PHYSICAL REVIEW B VOLUME 28, NUMBER 2 15 JULY 1983

s-*d*-band conductivity in liquid La

L. E. Ballentine and J. E. Hammerberg
Department of Physics and Theoretical Science Institute,
Simon Fraser University, Burnaby, British Columbia V5A 1S6, Canada

(Received 31 January 1983)

The electrical conductivity of liquid La is computed numerically from a linear combination of atomic orbitals description of a cluster of 364 atoms. Contrary to an earlier suggestion that the conduction should be mainly due to *s* states, we find that the *d* states are dominant. Although the diffusivity of *s* states is about 2.5 times greater than that of *d* states, the density of *d* states is so much greater than the density of *s* states that the conduction is mainly by *d* states.

The 6*s* and 5*d* valence bands of La are of nearly the same width and occupy nearly the same energy range. In order to calculate the electrical conductivity of liquid La, it has been assumed by some that only the *s* states are significant as current carriers, yielding 0.5 or fewer conduction electrons per atom,[1] whereas others have assumed that *s* and *d* states are equally effective as current carriers, yielding three conduction electrons per atom.[2]

Recently a linear combination of atomic orbitals (LCAO) calculation of the valence bands in liquid La was performed[3] for the purpose of elucidating the roles of the *s* and *d* states in electrical conduction. Using the recursion method,[4] one can calculate the projected density of states onto any chosen vector $|u\rangle$,

$$n_u(E) = \lim_{\epsilon\to 0} \frac{-1}{\pi} \operatorname{Im}\langle u|G(E+i\epsilon)|u\rangle = \sum_n |\langle u|\Psi_n\rangle|^2 \delta(E-E_n) \ . \qquad (1)$$

Here $G(E)=(E-H)^{-1}$, and the eigenvalues and eigenvectors of H are E_n and Ψ_n. The projected density of states onto a Bloch-type vector of the form

$$|u_{\vec{k}}^{(L)}\rangle = \sum_j e^{i\vec{k}\cdot\vec{R}_j}|\phi_j^{(L)}\rangle \qquad (2)$$

gives information about the propagating character of the states. In (2) the function $\phi_j^{(L)}$ is an atomic orbital of symmetry $L=(l,m)$ centered on atom j at the position $\vec{R}_j$. When applied to a crystal, this method yields a projected state density with peaks corresponding to the energy bands $E=E(\vec{k})$ of symmetry L. When applied to a liquid or amorphous metal, it yields a projected state density that may or may not have well-defined peaks.

For liquid La it was found (Ref. 3, Figs. 6 and 7) that the projected density for *s* states ($l=0$) has a well-defined peak at an energy that varies systematically with $\vec{k}$. However, the projected density of *d* states ($l=2$) is very broad, has very little dependence on $\vec{k}$, and differs little from the bulk density of *d* states. The existence of a vestigial dispersion relation for *s* states and the absence of one for *d* states suggested that the *s* states are propagating but the *d* states are not. That conclusion was, of course, only tentative, as was duly stressed in Ref. 3, and should be followed by a full calculation of the conductivity of liquid La, which we report in this paper.

We use the method of Stein and Krey,[5] which is essentially a generalization of the recursion method to evaluate Kubo's formula for the conductivity. The result, in a notation differing slightly from theirs, is

$$\sigma_{\mu\mu} = \frac{e^2}{\hbar}\frac{n(E_F)}{\Omega}(-1)\operatorname{Im}[\langle\chi_i|G(E_F+i\epsilon)|\chi_i\rangle]_{\text{av}} \ . \qquad (3)$$

Here $n(E_F)/\Omega$ is the total density of states per unit energy per unit volume at the Fermi energy. The vector

$$|\chi_i\rangle = [H,x_\mu]|\Psi_i\rangle \qquad (4)$$

is, apart from a trivial factor, equal to the velocity operator acting on an eigenvector of H at energy $E=E_F$. The notation of square brackets with subscripts "av" means an average over all states Ψ_i at the Fermi energy. Thus if one can obtain (approximate) eigenvectors Ψ_i then the conductivity can be calculated by using the recursion method to obtain the projected density of states onto the vector χ_i. We did not follow the method of Ref. 5 to obtain approximate eigenvectors. Instead we chose a random vector and repeatedly applied a filtering operator, $(H-a)(b-H)$, with a and b chosen to lie equidistant below and above E_F and to enclose the spectrum of H between them. This has the effect of damping out all components of the initial vector with energies $E \neq E_F$, and so yields an approximate eigenvector.

It seems intuitively plausible that a calculation on a finite cluster will be representative of the bulk conductivity provided the cluster is sufficiently large compared with the mean free path. Indeed, we find that the length of the cluster in the direction of con-

©1983 The American Physical Society

duction is the most important dimension, and computing time can be saved by using a long, thin cluster. Our results reported here were obtained for a cluster of 364 atoms whose length is eight times its transverse dimensions. Further details of our calculations, including a study of the dependence of the results on the size and shape of the cluster, and results for other metals, will be published elsewhere. We note, in passing, that our method automatically includes all s-d scattering and vertex corrections.

The electrical conductivity is related to an energy-dependent diffusivity[6] $D(E)$,

$$\sigma = e^2 \frac{n(E_F)}{\Omega} D(E_F) \quad ; \tag{5}$$

therefore, in evaluating (3) we are really calculating the diffusivity at the Fermi energy. In Table I we list the density of states per atom, the diffusivity (in atomic units: $\hbar = 2m = \text{Bohr radius} = 1$), and the conductivity. The first row is for our realistic model of hybridized s-d bands. The calculated resistivity is 151 $\mu\Omega$ cm, compared with the measured value[7] of 135 $\mu\Omega$ cm. As far as we know, this is the first time that the method of Ref. 5 has been applied to a realistic model of a conductor and quantitatively compared with experiment.

In order to estimate the relative importance of s and d states in the conduction process, we also performed the calculation for unhybridized s and d bands. We find that the tentative suggestion, based on the results of Ref. 3, that the s states should be dominant, is not correct. Indeed, the diffusivity of s states is greater than the diffusivity of d states, but the much greater density of d states causes them to dominate the conductivity. The effective mean free path for unhybridized s states is so long that our cluster is not quite long enough to yield a precise result for that case. Therefore no significance should be attached to the small difference between the conductivity for the hybridized bands and the sum of the conductivities for the unhybridized bands.

TABLE I. Density of states, diffusivity, and conductivity with and without hybridization.

	$n(E_F)$ [(Ry atom)$^{-1}$]	$D(E_F)$ (a.u.)	σ [$(\Omega\,\text{m})^{-1}$]
s-d	13.3	2.83	6.64×10^5
s	1.4	6.3	1.6×10^5
d	10.8	2.45	4.67×10^5

There have been a few previous calculations of d-band conductivity in liquid metals. Using the so-called s-d model, in which plane-wave s states hybridize with localized d states, ten Bosch and Bennemann[8] found that the d contribution to the conductivity could become as large as the s contribution, but the d contribution was never dominant. However, the significance of their results is cast into doubt because of several oversimplifications in their model. They did not take into account the degeneracy of the d state nor the angular dependence of the transfer matrix element and, furthermore, their model is biased in favor of s-state domination of the conductivity. Weir and Morgan[9] studied the diffusion of electrons as a function of time in computer models of liquids having s or d states (but not both together). In spite of the omission of s states and hybridization, they found that a pure d-state model could account for a large fraction of the conductivity of liquid Ni.

What then is the correct number of conduction electrons per atom to use in the Boltzmann equation? If the states at the Fermi energy are dominated by a characteristic wave vector k_0, then the n_e should be chosen so that $k_F \equiv (3\pi^2 n_e)^{1/3} = k_0$. However, Fig. 7 of Ref. 3 shows that there is no such characteristic wave vector for the d states, which dominate the conductivity of liquid La. We suggest that this means that electrical conduction takes place via a kind of diffusion process for which the usual Boltzmann-equation treatment is unjustifiable.

---

[1] B. Delley and H. Beck, J. Phys. F $\underline{9}$, 517 (1979).

[2] Y. Waseda, A. Jain, and S. Tamaki, J. Phys. F $\underline{8}$, 125 (1978).

[3] L. E. Ballentine, Phys. Rev. B $\underline{25}$, 6089 (1982).

[4] V. Heine, Solid State Phys. $\underline{35}$, 1 (1980); D. W. Bullett, *ibid.* $\underline{35}$, 129 (1980); R. Haydock, *ibid.* $\underline{35}$, 215 (1980); M. J. Kelly, *ibid.* $\underline{35}$, 295 (1980).

[5] J. Stein and U. Krey, Z. Phys. B $\underline{37}$, 13 (1980).

[6] P. N. Butcher, J. Phys. C $\underline{5}$, 3164 (1972).

[7] G. Busch, H.-J. Güntherodt, H. U. Künzi, and H. A. Meier, in *Proceedings of the 2nd International Conference on Liquid Metals, Tokyo, 1972,* edited by S. Takeuchi (Taylor and Francis, London, 1973), p. 263.

[8] A. ten Bosch and K. H. Bennemann, J. Phys. F $\underline{5}$, 1333 (1975).

[9] G. F. Weir and G. J. Morgan, J. Phys. F $\underline{11}$, 1833 (1981).