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Fermi surface of alkali metals using the full-potential linear muffin-tin orbital method and the generalized gradient approximation

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The Fermi surface (FS) of the alkali metals (Li, Na, K, Rb, and Cs) has been studied using a full-potential linear muffin-tin orbital (FPLMTO) method together with both the local-density approximation (LDA) and the generalized gradient approximation of Perdew and Wang (PW91). We demonstrate that FPLMTO calculations based on the LDA improve the FS of K, Rb, and Cs compared to LMTO calculations within the atomic-sphere approximation (ASA). Most importantly, our FPLMTO-LDA calculations reproduce all essential features of the FS of Cs, whereas the previous LMTO-ASA LDA calculations erroneously resulted in a FS which is open at the N point. The gradient-corrected FPLMTO calculations further improve the FS for K, Rb, and Cs and give results in good agreement with experiment. For Li and Na the FPLMTO calculations slightly worsen the FS, both when using the LDA and PW91.

I. INTRODUCTION

With the continuous improvement of the theories and the computational techniques of the electronic structure, one can hope to be able to determine material properties from first principles. For metals, Fermi surface (FS) studies are important as these can be used in considerations of properties such as superconductivity and phonon spectra. Moreover, calculations of the FS are important when introducing improvements of the basic theory, since the experimental data often are very accurate and give important information about the energy bands in the ground state. In this paper we report on self-consistent *ab initio* calculations for the FS of alkali metals. The alkali metals are of technological interest due to their use as liquid coolants for nuclear reactors. At room temperature and zero pressure all alkali metals are stable in the bcc phase. With decreasing temperature, Li and Na transform into a close-packed hexagonal phase (Sm type, also called $9R$). The character and nature of this martensitic phase transition make these materials interesting candidates for experimental and theoretical studies. Moreover, the unusually high compressibility of the alkali metals makes them suitable also for high pressure studies.[1] For instance, the heavy alkali metals (Cs and Rb) are prototype examples for where an $s \rightarrow d$ transition appears upon compression.[2] The crystallographic behavior of Cs within a rather moderate pressure range, caused by the $s \rightarrow d$ transition, has offered the possibility of an experimental as well as a theoretical investigation of this new type of d-band metal.[2]

Recent first principle calculations[3] of the FS of alkali metals have shown that linear muffin-tin orbital atomic-sphere approximation (LMTO-ASA) calculations are not able to predict the FS of Cs correctly, namely, these calculations[3] show that the FS of Cs is open at the N point. This finding is similar to earlier calculations[4] but it contradicts experiment,[5] which shows that the FS at the N point is closed just as in the other alkali metals. Furthermore, the calculated[3] anisotropy of the extremal cross-sectional Fermi surface areas is two to five times larger than the experimental anisotropy for Na, K, Rb, and Cs. The main purpose of this paper is to investigate the effects from an improved theoretical treatment of the exchange and correlation potential as well as the removal of geometrical constraints on the shape of the crystal potential, and hopefully to be able to improve on the agreement with experimental data for the FS, especially in the case of Cs.

Of particular interest in the present context is the fact that Perdew and Wang[6] (PW) have proposed a generalized gradient approximation (GGA) for the density functional. In the present work we have used the most recent version of GGA, which we will refer to as PW91.[7] It has been demonstrated that PW91 gives a considerable improvement for a number of ground state properties of

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many atomic, molecular, and solid state systems.[8] As an example of this we mention the recent work of Ozolins and Körling,[9] who have studied the structural and cohesive properties of transition metals using calculations based on a general potential and PW91 for the density functional. They have shown that gradient-corrected full-potential calculations give a significant improvement over calculations based on the local-density approximation (LDA). Further, they claim that the full-potential (FP) treatment is important when using gradient-corrected potentials. In the literature there is almost a complete lack of FS calculations using functionals which consider the electron density gradient for the exchange and correlation potential. An exception is the calculation by Barbiellini *et al.*,[10] who have performed LMTO-ASA calculations for the Fermi surface calipers of copper and nickel in certain directions and the N-centered ellipsoid areas of vanadium, using an older form (PW) of the gradient-corrected exchange and correlation potential.[6] For copper they found that the small changes in the Fermi surface calipers were in the right direction but that they were not sufficiently large and that the PW and LDA bands were actually almost identical. They also calculated the Fermi surface radii for the majority spin sixth band in Ni and found that the LDA and PW radii are very similar. Barbiellini *et al.* concluded that the gradient-corrected potentials are not yet sufficiently developed to replace the LDA potential. Our own attempts in this direction, although based on a modified version of the generalized gradient approximation, have met with considerable success and our conclusion is thus somewhat different than that of Barbiellini *et al.* Namely, our recent calculations on the FS of noble metals[11] using a FPLMTO calculation within the LDA gave an improvement over LMTO-ASA calculations and gradient-corrected FPLMTO calculations further improved the agreement with experiment. The main purpose of the present paper is to gain more experience and knowledge of whether gradient-corrected FPLMTO calculations improve the FS of solid state systems or not and we presently concentrate our efforts on the alkali metals.

Previous to the recent study of the FS of the alkali metals by Hjelm and Calais,[3] there have been a number of calculations[12–18] of the FS of the alkali metals. In the work by Hjelm and Calais cyclotron orbit areas, effective masses, and g factors for the alkali metals were calculated using the LMTO-ASA method. Moreover, Alouani *et al.*[19] have determined the FS contours for K using a relativistic LMTO-ASA method. In that work it was shown that under pressure the FS of K transforms continuously from a free-electron sphere into an object with complex shape due to the progressive filling of d states.

The rest of this paper is organized in the following way. In Sec. II we briefly give the details of the calculations, whereas results and discussion are given in Sec. III and conclusions are presented in Sec. IV.

II. DETAILS OF THE CALCULATIONS

In our calculations we have used a full-potential linear muffin-tin orbital technique.[20] The calculations were all electron, fully relativistic, with the spin-orbit coupling included at each variational step. The charge density and potential were allowed to have any shape inside the muffin tins as well as in the interstitial region. The basis set, charge density, and potential were expanded in spherical harmonic series (with a cutoff $l_{\max}=8$) within the nonoverlapping muffin-tin spheres and in a Fourier series in the interstitial region. The basis set was comprised of augmented linear muffin-tin orbitals.[21,22] The tails of the basis functions outside their parent spheres were linear combinations of Hankel or Neuman functions with nonzero kinetic energy. In the calculations reported here, two sets of energy parameters were used for Cs, one appropriate for the semicore $5p$ states, and the other appropriate for the valence states. The resulting basis formed a single, fully hybridizing basis set. The integration over the Brillouin zone was done using the special point sampling[23] with a Gaussian smearing of 20 mRy and 58 **k** points in the 1/48th part of the Brillouin zone. The calculations were all done at the experimental lattice constant and the ratio between the interstitial region and the unit cell volume was approximately 0.5. The potential was either treated in the local-density approximation (LDA) using the Hedin-Lundqvist[24] (HL) expression for the exchange and correlation potential or treated in the generalized gradient approximation of Perdew and Wang (PW91).[7] Using Stark's[25] area-mass routine, we have calculated FS orbital areas and masses. The area and mass of the computed surface in a plane normal to a given direction (equal to the direction of the magnetic field in the experiment) were found by numerical integration of the radii calculated at a fixed interval of rotation in that plane. In the calculations reported here the stepping angle $\delta\theta$ was taken to be 5°. When we modified this angle to be 2.5° the calculated areas changed by less than 0.5%. In the past, authors have taken a percentage error in the calculated FS area as a measure of the agreement with experiment. We take a different view, where the electronic structure calculations are the central issue, namely, that a more appropriate measure of the accuracy of the theory is to know the error in the eigenvalues. It would therefore be more appropriate to measure the agreement in terms of the shift in the Fermi energy, ΔE_F, required to bring the calculated extremal area into agreement with the experimental area. We define this shift as

$$\Delta E_F = \frac{1}{\pi}\frac{A_{\text{expt}} - A_{\text{calc}}}{m_b} , \qquad (1)$$

where m_b is the calculated band mass for the orbit. A_{expt} and A_{calc} are the experimental and calculated areas. We would like to stress that the area-mass codes calculate eigenvalues at each **k** point on the FS and use no fitting procedures.

III. RESULTS AND DISCUSSION

The crystal structure, lattice constants,[26] and Wigner-Seitz radii, along with the free-electron cross-sectional areas, used in the present calculations are collected in Table I. In Table II we give the calculated extremal

TABLE I. Crystal structure, lattice constant (a), Wigner-Seitz radius (S_{ws}), and free-electron model (FEM) cross-sectional area used in the present calculations.

Element	Crystal structure	a^a (Å)	S_{ws} (a.u.)	FEM (a.u.)
Li	bcc	3.480	3.2375	1.1040
Na	bcc	4.225	3.9311	0.7488
K	bcc	5.225	4.8616	0.4869
Rb	bcc	5.585	5.1966	0.4285
Cs	bcc	6.045	5.6246	0.3658

[a] Donohue (Ref. 26).

cross-sectional areas along with experimental areas for the alkali metals. As regards the areas all levels of approximations (ASA-LDA, FP-LDA, and FP-GGA) give good agreement with experiment. Notice that the replacement of the ASA with a general potential causes a larger shift compared to replacing the LDA with the GGA. Also, for Li and Na the ASA-LDA data agree best with experiment whereas for K, Rb, and Cs the FP-GGA give the best results. A better measure of the accuracy of the theory may be the anisotropy of the FS area (Table II). Notice from Table II that the largest change in the anisotropy is found when replacing the ASA with FP calculations. A replacement of the LDA with the GGA introduces only a small shift in the anisotropy. Overall, the agreement between experiment and theory is better for the full-potential calculations, and the GGA results improve the agreement further. However, Li is an exception, for which both these two modifications worsen the agreement with experiment.

In the present paper the calculation of the FS for Cs is especially important because the previous self-consistent LMTO-ASA band structure calculation by Hjelm and Calais[3] was not able to predict it correctly. The calculation of Ref. 3 shows a FS which is open at the N point, and this is in sharp disagreement with the experiment. Therefore Hjelm and Calais also modified their FS calculations for Cs by lowering the Fermi level artificially. In our FPLMTO self-consistent calculations we did not introduce any shifts in E_F and the computation correctly predicts the FS of Cs. Our calculated band structure for Cs is shown in Fig.1 and it is obvious from this figure that the Fermi level cuts one band at the N point, which gives rise to a closed Fermi surface at N. Our band structure for Cs is also very similar to the ones we calculate for the other alkali metals. Hjelm and Calais[3] have calculated the anisotropy of the FS area, with the above mentioned shifted Fermi level. They so obtained an anisotropy of 81.0×10^{-3}, whereas our self-consistent LDA calculation gives an anisotropy of 73.6×10^{-3}. This value is still too large in comparison with the experimental data of 36.0×10^{-3}.[5] Using the gradient-corrected FPLMTO calculation, the calculated anisotropy is reduced to 62.6×10^{-3}, bringing it closer to experiment.

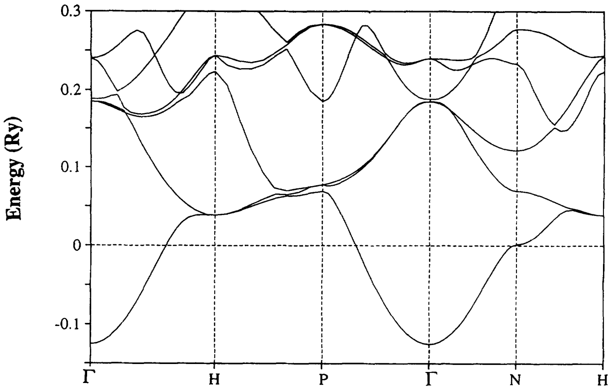

FIG. 1. Relativistic band structure of Cs along the major symmetry directions using PW91. The Fermi level (E_F) is set to be at zero energy and is marked by a dashed line. The energy is in rydbergs.

In Table III, we have shown the calculated values of ΔE_F for all alkali metals. Here we notice that the largest improvement is again found when replacing the ASA with the FP, whereas replacing the LDA with the GGA produces smaller modifications. With two exceptions—Li and Na—the agreement is better for the more elaborate theory.

TABLE II. Calculated and experimental cross-sectional area (in a.u.) as well as anisotropy (in 10^{-3}) for alkali metals.

Element	Expt. area	Previous calc. area[a]	Present calc. area		Expt. anis.	Previous calc. anis.[a]	Present calc. anis.	
		ASA-LDA	LDA	PW91		ASA-LDA	LDA	PW91
Li	1.10(mean)[b]	1.0956–1.1290	1.1173–1.1596	1.1195–1.1594	30[c]	30	38	36
Na	0.7479(mean)[b]	0.7495–0.7508	0.7564–0.7567	0.7563–0.7567	0.92[d]	1.7	0.4	0.6
K	0.4886(mean)[e]	0.4890–0.4938	0.4882–0.4907	0.4885–0.4909	2.0[f]	9.6	5.1	4.9
Rb	0.4268–0.4305[g]	0.4250–0.4385	0.4231–0.4317	0.4236–0.4304	8.9[g]	31.0	20.0	16.0
Cs	0.3621–0.3755[g]	0.3348–0.3628	0.3544–0.3814	0.3541–0.3770	36.0[g]	81.0	73.6	62.6

[a] Hjelm and Calais (Ref. 3).
[b] Randles and Springford (Ref. 27).
[c] Hunt *et al.* (Ref. 30).
[d] Lee (Ref. 16).
[e] Shoenberg and Stiles (Ref. 29).
[f] Templeton (Ref. 28).
[g] Gaertner and Templeton (Ref. 5).

TABLE III. ΔE_F (in mRy) for alkali metals.

Element	Previous calc.[a] ASA-LDA	Present calc. LDA	PW91
Li	-2.51	-7.10	-7.37
Na	-0.7	-2.7	-2.6
K	-0.8	-0.2	-0.3
Rb	-0.9	0.4	0.5
Cs	4.2	0.2	0.6

[a] Hjelm and Calais (Ref. 3)

IV. CONCLUSIONS

We have reported on FPLMTO calculations for the FS of all the alkali metals, within both the LDA and the GGA (PW91). Quite generally there is a larger change in the electronic structure when replacing the ASA with a general potential compared to exchanging the LDA with the GGA. Concerning the FS areas the LMTO-ASA calculations give better data for Li and Na whereas for K, Rb, and Cs the FP-GGA data are better. Our FP calculations correctly predict the FS of Cs to be closed at the *N* point in agreement with experiment but in contrast to a previous LMTO-ASA calculation.[3] Moreover, the experimental anisotropy increases with atomic number as we go from Na → Cs as well as showing a large anisotropy for Li, and our calculations reproduce this trend. Furthermore, the calculation using the FP-LDA reduces the anisotropy in comparison to the ASA-LDA calculation[3] and brings it closer to the experimental data, suggesting that a full-potential treatment is necessary for obtaining good agreement with the experimental FS in alkali metals. Gradient-corrected FPLMTO calculations further reduce the anisotropy, showing that a nonlocal potential also has an effect on the FS, although smaller than the FP treatment. We finally conclude that the calculations give good agreement with experiment and the effect of the GGA on the FS properties is encouraging, especially for K, Rb, and Cs, which is in agreement with our earlier experience.[11]

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