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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 Mattheiss [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 constructed using the Hedin–Lundqvist [11] form of 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

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

for the linear coefficient of the specific heat γ to the experimental value [13] $\gamma = 3.06$ mJ mole^{-1} deg^{-2}, with $n_t(E_F) = 3.475$ 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 Dynes [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 Dynes [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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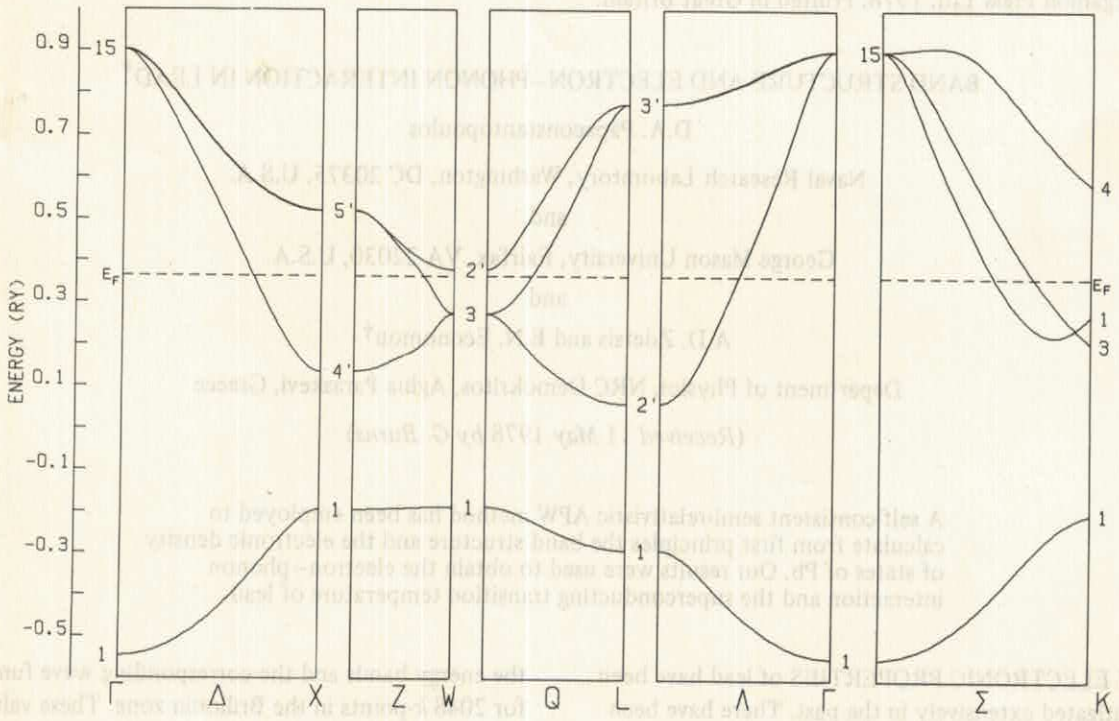

Fig. 1. Energy bands of Pb.

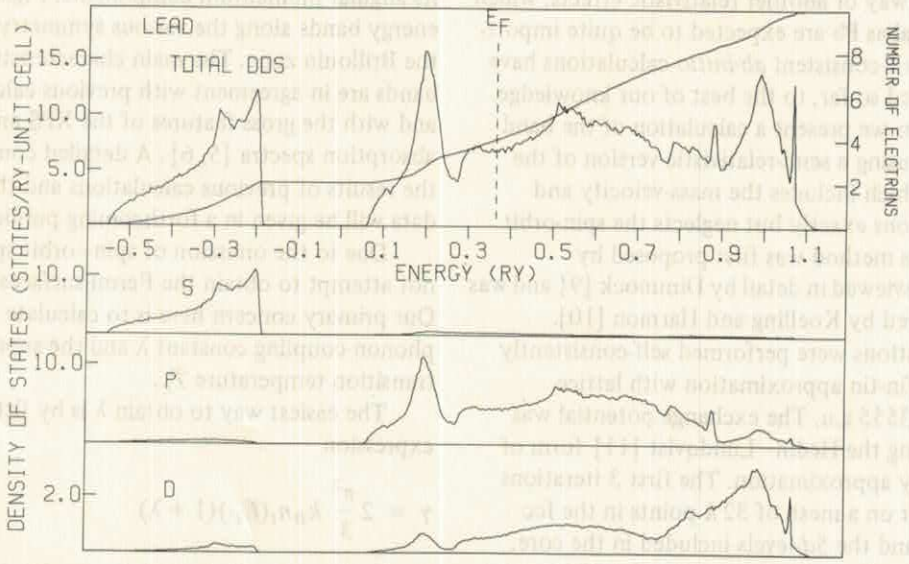

Fig. 2. Total electronic density of states of Pb and its decomposition into *s*-, *p*-, *d*-like components, inside the muffin-tin spheres.

The value of λ 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 η; λ 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 η or λ 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_l DOS; of the ratios $n_l/n_l^{(1)}$; of phase shifts δ_l and of η, λ, μ^*, T_c for Pb

		RMT[a]	AMT[b]
E_F (Ry)		0.365	0.215
n_t		3.475	3.475
n_s	States per	0.185	–
n_p	Ry-atom-spin	2.252	–
n_d		0.292	–
n_f		0.060	–
		Ratios[c]	$n_l/n_l^{(1)}$
s		1.164	1.164
p		0.698	0.698
d		1.158	1.158
f		1.933	1.933
		Phase shifts	
δ_s		1.337	−1.377
δ_p		0.921	1.540
δ_d		0.000	0.014
δ_f		0.004	0.001
η (eV Å^{-2})		1.199	1.773
$M\langle\omega^2\rangle$ (eV Å^{-2})		1.434[d]	1.434[d]
λ		0.836	1.236
μ^*		0.088	0.088
T_c (calc) (K)		3.3	5.8
T_c (meas) (K)		7.19	

[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 $E_F^* = \frac{1}{3}E_F^0 = 0.215$ Ry where E_F^0 is the free-electron Fermi energy equal to $(9\pi/4)^{1/3}(1/r_{ws})$ with r_{ws} the Wigner–Seitz radius. It was pointed out to us by Butler [19] that we can use E_F^* in the frame work of the Gaspari–Gyorffy theory provided that we calculate phase shifts δ_l^* at E_F^* and r_{ws}, 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 $\sin(\delta_l - \delta_{l+1})$ in the Gaspari–Gyorffy formula to $c_l c_{l+1} \sin(\delta_l^* - \delta_{l+1}^*)$ with

$$c_l = \frac{R_l}{R_l^*}$$

where

$$R_l = j_l(\sqrt{E_F} r_{ws}) \cos\delta_l - n_l(\sqrt{E_F} r_{ws}) \sin\delta_l$$

and

$$R_l^* = j_l(\sqrt{E_F^*} r_{ws}) \cos\delta_l^* - n_l(\sqrt{E_F^*} r_{ws}) \sin\delta_l^*$$

where j_l and n_l 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 η and λ 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 covalent instability [14] or Umklapp processes [20] have been proposed as factors enhancing the value of λ obtained from normal phonon processes. These ideas are under further examination in light of our band structure results

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