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Ab initio bandstructure of lead†

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Abstract. The self-consistent semi-relativistic APW method has been employed to calculate the bandstructure of lead and its electronic density of states from first principles. The results of the calculation agree with optical and specific heat data to within 30 and 1% respectively. Calculated frequencies for the second band hole surface agree with experimental Fermi surface results to within 4%. An application of our bandstructure results to the study of the electron–phonon interaction and superconductivity is made including the variation of these properties upon alloying lead with bismuth. These results are also in good agreement with experiment and demonstrate the increase of the superconducting transition temperature for the Pb–Bi alloys.

1. Introduction

There have been several calculations of the energy bands of Pb using a variety of methods. Anderson and co-workers (Anderson and Gold 1965, Anderson *et al* 1972) fitted their de Haas–van Alphen effect measurements with an OPW scheme and a model pseudopotential. Loucks (1965) performed an *ab initio* fully relativistic but non-self-consistent calculation using the relativistic augmented plane wave (RAPW) method. The convergence properties of the pseudopotential model for Pb were discussed by Van Dyke (1973). Breeze (1975) reported a linear combination of atomic orbitals (LCAO) calculation parametrised to fit the XPS spectrum (Ley *et al* 1972). Another LCAO calculation adjusted to fit the experimental results with and without spin–orbit interaction was done by McFeely *et al* (1975). Finally a calculation by the relativistic Green function method was performed more recently by Neto and Ferreira (1976). These calculations have included directly or indirectly relativistic effects, which for a heavy metal such as Pb are expected to be quite important. However, self-consistent *ab initio* calculations have not been reported so far by other investigators, to the best of our knowledge. In this paper we present a self-consistent calculation of the bandstructure of Pb using a semi-relativistic version of the APW method (Mattheiss 1966, Koelling and Harmon 1977). This calculation, in addition to its application to the study of the electron–phonon (EP) interaction, and its good agreement with experiment, should be very useful on its own merit in view of the differences found in some of the aforementioned calculations.

In §2 we present the bandstructure calculation which includes the computation of the dispersion curves and the density of states together with some comparisons with previous calculations. Our results are compared with optical, specific heat and Fermi surface experimental data in §3. The application of our results to the calculation of the EP interaction and superconducting transition temperature, T_c, is given in §4. Using the rigid band approximation we have extended these calculations to study the super-conducting properties of Pb–Bi alloys.

2. Bandstructure calculation

2.1. Dispersion curves

The present *ab initio* calculation is based on a semi-relativistic version of the APW method, which includes the mass-velocity and Darwin corrections exactly, but neglects the spin–orbit interaction. The spin–orbit interaction, although very important for the details of the Fermi surface, is not expected to introduce significant differences in the density of states which is our primary concern here. The present method was first proposed by Mattheiss (1966) and was reviewed in detail by Dimmock (1971). Koelling and Harmon (1977) have further improved this method by introducing a computationally convenient way to handle double asymptotes in the APW program.

Our calculations, a preliminary report of which was published earlier (Papaconstantopoulos *et al* 1978), were performed self-consistently within the muffin-tin approximation and with lattice constant of 9·3555 au. The exchange potential was constructed using the local-density approximation of the Hedin–Lundqvist (1971) form. According to Hedin and Lundqvist (1971) the exchange and correlation potential is given by

$$V_{EC} = \beta(r) V_{KS}(r), \qquad (2.1)$$

where $V_{KS}(r)$ is the well known Kohn–Sham exchange potential equal to $\frac{2}{3}$ of the $\rho^{1/3}$ Slater potential, and $\beta(r) = 1 + B x \ln(1 + x^{-1})$, where $B = 0·7734$ and $x = \frac{1}{21}(3/4\pi\rho(r))^{1/3}$ with $\rho(r)$ the electronic charge density.

The first three iterations of our self-consistency cycle were carried out on a mesh of $32 k$ points in the FCC Brillouin zone with the 5d levels included in the core. We then performed another five iterations for $256 k$ points in the zone, treating the 5d levels as bands. In each iteration the core levels were recalculated in an atomic-like way using a modified version of the Libermann computer code (Libermann *et al* 1971). After eight iterations the energy eigenvalues converged to within 1 mRyd from the results of the seventh iteration. The energy bands of lead, calculated by employing the final potential are shown in figure 1 along the main symmetry directions of the Brillouin zone. The overall shape of the bands is similar to the ones obtained by the parametrised LCAO scheme (Breeze 1974, McFeely *et al* 1975). The 5d levels, not shown in figure 1, lie approximately 0·3 Ryd below the Γ_1 point and have a width of 0·035 Ryd. Further comparisons with other calculations and experimental results will be given below in §2.3 and §3.

2.2. Density of states

For the computation of the density of states (DOS) we have used the final muffin-tin potential to calculate the energy bands and the corresponding wavefunctions for
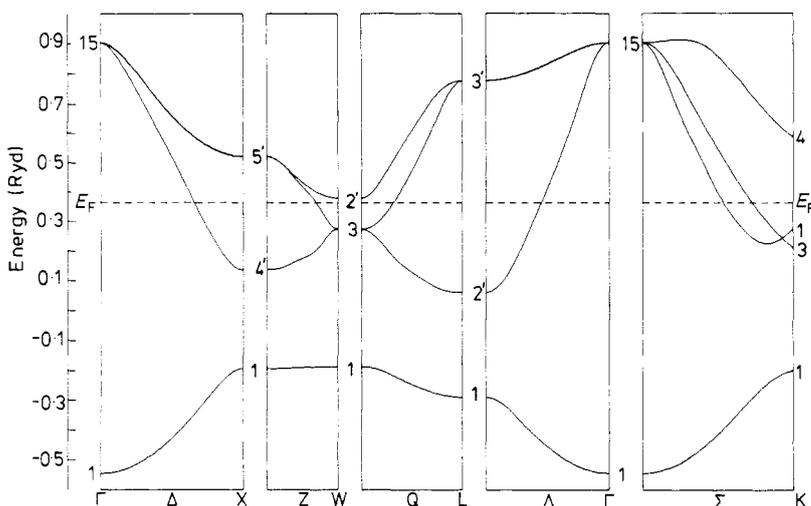
Figure 1. The energy bands of Pb. The 5d levels are located at 0·3 Ryd below Γ_1.

2048 k points in the Brillouin zone. These values were then interpolated to a random mesh of 128000 k points by our modified version of the QUAD method (Mueller *et al* 1971). In addition to the total density of states, we have calculated its angular momentum components n_l inside the APW spheres,

$$n_l = \sum_n \int_s \frac{Q_{n,l}(k)}{|\nabla E_n(k)|} \, ds \tag{2.2}$$

where $Q_{n,l}(k)$ are the electronic charges inside the muffin-tin spheres as defined by Mattheiss *et al* (1968). The RMS fitting error for the energies was approximately 12·5 mRyd for the higher fifth band and 2·2 mRyd for the lower band. The calculated total density of states $n_t(E)$ together with its s, p and d components are shown in figure 2. A similar calculation using the tetrahedron technique (Lehmann and Taut 1972) did not give any substantial differences.

2.3. Comparisons with other calculations

The gross features of the $n_t(E)$ curve and of the energy bands calculated here are similar in shape to the LCAO results (Breeze 1974, McFeely *et al* 1975). Closer inspection, however, shows the existence of substantial discrepancies. This can be seen from table 1 where we compare various bandwidths and separations according to the existing calculations. The largest discrepancy between the LCAO and the present results occurs at the point K. Due to this discrepancy, McFeely *et al* (1975) have attributed the 5·3 eV peak, found by a Kramers–Kroning analysis of the optical data of Liljenvall *et al* (1970), to the point L. Our calculation, as well as the three non-LCAO calculations, confirms the suggestion of Liljenvall *et al* (1970) who have proposed that this peak is due to the K_4–K_3 transition. One feature shared by our calculation, the LCAO results, and the calculations of Loucks (1965) and of Neto and Ferreira (1976) is the lower position of the s band relative to the p bands, compared to the results of Anderson and Gold (1965). This should be attributed to the fact that Anderson's energy bands, since they were obtained by fitting his Fermi surface measurements, are expected to be reliable only near the Fermi level. In general our results are in close agreement with the results of the RAPW and to a lesser extent to the Green function method, except
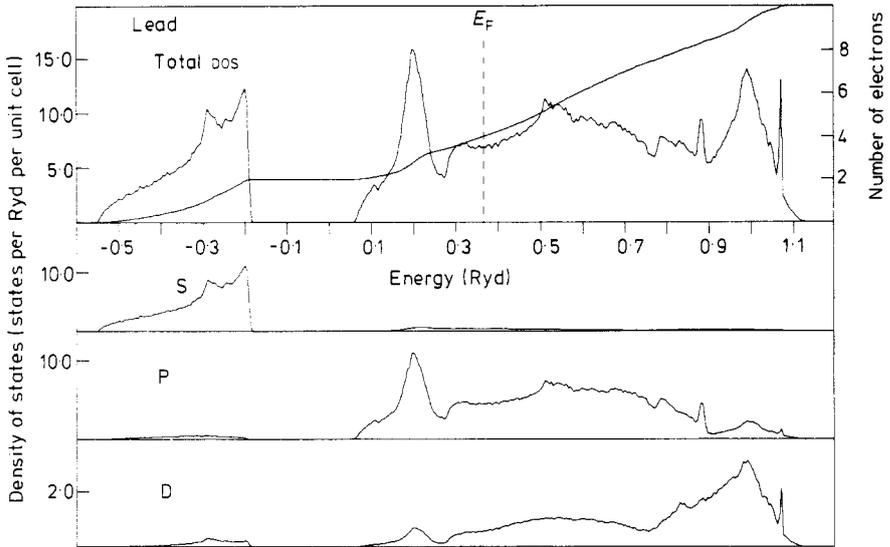
Figure 2. Electronic density of states (DOS) of Pb and its s-, p- and d-like components, inside the muffin-tin spheres.

around the X'_5, X'_4 and W_3 points, where the spin–orbit interaction splittings obscure the comparison. Thus the two-fold degenerate level X'_5 is split into X_6^- and X_6^+ and the band crossing at W_3, which lies very close to the Fermi energy, is lifted with the introduction of a gap of approximately 1 eV between the lowest p bands at this point. The remaining differences between our results and the results of the other *ab initio* relativistic calculations are mainly due, besides the spin–orbit interaction, to the lack

Table 1. Comparisons of characteristic bandwidths and separations. Most of the numbers quoted (other than those of the present calculations) have been read out from the corresponding figures (the error due to misreading should be ±1%).

	Anderson *et al* (1972)	Loucks (1965)	McFeely *et al* (1975)	Breeze (1974)	Present
Occupied bandwidths (eV)					
$E_1-\Gamma_1$	9·8	11·4	11·9	12·0	12·4
$E_1-X'_4$	3·4	3·5	3·0	2·7	3·1
$E_1-L'_2$	4·4	4·5	3·6	3·0	4·1
W'_2-E_1	0·1	0·2	0·3	0·4	0·2
s–p separations (eV)					
X'_4-X_1	1·8	3·3	3·8	4·0	4·5
W_3-W_1	4·7	5·6	5·5	5·4	6·3
L'_2-L_1	2·6	3·8	4·6	4·8	4·7
K_3-K_1	2·2	3·9	5·0	4·7	5·5
p bandwidths (eV)					
$X'_5-X'_4$	5·7	6·2	3·5	3·4	5·2
W'_2-W_3	1·8[a]	1·8[a]	1·5	1·8	1·4
$L'_3-L'_2$	10·4	—	5·7	4·9	9·7
K_4-K_3	6·7	5·3	3·0	3·1	5·2

[a] This value corresponds to the average of these two spin–orbit split separations.

of self-consistency in the other calculations and to the different treatment of the exchange potential.

3. Comparison with experiment

3.1. Optical data

As was mentioned earlier, the present calculation, contrary to the LCAO results, gives the correct prediction about the 5·3 eV peak, found by Kramers–Kroning analysis of the optical data of Liljenvall *et al* (1970). Our calculation confirms the suggestion of Liljenvall *et al* (1970) who have identified this peak as due to the K_4–K_3 transition. We also share the reservation expressed by these authors concerning the contributions to the same peak from the X'_5–X'_4 transitions, as can be seen in table 1. Moreover, our results show that the second unidentified peak at about 3·9 eV can be associated with the K_4–K_1 transition as Liljenvall *et al* (1970) have proposed.

Also, from our densities of states figure 2, we have found a 3·3 eV gap between the s-like and p-like bands, and an occupied p bandwidth of 4·1 eV. The corresponding values deduced from the XPS spectrum are about 2·5 eV and about 3·5 eV respectively. This represents a 15–30% deviation between theory and experiment.

3.2. Electronic specific heat coefficient γ and mass enhancement factor λ

The linear coefficient γ of the electronic specific heat is related to the electron–phonon mass enhancement λ by the following relation

$$\gamma = \tfrac{2}{3}\pi^2 \, k_B n_t(E_F)(1 + \lambda). \tag{3.1}$$

In the above expression k_B is the Boltzman's constant, and $n_t(E_F)$ is the total density of states at the Fermi level. The experimentally measured value of γ is 3·06 mJ mol^{-1} deg^{-2} (Van der Hoeven and Keesom 1965) and according to the present calculation, $n_t(E_F) = 3\cdot475$ states per Ryd per spin per atom. Thus substituting these values in (3.1) we obtain $\lambda = 1\cdot51$. This value is in excellent agreement with the value $\lambda_{\text{exp}} = 1\cdot55$ deduced from tunnelling experiments (see, e.g., Allen and Dynes 1975). A direct determination of γ using $n_t(E_F)$ and our calculated value of λ, presented in §4.1, gives $\gamma = 3\cdot10$ mJ mol^{-1} deg^{-2} in very good agreement with experiment (1%).

3.3. Fermi surface data

Using our energy bands we have calculated the frequencies of the ψ orbit of the Fermi surface of Pb. This orbit is a contribution to the Fermi surface resulting from the second band and is centred at Γ; it should not be affected by spin–orbit splittings. Our results shown in table 2 agree with the measurements of Anderson *et al* (1972) to

Table 2. Fermi surface frequencies expressed in MG.

Orbit	Direction	Exp[a]	Cal
ψ	100	204·4	199·6
ψ	110	159·1	153·2
ψ	111	155·8	149·1

[a] Measurements of Anderson *et al* (1972).

within 4%. We have not attempted to calculate the frequencies of any of the other orbits measured by Anderson *et al* (1972) because these orbits depend on the position of the level W_3 which is affected seriously by the spin–orbit coupling.

4. Applications to electron–phonon interaction and T_c

The value of the electron–phonon mass enhancement λ, obtained in §3.2 by resorting to experimental measurements of γ, can be calculated *ab initio* from our bandstructure results. This can be done by employing the theory of Gaspari and Gyorffy (1972). This theory, within the rigid muffin-tin approximation gives the electron–phonon inter-action η and hence λ in terms of partial densities of states and phase shifts readily available from our bandstructure results, provided that the average phonon frequency $\langle \omega^2 \rangle$ is known from experiment. We have found a value of $\eta = 1\cdot23 \, \text{eV Å}^{-2}$ with a corresponding value for $\lambda = 0\cdot836$ which is almost half the experimental value. The reasons for this large discrepancy should certainly be related to the validity of the approximations underlying the Gaspari–Gyorffy theory; namely the spherical, the local and the rigid muffin-tin approximations. It has been illustrated by Zdetsis *et al* (1979) that the first two approximations are not important for lead, the main reason for the discrepancy being the rigid muffin-tin approximation (RMTA). The RMTA assumes that the effective electron–ion potential as the ions move is the same as the muffin-tin potential used to obtain the bandstructure. For transition metals, for which the Gaspari–Gyorffy theory was originally designed, the scattering of the electrons is dominated by the atomic potential inside the muffin-tin sphere and the RMTA should be quite good. For simple metals however, it is very unlikely that this is the case and one must go beyond the RMTA to obtain good estimates of η and, in turn, of λ. This has been attempted in two previous publications (Papaconstantopoulos *et al* 1978, Zdetsis *et al* 1979) using different approaches. Both methods are based on the idea of adjusting the muffin-tin potential so that the $q = 0$ Fourier component of the electron–ion pseudopotential equals $-Z/2n_t(E_F)$, where Z is the valency (Ziman 1960). The main difference is that the first method (Papaconstantopoulos *et al* 1978) employs the eigenfunctions corresponding to the adjusted muffin-tin potential while the second (Zdetsis *et al* 1979) leaves the eigenfunctions unaltered. Because of this difference the

Table 3. Calculated values of the Fermi level, E_F; of total $n_t(E_F)$ and partial $n_l(E_F)$ DOS; of the free scatterer $n_l^{(1)}$; of phase shifts δ_l and of η. λ and T_c for Pb. The renormalised values η^*, λ^*, T_c^* are those corrected for the RMTA.

States per Ryd per atom per spin								
n_t	n_s	n_p	n_d	n_f	$n_s^{(1)}$	$n_p^{(1)}$	$n_d^{(1)}$	$n_f^{(1)}$
3·475	0·185	2·252	0·292	0·060	0·159	3·226	0·252	0·031
μ^*	δ_s	δ_p	δ_d	δ_f	E_F(Ryd)		$m\langle \omega^2 \rangle$ (eV Å^{-2})	
0·088	1·337	0·921	0·000	0·004	0·365		1·434	

RMTA			Present method			Experimental	
η (eV Å^{-2})	λ	T_c (K)	η^* (eV Å^{-2})	λ^*	T_c^* (K)	λ	T_c (K)
1·199	0·836	3·3	2·216	1·545	6·99	1·55	7·19

Table 4. Variation of the superconductivity parameters of lead by alloying with bismuth. Symbols as in table 3.

Pb–Bi concentration	No of electrons per atom	λ/λ_{Pb} Calculated	λ/λ_{Pb} Exp[a]	$T_c/T_{c,Pb}$ Calculated	$T_c/T_{c,Pb}$ Exp[a]
$Pb_{0.9}\ Bi_{0.1}$	4·1	1·04	1·07	1·03	1·06
$Pb_{0.8}\ Bi_{0.2}$	4·2	1·10	1·21	1·12	1·10
$Pb_{0.7}\ Bi_{0.3}$	4·3	1·18	1·30	1·24	1·17
$Pb_{0.65}\ Bi_{0.35}$	4·35	1·21	1·37	1·27	1·24

[a] Taken from Allen and Dynes (1975).

second approach appears to be physically more reasonable, and the results for Pb, given in table 3, confirm this expectation displaying an excellent agreement with experiment. We have also compared the two approaches for several other simple metals; results and discussion will be given elsewhere.

Having λ, the superconducting transition temperature T_c can be calculated by the well known McMillan formula (McMillan 1968) or its improved Allen–Dynes version (Allen and Dynes 1975). Besides λ, the other key parameter entering McMillan's formula is the Coulomb pseudopotential μ^*. The parameter μ^* was obtained from the density of states $n_t(E_F)$ using the formula of Bennemann and Garland (1972) giving $\mu^* = 0.088$. The value of T_c in table 3 has been calculated by the Allen–Dynes equation and our computed values, of λ and μ^*. Note that the experimental value of λ quoted in table 3 is that obtained by Allen and Dynes using $\mu^* = 0.1$.

Alloying lead with elements of the nearby columns of the periodic table (such as Tl and Bi) can substantially change the superconducting properties of Pb. In particular, alloying with Bi, which increases the electronic content of the unit cell, is known to increase T_c (see Allen and Dynes 1975).

Here, we can reproduce this trend by using our results for lead and employing the rigid band approximation. This approximation, which assumes that the electronic bands of Pb remain rigid as Bi is added, is expected to be reliable especially for low concentrations of Bi. Thus, considering that adding Bi changes only the position of the Fermi level and therefore the n_l and $n_t(E_F)$, we have constructed table 4. This table shows the variation of λ and T_c with increasing concentration of Bi. As can be seen in table 4, the experimentally found trends are well reproduced here. Since we are interested only in showing the trends in the variation of λ and T_c, we have not attempted any RMTA corrections as we have done for pure lead.

Acknowledgment

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