BAND STRUCTURE AND ELECTRON–PHONON INTERACTION IN LEAD∗

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A self-consistent semi-relativistic APW method has been employed to
calculate from first principles the band structure and the electronic density
of states of Pb. Our results were used to obtain the electron–phonon
interaction and the superconducting transition temperature of lead.

THE ELECTRONIC PROPERTIES of lead have been
investigated extensively in the past. There have been
several calculations of the energy bands of Pb using a
variety of methods [1–7]. These calculations have
included in one way or another relativistic effects, which
for a heavy metal as Pb are expected to be quite important.
However, self-consistent ab-initio calculations have
not been reported so far, to the best of our knowledge.

In this paper we present a calculation of the band
structure of Pb using a semi-relativistic version of the
APW method which includes the mass-velocity and
Darwin corrections exactly but neglects the spin-orbit
interaction. This method was first proposed by
Matthiess [8], reviewed in detail by Dimmock [9] and was
recently improved by Koelling and Harmon [10].

Our calculations were performed self-consistently
within the muffin-tin approximation with lattice
constant a = 9.3555 a.u. The exchange potential was
the local density approximation. The first 3 iterations
were carried out on a mesh of 32 k points in the fcc
Brillouin zone and the 5d-levels included in the core.

We then performed another 5 iterations for 256 k-points
in the zone, treating the d-levels as bands. In each
iteration, the core levels were recalculated atomic-like.
After 8 iterations the energy eigenvalues converged to
within 1 mRy from the results of the seventh iteration.

The final, self-consistent, potential was used to calculate

the energy bands and the corresponding wave functions
for 2048 k-points in the Brillouin zone. These values
were then interpolated by our modified version of the
Quad method [12], to obtain the density of states and
its angular momentum components. Figure 1 shows the
energy bands along the various symmetry directions in
the Brillouin zone. The main characteristics of these
bands are in agreement with previous calculations [1–7]
and with the gross features of the XPS and the optical
absorption spectra [5, 6]. A detailed comparison with
the results of previous calculations and the experimental
data will be given in a forthcoming publication.

Due to the omission of spin–orbit splitting we will
not attempt to obtain the Fermi surfaces in this report.
Our primary concern here is to calculate the electron–
phonon coupling constant λ and the superconducting
transition temperature $T_c$.

The easiest way to obtain λ is by fitting the
expression

$$\gamma = 2 \frac{\pi^2}{3} k_B n_t(E_F) (1 + \lambda)$$

(1)

for the linear coefficient of the specific heat γ to the
experimental value [13] $\gamma = 3.06 \text{ mJ mole}^{-1} \text{ deg}^{-2}$,
with $n_t(E_F) = 3.475 \text{ states/Ry-spin-unit cell}$, according
to the present calculation. We obtain $\lambda = 1.51$ in
excellent agreement with the value $\lambda = 1.55$ deduced
from tunneling experiments (see, e.g. [14]). To obtain
$T_c$ we employed the Allen and Dyines [14] equation
with $\lambda = 1.51$, $\mu^* = 0.088$ (from the Bennemann and
Garland [15] formula) and the required moments of the
phonon spectrum as given by Allen and Dyines [14].
Our result for $T_c$ is 7.5 K in very good agreement with
the observed value of $T_c = 7.19$ K.

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Fig. 1. Energy bands of Pb.

Fig. 2. Total electronic density of states of Pb and its decomposition into s-, p-, d-like components, inside the muffin-tin spheres.

The value of $\lambda$ can also be obtained, within the rigid-muffin-tin approximation, by the Gaspari and Gyorffy [16] theory. The latter uses the partial DOS and phase shifts (obtained by the present calculation and given in Table 1) to calculate the electron-phonon interaction $\eta$; $\lambda$ is then given by $\eta/M\langle\omega^2\rangle$, where $M\langle\omega^2\rangle$ is taken from [14].

It can be seen from Table 1 (first column) that $\eta$ or $\lambda$ are underestimated by the rigid-muffin-tin approximation. This is consistent with previous calculations [17] for a number of simple and noble metals. The value of $T_c$, corresponding to the calculated value of $\lambda = 0.84$ is 3.3 K which is an underestimation. Nevertheless, this value of $T_c$ shows that Pb stands out (in comparison with the results of similar calculations in other simple metals) as a high $T_c$ material.
Table 1. Calculated values of the Fermi level, $E_F$, of total $n_t$ and partial $n_t$ DOS; of the ratios $n_t/n_t^{(1)}$; of phase shifts $\delta_i$ and of $\eta$, $\lambda$, $\mu^*$, $T_c$ for Pb

<table>
<thead>
<tr>
<th></th>
<th>RMT$^a$</th>
<th>AMT$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_F$ (Ry)</td>
<td>0.365</td>
<td>0.215</td>
</tr>
<tr>
<td>$n_t$</td>
<td>3.475</td>
<td>3.475</td>
</tr>
<tr>
<td>$n_s$ States per</td>
<td>0.185</td>
<td>-</td>
</tr>
<tr>
<td>$n_p$ Ry-atom-spin</td>
<td>2.252</td>
<td>-</td>
</tr>
<tr>
<td>$n_d$</td>
<td>0.292</td>
<td>-</td>
</tr>
<tr>
<td>$n_f$</td>
<td>0.060</td>
<td>-</td>
</tr>
<tr>
<td>Ratios$^c$</td>
<td>$n_t/n_t^{(1)}$</td>
<td>$R_1/R_1^*$</td>
</tr>
<tr>
<td>$s$</td>
<td>1.164</td>
<td>1.164</td>
</tr>
<tr>
<td>$p$</td>
<td>0.698</td>
<td>0.698</td>
</tr>
<tr>
<td>$d$</td>
<td>1.158</td>
<td>1.158</td>
</tr>
<tr>
<td>$f$</td>
<td>1.933</td>
<td>1.933</td>
</tr>
<tr>
<td>Phase shifts</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\delta_s$</td>
<td>1.337</td>
<td>-1.377</td>
</tr>
<tr>
<td>$\delta_p$</td>
<td>0.921</td>
<td>1.540</td>
</tr>
<tr>
<td>$\delta_d$</td>
<td>0.000</td>
<td>0.014</td>
</tr>
<tr>
<td>$\delta_f$</td>
<td>0.004</td>
<td>0.001</td>
</tr>
<tr>
<td>$\eta$ (eV Å$^{-2}$)</td>
<td>1.199</td>
<td>1.773</td>
</tr>
<tr>
<td>$M(\omega^2)$ (eV Å$^{-2}$)</td>
<td>$1.434^d$</td>
<td>$1.434^d$</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.836</td>
<td>1.236</td>
</tr>
<tr>
<td>$\mu^*$</td>
<td>0.088</td>
<td>0.088</td>
</tr>
<tr>
<td>$T_c$(calc) (K)</td>
<td>3.3</td>
<td>5.8</td>
</tr>
<tr>
<td>$T_c$(meas) (K)</td>
<td></td>
<td>7.19</td>
</tr>
</tbody>
</table>

$^a$ Rigid muffin-tin approximation.
$^b$ Adjusted muffin-tin (see text).
$^c$ For definition see Ref. [14].
$^d$ Ref. [14].

A more quantitative agreement between theory and experiment can be achieved if we adjust the Fermi level $E_F$ according to the pseudopotential approach of Lee and Heine [18]. Following their prescription we have shifted our Fermi level to the value $E_F^\ast = \frac{1}{3}E_F^0 = 0.215$ Ry where $E_F^0$ is the free-electron Fermi energy equal to $(9\pi/4)^{1/3}(1/r_{uw})$ with $r_{uw}$ the Wigner–Seitz radius. It was pointed out to us by Butler [19] that we can use $E_F^\ast$ in the frame work of the Gaspari–Gyorffy theory for $\xi_i$ at $E_F^\ast$ and $r_{uw}$, rather than at $E_F$ and the muffin-tin radius $r_{MT}$. This will require, as shown by Butler [19], a renormalization of the term sin $(\delta_i - \delta_{i+1})$ in the Gaspari–Gyorffy formula to $c_i c_{i+1} \sin (\delta_i^\ast - \delta_{i+1}^\ast)$ with

$$R_1 = j_1(\sqrt{E_F r_{uw}}) \cos \delta_i - n_t(\sqrt{E_F r_{uw}}) \sin \delta_i$$

and

$$R_1^\ast = j_1(\sqrt{E_F^\ast r_{uw}}) \cos \delta_i^\ast - n_t(\sqrt{E_F^\ast r_{uw}}) \sin \delta_i^\ast$$

where $j_i$ and $n_t$ are spherical Bessel and Neumann functions.

The results of this correction to the rigid-muffin-tin approximation are given in Table 1 (second column).

We note that the $\eta$ and $\lambda$ values are now closer to the values extracted [14] from tunneling measurements; and the calculated $T_c$ in reasonable agreement with experiment. It must be pointed out that the instability [14] or Umklapp processes [20] have been proposed as factors enhancing the value of $\lambda$ obtained from normal phonon processes. These ideas are under further examination in light of our band structure results.

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