15]:

$$\epsilon(q) = 1 + (4\pi/q^2)G(q)$$

where

$$G(q) = G_0(q)/[1 - (4\pi/k_{\text{TF}}^2)G_0(q)(1 - L)]$$

and  $G_0(q)$  is the usual Lindhard polarisability,  $k_{\text{TF}}$  is the Thomas–Fermi screening constant, and  $L$  is the ratio

$$L = (\partial\mu/\partial r_s)/(\partial E_{\text{F}}/\partial r_s).$$

In equation (6)  $\mu$  is the chemical potential,  $E_{\text{F}}$  is the Fermi energy and

$$\mu(r_s) = E_{\text{F}}(r_s) + \mu_{\text{xc}}(r_s)$$

where  $\mu_{\text{xc}}(r_s)$  is the exchange–correlation contribution to the chemical potential.

Using the expression of Gunnarson and Lundqvist [16], for exchange–correlation (which is the one we used in the calculation of the induced electronic density), the corresponding value of  $L$  is

$$L = 1 - (4/9\pi^4)^{1/3} r_s(1 + 0.6213 r_s/(r_s + 11.4)).$$

Notice that the value of  $v(q = 0)$  is  $-(2/3)E_{\text{F}_0}$ , where  $E_{\text{F}_0}$  is the Fermi energy of the free electron gas. The corresponding Friedel sum is the valence of the metal ion.

### 3. Phonons, elastic constants and specific heat

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

From the interionic potential we calculated the phonons and associated force constants, using the harmonic approximation.

From the tensor force model and using the notation of [17], the force matrix with elements  $\Phi_{ij}$  is defined as the force on the origin atom in the  $i$  direction when atom  $S$  moves one unit distance in the  $j$  direction. This force matrix is symmetric and it is denoted by

$$(\Phi_{ij}^{(S)}) = \begin{bmatrix} \alpha_1^S & \beta_3^S & \beta_2^S \\ \beta_3^S & \alpha_2^S & \beta_1^S \\ \beta_2^S & \beta_1^S & \alpha_3^S \end{bmatrix}. \quad (4)$$

The point  $S$  is one of a set of points according to the symmetry of the lattice. This set of points is denoted by  $S$ , where  $S = 1, 2, 3$ , etc, corresponding to each shell of neighbours. The force matrices of the other members of the set consist of rearrangements of the same set of force constants.

The elastic constants,  $C_{11}$ ,  $C_{44}$ ,  $C_{12}$  are given by [17]

$$\begin{aligned} aC_{11} &= 8\tau \sum_S \frac{n^S}{48} \sum_j (h_j^S)^2 \alpha_j^S \\ aC_{44} &= 4\tau \sum_S \frac{n^S}{48} \sum_j [(h_{j+1}^S)^2 + (h_{j+2}^S)^2] \alpha_j^S \\ a(C_{11} + C_{44}) &= 16\tau \sum_S \frac{n^S}{48} \sum_j h_{j+1}^S h_{j+2}^S \beta_j^S \end{aligned} \quad (5)$$

where  $a$  is the lattice constant,  $n^S$  is the number of lattice points for the neighbouring shell  $S$ ;  $h_j^S$  corresponds to three non-negative integers such that  $h_1 > h_2 > h_3$  and the coordinates of a point in shell  $S$  are  $h_1\alpha/2$ ,  $h_2\alpha/2$ ,  $h_3\alpha/2$ . For FCC  $\tau = 1$  and for BCC  $\tau = 1/2$ .

The relations between the force constants of the tensor force model and the axially symmetric model are [18]:

$$\begin{aligned} \alpha_1^S &= C_B(S) + (h_1^2/h^2)k_1(S) & \beta_1^S &= (h_2h_3/h^2)k_1(S) \\ \alpha_2^S &= C_B(S) + (h_2^2/h^2)k_1(S) & \beta_2^S &= (h_3h_1/h^2)k_1(S) \\ \alpha_3^S &= C_B(S) + (h_3^2/h^2)k_1(S) & \beta_3^S &= (h_1h_2/h^2)k_1(S) \end{aligned} \quad (6)$$

where  $h^2 = h_1^2 + h_2^2 + h_3^2$ , and  $k_1(S)$  and  $C_B(S)$  are the two force constants of the axially symmetric model for the  $S$ th shell of neighbours [18].

We can easily relate the force constants  $k_1(S)$  and  $C_B(S)$  to the derivatives of the interionic potential to give

$$k_1(S) = [d^2V(r)/dr^2 - (1/r) dV(r)/dr]_{(S)} \quad (7)$$

and

$$C_B(S) = [(1/r) dV(r)/dr]_{(S)}. \quad (8)$$

In this way, once we know the interionic potential  $V(r)$ , we can find  $k_1(S)$  and  $C_B(S)$  and using equations (5) and (6) we can calculate the elastic constants.

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 [19]. This method consists of solving the secular equations associated with the dynamical matrix only at a relatively small number of points in the irreducible first

Brillouin zone. Then, by means of linear extrapolation, the other phonon eigenfrequencies are extracted from within small cubes, each centred at one point. These cubes can be arranged to fill the entire irreducible first Brillouin zone and thus can yield the complete frequency distribution of the crystal.

Having the phonon spectrum,  $F(\nu)$ , the specific heat is calculated numerically by the integral

$$C_v = \frac{\partial \langle E \rangle}{\partial T} = k_B \int_0^{\nu_m} d\nu \left( \frac{\beta h \nu}{2} \right)^2 \frac{F(\nu)}{\sinh(\beta h \nu / 2)} \quad (9)$$

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

For high temperatures (for example, larger than the corresponding Debye temperatures) the anharmonic effects become more important, as happens with the specific heat [20–22].

We believe that our calculations will be sufficient to explore the applicability of our pseudopotential in the prediction of the lattice specific heat and elastic constants of sodium and potassium from first principles.

#### 4. Results and conclusions

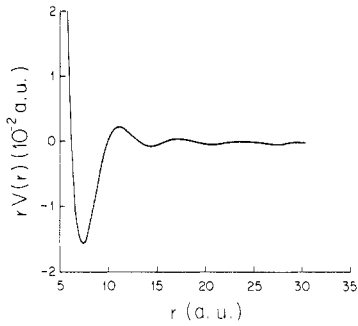
We started our calculations by obtaining the induced densities according to equation (2) and using the density functional formalism. For this is necessary to calculate the displaced electronic densities around a nucleus embedded in a jellium vacancy and also the displaced electronic density around a vacancy alone. We made the calculations for nuclei of sodium and potassium respectively, and jelliums corresponding to sodium and potassium. After this, a smoothing of the densities near the ions is done in order to construct the displaced electronic pseudodensities.

The following step was to calculate the Fourier transform of the pseudodensities. This was achieved using the asymptotic form for  $\delta n(r)$  given by:

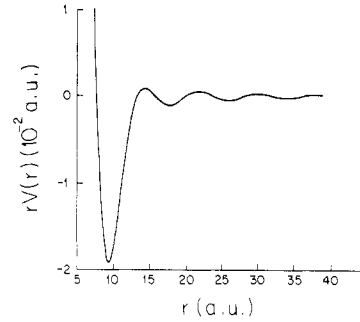
$$\delta n(r) = B \cos(2k_F r + \varphi) / r^3,$$

where the constants  $B$  and  $\varphi$  were obtained using the last points in our calculation of  $\delta n(r)$ . This asymptotic form was taken for distances larger than  $R_{\max} = 15.04 a_0$ , where  $a_0$  is the Bohr radius ( $a_0 = 0.529 \text{ \AA}$ ). The accuracy of the Fourier transform was tested taking the inverse Fourier transform of  $\delta n(q)$  and the resulting difference with respect to the original values of  $\delta n(r)$  was less than 0.1% for each point.

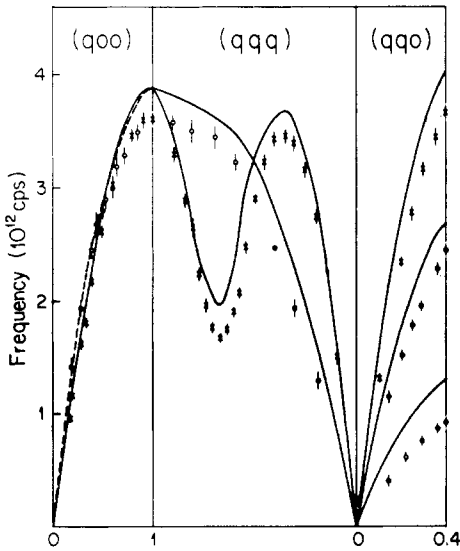
With  $\delta n(q)$  and the dielectric function defined in section 3 we could evaluate the interionic potential using equation 1. In figures 1 and 2 we show the resulting interionic potentials for sodium and potassium respectively. From these interionic potentials we calculated the derivatives to be used in (7) and (8) in order to calculate the elastic constants for each material. Also, from the interionic potential we obtained the phonons and the force constants by the harmonic approximation. The resulting phonons for sodium and potassium are shown in figures 3 and 4 respectively. We can see from these figures a good agreement with the experimental results [23, 24] and from this we should expect a good prediction for the elastic constants and the lattice specific heats, as in fact happened. Using the elastic constants and the method of Gilat and Raubenheimer [19], we obtained the phonon spectra to be employed to calculate numerically the lattice contribution to the specific heat.



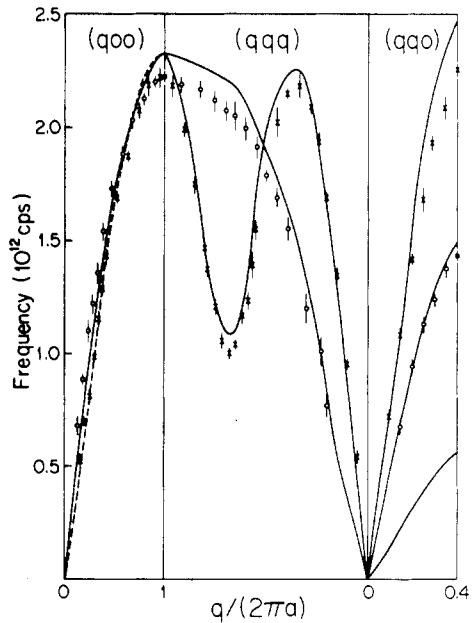
**Figure 1.** The calculated interionic potential for sodium. In this figure we are using  $r_s = 3.93 a_0$ , where  $a_0$  is the Bohr radius.



**Figure 2.** The calculated interionic potential for potassium. In this case we are using  $r_s = 4.86 a_0$ , where  $a_0$  is the Bohr radius.

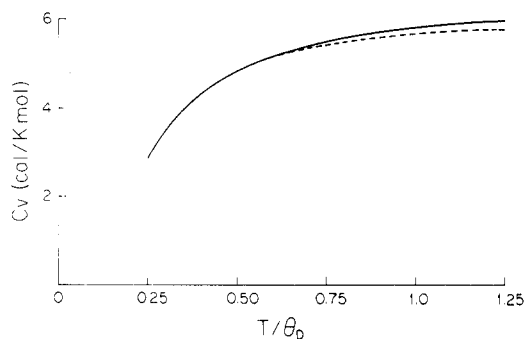


**Figure 3.** Phonons for sodium. Results of this work: full curve; experimental results [23, 24]: ○, ×.

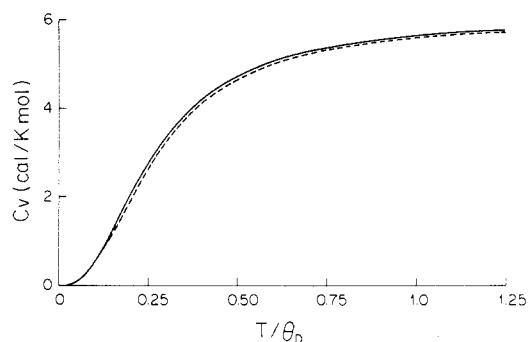


**Figure 4.** Phonons for potassium. Results of this work: full curve; experimental results [23, 24]: ○, ×.

The results for the lattice specific heats for sodium and potassium are shown in figures 5 and 6 respectively, where we also show a comparison with the experimental results [20–22]. We consider a range of temperatures in both cases up to a maximum slightly above the Debye temperatures. From these figures we can see a good agreement between our first principles calculations and the experimental results. It is known that for sodium there exists a martensitic transformation below 35 K, therefore we are not considering temperatures below this for sodium. The range of temperatures we are considering for potassium begins at 0 K. We can see from these figures a good agreement between our prediction and the experimental results.



**Figure 5.** Constant volume lattice specific heat of sodium. Prediction of this work: broken curve. Experimental results [20–22]: full curve. The Debye temperature for sodium is 156 K.



**Figure 6.** Constant volume lattice specific heat of potassium. Prediction of this work: broken curve. Experimental results [20–22]: full curve. The Debye temperature of potassium is 90.6 K.

**Table 1.** Elastic constants of sodium, as functions of temperature, predicted with our first principles calculation and experimental results from [23]. Sodium undergoes a martensitic transformation below 35 K to an FCC structure. The Debye temperature for sodium is 156 K.

$T$ (K)	$C_{44}$ (calc.)	$C_{44}$ (exp.)	$C_{11}$ (calc.)	$C_{11}$ (exp.)	$C_{12}$ (calc.)	$C_{12}$ (exp.)
50	0.564	0.619	0.646	0.617	0.442	0.469
90	0.558	0.586	0.619	0.603	0.411	0.458
140	0.552	0.550	0.587	0.583	0.374	0.443
200	0.542	0.501	0.560	0.560	0.338	0.428

It is convenient to mention here that in order to calculate the lattice specific heat and elastic constants for each temperature, it was necessary to evaluate the interionic potential and the phonon frequencies for the corresponding lattice parameter at each temperature.

Our calculated elastic constants, for different temperatures are shown in tables 1 and 2, for sodium and potassium, respectively, where we also show experimental results from [25, 26]. We can see that there is good agreement between our predictions and the experiments.

From above it is clear that our pseudopotential is appropriate for the calculation of the elastic constants and the lattice specific heat, as functions of the temperature, for sodium and potassium and that a good agreement with experimental results can be seen



**Table 2.** Elastic constants of potassium, as functions of temperature, predicted with our first principles calculation and experimental results from [24]. The Debye temperature for potassium is 90.6 K.

$T$ (K)	$C_{44}$ (calc.)	$C_{44}$ (exp.)	$C_{11}$ (calc.)	$C_{11}$ (exp.)	$C_{12}$ (calc.)	$C_{12}$ (exp.)
4	0.263	0.284	0.400	0.427	0.358	0.354
50	0.259	0.268	0.388	0.417	0.356	0.347
90	0.247	0.255	0.386	0.410	0.335	0.342
130	0.224	0.241	0.381	0.402	0.342	0.336
200	0.205	0.218	0.363	0.389	0.327	0.327

for the range of temperatures for which our calculations are expected to be applicable. This is without any phenomenological adjustments.

Finally, it is convenient to mention that the only previous articles where a first principles pseudopotential is used to calculate successfully phonons for sodium and potassium are [3] (for sodium) and [4] (for potassium). In these references, a non-local, first principles pseudopotential is used, but there were no reports on elastic constants nor on the lattice specific heat for sodium or potassium in them.

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