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1994 J. Phys.: Condens. Matter 6 2145

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An electronic structure and resistivity calculation for liquid La

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Received 21 June 1993, in final form 7 December 1993

Abstract. We present a first-principles parameter-free calculation of the electronic densities of states, spectral functions and electrical resistivity of liquid La based on the tight-binding linear muffin-tin orbitals (TB-LMTO) and the recursion method. Computer-generated 600-particle cubic clusters are used as models of liquid La. Electrical resistivity is calculated using the Kubo-Greenwood formula and the recursion method applied to the TB-LMTO Hamiltonians for the model clusters. Partial decomposition of conductivity, in order to assess the separate contributions from the (TB-LMTO) s, p and d states, is presented. The contribution of the cross channels (s-p, p-d, and s-d) to the diffusivity function is found to be substantial and negative, reducing the total value of the conductivity by almost 50%. The calculated resistivity is about 23% in excess of the measured value. Sources of error in our calculation are discussed and ways of improving the results within the framework of the TB-LMTO scheme are suggested.

1. Introduction

Electronic structure and electrical resistivity of liquid La, and several other transition metals, have been calculated by Ballentine and co-workers [1–4] using a linear combination of atomic orbitals (LCAO) basis. These authors used computer-generated model clusters of 365 atoms to represent the liquids, and the recursion method [5] together with the Kubo-Greenwood formula [6, 7] was employed to compute the electronic density of states (DOS) and resistivity. The resistivity of liquid La was found to be dominated by the d states, i.e., the eigenstates that could be described mainly by a superposition of d orbitals centred on various atoms. The situation was found to be similar in other liquid transition metals where the Fermi level is well inside the d band. These calculations revealed the inappropriateness of the use of the diffraction model [8], or the extended Ziman theory, in describing the electronic conduction in strong-scattering disordered metals. The diffraction model assumes that the conduction electrons possess well defined wave vectors, and describes their propagation via the Boltzmann equation. However, the wave vector k associated with an electron state has an uncertainty of approximately the reciprocal of the mean free path, which can be as small as the average interatomic spacing in these highly resistive disordered metallic systems. Clearly k is no longer a good quantum number to describe the electron states. The calculations of Ballentine and co-workers have clearly shown that in these partially filled d-band liquid metals conductivity is dominated by d states, that do not possess well defined k vectors. Even if one assumes that conduction is via states that can be labelled with k vectors (e.g. the s states), a practical difficulty in employing the diffraction model arises in the estimation of the Fermi wave vector k_F , determined by the number density of

such electrons [9, 10]. In order to calculate the resistivity of liquid La, Delley and Beck [9] assumed that conduction was via *s* states only, yielding 0.5 or fewer current carriers per atom, whereas Waseda and co-workers [10] assumed that *s* and *d* states were equally conductive, yielding three carriers per atom.

On the grounds of the reasons discussed above Ballentine and co-workers [3, 4, 11, 12] argued that the conductivity of strong-scattering *s*-*d*-band metallic systems is best calculated via methods that treat all electronic states on equal footing, without any *a priori* assumption regarding their role in the process of conduction. They proposed a calculation scheme based on the Kubo-Greenwood formula [6, 7] and the recursion method [5], which provides a real-space (as opposed to *k*-space) treatment of the properties of topologically disordered systems in a tight-binding (TB) basis. Ballentine and co-workers used the Anderson-Bullett [13, 14] (chemical pseudopotential) scheme to obtain TB-LCAO Hamiltonians for computer-generated clusters representing liquid La and other liquid transition metals. In implementing the Anderson-Bullett scheme the authors were forced to use two adjustable parameters that were fitted to the band structure of solid (FCC) La and used subsequently in the liquid-state calculation.

In this work we present the electronic structure and the conductivity of liquid La by using the method of Ballentine and co-workers [1-4, 11, 12] together with the first-principles TB linear muffin-tin orbital (LMTO) [15-17] basis. The motivation here is to perform a first-principles calculation of electronic structure and conductivity of liquid La (i) based on density functional theory, (ii) without the use of any parameters fitted to experiments, and (iii) without the *a priori* assumption of the existence of *k* vectors labelling the conduction-electron states. Recently we have presented similar calculations for the 3d liquid transition metals [18], along with a detailed discussion of the natural advantage and suitability of the TB-LMTO basis for such calculations.

The remainder of this paper is divided into the following sections. In section 2 we describe the construction of the 600-particle clusters used in the calculation. In section 3 we describe the electronic structure. In section 4 we present the TB-LMTO recursion calculation of resistivity. In section 5 we discuss possible sources of errors and ways of improving the present resistivity calculation. To our knowledge the only other first-principles real-space calculation of transport properties in disordered metals is that of Zhao *et al* [19, 20], who have studied the transport and optical properties in some metallic glasses using the orthogonalised linear combination of atomic orbitals (OLCAO) method. Instead of using the recursion method, they used exact diagonalization of the matrices involved in order to compute the eigenfunctions and related properties.

2. Simulation of the liquid clusters

600-particle clusters with cubic boundaries were generated using the Monte Carlo method based on the Metropolis [21] algorithm discussed extensively in the literature [22]. We considered the two-body potential proposed by Ballentine [1] in calculating the energies of various configurations. The number density for the clusters was chosen to be 0.0257 \AA^{-3} , which corresponds to the experimental number density in liquid La at 1070°C [23]. The clusters were surrounded by periodic replicas, thus avoiding the surface effects in considering the energy of interaction of an atom with its neighbours. The simulation was continued until the fluctuations in energy no longer showed any systematic component, and the pair distribution function, $g(r)$, calculated for the cluster reached a stable limit. The form of the

two-body potential for liquid La given by Ballentine [1] is

$$U(r) = \begin{cases} c(X^{-6} - X^{-4}) + H & X < 2 \\ 0 & X > 2 \end{cases} \quad (1)$$

with $X = r/r_0$, $r_0 = 5.669$ a.u., $c = 1.3$ eV, and $H = 0.0469$ eV. This form was suggested by inversion of the hypernetted-chain equation [24] based on the measured structure factor [23]. The value of the scale parameter r_0 was adjusted to produce the correct radius of the repulsive core. The simulation was carried out for about 3000 steps, i.e., each particle was given 3000 trials to move. The actual temperature of simulation was 1700 K, higher than the temperature (1343 K) at which the experimental pair distribution function was considered, simply to improve the agreement between theory and experiment for this quantity. The pair distribution functions, $g(r)$, of two such clusters thus generated (histogram) are compared with the experimental result [23] (smooth curve) in figure 1. We tried changing the parameters r_0 and using two different constants in front of the inverse sixth- and fourth-power terms in (1) in order to obtain a better agreement between the theoretical and experimental $g(r)$. No significant improvement over the pair distribution function shown in figure 1 was achieved.

3. Electronic structure

In the LMTO method [16, 17] space is divided into muffin-tin spheres centred at various atomic (if necessary, also interstitial) sites R . In the tightest-binding representation, α , an LMTO basis orbital of (collective) angular momentum index $L = (\ell, m)$, centred at site R , is given, in the atomic sphere approximation (ASA) by the expression

$$\chi_{RL}^\alpha(\mathbf{r}_R) = \phi_{RL}(\mathbf{r}_R) + \sum_{R'L'} \dot{\phi}_{R'L'}^\alpha(\mathbf{r}_{R'}) h_{R'L',RL}^\alpha \quad (2)$$

The function ϕ_{RL} is the solution of the wave equation inside the sphere of radius s_R at R for some reference energy $E_{\nu R\ell}$ and is normalized within the sphere. The potential inside the spheres is calculated using the density functional theory. The radial part of the function $\dot{\phi}_{RL}^\alpha$ is related to the energy derivative of $\phi_{R\ell}(r_R)$ at the reference energy. The expansion coefficients h^α in (2) are given by

$$h_{RL,R'L'}^\alpha = (c_{R\ell}^\alpha - E_{\nu R\ell}) \delta_{RR'} \delta_{LL'} + (d_{RL}^\alpha)^{1/2} S_{RLR'L'}^\alpha (d_{R'L'}^\alpha)^{1/2} \quad (3)$$

where $c_{R\ell}^\alpha$ and $d_{R\ell}^\alpha$ are potential parameters (PPs) to be obtained from the function $\phi_{R\ell}^\alpha$ at the sphere boundary at R (see (3.52) and (3.53) of [17]). S^α is the screened structure matrix whose elements, in the tightest-binding representation, are essentially zero beyond the second shell of neighbours in all close-packed structures. The functions ϕ and $\dot{\phi}^\alpha$ are truncated outside the sphere at R . Thus all TB-LMTO orbitals, irrespective of the L character of the function ϕ in (2), are short-ranged. Through the second term on the RHS of (2) a TB-LMTO orbital centred about the site R depends on the spatial arrangement and the chemical nature of the atoms in the neighbourhood of R . This makes them a natural choice for the description of topologically disordered systems. Note also that the L' sum in (2) destroys the pure $L(\ell, m)$ character of a TB-LMTO orbital $\chi_{R'L'}^\alpha$, although, in many cases, the deviation from the pure L character may be small.

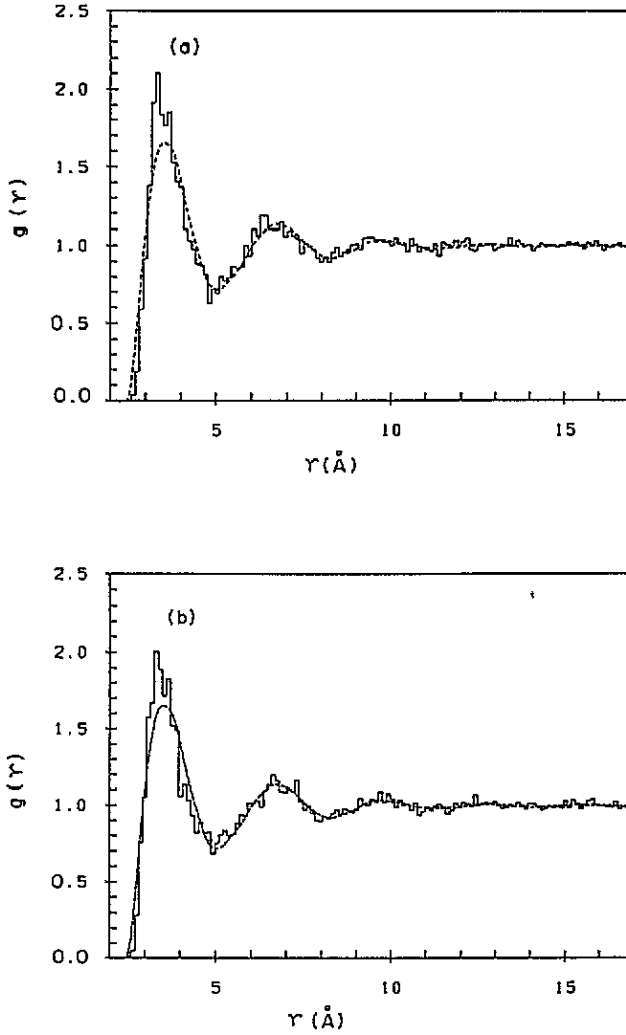


Figure 1. A comparison of the experimental pair distribution function $g(r)$ [23] in liquid La at 1070°C (smooth dashed curve) with those calculated (histogram) for the 600-particle liquid La clusters.

The Hamiltonian and the overlap matrices for the basis represented by (2) are given by (with the neglect of a small term)

$$\mathbf{H} = \mathbf{h} + \mathbf{hoh} + (\mathbf{1} + \mathbf{ho})E_v(\mathbf{1} + \mathbf{oh}) \quad (4)$$

$$\mathbf{O} = \langle \chi | \chi \rangle = (\mathbf{1} + \mathbf{ho})(\mathbf{1} + \mathbf{oh}). \quad (5)$$

In (4) and (5), $\mathbf{1}$ is the unit matrix and we have consistently dropped the subscripts R and L as well as the superscript α . The matrix \mathbf{o} is diagonal in RL representation and its value is determined by the logarithmic derivative of the function ϕ at the sphere boundary at R (see (3.48) of [17]). The Löwdin-orthonormalized Hamiltonian in the ASA assumes the form

$$\mathbf{H}^{(2)} = E_v + \mathbf{h} - \mathbf{hoh} + \mathbf{hohoh} - \mathbf{hohohoh} + \dots = \mathbf{H}^{(1)} - \mathbf{hoh} + \mathbf{hohoh} - \mathbf{hohohoh} + \dots \quad (6)$$

$$\mathbf{H}^{(1)} = E_v + \mathbf{h}. \quad (7)$$

As shown in (5), the parameter α determines the degree of non-orthogonality of the basis. Solving the eigenvalue problem for $\mathbf{H}^{(1)}$ only is equivalent to neglecting the non-orthogonality of the TB-LMTO basis. As seen from (6) this non-orthogonality can only be incorporated at the cost of increasing the range of the Hamiltonian. Although the recursion calculation can be carried out with an approximate form of $\mathbf{H}^{(2)}$ ($= \mathbf{H}^{(1)} - \mathbf{hoh}$) [25], in this work we restrict ourselves to $\mathbf{H}^{(1)}$ in calculating the DOS and conductivity. The Fermi level, E_F , determined from the DOS obtained with $\mathbf{H}^{(1)}$ is close to the reference energy, E_v , for d orbitals (see table 1 and figure 2). So the error in the DOS near E_F due to the use of $\mathbf{H}^{(1)}$ is expected to be small.

Table 1. TB-LMTO potential parameters obtained by performing self-consistent LMTO calculations for FCC La at the density of liquid La at 1070 °C (0.0257 atoms \AA^{-3}).

	E (Ryd)	c (Ryd)	$d^{1/2}$ (Ryd $^{1/2}$)	α (Ryd $^{-1}$)
s	-0.258 25	-0.183 83	0.290 72	-0.987 88
p	-0.205 51	0.109 20	0.142 58	-1.773 96
d	-0.202 04	-0.008 51	0.140 24	-0.886 36

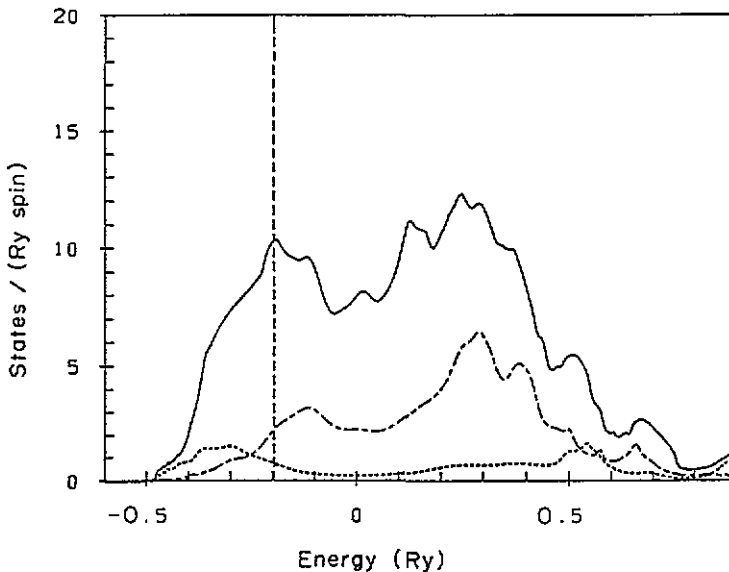


Figure 2. The density of electronic states for the 600-particle liquid clusters obtained with the TB-LMTO Hamiltonian $\mathbf{H}^{(1)}$ (see text for details): short-dashed line, s component; long-short-dashed line, p component; solid line, total DOS. The vertical line shows the position of the Fermi level.

We have used the TB-LMTO Hamiltonian $\mathbf{H}^{(1)}$ to calculate the DOS for the 600-particle liquid clusters with periodic boundary conditions using the recursion method [5]. Although self-consistency in an average sense could be achieved as in the TB-LMTO recursion calculation of Nowak *et al* [26], we have relied on the fact that the potential parameters are the true atomic quantities in the Hamiltonian. They are obtained from the solutions of the

wave equation at the sphere boundary, and hence depend on the volume per atom. We have performed self-consistent scalar-relativistic LMTO-ASA calculations using an s, p, d basis and combined corrections for La in the FCC structure with lattice parameters determined by the number density in the liquid phase [23]. The potential parameters thus obtained are used in the construction of the liquid-state Hamiltonian. The FCC structure was chosen to obtain the potential parameters because the coordination number in the liquid is close to that of an FCC solid. In table 1 we present the TB-LMTO PPs for FCC La at a number density of $0.0257 \text{ atoms } \text{\AA}^{-3}$, the density of liquid La at 1070°C [23]. In the TB-LMTO recursion calculation of [26], where self-consistency was achieved in the potential averaged over a number of atoms, the PPs were found to vary very little from one atom to another [27]. Thus we believe that our method of determining the PPs for the liquid state is quite reliable. Note also that our PPs are based on first-principles calculations and are not empirical.

Local densities of states (LDOSs) of twenty atoms in the inner region of two clusters were averaged to obtain the DOS for liquid La. The continued-fraction expansion of the Green function was terminated using the prescription of Allan [28] (see [26] for a discussion of the actual version of the terminator used), and Beer and Pettifor [29]. The two methods of terminating the Green function yielded very similar results. In figure 2 we show the DOS for liquid La obtained with the Hamiltonian $\mathbf{H}^{(1)}$ using the Beer-Pettifor [29] terminator. For reference purposes, in figures 3 and 4 we show the band structure and the DOS, respectively, for FCC La with a lattice parameter corresponding to liquid La density, obtained by the standard LMTO-ASA method. The DOS in figure 2 has a much smaller band width than that in figures 3 and 4, indicating the main difference between the TB-LMTO and standard LMTO Hamiltonians. Because states are squeezed into a smaller band width, the value $n(E_F)$ of the DOS at the Fermi level, obtained via $\mathbf{H}^{(1)}$, is somewhat larger than is expected from the standard LMTO result. However, for the same reason the diffusivity of the eigenstates of $\mathbf{H}^{(1)}$ should be lower than that of the eigenstates of the standard LMTO Hamiltonian. This means that the error in the conductivity, which is the product of $n(E_F)$ and the diffusivity (see next section), due to the use of $\mathbf{H}^{(1)}$, is smaller than the errors in $n(E_F)$ and diffusivity individually.

Spectral functions [1, 25, 30] are useful in studying the effect of disorder on the various spectral (s, p, or d) components of the energy eigenstates and in examining the presence of residual dispersion (energy versus wave vector) relations in the disordered phase. Since, unlike LCAO or similar bases, the TB-LMTO orbitals lack pure *L* character, resolution of the eigenfunctions into pure s- or d-like components is not possible. However, a study of TB-LMTO spectral functions is still of interest. We consider the DOS projected onto a running wave of the form

$$|u_k^{\ell,m}\rangle = \sum_j e^{ik \cdot R_j} |\chi_{R_j}^\alpha\rangle \quad (8)$$

and compute the spectral functions

$$n_k^\ell(E) = \sum_m n_k^{\ell,m}(E) \quad (9)$$

$$n_k^{\ell,m}(E) = -\frac{1}{\pi} \lim_{\epsilon \rightarrow 0^+} \text{Im} \langle u_k^{\ell,m} | G(E + i\epsilon) | u_k^{\ell,m} \rangle.$$

Here R_j represent the (atomic) sites at which the TB-LMTOs are centred. In figure 5(a) and (b) we show two views of the spectral functions calculated for the TB-LMTO s and d orbitals, respectively, for liquid La. The front view is useful in picking up any change in

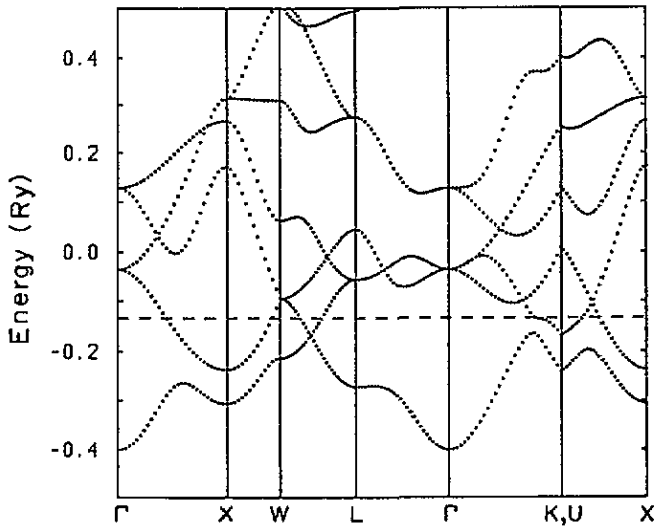


Figure 3. The band structure of FCC La at a number density equal to that of liquid La at 1070°C using the standard LMTO-ASA method.

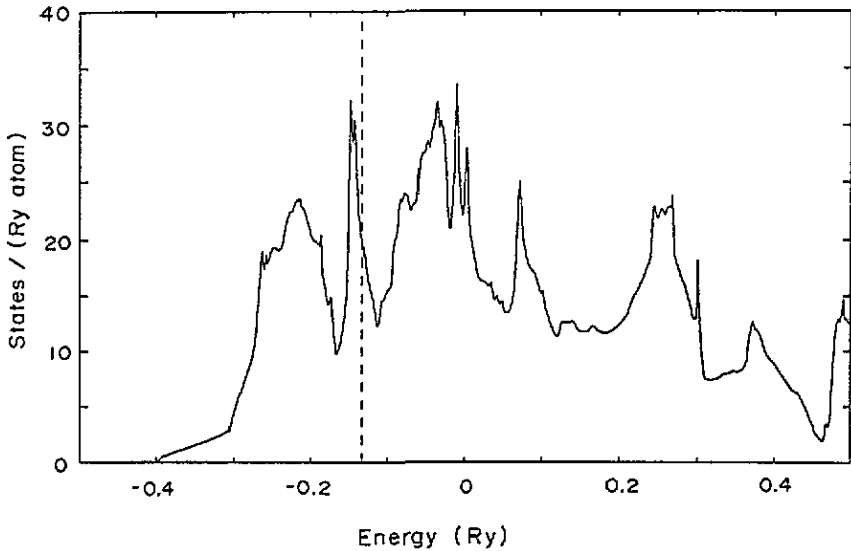


Figure 4. The density of states of FCC La at a number density equal to that of liquid La at 1070°C using the standard LMTO-ASA method.

the position of the peak as a function of k , while the side view shows clearly the change in the height of the peaks. The k values chosen extend from zero to $2\pi/a$, where a is the lattice parameter for FCC La at the liquid La density. For low k both s and d spectral functions are peaked, but about halfway between the k values corresponding to Γ and X points the peaked structure is lost, and the spectral functions resemble the average s and d DOS, indicating that the coherence between various terms in (7) has been lost. There is

very little dispersion to be discerned from the d spectral functions, while the dispersion in the s spectral function is much less than expected from the band structure in the FCC phase (figure 3). The p spectral functions (not shown here) are qualitatively similar to d spectra, i.e., exhibit some peaks for low k , soon changing to local average p DOS. The behaviour of s spectral functions is in particularly sharp contrast with the s-state spectral functions in an LCAO basis where, as discussed in detail in [1], they are found to retain their propagating character and display distinct dispersion relations, for low as well as high k values. The difference is primarily due to the fact that the TB-LMTO s orbitals show deviations from spherical symmetry, and thus are influenced by positional disorder to a larger extent than atomic s orbitals with full spherical symmetry. Note also that the dispersion shown by even the propagating states of $\mathbf{H}^{(1)}$ would be smaller than that gleaned from the band structure of figure 3 (due to the standard LMTO Hamiltonian) because of the smaller band width of $\mathbf{H}^{(1)}$.

4. Resistivity

The Kubo–Greenwood [6, 7] formula for the diagonal elements of the zero-temperature DC conductivity tensor in the eigenfunction representation can be written as

$$\sigma_{jj} = \frac{e^2 \hbar}{\Omega} \sum_{m,n} |(E_m | v_j | E_n)|^2 \delta(E_m - E_F) \delta(E_n - E_F) \quad (10)$$

where Ω is the volume of the sample, \hbar is Planck's constant, E_F is the Fermi energy, and v_j is the j component of the velocity operator. Relating the delta function to the imaginary part of the Green function and using the expression

$$\sum_m \delta(E - E_m) \langle E_m | f(E) | E_m \rangle = g(E) \{f(E)\}_{E_m=E} \quad (11)$$

where $\{\dots\}_{E_m=E}$ implies an average over the eigenfunctions with energy E , and $g(E)$ is the sample DOS at energy E , (10) can be written in the physically transparent form [31]

$$\sigma_{jj} = \frac{e^2}{\Omega_a} n(E_F) D(E_F). \quad (12)$$

Here Ω_a is the volume per atom, $n(E_F)$ is the DOS per atom, and $D(E_F)$ is the diffusivity given by

$$D(E_F) = -\hbar \lim_{\epsilon \rightarrow 0} \text{Im} \{ \langle E_m | v_j G(E_F + i\epsilon) v_j | E_m \rangle \}_{E_m=E_F}. \quad (13)$$

$D(E_F)$ is proportional to the average local DOS projected on to the states $v_j | E_m \rangle$ and can be calculated using the recursion method [5]. The eigenvectors $| E_m \rangle$ are calculated by the same filtering technique as used by Ballentine and co-workers [2–4, 11, 12, 30] and given originally by Kramer and Weaire [32].

The velocity operator is given by

$$v_j = [\mathbf{H}, x^j] i / \hbar. \quad (14)$$

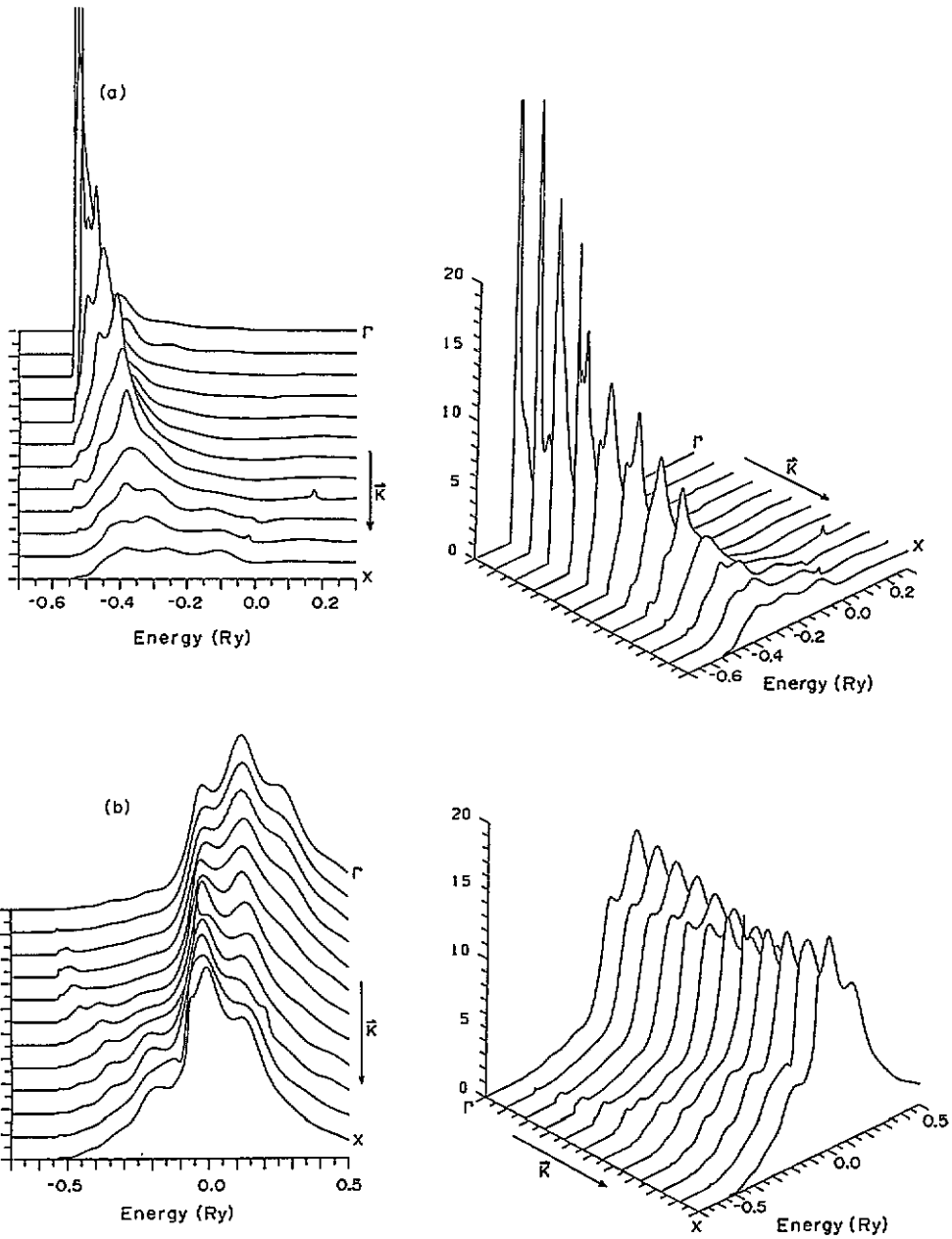


Figure 5. (a) s- and (b) d-state spectra in liquid La obtained by using the Hamiltonian $H^{(1)}$. The k -values range from zero to $2\pi/a$, where a is the lattice parameter of FCC La at the density, $0.0257 \text{ atoms } \text{\AA}^{-3}$, of liquid La at 1070°C .

The matrix elements of the velocity operator in the TB-LMTO basis (2) are

$$(v_j)_{\beta\gamma} = \sum_{\delta} (H\beta\delta x_{\delta\gamma}^j - x_{\beta\delta}^j H\delta\gamma) i/\hbar \tag{15}$$

where the subscripts denote the combined angular momentum and site indices (R, L). The

matrix elements, $x_{\gamma\beta}^j$, of the position operator can be written as

$$x_{\gamma\beta}^j = \langle \chi_\gamma^\alpha | x^j | \chi_\beta^\alpha \rangle - \frac{1}{2}(x_\gamma^j + x_\beta^j) O_{\gamma\beta}^\alpha + \langle \chi_\gamma^\alpha | [x^j - \frac{1}{2}(x_\gamma^j + x_\beta^j)] | \chi_\beta^\alpha \rangle \quad (16)$$

where x_β^j is the x^j coordinate of the atomic nucleus on which the orbital β is centred. The second term on the RHS of (16), the dipole term, is assumed to be small and neglected as in the previous LCAO recursion calculations [11, 12]. In the present calculation we also neglect the non-orthogonality of the TB-LMTO basis. Then from (15) the matrix elements of the velocity operator neglecting the dipole term, are

$$(v_j)_{\beta\gamma} = H_{\beta\gamma}(x_\gamma^j - x_\beta^j)i/\hbar. \quad (17)$$

In this work we have performed all calculations of the diffusivity function using (17). In [18] we presented results for the resistivity of liquid 3d transition metals, where the non-orthogonality of the TB-LMTO basis in evaluating the matrix elements of the velocity operator is taken into account in an approximate way. Partial justification for the neglect of the non-orthogonality of the basis in this calculation is the small difference between the Fermi level and the reference energy, E_v , for the d orbitals.

Obtaining the eigenvectors via the filtering method [32] discussed above is the most time-consuming part of the calculation. The larger the band width, the larger is the computation time. For the Hamiltonian $\mathbf{H}^{(1)}$, 1900–2200 filtering operations were typically needed to reduce the RMS energy spread, ΔE , to less than 0.02 Ryd. The CPU time required for this on a Cray XMP/24 machine was ~ 250 s (less than 5 min). For the Hamiltonian $\mathbf{H}^{(2)}$, which has a much larger band width, filtering to within $\Delta E = 0.02$ Ryd was not possible even with half an hour of CPU time on the same machine. This forced us to calculate the diffusivity with the first-order Hamiltonian $\mathbf{H}^{(1)}$ only. Fifteen eigenvectors from each of the two clusters, with energy within 0.02 Ryd of E_F , were used in computing the diffusivity.

In calculating the diffusivity via the recursion method one faces the problem of terminating the continued-fraction representation of the Green function, just as in computing a local DOS. A discussion on the various ways of terminating the continued fraction, and their effect on the calculated diffusivity, appears in our recent publication [18]. The fluctuations in the diffusivity from one eigenvector to another were larger (~ 10 –15%) than the fluctuations in the diffusivity for the same eigenvector calculated with various terminators. The results presented here are based on the Beer–Pettifor [29] terminator. The average value of the calculated resistivity was $\sim 185\mu\Omega$ cm (with $\sim 15\%$ total spread), 23% higher than the measured value of $\sim 150\mu\Omega$ cm [33]. Although the calculated value is high compared with experiment, the agreement is satisfactory in view of the fact that the calculation is free from parameters fitted to either experiments or crystal band structure. Readers should also note that in order to calculate the conductivity, we have used (9), the zero-temperature expression. This expression results from the finite-temperature Kubo–Greenwood formula by replacing the Fermi–Dirac distribution function with a step function appropriate for zero temperature. The effect of replacing the Fermi–Dirac distribution function with the step function is negligible, because the liquid temperature is much smaller than the Fermi temperature. The main temperature dependence of the conductivity originates from the changes in the structure of the liquid with temperature. Thus in the present approach, a proper temperature-dependent calculation is possible only if the structure of the liquid at different temperatures is properly represented via the clusters used in the calculation. Since our cluster was prepared to match the experimental pair distribution function at 1070 °C,

we can say our calculated resistivity is for that temperature. The experimental value of $150\mu\Omega$ cm quoted above (see *Metals Reference Book* [33]) is for 1100°C .

By resolving the eigenvectors at E_F into their orbital components we can estimate the contribution to the resistivity purely from the (diagonal) s, p, and d channels as well as the contributions from the mixed (off-diagonal) channels. Following the notation of [3], [4], [11], [12], and [30], we denote by D_s , D_p , and D_d the contribution of s, p, and d orbitals, respectively, to the full diffusivity divided by the fractional s, p, or d component of the DOS. The s and p characters of the states at the Fermi level fluctuate between 10 and 15% each, while 70–80% of the states are d like. The diffusivities D_d and D_p of the d and p channels, respectively, are similar and about a factor of three to four lower than the diffusivity D_s of the s channel. Thus the contribution of the p states to the conductivity is the least, being about 17% of the d contribution, while the contribution of the s states to the conductivity is about half the d contribution. The relative magnitudes of the s- and d-state contributions to the conductivity is thus somewhat different from the empirical LCAO (s–d band, without p states) calculation of Ballentine and co-workers [3, 4] (the agreement improved if the p- and d-state contributions in our calculation are added and then compared with the s-state contribution), but the conclusion that the conductivity is dominated by the slow-moving d states due to their larger weight at the Fermi level is still maintained. One important difference from the previous LCAO calculations [3, 4] is that the contribution from the off-diagonal channels or the cross terms is significant. The off-diagonal contribution to conductivity is negative, and roughly 40–50% of the diagonal contribution. In the calculations of [3] and [4] the off-diagonal contribution was found to be negligible (less than 2% of the diagonal contribution). Thus hybridization between the s, p, and d orbitals has strong effect on the conductivity, seriously impeding the process of conduction.

5. Summary and discussion of results

The principal features of the present calculation are that it is free from any fitted parameters, and it could be carried out with the computational ease of an empirical tight-binding calculation. However, the computational ease causes some loss of accuracy. The sources of errors, in order of perceived importance, can be described as follows. (i) The velocity matrix elements were calculated using (17), i.e., by replacing the overlap matrix \mathbf{O} by the identity matrix and by neglecting the dipole term. Although the neglect of the non-orthogonality of the basis can be justified due to the small difference between E_F and the d-orbital reference energy, the smallness of the dipole term in (16) is an untested assumption. It is possible that in the LCAO calculations of [3], [4], [11], [12], and [30], where the basis consisted of only s and d atomic-like orbitals, the relative error due to this neglect was small, since the s and d orbitals on the same atom could not be connected via the position operator, and the matrix elements connecting neighbouring orbitals are expected to be small. In calculations including the p orbitals, the s–p and p–d matrix elements for the same atom are non-zero, and neglecting all such terms is not readily justified. In fact, large negative contributions to the conductivity from the cross (non-diagonal) channels in our calculation may be partly due to errors in the velocity matrix elements. (ii) The calculations of diffusivity should be performed with a Hamiltonian more accurate than $\mathbf{H}^{(1)}$. Diffusivity is crucially dependent on the nature of the eigenfunctions at the Fermi level. Although the eigenvalues and therefore $n(E_F)$ obtained with $\mathbf{H}^{(1)}$ may be accurate, the eigenfunctions of $\mathbf{H}^{(1)}$ themselves may not be accurate enough for calculating conductivity.

(iii) It is quite likely that there are non-negligible contributions from the f states that have not been considered in the present calculation. The omission of the f orbitals may partly be responsible for the large d contribution to the conductivity. However, in the present cluster calculation with 600 particles, the inclusion of seven f orbitals per particle will increase the size of the Hamiltonian matrix well beyond the available computer memory. Thus although we recognize the potential importance of the d states, we are unable to include these in the calculation. (iv) There are errors due to the real-space method used, associated with the finite cluster size (which affects the values of the calculated recursion coefficients), and the energy window used in filtering the eigenvectors out of the initial randomly chosen vectors in the TB-LMTO space. Finite cluster size affects the diffusivity results, via errors in the eigenfunctions as well as the recursion coefficients, more severely than the DOS. Also, for a better configurational averaging one should consider a large number of clusters, possibly obtained via different choices of pair potentials, and different techniques. Our results are based on two clusters. Additional studies involving similarly prepared clusters (i.e., using Monte Carlo simulation and the same pair potential) did not significantly alter these results. This is perhaps because they all had similar $g(r)$, with the first peak somewhat higher and narrower than seen by the experiment. In principle, even clusters with very similar $g(r)$ can give rise to different results, because of differences in higher-order correlation functions. However, our clusters did not reveal such differences.

One can question the appropriateness of the Kohn–Sham orbitals for calculating transport properties, as these can be viewed simply as theoretical artifacts of a total-energy calculation, and not as the true eigenfunctions. However, they are known to describe some Fermi-surface properties correctly, and the present calculation is based on an *a priori* assumption of their suitability in describing electronic transport.

The validity of the Kubo–Greenwood formula [6, 7] itself for the calculation of resistivity of highly disordered and inhomogeneous systems has been addressed by Morgan and Ghassib [34]. They considered the effect of the internal fields (due to non-uniform charge distribution) on the scattering of electrons. The effect of the correction to the Kubo–Greenwood formula proposed by them is expected to be important only in multicomponent systems, with the components having vastly different conductivities.

Point (i) can be addressed at the cost of some additional computation. Since the expressions of the TB-LMTO orbitals are available, the matrix element of the position operator for two such orbitals can be calculated exactly, instead of using (16) and neglecting the dipole term. Point (ii) involves the use of the proper Hamiltonian in the calculation of diffusivity. Although the DOS calculation with $\mathbf{H}^{(1)}$ can be justified to some extent on account of the small difference between E_F and the reference energy, E_v (for the d orbitals), the diffusivity calculation with $\mathbf{H}^{(1)}$ is not sufficiently accurate. Since the computation of diffusivity with $\mathbf{H}^{(2)}$ is prohibitively time consuming, what we need is a Hamiltonian that is as tight binding as $\mathbf{H}^{(1)}$, and at the same time describes the states at the Fermi level accurately. One way to tackle the problem within the TB-LMTO scheme would be to recalculate the potential parameters (to be used in the diffusivity calculation) by shifting the reference energies, E_v , to the Fermi level. This has been discussed in greater detail in our recent publication [18].

To summarize, we have used the TB-LMTO recursion method for a first-principles calculation of resistivity of liquid La. The calculation is free from fitted parameters and is based on density functional theory. The calculated resistivity is around 23% in excess of the measured value. s states at the Fermi level are found to be three to four times more diffusive than the p and d states, but the contribution to the conductivity from the d states is roughly double that from the s states. The cross-channels (s – p , p – d , s – d) are found to

have a negative contribution to conductivity, amounting, in magnitude, to approximately half the contribution from the direct (s-s, p-p, d-d) channels. We have indicated the likely sources of error in our calculation and suggested ways of overcoming them within the LMTO formalism.

Acknowledgments

Financial support for this work was provided by the Natural Science and Engineering Research Council of Canada. One of the authors (SKB) would like to thank members of the Max-Planck-Institut, Stuttgart, where the initial part of this work was carried out.

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