Self-Consistent Energy Bands of Calcium by the Green's-Function Method*

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The nonrelativistic Green's-function method is used to compute self-consistent energy bands of calcium. The results show the state U to be occupied in the metal and the state W to be unoccupied. Corrections due to relativistic effects and to unfreezing of the core are discussed.

I. INTRODUCTION

There exists in the literature some disagreement concerning the electron-energy-band structure of calcium. An early band-structure calculation for calcium was carried out by Manning and Krutter[1] using the cellular method. They found unoccupied states in the first zone near what would now be called the point W, and occupied states in the second zone, presumably near L. A more recent calculation for calcium has been made by Harrison[2] using a few weak constant orthogonalized-plane-wave (OPW) matrix elements. He found a band structure very like that for free electrons, with a Fermi surface consisting of a first-zone monster and second-zone caps at L.

Altmann and Cracknell[3] have used the modified cellular method of Altmann[4] to calculate the energy bands. They find a band structure that is much less free-electron-like than is the model proposed by Harrison. They find a Fermi surface that consists of small kidney-shaped pockets of holes centered at K and U in the zone and a saucer-shaped region of electrons at L.

The band structure of calcium has been calculated also by Vasvari, Animalu, and Heine,[5] using the model potential of Abarenkov and Heine.[6] Depending upon the choice of the Fermi level, they find[7,8] a first-zone hole surface differing from that given by Harrison and from that given by Altmann and Cracknell, and consisting of hole pockets centered at W.

Ordinarily, these differences could be resolved by appeal to experimental measurements of the Fermi surface, in particular, to measurements of the de Haas–van Alphen effect. Unfortunately, however, in the case of calcium the measurements[9,10] are incomplete and were made on samples that turned out to be microcrystalline aggregates. As a result, the measurements are subject to differing interpretations and it is possible to make from them a more or less reasonable argument in support of each of the various calculations. Thus, we feel that a reasonably careful first-principles calculation will be useful and will help to choose among the various models proposed for the energy-band structure of calcium.

We have carried out a self-consistent energy-band calculation for calcium using the Green's-function method of Korringa[11] and Kohn and Rostoker.[12] We find the state K to be occupied in the first zone and the state W to be unoccupied, the first-zone Fermi surface consisting of pocket of holes about W. The second-zone surface consists of the usual saucer-shaped region of electrons at L.

II. RESULTS

The first Brillouin zone for the fcc calcium lattice is shown in Fig. 1, where the various symmetry points are labeled.[13] The calculations were carried out for values of $\mathbf{k}$ in 1/48 of the zone, corresponding to 2048 equally spaced points in the full zone. The lattice constant for calcium was chosen as 10.5296 a.u. This value is based upon the measurements of Smith, Carlson, and Vest[14] and includes an estimated correction for thermal contraction to 0°K.

The numerical integrations of the radial Schrödinger equation were carried out for a logarithmic mesh given by

$$x=\ln r=x_0+(N-1)\Delta x,$$

with $x_0=-9$ and $\Delta x=0.025$. The inscribed sphere radius corresponded to $N=413$, which gives a value slightly smaller than half the nearest-neighbor distance. The integrations were carried out using a modified Milne method, with the starting values generated by a series expansion near the origin.

The calculations were done nonrelativistically and without spin-orbit coupling since it was felt that the extra computer time that would be needed for relativistic calculations was not justified. These corrections are shown to be small in Sec. III. The calculations were carried out self-consistently, using a procedure generally similar to that described by Snow and Waber[15] in their self-consistent calculation for copper. The calculations were carried out until for all occupied states the energy eignevalues differed by less than 0.002 Ry between the two final steps.

The starting potential was generated from a superposition of the free-atom charge densities.[16] The crystal-core charge density was calculated from the free-atom core with nearest-neighbors overlap and its value frozen for subsequent steps of the calculation (the effect of removing this restriction is discussed in Sec. III). The potential for succeeding steps in the self-consistent procedure was computed from the

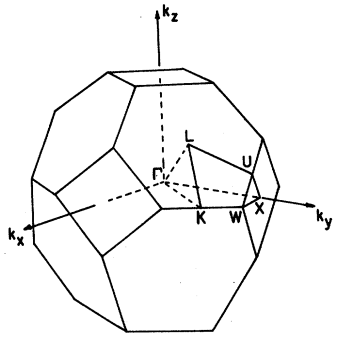

FIG. 1. First Brillouin zone for fcc calcium.

frozen-core density and an average of the conduction electron densities found in the two preceding steps of the calculations. The crystal muffin-tin potential was calculated using the formulation suggested by Liberman,[17] which is particularly suited to this type of calculation. The structure parameters needed for computing the potential from this formulation were found to be

$$\langle 1/r\rangle_R = 1/(0.37832a),$$
$$\langle 1/r_{12}\rangle_{RR} = 1/(0.38157a),$$

where a is the lattice constant. The values include the correction to apply to the inscribed sphere radius used here and have an estimated uncertainty of about 0.05 and 0.25%, respectively. Liberman's formulation uses the Kohn-Sham[18] exchange potential, which is $\frac{2}{3}$ as large as that proposed by Slater.[19] Snow and Waber,[15] in their work on copper, found better results by using a value somewhat between these two. We have not investigated the effect of varying this factor for calcium.

As shown by Ham and Segall,[20] it is convenient to expand the wave function used in the Green's-function method in the form

$$\psi = \sum_{l,m} i^l d_{lm} R_l(r)\, Y_{lm}(\theta, \phi),$$

where the Y_{lm} are real angular functions. This form allows the expansion coefficients to be chosen real and leads to real matrix elements. For these calculations we have included in the expansion all terms through $l=4$. The effect on the convergence of the energy eigenvalues of including the higher l components in the wave function is indicated in Table I. This table gives for some representative points the variation of the computed energy eigenvalue as higher l values are added to the trial wave function. Particularly noticeable from this table is the large effect produced by the inclusion of the $l=2$ terms. The importance of these d terms for calcium has already been stressed by Vasvari, Animalu, and Heine.[5]

Equally important for a self-consistent calculation is the convergence of the wave function itself. An approximate, but convenient, measure of this convergence is afforded by the variation with l of the fraction of the wave function outside the inscribed sphere. This fraction ω, which is needed in the calculations, can conveniently be found by the method given by Ham and Segall.[20] The variation of this fraction with l is shown for some representative points in Table II, which indicates the degree of convergence obtained for the wave functions used in the calculations.

The final computed energy eigenvalues are given in Table III and the resulting band structure is shown

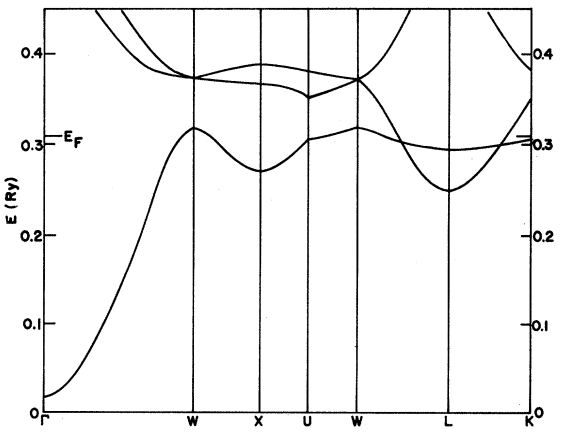

FIG. 2. Self-consistent energy bands for calcium.

TABLE I. Convergence of energy eigenvalues for representative points in the zone. The computed eigenvalues are shown as a function of the maximum l value included in the trial wave function. The units of k are $\pi/4a$ and the energy is given in Ry.

k	$l=0$	$l=1$	$l=2$	$l=3$	$l=4$
110	0.02934	0.03029	0.03023	0.03023	0.03023
340	0.18638	0.19833	0.18352	0.18336	0.18336
282	−0.15224	−0.15224	0.30672	0.30593	0.30585
480	−0.15224	−0.15224	0.31887	0.31770	0.31765

TABLE II. Convergence of the wave function for representative points in the zone. The table gives the fraction ω of the wave function outside the inscribed sphere shown as a function of the maximum l value included in the trial wave function. The variation of this fraction is assumed to be a measure of convergence. The first column gives k in units of $\pi/4a$.

k	$l=0$	$l=1$	$l=2$	$l=3$	$l=4$
110	0.36125	0.33670	0.33645	0.33650	0.33650
340	0.66395	0.37545	0.32760	0.32670	0.32660
282			0.34235	0.33710	0.33645
480			0.34315	0.33575	0.33540

TABLE III. Eigenvalues for points in 1/48 of the Brillouin zone considering 2048 points in the entire zone. The units for k are $\pi/4a$ and the energy eigenvalues are given in Ry, relative to the constant value $V_c = -0.3947$ between spheres.

	Band 1	Band 2	Band 3
k	E_1	E_2	E_3
000	0.0173	0.4992	0.5792
010	0.0238	0.4918	0.5713
020	0.0429	0.4728	0.5501
030	0.0737	0.4478	0.5184
040	0.1144	0.4220	0.4819
050	0.1620	0.3992	0.4467
060	0.2114	0.3816	0.4171
070	0.2529	0.3706	0.3959
080	0.2705	0.3669	0.3874
110	0.0302	0.4846	0.5693
120	0.0492	0.4669	0.5526
130	0.0798	0.4436	0.5036
140	0.1202	0.4194	0.4763
150	0.1675	0.3978	0.4431
160	0.2167	0.3811	0.4145
170	0.2581	0.3706	0.3940
180	0.2758	0.3670	0.3858
220	0.0677	0.4520	0.4999
230	0.0976	0.4326	0.4875
240	0.1371	0.4123	0.4628
250	0.1835	0.3940	0.4330
260	0.2319	0.3797	0.4068
270	0.2728	0.3706	0.3886
280	0.2903	0.3675	0.3815
330	0.1263	0.4182	0.4688
340	0.1642	0.4030	0.4437
350	0.2087	0.3892	0.4161
360	0.2549	0.3784	0.3930
370	0.2931	0.3714	0.3796
380	0.3084	0.3690	0.3765
440	0.1998	0.3933	0.4188
450	0.2408	0.3846	0.3926
460	0.2818	0.3724	0.3779
470	0.3104	0.3671	0.3735
480	0.3176	0.3721	0.3721
550	0.2757	0.3675	0.3810
560	0.3045	0.3518	0.3784
570	0.3105	0.3600	0.3770
660	0.3058	0.3509	0.3798
111	0.0366	0.4772	0.5726
121	0.0554	0.4599	0.5572
131	0.0857	0.4377	0.5023
141	0.1258	0.4146	0.4748
151	0.1729	0.3939	0.4426
161	0.2218	0.3777	0.4144
171	0.2633	0.3682	0.3936
181	0.2810	0.3662	0.3844

	Band 1	Band 2	Band 3
k	E_1	E_2	E_3
221	0.0737	0.4438	0.5040
231	0.1033	0.4237	0.4928
241	0.1424	0.4029	0.4686
251	0.1885	0.3838	0.4396
261	0.2367	0.3689	0.4135
271	0.2777	0.3615	0.3925
281	0.2949	0.3624	0.3810
331	0.1316	0.4062	0.4782
341	0.1691	0.3876	0.4568
351	0.2132	0.3698	0.4325
361	0.2594	0.3556	0.4106
371	0.2974	0.3511	0.3914
381	0.3105	0.3600	0.3770
441	0.2041	0.3703	0.4399
451	0.2447	0.3523	0.4218
461	0.2860	0.3378	0.4060
471	0.3099	0.3431	0.3909
551	0.2796	0.3330	0.4108
561	0.3051	0.3246	0.4014
222	0.0915	0.4259	0.5072
232	0.1201	0.4049	0.4979
242	0.1582	0.3835	0.4755
252	0.2031	0.3636	0.4485
262	0.2507	0.3482	0.4223
272	0.2912	0.3427	0.3973
282	0.3058	0.3509	0.3798
332	0.1473	0.3833	0.4910
342	0.1834	0.3613	0.4745
352	0.2260	0.3406	0.4521
362	0.2718	0.3238	0.4279
372	0.3051	0.3246	0.4014
442	0.2164	0.3384	0.4647
452	0.2550	0.3167	0.4490
464	0.2948	0.3001	0.4299
552	0.2832	0.2982	0.4405
333	0.1725	0.3585	0.4934
343	0.2058	0.3342	0.4831
353	0.2448	0.3120	0.4646
363	0.2832	0.2982	0.4405
443	0.2339	0.3091	0.4809
453	0.2587	0.2949	0.4689
444	0.2457	0.2934	0.4863

in Fig. 2. By assigning an appropriate weight[15] to each of the states given in the table, we find for the Fermi energy, relative to the bottom of the band, the value

$$E_F = 0.3091 - 0.0173$$

$$= 0.2918 \text{ Ry}.$$

This value is indicated in Fig. 2. It is particularly to be noted from the table and the figure that we find the point W to lie above the Fermi level and the point U to lie below. This is in contrast to the findings of Altmann and Cracknell,[3] but agrees with the conclusions reached by Vasvari.[8] The resulting Fermi surface is very similar to that given and discussed by Vasvari.

III. ENERGY CORRECTIONS

In this section we discuss two of the corrections—not necessarily the largest—that apply to the calculations discussed above. These corrections involve relativistic effects, including particularly spin-orbit coupling, and the effect of unfreezing the crystal-core charge density. Both corrections are expected to be small for calcium.

Although the calculations discussed in the preceding section were carried out using the nonrelativistic version of the Green's-function method, we have also written programs that are being used for other calculations which use a relativistic version[21,22] of the method. Thus, it was comparatively easy to investigate relativistic corrections to the computed energy eigenvalues. We have used the final crystal muffin-tin potential generated in the nonrelativistic calculations to recompute the energy eigenvalues for a few representative points with the relativistic version of the program. The results of these calculations are shown in Table IV. It is seen from this table that the relativistic corrections are indeed small for calcium and have the effect of further depressing U relative to W.

It is customary in self-consistent energy-band calculations to consider only the variation of the conduction-electron charge density, with the core being frozen at the free-atom value. However, changes in the outer-electron charge density will, of course, react back on the core and this in turn will affect the potential seen by the conduction electrons. To investigate the size of this effect in calcium, we have computed the change in the energy eigenvalues which is produced by unfreezing the core. For this purpose we have first recalculated the free-atom charge density, using a method similar to that described by Liberman, Waber, and Cromer.[16] This preliminary step was necessary to ensure that possible differences in details of methods of calculation would not mask the effect being investigated. The core charge density was then recalculated using the same program, but with the outer $4S\frac{1}{2}$ conduction-electron charge density frozen at the final value computed in the previous section. The difference between the recalculated free-atom core density and the core density as computed with the frozen $4S\frac{1}{2}$ electron density was taken to be the correction that is to be added to the crystal-core density used for the calculations described in the preceding section. A new crystal muffin-tin potential was then calculated from this new core density and the final conduction-electron density, as described in Sec. II. The change in the energy eigenvalues that resulted from using this new potential are shown[23] for some representative points in Table IV. It is seen from this table that the correction is reasonably small. This is, of course, not surprising, since the conduction electrons in calcium account for only 10% of the total charge density and, as indicated in Table III, 30% of this is outside the core region. Thus, changes in the conduction-electron charge density from the free-atom value should have a rather small effect on the core. The corrections, however, could be considerably larger for cases, such as copper, where the band electrons account for a proportionately larger fraction of the total charge.

TABLE IV. Energy corrections for representative points in the zone. The first column gives k in units of $\pi/4a$ and the second column gives the uncorrected energy eigenvalue in Ry. The third and fourth columns give the energy corrections due to relativistic effects and to unfreezing of the core, respectively.

k	E	ΔE (rel.)	ΔE (core)
110	0.03023	−0.00472	−0.00272
340	0.18336	−0.00399	−0.00338
282	0.30585	−0.00116	−0.00534
480	0.31765	−0.00088	−0.00564

Note added in proof. A calculation of the energy-band structure of calcium by the OPW method has recently been reported by Chatterjee and Chakraborti [S. Chatterjee and D. K. Chakraborti, J. Phys. C **3**, S120 (1970)]. These authors find the state W to be occupied in calcium and the state K to be unoccupied. This agrees with the conclusions of Altmann and Cracknell,[3] but disagrees with the calculations of Vasvari, Animalu, and Heine[5] and with the calculations reported here.

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[23] The magnitude of the entries given in Table IV have been reduced by 0.00068 Ry to account for a change in the constant potential between spheres.

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Interaction of Dislocations with Electrons and with Phonons*

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The interaction parameter of moving dislocations with electrons and with phonons was determined in aluminum, in the temperature range 10 to 250°K. A new technique, involving a "dynamic bias stress", was developed for measuring ultrasonic-attenuation changes $\Delta\alpha$. The numerical values of the interaction parameter were obtained from the measured $\Delta\alpha$ by means of an analysis which does not require any knowledge of the dislocation density or of other inaccurately known features of the dislocation network. The results indicate that the dislocation interaction with electrons is temperature independent and the interaction with phonons increases with increasing temperature. These results are consistent with theoretical predictions.

I. INTRODUCTION

When a dislocation in a crystal is set in motion, it experiences a resistive force against its motion. In the string model of a vibrating dislocation, this frictional force, or damping, is usually assumed to be proportional to the dislocation velocity and is described formally by the following equation:

$$Bv = b\tau, \tag{1}$$

where $b\tau$ is the force per unit length acting on a dislocation moving with velocity v, b is Burgers's vector, τ is the resolved shear stress on the dislocation slip system, and B is the damping constant. This damping constant is assumed here to consist of two parts, one due to interactions of dislocations with phonons ($B_{\rm ph}$) and the other due to interactions with conduction electrons (B_e). It is further assumed that these parts are additive, i.e., $B = B_{\rm ph} + B_e$.

Theoretical attempts to predict the magnitude and temperature dependence of $B_{\rm ph}$ have been made in the past by a number of people including Eshelby,[1] Leibfried,[2] Nabarro,[3] Lothe,[4] Weiner,[5] Mason,[6] and Seeger[7]; and for the electron contribution B_e, by Mason,[8] Kravchenko,[9] Holstein,[10] and Brailsford.[11] Comparison and discussion of some of these predictions are presented by Nabarro.[12]

Commonly used techniques for experimental determination of the damping constant B are (i) direct observation by etch pits[13] or x rays[14] of the displacement of individual dislocations produced by stress pulses of known magnitude and duration, (ii) ultrasonic-attenuation methods,[15–18] and (iii) macroscopic mechanical tests.[19–21] Discussions concerning the relation between the values of damping constants deduced by these methods were given by Fanti *et al.*[22] and by Gillis *et al.*[23] The purpose of this paper is to discuss a new method of obtaining the damping constant by means of ultrasonic measurements and to present experimental values deduced from this approach. With this new method we have overcome many difficulties previously encountered both in the analysis and in the experimental technique. The analysis is applied to the case of aluminum and the value of B thus derived and its temperature dependence are presented.

In Sec. II, the method of analysis is described. The new experimental technique, a dynamic bias stress method, is outlined in Sec. III. The results obtained in aluminum single crystals are given in Sec. IV and