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E.A. Mendoza, G.J. Vázquez, L.F. Magaña. A first principles pseudopotential in the calculation of the phonon limited resistivity of sodium and potassium. *Journal de Physique*, 1989, 50 (24), pp.3489-3496. 10.1051/jphys:0198900500240348900 . jpa-00212341

HAL Id: jpa-00212341

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Submitted on 4 Feb 2008

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Classification
Physics Abstracts
72.15E

A first principles pseudopotential in the calculation of the phonon limited resistivity of sodium and potassium

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(Reçu le 13 juillet 1989, accepté le 8 septembre 1989)

Résumé. — Nous avons calculé la résistivité de phonons à volume constant et à pression constante dans le sodium et le potassium en utilisant un pseudopotentiel local déterminé à partir des premiers principes. Ce type de pseudopotentiel s'est révélé utile dans le calcul des propriétés de l'aluminium et du lithium. Il s'obtient à partir de la densité électronique induite autour d'un ion dans le gaz d'électrons correspondant. A partir de ce pseudopotentiel, nous avons obtenu le potentiel interionique, les phonons (que nous calculons dans l'approximation harmonique) et, finalement, la résistivité de phonons. Les résultats sont en bon accord avec l'expérience.

Abstract. — We have calculated the constant volume and the constant pressure phonon limited resistivity of sodium and potassium using a local, first principles pseudopotential. This kind of pseudopotential has been useful in the calculation of properties of aluminum and lithium. It is obtained from the induced electron density around an ion in the corresponding electron gas. From this pseudopotential we obtained the interionic potential, the phonons (which are calculated by the harmonic approximation) and finally the phonon limited resistivity. The results are in good agreement with experimental results.

1. Introduction.

It is clear at present that a pseudopotential determined in an empirical way can not be considered as weak always [1], so that its use in the calculation of the interionic potential and from this, the phonons to calculate the electron-phonon interaction to predict the resistivity and other properties of metals is not justified.

We employ a local, first principles pseudopotential constructed following a method proposed by Manninen *et al.* [2], who followed the spirit of the method of Rasolt *et al.* [3].

In the method we have used the starting point is 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 made by non-linear screening theory, and 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. The latter satisfies, by construction, the compressibility theorem which is important in connection with the interionic potential [2, 4]. With this definition of the pseudopotential, some of the non-linear screening effects are included into the pair potential obtained from the pseudopotential.

In the approach of Rasolt *et al.* [2] the displaced electronic density around an impurity in an electron gas is also previously calculated by non-linear screening theory. Then a non-local pseudopotential is defined in order to reproduce, as close 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 also partially included.

In previous work we have employed the same kind of pseudopotential we used in this work, and also within the model of the nucleus embedded in a jellium vacancy, with success in the calculation of the lattice specific heat of lithium [5], and aluminum [6], and of the pressure dependence of the lattice specific heat of lithium [7], and aluminum [6], and also in the calculation of the pressure dependence of the elastic constants of aluminum and lithium [8]. More recently we also explored, with good results, its application in the calculation of the phonon limited resistivity of aluminum [9].

In this work we calculated the corresponding local, first principles pseudopotentials for sodium and potassium and employed them in the calculation of the constant volume and constant pressure phonon limited resistivity of these materials.

Shukla and Taylor [15] have calculated the constant volume and the constant pressure resistivity of sodium and potassium using the non-local first principles pseudopotential defined in reference [3], with very good results. The results we have obtained in this work using local, first principles pseudopotentials are very similar to theirs.

In the second section we describe briefly the method to construct the pseudopotential from the displaced electron density. We also exhibit the dielectric function we have used in this work, and the vertex correction for the screened pseudopotential form factor, which is important in the calculation of the phonon limited resistivity.

We use the third section to describe the calculation of phonons and to discuss the application of the expression for the phonon limited resistivity we have employed. Section 4 is for results and conclusions.

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

2. The pseudopotential and interionic potential.

The first step was to calculate, using the density functional formalism [10, 11], the displaced electron densities around a nucleus embedded in a jellium vacancy for sodium (Na) and potassium (K). 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 pseudopotential theory and linear response theory [12], the interionic potential is given by :

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

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] :

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

where $n(r)$ is calculated with the total charge density corresponding to a nucleus located at the center of a vacancy in jellium, and $n_v(r)$ is the electron density around a jellium vacancy alone. Charge neutrality of the metal is a necessary condition. Bound states are represented by ψ_b .

The unscreened pseudopotential form factor, $\nu(q)$, is related to the Fourier transform of the induced charge pseudodensity, $\delta n(q)$, by :

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

We calculated $\delta n(q)$ using the induced electronic density, $\delta n(r)$, which was computed by the density functional formalism, [10], [11], with a smoothing in a region near the origin [2]. 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, is imposed [2]. Then, 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. It should be remarked 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 dielectric function we used, as we have already said, satisfies by construction, the compressibility theorem which is important in connection with the interionic potential [2, 4]. The dielectric function is [2, 13] :

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

where :

$$G(q) = \frac{G_0(q)}{1 - (4 \pi / k_{TF}^2) G_0(q) (1 - L)} \quad (5)$$

and $G_0(q)$ is the usual Lindhard polarizability, k_{TF} is the Fermi-Thomas screening constant, and L is the ratio :

$$L = \left(\frac{\partial \mu}{\partial r_s} \right) \bigg/ \left(\frac{\partial E_F}{\partial r_s} \right). \quad (6)$$

In equation (6) μ is the chemical potential, E_F is the Fermi energy and

$$\mu(r_s) = E_F(r_s) + \mu_{xc}(r_s),$$

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

On the other hand, the screened pseudopotential form factor, $W(q)$, given by

$$W(q) = \frac{\nu(q)}{\varepsilon(q)} C(q), \quad (7)$$

is important in the calculation of the resistivity. The vertex correction is $C(q)$ which, following the work of Rasolt [14] and the work of Shukla and Taylor [15] is given by :

$$C(q) = \frac{1}{H(E_F)} \left[1 - \frac{G(q)}{G(0)} \left(1 - \frac{H(E_F) B}{B_0} \right) \right],$$

where $H(E_F)$ is the quasiparticle renormalization constant at the Fermi level given by Hedin [16] and it is a function of r_s , (B/B_0) is the ratio of the electron gas compressibility (B) with that of the non-interacting electron gas (B_0), and the quasiparticle electron mass has been taken equal to the electron mass. In table I we reproduce the tabulated values of $H(E_F)$, from the work by Hedin [16].

Table I. — *Quasiparticle renormalization constant at the Fermi level as given by Hedin [16]. It is a function of r_s .*

r_s	1	2	3	4	5	6
$H(E_F)$	1.164	1.302	1.429	1.547	1.660	1.766

In the derivation of this expression for $C(q)$, a non local electron-electron interaction, and scattering on the Fermi surface were considered [14, 15].

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

$$L = 1 - \left(\frac{4}{9\pi^4} \right)^{1/3} r_s \left(1 + \frac{0.6213}{r_s + 11.4} r_s \right). \quad (8)$$

3. Resistivity and phonons.

The expression for the resistivity, $\rho(T)$, as function of the temperature, T , we use in this work has been derived and discussed by several authors [18, 19] :

$$\rho(T) = A \sum_{\lambda} \int_{2k_F} \frac{|\mathbf{q} \cdot \boldsymbol{\epsilon}(q, \lambda)|^2 |W(q)|^2 \beta q d^3q}{[\exp(\beta \omega(q, \lambda)) - 1][1 - \exp(-\beta \omega(q, \lambda))]} \quad (9)$$

where $W(q)$ is the screened pseudopotential form factor. $\boldsymbol{\epsilon}(q, \lambda)$ is the polarization vector of the lattice vibration with wave vector $\mathbf{q}$ and frequency $\omega(q, \lambda)$, β is $1/k_B T$, k_B being the Boltzmann constant and A is a constant given by :

$$A = \frac{3 \Omega_0}{16 M V_F^2 k_F^4}, \quad (10)$$

where M is the ion mass, V_F and k_F are the electron velocity and wave vector at the Fermi level, respectively.

The integral in equation (9) is over a sphere of radius $2k_F$. The pseudopotential describing electron scattering at the Fermi surface is assumed to depend only on momentum transfer $\mathbf{q}$. The Fermi surface is taken as spherical so that the two surface integrals describing transitions

from an initial to a final state on the Fermi surface can be converted to a three dimensional integral over $\mathbf{q}$. A one phonon approximation is considered when equation (9) is derived [18, 19]. In sodium and potassium the Fermi surface is free electron-like and only very slightly distorted. We should expect that multiple plane wave effects are not very important. At low temperatures this same pseudopotential could be used but we believe that it is necessary to consider the anisotropy in the electron-scattering probability. This anisotropy can be considerable as a result of the strong orientational dependence of the electron-phonon Umklapp interaction at low temperatures [20] (i.e. temperatures below $\theta_D/5$, where θ_D is the Debye temperature).

For high temperatures (for example, larger than the corresponding Debye temperatures) we expect that anharmonic effects become more important, as it happens with the specific heat [21, 22].

We believe that our calculation will be sufficient to explore the applicability of our pseudopotential in the calculation of the phonon limited resistivity of sodium and potassium. A careful calculation of this property, for low temperatures, using our pseudopotential, can be performed following the method given in reference [20] for potassium, where different pseudopotentials are employed.

It is clear, from equation (9), that we need information about the phonon frequencies and polarization vectors and that we also need the screened pseudopotential form factor.

From the induced pseudodensity and the dielectric function, we obtained the interionic potential, given by equation (1). From this interionic potential we calculated the phonons to be employed in the expression for the resistivity. The force constants associated to our interionic potential were calculated using the harmonic approximation.

To calculate all the phonon frequencies and polarization vectors entering in the expression for the resistivity, equation (9), from the force constants obtained in the phonon dispersion curve, we followed the method of Gilat and Raubenheimer [23]. This method consists of solving the secular equations associated with the dynamical matrix only at a relatively small number of points (3000) in the irreducible first Brillouin zone. Then, by means of linear extrapolation the other phonon eigenfrequencies are extracted from within small cubes, each centered 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. Simple translations of vectors $\mathbf{q}$ are used to complete the integration region up to $2k_F$.

4. Results and discussion.

In order to calculate the resistivities we started 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 into a jellium vacancy and also the displaced electronic density around a vacancy alone. We made the calculations for nucleus 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. In figures 1 and 2 we show the displaced electronic densities calculated using equation (2) and the corresponding smoothed densities for sodium and potassium.

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 :

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

where the constants B and ϕ 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

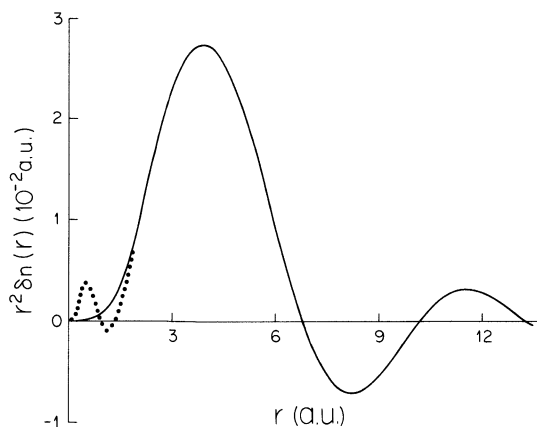


Fig. 1

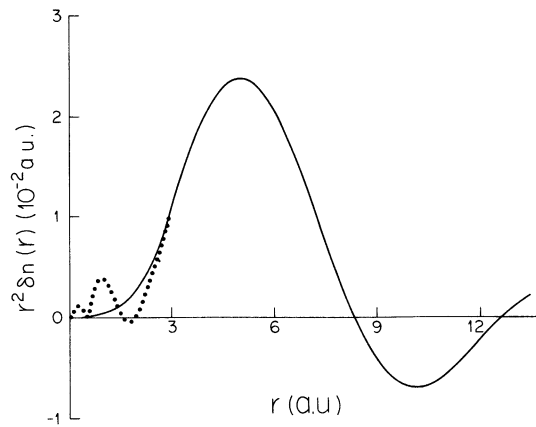


Fig. 2

Fig. 1. — Electronic densities for sodium. Calculated displaced electronic density : (...); displaced electronic pseudodensity which is obtained by smoothing the calculated displaced electronic density : (—). In this case we are taking $r_s = 3.93 a_0$. The Debye temperature of sodium is 156 K.

Fig. 2. — Electronic densities for potassium. Calculated displaced electronic density : (...); displaced electronic pseudodensity which is obtained by smoothing the calculated displaced electronic density : (—). In this case we are taking $r_s = 4.86 a_0$. The Debye temperature for potassium is 90.6 K.

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 functions defined in section 3 we could calculate the interionic potential, using equation (1). From this interionic potential we found the force constants by the harmonic approximation, and using these and the method of Gilat and Raubenheimer [23], we obtained the phonon frequencies and polarization vectors to be used in equation (9) in order to calculate the phonon limited resistivity.

The results for the constant volume resistivity are shown in figures 3 and 4, for sodium and potassium respectively. In these figures we make a comparison between experimental results [24, 25], and the results from our first principles calculation. We considered maximum temperatures a little bit above the Debye temperature, for each material. It is known that for sodium exists a martensitic transformation below 35 K. We are not considering temperatures below this for sodium. The range of temperatures we are considering for potassium begins at 20 K. We can see from these figures a good agreement between our prediction and experimental results. In figures 5 and 6 we show a comparison between the experimental results [24, 25] and ours, for the constant pressure resistivity, for the same range of temperatures for both materials. Again, we can see a good agreement between our predictions and experiment. It is convenient to mention that to calculate the constant pressure resistivity it is necessary to evaluate the interionic potential and the phonon frequencies for the corresponding lattice parameter at each temperature.

We should mention that it is not our goal in this work to perform a precise calculation of the phonon limited resistivity of sodium and potassium for the whole range of temperatures. We want only to assess the suitability of our pseudopotential for the calculation of this property for these materials.

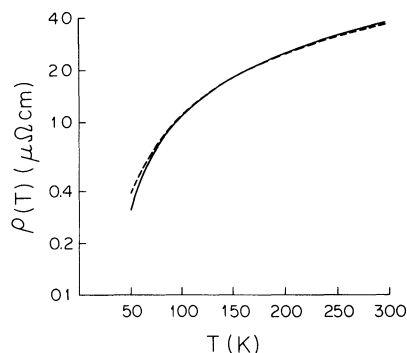


Fig. 3

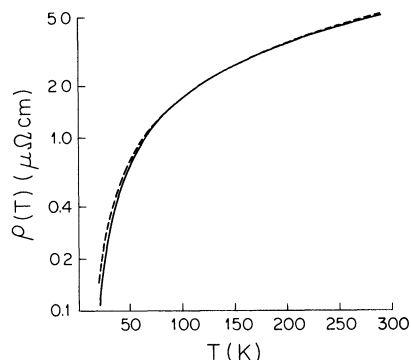


Fig. 4

Fig. 3. — Constant volume phonon limited resistivity of sodium. Experimental results [24, 25] : (—) ; result of this work : (---) ; results of reference [15] are very similar to the results of this work.

Fig. 4. — Constant volume phonon limited resistivity of potassium. Experimental results [24, 25] : (—) ; result of this work : (---) ; results of reference [15] are very similar to the results of this work.

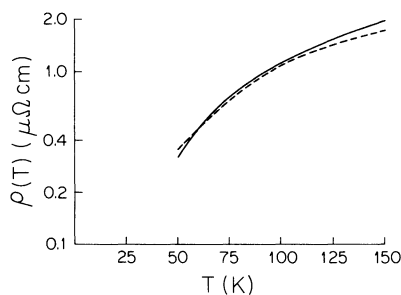


Fig. 5

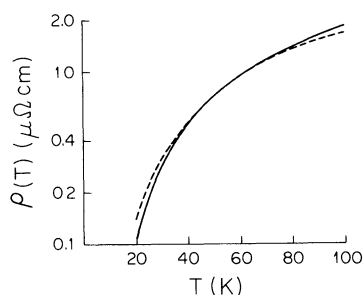


Fig. 6

Fig. 5. — Constant pressure phonon limited resistivity of sodium. Experimental results [24, 25] : (—) ; result of this work : (---) ; results of reference [15] are very similar to the results of this work.

Fig. 6. — Constant pressure phonon limited resistivity of potassium. Experimental results [24, 25] : (—) ; result of this work : (---) ; results of reference [15] are very similar to the results of this work.

From above we can say that our pseudopotential is adequate for the calculation of the phonon limited resistivity of sodium and potassium, and that a good agreement with experimental results can be seen for the range of temperatures for which our calculations are expected to be applicable.

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