Mead can be explained in terms of barrier distortion due to negative space charge within the insulator arising due to the occupation by electrons of deep traps therein.

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[3] The localized states near the top of the valence band are of no interest to us here, since we are concerned with conditions existing in the *upper* half of the energy gap of the insulator.

[4] Here we are assuming that the insulator is thin enough so that the lowest trap level does not rise above the electrode Fermi level. Thus we are confining ourselves to barrier heights lying in the range φ_0 to $\varphi_0 + (E_{Fe} - E_t)$. In actual fact the maximum height above the electrode Fermi level which the conduction band can attain is $\varphi_0 + (E_{Fe} - E_{Fi})$. In this case, traps at the center of the insulator will lie above the electrode Fermi level. However, for barrier heights in excess of $\varphi_0 + (E_{Fe} - E_t)$ the barrier is an extremely slow function of the insulator thickness.

[5] The effect of image forces are negligible in the results presented here [see J. G. Simmons, J. Appl. Phys. 34, 1793 (1963)]. It would be of significance only when the voltage bias is greater than that for which the virtual cathode is positioned at the cathode-insulator interface, where a modified form of Schottky lowering of the interfacial barrier would become apparent.

[6] Note this process is simply an artifice for assigning a value to φ_0, which would otherwise have to be quantified arbitrarily, and is not suggested to be the actual value of the interfacial barrier. Furthermore, it will be apparent that φ_0 is one of the less important parameters considered here, and hence a knowledge of its precise value is relatively unimportant.

NEW APPROACH TO ENERGY-BAND CALCULATIONS WITH RESULTS FOR LITHIUM METAL*

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A new method, the GI method, for electronic wave functions has been applied to the study of energy bands in bcc lithium metal. The GI method leads to energy bands for lithium comparable with the Hartree-Fock bands except that small gaps occur within the first Hartree-Fock Brillouin zone. This leads to a compelling interpretation of several anomalous experimental properties of alkali metals (such as the very low optical absorption threshold and the lack of saturation of the transverse magnetoresistance).

Band structures for solids have usually been calculated using the Hartree-Fock (HF) method.[1] In this method the total wave function is a Slater determinant of spin orbitals,

$$\alpha\Psi, \tag{1}$$

where Ψ is a product of spin orbitals and α is the antisymmetrizer. For a singlet state, the spin orbitals are required to occur in pairs which involve the same spatial orbitals but different spins, say $\varphi_i\alpha$ and $\varphi_i\beta$ (i.e., the orbitals φ_i are doubly occupied) in order that the total wave function have the correct spin symmetry. One of the most valuable features of the HF method is that each orbital can be interpreted as the eigenstate of an electron moving in the average field due to the other electrons.

Recently it has been shown that it is possible to go beyond the HF framework while retaining an independent particle interpretation.[2] In the GI method[2] the antisymmetrizer in (1) is replaced by the group operator[3] G_i^{γ}, which ensures that

$$G_i^{\gamma}\Psi \tag{2}$$

is an eigenfunction of $\hat{S}^2$ and satisfies the Pauli principle for all choices of orbitals in Ψ. Thus every spatial orbital is allowed to be different (no double occupation). This method has been applied to a number of atoms and molecules, including Li[4] and Li_2,[5,6] and always leads to a better energy than HF. In calculations on Li it was found that the core orbitals could be *exactly* replaced by an effective local potential (the *ab initio* pseudopotential),[7] and it was found that this potential accurately reproduces the states of Li_2.[6] In Li_2, instead of one symmetric (σ_g) doubly occupied bonding orbital as in the HF method, we obtain two bonding orbitals, each concentrated on one of the respective Li centers.

We have now applied the GI method to studying the band structure of Li metal. Just as in the Li_2 molecule, the GI orbitals have lower symmetry than the HF orbitals. In order to describe the states of Li metal, it is convenient to view the bcc lattice in terms of the two equivalent interpenetrating simple cubic (sc) sublattices. The GI conduction orbitals divide into two sets: The

a orbitals $\{\varphi_{ia}\}$ are mutually orthogonal, are eigenfunctions of the one-electron self-consistent-field Hamiltonian H_a, and are concentrated (or localized) more on the a sublattice (sc_a); similarly the b orbitals $\{\varphi_{ib}\}$ are orthogonal, are eigenfunctions of a different Hamiltonian H_b, and are concentrated more on the b sublattices (sc_b).[8] No orthogonality conditions exist between the sets $\{\varphi_{ia}\}$ and $\{\varphi_{ib}\}$, but they are related by the translation vectors between sc_a and sc_b. The GI orbitals are Bloch functions, but only for the sc space group, not for the bcc space group; however, the many-electron wave function (2) still transforms according to the bcc space group. Hence, since the unit cell for sc is twice the volume of the bcc unit cell, the resulting sc Brillouin zone (BZ) is only half the volume of the bcc BZ and is a cube inscribed in the HF dodecahedral BZ. In terms of this reduced sc BZ each HF band becomes two bands, and in this new context it is possible for small energy-band gaps to occur on the boundary of the sc BZ. We will see below that since this first BZ has the same volume as the Fermi surface, and since the Fermi surface is roughly spherical, the Fermi surface overlaps the first two GI bands.

As discussed below, the existence of two partially filled bands seems to provide a cogent explanation of several properties observed in the alkalis which afford no natural explanation within the HF framework. These properties are the following: (1) The observed linearity of the transverse magnetoresistance[9,10] of the alkalis is in contradiction to the saturation in high fields expected for the closed orbits found in HF.[11] (2) The Hall coefficient[12] exhibits a significant decrease in increasing fields which is not expected for the HF schema. (3) The optical absorption threshold observed for alkali metals is far lower than expected from the HF energy bands.[13] (4) The soft-x-ray spectra[14] are difficult to explain for the HF energy band.

We have carried out GI calculations for band states at the center and at three symmetry points[15] on the surface of the sc BZ. The wave functions were expanded in plane waves and solved in the field of the Li atom *ab initio* effective potential[7,16] centered at the center of the cell. As for Li_2,[6] the potential is angular-momentum dependent (i.e., different for s and p states). The energies of the states calculated using the GI approach and the connectivity of these states are shown in Fig. 1.

We find that the splittings are small, 0.5 eV at $k=(2\pi/a)(\frac{1}{2},0,0)$ and dropping to 0.0 at $k=(2\pi/a)\times(\frac{1}{2},\frac{1}{2},0)$. Thus the Fermi surface should be nearly spherical. However, the Fermi surface overlaps the first two GI bands and intersects the sc BZ at about 0.734 of the distance from $k=(2\pi/a)(\frac{1}{2},0,0)$ to $k=(2\pi/a)(\frac{1}{2},\frac{1}{2},0)$, at which point ($k_{\mathrm{F}}=0.59a_0^{-1}$) the energy gap should be about 0.08 to 0.16 eV.[17] This gap size should cause little distortion from sphericity for the Fermi surface, which is in agreement with de Haas-van Alpen,[18] cyclotron-resonance,[19] and positron-annihilation experiments,[20] and with the x-ray determination of electron moments.[21] But optical transitions are now allowed between occupied states of the first band and empty states of the second band, and thus the threshold for optical transitions

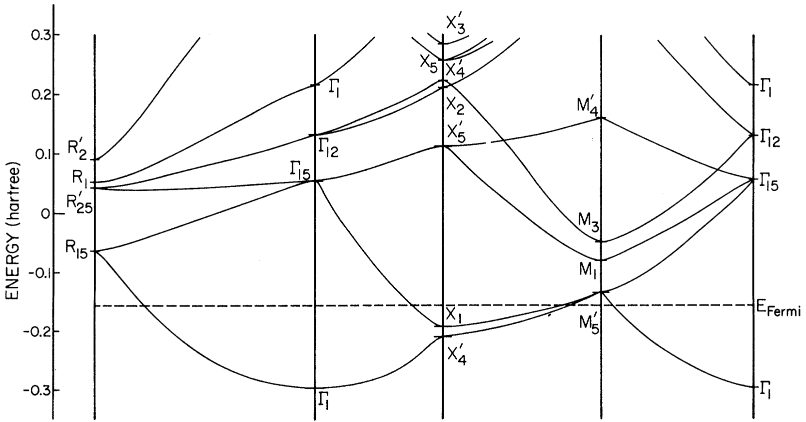

FIG. 1. GI energy-band states at the center and at high-symmetry points on sc BZ boundary for bcc lithium metal. [All quantities are in Hartree atomic units (the unit of energy is the Hartree = 27.211 eV). A lattice constant of $6.575a_0$ has been used.] Lines indicate only the connectivity of the states and the dashed line denotes the approximate location of the Fermi level.

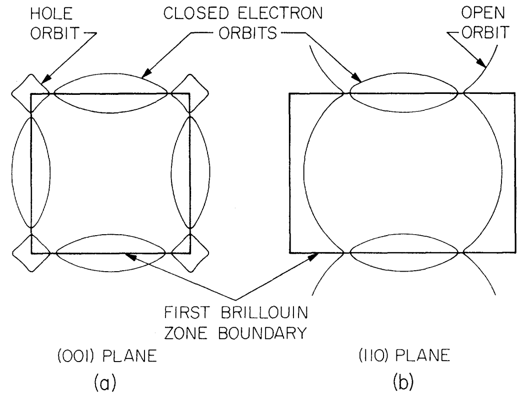

FIG. 2. Maximum orbitals in k space (Fermi-surface radius $k_F = 0.5298 a_0^{-1}$). (a) The (001) plane (appropriate for $B \parallel [001]$); $\theta = 72°$; $\theta' = 18°$; side of square $= 0.9556 a_0^{-1}$. (b) The (110) plane (appropriate for $B \parallel [110]$); $\theta = 72°$; $\theta' = 108°$; sides of rectangle $= 0.9556 a_0^{-1}$ and $1.3514 a_0^{-1}$.

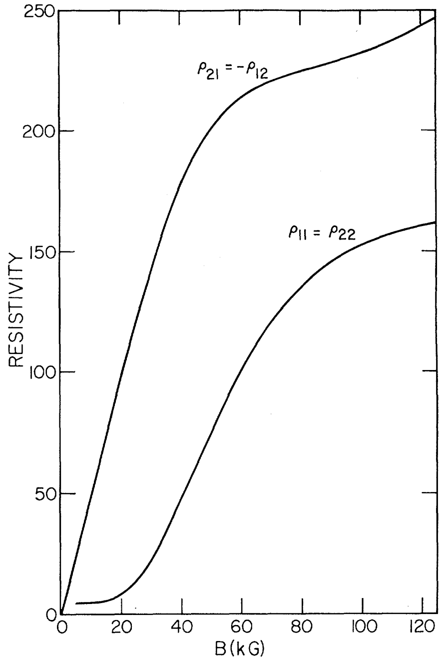

FIG. 3. The lithium-metal resistivity components $\rho_{11} = \rho_{22}$ and $\rho_{21} = -\rho_{12}$ as a function of the magnetic field (oriented in the [001] direction). Calculations were carried out allowing transitions between orbits. An energy gap of 0.08 eV = 0.002 94 Hartrees and a relaxation time $\tau = 0.7 \times 10^{-10}$ sec were used.

should be very small. These new transitions from the first to the second GI band correspond to indirect (or k-symmetry-forbidden) transitions in terms of the HF band. Such indirect transitions have also been detected in other materials[22] and it may be that GI energy bands could be used to explain these.

As shown in Fig. 2(b) it is possible to have open orbitals in some planes [e.g., (110)] whereas for other planes [e.g., (001) in Fig. 2(a)] both the electron and hole orbits are closed. The very small energy gap is expected to allow magnetic breakdown which would lead to transitions between open and closed orbits and between closed orbits. As discussed by Falicov and Sievert[23] such band-to-band transitions can lead to unusual variations in the magnetoresistance as a function of magnetic field. We have carried out similar calculations for the cases in Fig. 2 and find results similar to theirs. In order to make a relevant comparison with experimental results, we have extended the calculation to an integration over the entire Fermi surface rather than just over the maximal orbits. Our results for the field in the [001] direction are reported in Fig. 3. We find a distinctly linear behavior (20 to 80 kG) in the transverse magnetic resistance over a large part of the field range (10 to 60 kG) investigated by Penz and Bowers.[9] In addition we find that ρ_{21} (the Hall coefficient R times the magnetic field) is linear at low fields, decreases in slope at intermediate fields, and is again linear (with smaller slope) at high fields. This is consistent with the decrease in R found by Penz for intermediate fields. The large slope at small fields occurs because of the large fraction of hole orbits. On account of magnetic breakdown in the limit of high fields all orbits are electron orbits. On the basis of the band-structure calculations the ratio of these slopes is expected to be about 4:1, which is consistent with the ρ_{21} calculations for various values of the energy gap and relaxation time (τ).

The HF wave function for Li has a half-filled conduction band for all lattice constants, including $a = \infty$. However, as noted by Mott[24] this cannot be correct for large a since the system must be an insulator at sufficiently large internuclear separations. This is known as the Mott paradox[11] and has been explained in terms of electron correlation.[11,24] We have carried out GI calculations on Li at larger internuclear distances and find that the energy gap increases and the bandwidths decrease with internuclear distance until for large a ($15a_0$) the gap corresponds approximately to the Li atom $2s$-$2p$ excitation energy and the width of the first band is negligible. Thus the first cubic BZ is completely filled and the second zone completely empty, and bcc Li is an insulator at larger distances, just as it should be. That is, for the GI band structure, bcc Li changes continuously from an insulator at large a to a metal at small a, and we see that the Mott paradox merely arises as an artifact of the HF band scheme. (It actually results because the HF orbitals are forced to be doubly occupied which results in an incorrect dissociation of the wave function as $a \rightarrow \infty$. The analogous incorrect behavior also occurs for the HF wave function of Li_2 molecule.)[8] It may be that a study of the GI band structure of transition-metal oxides would provide an understanding of the Mott-like transitions which occur in these and related systems.[24,25]

In addition to the aforementioned properties, it may be possible to explain the anomalous soft x-ray emission spectrum[14] of Li from the GI energy bands. However, here it is essential to calculate the states within the sc BZ. We are now in the process of carrying out such calculations, which are required for a consideration of the intensities of both optical and x-ray transitions and are also necessary for a more accurate determination of the magnetoresistance.

Other attempts to explain the anomalous properties of the alkali metals have been made by Phillips and Cohen,[26] postulating a collective resonance state, and by Overhauser and co-workers,[27] postulating spin-density or charge-density waves. The GI wave function (2) for Li leads to an alternative to these explanations; however, it retains the correct bcc periodicity and is exactly a singlet state with no net spin density anywhere.

In conclusion, we find that the band structure of Li metal obtained directly from GI calculations leads to two partially filled bands and small energy gaps. The existence of these gaps leads to a direct and simple explanation of several anomalous properties of alkali metals.

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