PHYSICAL REVIEW VOLUME 167, NUMBER 3 15 MARCH 1968

Calculation of the Band Structure for Copper as a Function of Lattice Spacing*

HAROLD L. DAVIS, J. S. FAULKNER, AND H. W. JOY
Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

(Received 9 August 1967; revised maunscript received 2 November 1967)

Calculations are described which relate to the change in the electronic band structure of copper with change in lattice spacing. The calculations were performed using previously described constant-energy search techniques based on the Korringa-Kohn-Rostoker method for band-theory calculations. Included in the results are a total of 26 066 points on each of three Fermi surfaces corresponding to lattice spacings a, $0.995a$, and $0.99a$, with a being the normal lattice constant of copper. Using the measured value for the volume compressibility, our results give calculated changes in the Fermi surface with pressure which agree very well with recent de Haas–van Alphen experimental results. The calculated results are also consistent with the pressure dependence of reflectivity measurements, and with experiments thermodynamically related to the pressure dependence of the density of states at the Fermi energy. These results are based on band structures obtained from potentials calculated by a commonly invoked prescription using free-atom charge densities and Slater exchange. When considering the uncompressed metal, this prescription has been found to generate potentials giving widely varying band structures when different free-atom charge densities are used. However, once free-atom charge densities have been found which generate a reasonably accurate potential for the uncompressed metal, we conclude from the present results that the potential prescription appears to be very promising in its ability to accurately describe changes in metallic band structures with changes in lattice spacing.

I. INTRODUCTION

USING the Korringa-Kohn-Rostoker (KKR)[1,2] method for investigating electronic energy bands in metals, we have recently described[3] techniques for tracing out constant-energy surfaces, within the Brillouin zone, from given one-electron band theoretic potentials. Although previous work by Ham and Segall[4–7] had established the calculational reliability of the KKR method, one of the innovations of Ref. 3 was the demonstration that a careful treatment of the computational problems allows efficient calculation of the bands at a large number of points in the Brillouin zone, with modest expenditures of computer time.[8] Our first application of the resulting computer programs was the determination of numerous constant energy surfaces for metallic copper.[3] The present work is also concerned with copper, but here the variation of its band structure with lattice parameter will be considered.

There exist various motivations for our consideration of the general problem of variation of electronic band structure as a function of lattice parameter, and in using copper for this investigation. From previous work[3,6,9] there exists a detailed understanding of the band structure of copper at normal lattice spacing, and this knowledge is valuable when studying the variation with lattice spacing. Copper is also a good example, owing to recent experimental work of Templeton[10] who has obtained the pressure variation of two de Hass–van Alphen orbits on the Fermi surface of copper, and of Gerhardt, Beaglehole, and Sandrock[11] who have measured the strain-induced change of the reflectance. The precision of these measurements provides an excellent check on the validity of any theoretical calculations.

A more general motivation concerns the problem of the potential. In order to do calculations pertaining to the variation of any electronic band structure with lattice parameter when using a first-principles method, it is necessary to have some mechanism to change the one-electron potential as the lattice parameter changes. Even though some band-structure calculations have been made as a function of lattice parameter and/or deformation,[7,12–15] and very extensive experimental data exist which are directly or indirectly related to the variation of band structure with pressure,[15] very little detailed quantitative understanding exists on how the one-electron potential changes with lattice parameter. However, a whole host of reasonably successful band-theory calculations have been done for various materials at their normal lattice spacing by using potentials generated by a relatively simple prescription[16] based on the

---

* Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

[1] J. Korringa, Physica **13**, 392 (1947).

[2] W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954).

[3] J. S. Faulkner, H. L. Davis, and H. W. Joy, Phys. Rev. **161**, 656 (1967).

[4] F. S. Ham and B. Segall, Phys. Rev. **124**, 1786 (1961).

[5] B. Segall, Phys. Rev. **124**, 1797 (1961).

[6] B. Segall, Phys. Rev. **125**, 109 (1962).

[7] F. S. Ham, Phys. Rev. **128**, 82 (1962).

[8] At the time this research was performed, our programs required less than 10 minutes on an IBM System/360 Model 75 Computer to calculate the 561 **k** points necessary for a $M(E)$ entry of Table III.

[9] G. A. Burdick, Phys. Rev. **129**, 138 (1963).

[10] I. M. Templeton, Proc. Roy. Soc. (London) **A292**, 413 (1966).

[11] U. Gerhardt, D. Beaglehole, and R. Sandrock, Phys. Rev. Letters **19**, 309 (1967).

[12] F. S. Ham, Phys. Rev. **128**, 2524 (1962).

[13] L. G. Ferreira, Phys. Rev. **137**, A1601 (1965).

[14] L. Johnson, MIT, Solid State and Molecular Theory Group Quarterly Progress Report No. 42, 1961 (unpublished).

[15] See articles in *Physics of Solids at High Pressure*, edited by C. T. Tomizuka and R. M. Emrick (Academic Press Inc., New York, 1965).

[16] L. F. Mattheiss, Phys. Rev. **133**, A1399 (1964).

superposition of single-atom (ion) charge densities. Thus it was felt an investigation was in order to see if this simple prescription would also have the facility of generating potentials which would account for variation of band structures with lattice parameter.

II. DISCUSSION OF THE KKR METHOD AND NUMERICAL TECHNIQUES

Although not required by the basic formalism of the KKR method, use of a muffin-tin potential greatly reduces the amount of labor and computer time required to do band-theory calculations with this and other methods. At the same time, calculations on models[4] and real systems[6,17] have shown that approximating a crystal potential by a muffin-tin potential does no great damage to the resulting electronic band structure. Our main interest in the present investigation is in relative changes as the lattice parameter is varied, and use of muffin-tin potentials would be expected to have less effect on relative changes than on absolute quantities. For the above reasons, muffin-tin potentials have been used throughout the present investigation.

For a muffin-tin potential, the one-electron wave function within the muffin-tin spheres is expanded in the KKR method in terms of spherical harmonics $Y_{lm}(\theta,\phi)$, with the expansion being truncated as some l value denoted by $l_{\max}$. Results obtained by Ham and Segall[4–7] have shown that errors of at most a few thousandths of a Ry are made in energy eigenvalues at particular $\mathbf{k}$ values when $l_{\max}=2$ is used. We have previously shown[3] that the same truncation leads to errors of only a few tenths of one percent in dimensions of constant-energy surfaces in general and Fermi surfaces in particular. We expect relative changes of the Fermi surface and particular $\mathbf{k}$ energy eigenvalues to be less sensitive to the value of $l_{\max}$ than absolute quantities. For the above reasons, we believe use of $l_{\max}=2$ is more than adequate for the present investigation, and all calculations reported here have been done with this truncation.

The numerical techniques used in this investigation for the calculation of constant-energy surfaces were the same as previously reported.[3] With these techniques, 561 points were obtained in 1/48th of the Brillouin zone for each of the constant-energy surfaces necessary in the present investigation. By symmetry, this means a total of 26, 066 points on each of the constant-energy surfaces. Each such point is specified by a vector from Γ, the center of the zone, to the constant-energy surface. The directions of the vectors are specified by a search pattern and are thus exactly known. After specification of the value of $l_{\max}$, the numerical procedures used in the calculation are such that we are able to claim knowledge of the length of each of the vectors to at least four figures. This precision enables the volume contained by a constant-energy surface and hence the integrated density of states for the same energy to be accurate to about four decimal places.

We also have available computer programs for constant-$\mathbf{k}$ searches which use some of the same computer subprograms used in the constant-E searches described above. For clarity, it is best to emphasize explicitly that all results quoted in this paper have been obtained by direct numerical solution of the one-particle band theoretic eigenvalue problem without any recourse to an interpolation or extrapolation scheme.

III. CALCULATION OF POTENTIALS

The muffin-tin potentials used in this investigation were generated using a prescription described by Mattheiss.[16] In this prescription a crystal potential $V(r)$ is approximated as

$$V(r)=V_{\mathrm{coul}}(r)+V_{\mathrm{exc}}(r), \tag{1}$$

and both the Coulomb part, $V_{\mathrm{coul}}(r)$, and the exchange part, $V_{\mathrm{exc}}(r)$, are obtained using free-atom wave functions. At a given lattice site, which is taken as the coordinate origin, the Coulomb part is taken as the sum of both the Coulomb potential located at the origin, obtained from the free-atom wave functions, and contributions from the same Coulomb potential situated on neighboring lattice sites. The contributions from neighboring sites are obtained by expanding the neighboring Coulomb potentials in terms of spherical harmonics about the origin, using Löwdin's α-function expansion.[18] When obtaining a muffin-tin potential, which is spherically symmetric, only the $l=0$ term in this expansion need be retained. The exchange part of the potential is obtained, using Slater's free-electron approximation,[19]

$$V_{\mathrm{exc}}(r)=-6[3\rho(r)/8\pi]^{1/3}. \tag{2}$$

The charge density, $\rho(r)$, used in this expression is the spherically symmetric superposition of the atomic charge densities and is obtained in a manner analogous to the method used for $V_{\mathrm{coul}}(r)$.

The main motivation of the present work is to see how accurately this relatively simple prescription will yield potentials that can be used to predict the experimentally determined relative pressure effects on the electronic band structure of copper. That is, we are not attempting to answer the question, "How are atomic charge densities to be determined which when used in this prescription generate a reasonably accurate one-electron potential for band theoretic studies?," but only the question, "Given atomic charge densities which generate a reasonably accurate potential for normal lattice spacing, how accurate is the prescription in describing relative effects on the band structure with

---

[17] P. D. deCicco, Phys. Rev. **153**, 931 (1967).

[18] P. O. Löwdin, Advan. Phys. **5**, 1 (1956).

[19] J. C. Slater, Phys. Rev. **81**, 385 (1951).

changes in lattice parameter?" Of course, by using the same atomic charge densities for different lattice spacings, the only way lattice spacings effects will enter the calculations are through changes in the lattice sums used to obtain the Coulomb and exchange parts of the potential.

The decision as to what atomic charge densities to use in the investigation was made after consideration of the following information. Previously we had investigated the band structures corresponding to three distinct copper potentials, which had been obtained by inserting three different atomic charge densities into the above prescription. In calculating these potentials, the atomic charge densities inserted into the prescription were calculated for an assumed $3d^{10}4s^1$ configuration from (1) the atomic Hartree-Fock-Slater wave functions tabulated by Herman and Skillman[20] and calculated for a $3d^{10}4s^1$ configuration; (2) the atomic Hartree-Fock wave functions calculated by Synek[21] for a $3d^{10}4s^1$ configuration; (3) the atomic Hartree-Fock wave functions calculated by Watson[22] for a $3d^9 4s^2$ configuration. The first of these potentials has been found to yield a Fermi surface which does not make contact with the hexagonal faces of the Brillouin zone,[3] which disagrees with the experimentally established fact that copper's Fermi surface does contact the hexagonal faces. The band structure calculated from the second potential had its five lowest-energy d bands all below the energy of the Γ_1 state for the conduction sp band,[23] which is in violent disagreement with well-established features of copper's band structure. The third potential is identical or very close[24] to a potential used by Mattheiss[25] for the calculation of copper's band structure along the Δ symmetry direction in the Brillouin zone. We have shown[3] that the third potential gives a resulting band structure reasonably approximating the experimentally determined band structure, especially in the vicinity of the Fermi energy where the most direct comparisons can be made between experimental and calculated quantities.[26] It is seen that neither of the first two potentials provides an accurate enough initial potential to serve as a basis for an investigation concerning relative changes with change in lattice spacing. But the third potential does provide an adequate enough initial potential, so it thus was decided to generate the potentials necessary for this investigation by use of Watson's wave functions inserted into a $3d^{10}4s^1$ configuration.

TABLE I. Values of the potentials $V(r)$ corresponding to the three lattice spacings a, $0.995a$, and $0.99a$ for selected radial distances, r. The tabulated values are $-rV(r)$. The units of V are rydbergs while r is in atomic units. The r_s entries are the muffin-tin sphere radii, and the V_0 are the calculated average values of the potentials in the void between the muffin-tin spheres.

r	a	$0.995a$	$0.99a$
0.10	41.262	41.262	41.262
0.20	31.478	31.479	31.479
0.30	24.703	24.704	24.704
0.40	19.741	19.742	19.743
0.60	13.046	13.047	13.049
0.80	8.946	8.948	8.950
1.00	6.490	6.493	6.496
1.20	4.998	5.002	5.006
1.40	4.052	4.057	4.063
1.60	3.438	3.445	3.453
1.80	3.049	3.058	3.069
2.00	2.825	2.840	2.855
2.20	2.739	2.759	2.779
2.40	2.773	2.800	2.828
2.60	2.923	2.959	2.997
r_s	2.4151	2.4030	2.3909
V_0	−1.1394	−1.1539	−1.1686

With small changes in lattice spacing, variations in the resulting band structure are expected to be linear. This expectation enables us to perform an additional check on the calculational precision of our computer programs. For this reason, we decided to do calculations for lattice spacings of a, $0.995a$, and $0.99a$, with a being the normal lattice constant of copper that has been taken equal to the room-temperature value of 6.8309 au tabulated by Pearson.[27] Using these three lattice spacings, potentials were generated by performing the necessary lattice sums over seven neighboring shells about a lattice site. To illustrate the minor changes in the resulting potentials, they are given in Table I at

TABLE II. Energy eigenvalues at some high-symmetry points using the potentials corresponding to lattice spacings a, $0.995a$, and $0.99a$. The energies are expressed in rydbergs. The energy for the state Γ_1 is expressed relative to the same energy zero used in specifying the V_0 of Table I. All other state energies are specified relative to Γ_1 for the potential of interest.

State	a	$0.995a$	$0.99a$
Γ_1	−1.1474	−1.1571	−1.1661
$\Gamma_{25'}$	0.4654	0.4709	0.4767
Γ_{12}	0.5211	0.5280	0.5352
X_1	0.3192	0.3212	0.3233
X_3	0.3657	0.3687	0.3720
X_2	0.5596	0.5674	0.5756
X_5	0.5730	0.5811	0.5897
$X_{4'}$	0.7995	0.8074	0.8152
L_1	0.3207	0.3233	0.3260
L_3	0.4606	0.4660	0.4716
$L_3^{(2)}$	0.5621	0.5699	0.5782
$L_{2'}$	0.5903	0.5954	0.6003
$L_1^{(\mathrm{up})}$	0.9677	0.9820	0.9965

---

[20] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

[21] M. Synek, Phys. Rev. **131**, 1572 (1963).

[22] R. E. Watson, Phys. Rev. **119**, 1934 (1960).

[23] J. S. Faulkner and H. L. Davis, unpublished results.

[24] There may exist minor numerical differences between our potential and the one used by Mattheiss in the third or fourth significant figure due to different numerical methods.

[25] L. F. Mattheiss, Phys. Rev. **134**, A970 (1964).

[26] See Ref. 3 for a detailed discussion of the minor differences which exist between the calculated and experimentally determined band-structural information.

[27] W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press, Inc., New York, 1958).

TABLE III. Integrated density of states $M(E)$ and linear and a real constant-energy surface dimensions for energies in the immediate vicinity of the Fermi energy for the potentials corresponding to lattice spacings, a, $0.995a$, and $0.99a$. The energies are in rydbergs and expressed relative to the Γ_1 energy for each potential. The second energy for each potential is taken as the calculational Fermi energy. The linear dimensions k_{100} and k_{110} are the distances from Γ to the constant energy surface along the $\langle 100\rangle$ and $\langle 110\rangle$ directions, respectively, measured in units of the radius of the free-electron sphere k_{fe}. This unit changes with potential, since $k_{\text{fe}}=(3\pi^2 n)^{1/3}$, with n being the number of lattice sites per unit volume. k_{neck} is the radius of the neck, as measured from L, in the same units. The neck is circular to the quoted accuracy. The A_{100}, A_{111}, and A_{db} are cross-sectional areas for the [100] belly orbit, the [111] belly orbit, and the dog's bone orbit, respectively, in units of πk_{fe}^2.

	Lattice spacing $=a$			Lattice spacing $=0.995a$			Lattice spacing $=0.99a$		
E	0.6754	0.6796	0.6839	0.6841	0.6884	0.6927	0.6931	0.6974	0.7017
$M(E)$	0.98224	0.99992	1.01745	0.98248	1.00017	1.01777	0.98216	0.99994	1.01763
k_{100}	1.0605	1.0658	1.0710	1.0621	1.0673	1.0726	1.0637	1.0690	1.0743
k_{110}	0.9359	0.9426	0.9492	0.9349	0.9417	0.9483	0.9337	0.9405	0.9472
k_{neck}	0.2066	0.2146	0.2225	0.2090	0.2170	0.2248	0.2113	0.2192	0.2270
A_{100}	0.9628	0.9746	0.9862	0.9627	0.9745	0.9861	0.9621	0.9738	0.9857
A_{111}	0.9310	0.9434	0.9558	0.9304	0.9429	0.9553	0.9293	0.9418	0.9543
A_{db}	0.4153	0.4054	0.3952	0.4147	0.4047	0.3944	0.4143	0.4041	0.3938

selected radial distances. Also listed in Table I are the muffin-tin sphere radii for the three lattice spacings and the values used for the constant potential V_0 in the voids between the muffin-tin spheres and the Wigner-Seitz polyhedra. These V_0 are used to adjust the zero of energy in the calculation in order to have the potential zero in the voids, and were approximated by the average value of $V(r)$ in the voids.

IV. ENERGY EIGENVALUES AT SELECTED HIGH-SYMMETRY POINTS

Using the potentials described in Sec. III, the energy eigenvalues of the resulting bands were determined at the high-symmetry points Γ, X, and L in the Brillouin zone using our constant-**k** energy survey techniques. The resulting energy eigenvalues are presented in Table II,[28] and linearity with lattice spacing is observed in the energy eigenvalues to within a few ten-thousandths of a rydberg.

V. DENSITY-OF-STATES RESULTS

By calculating the volume enclosed by a constant-energy surface within the Brillouin zone, the integrated density of states $M(E)$ may be obtained for a given energy E. Since our primary interest in the present work is the variation of copper's Fermi surface with lattice parameter, $M(E)$ needed to be calculated only in the immediate vicinity of the Fermi energy for each of the three potentials being considered. From inspection of the energy eigenvalues given in Table II, one expects the Fermi energy to vary only slightly for the potentials considered here. At the start of this investigation we had an accurate knowledge of the Fermi energy for the potential corresponding to normal lattice spacing a.[3] It was thus possible to estimate energies which would bracket the Fermi energies for the potentials corresponding to the lattice spacings $0.995a$ and $0.99a$. The $M(E)$ were calculated for these energies, and a simple interpolation then enabled finer bracketing energies to be obtained. The $M(E)$ were calculated for these new energies. and the process repreated until the Fermi energies were obtained to four figure accuracy for each of the potentials.

In Table III some results of the $M(E)$ calculations are given for energies in the vicinity of the Fermi energy for each of the three potentials.[29] The results in this table are expected to be accurate to about four figures. The Fermi energy for a potential has been taken as the second of the three energies tabulated since, as is seen in Table III, $M(E)$ for that energy equals unity to one part in 10^4.

By numerical differentiation of the $M(E)$ results, we find the density of states at the Fermi energy $\rho(E_f)$ equals 4.16, 4.13, 4.11 states/atom-Ry for the potentials corresponding to lattice spacings of a, $0.995a$, and $0.99a$, respectively. These values give 0.720, 0.716, 0.712 mJ/mole-°K^2, respectively, for the low-temperature electronic specific-heat coefficient γ. Because of loss of precision in obtaining numerical derivatives, the values obtained for $\rho(E_f)$ and γ are expected to be precise to three figures, and linearity with lattice spacing is obtained to this precision.

VI. DIMENSIONS OF CONSTANT-ENERGY SURFACES

The procedures described above give more information than values of $M(E)$ and $\rho(E)$ for a given potential, since they enable linear dimensions and cross-sectional areas of a given constant-energy surface to be obtained to at least four figure accuracy. The importance of such linear and areal dimensions is immediately evident, since they are related to quantities

---

[28] Some of the results quoted in this paper for the potential corresponding to the lattice spacing a have already been reported in Ref. 3. They are also reported here for ease of comparison with the results obtained from the other two potentials.

[29] If the demand is not too great, we can make available to those who have a use for them, decks of IBM cards containing all of the calculated points on some of the constant energy surfaces obtained in this investigation.

measured e.g., in, magnetoresistance, magnetoacoustic, de Haas–van Alphen, and cyclotron resonance experiments.

In Table III we present a limited listing of linear and areal dimensions which have been obtained in this work. Linearity with energy for each lattice parameter is obtained over the small range of energies tabulated in Table III, and linearity in the change of the dimensions of the Fermi surface with lattice parameter may be exhibited by expressing such dimensions in atomic units. In addition to the areal dimensions given in Table III, we have also investigated the changes in cross-sectional area for slices of the Fermi surface perpendicular to the $\langle 111\rangle$ direction, moving away from the slice containing Γ. For the potential corresponding to the lattice spacing a, we find the slice which is 1.563%, from Γ, of the distance between Γ and L to have a cross-sectional area of 0.9642 in the same areal units used in Table III. For a slice removed 3.125% the cross-sectional area is 0.9851. Thus, we calculate the [111] central extremal area to be a minimum. This agrees with Roaf's[30] analytical fit to Shoenberg's[31] de Haas–van Alphen data and recent data of Joseph, Thorsen, Gertner, and Valby.[32]

Using the dimensions for the constant energy surfaces given in Table III, some de–Hass van Alphen frequencies and cyclotron reasonance masses have been calculated and are expressed in Table IV. Since the energy derivatives required to obtain the cyclotron masses were obtained numerically, it was initially expected that the masses would be precise to only two decimal places. However, it is seen that approximate linearity with lattice spacing does appear in the third decimal place in the calculated masses, and our feeling now is that the masses are precise to slightly more than two decimal places. In any event, the trend of the change of these masses with lattice spacing is undoubtedly an accurate representation of the potentials used in this work.

The largest relative change with lattice spacing in the de Haas–van Alphen frequencies is seen to occur for the neck orbit. However, if an error of $+0.002$ Ry had been made in obtaining the Fermi energy for the potential corresponding to the lattice spacing a, and an error of -0.002 Ry made in obtaining the Fermi energy for the potential corresponding to the lattice spacing $0.99a$, the calculated change in the neck frequency would have been a *decrease* with *decrease* in lattice spacing. The precisely calculated change, from Table IV, is an *increase* with *decrease* in lattice spacing. Similar errors of ± 0.0015 Ry would also similarly affect the relative change in the dog's bone frequency. Also, errors of the same order in Fermi energies would wash out the trend observed in the cyclotron resonance masses. These examples serve to illustrate the advantages and sometimes the necessity of being able to calculate the Fermi energy and Fermi surface dimensions to the four-figure precision used in the present work.

TABLE IV. Calculated de Haas–van Alphen frequencies and cyclotron resonance masses for the three potentials corresponding to lattice spacings a, $0.995a$, and $0.99a$. The de Haas–van Alphen frequencies F_{100}, F_{110}, $F_{\rm neck}$, and $F_{\rm db}$ are for the [100] belly orbit, the [111] belly orbit, the neck orbit, and the dog's bone orbit, respectively, and are expressed in units of 10^8 G. Similar notation applies to the cyclotron masses m^*, which are expressed in units of the free electron's mass.

	a	$0.995a$	$0.99a$
F_{100}	5.920	5.979	6.036
F_{111}	5.731	5.785	5.837
$F_{\rm db}$	2.462	2.483	2.505
$F_{\rm neck}$	0.280	0.289	0.298
m^*_{100}	1.429	1.433	1.440
m^*_{111}	1.515	1.521	1.529
$m^*_{\rm db}$	1.228	1.243	1.250
$m^*_{\rm neck}$	0.417	0.418	0.420

VII. DISCUSSION

A number of experimental results can be compared with the calculations presented in Tables II, III, and IV. First, Templeton[10] has recently measured the change with hydrostatic pressure of the de Hass–van Alphen frequencies for the neck and [111] belly orbits of copper's Fermi surface. These measurements enabled him to quote values for the relative pressure change of the cross-sectional areas, $(\Delta A/A)/\Delta P$, of $+1.93\times10^{-6}$ cm^2/kg and $+4.21\times10^{-7}$ cm^2/kg for the neck and [111] belly orbits, respectively. Using the results of Table III and the experimental[33] volume compressibility, $(\Delta V/V)/\Delta P=-6.907\times10^{-7}$ cm^2/kg, our calculations give $+1.50\times10^{-6}$ cm^2/kg and $+4.27\times10^{-7}$ cm^2/kg, respectively, for the same quantities. Reasonably good agreement between calculation and experiment is thus obtained, in contrast with a previous attempt[34] to calculate one of these quantities which predicted $(\Delta A/A)/\Delta P$ to be *negative* for the neck orbit.

We feel that the fact that the present calculation underestimates the value of $(\Delta A/A)/\Delta P$ for the neck is predominantly due to the potential corresponding to the uncompressed lattice predicting a neck area about 28% larger[3] than the experimentally observed neck area rather than to the method used to obtain the potentials for the three lattice spacings. That is, if the potential, corresponding to the lattice spacing a, had led to a smaller cross-sectional area for the neck, we would expect the calculated relative change with pressure to be larger and move toward better agreement with Templeton's experimental value. No such difficulty is encountered with the calculated value for the [111] belly orbit, since the potential corresponding to the uncompressed lattice overestimates the experimental[31]

---

[30] D. J. Roaf, Phil. Trans. Roy. Soc. London **A255**, 135 (1962).

[31] D. Shoenberg, Phil. Trans. Roy. Soc. London **A255**, 85 (1962).

[32] A. S. Joseph, A. C. Thorsen, E. Gertner, and L. E. Valby, Phys. Rev. **148**, 569 (1966).

[33] W. C. Overton and J. Gaffney, Phys. Rev. **98**, 969 (1955).

[34] D. Caroline and J. E. Schirber, Phil. Mag. **8**, 71 (1963).

de Hass–van Alphen frequency, 5.742×10^8 G, by less than 1% (see Table IV).

The calculated $(\Delta A/A)/\Delta P$ for the [100] belly and the dog's bone orbits are, respectively, $+4.53\times10^{-7}$ cm^2/kg and $+3.96\times10^{-7}$ cm^2/kg. After the calculation was made, O'Sullivan and Schirber[35] measured this quantity for the dog's bone and obtained $4.0\pm0.2\times10^{-7}$ cm^2/kg, giving agreement with the calculation. We should like to suggest further experimental work to obtain the value for the [100] belly orbit and the value for the dog's bone orbit to higher precision, in order to see if the relative ordering in magnitude calculated in this work for $(\Delta A/A)/\Delta P$ for the neck, [100] belly, [111] belly, and dog's bone orbits has the excellent agreement with experiment all present work appears to indicate.

The present calculations give definite predictions concerning the pressure change of the density of states at the Fermi energy, and hence the electronic specific heat. We know of no direct experimental results on the change of the electronic specific heat of copper with pressure. However, as is discussed, e.g., by Green,[36] thermodynamic considerations lead to the desired result being related to the electronic Grüneisen constant

$$(\partial \ln\gamma/\partial \ln V)_T = 3\alpha_e VK/(\gamma T), \qquad (3)$$

where γ is the electronic specific-heat coefficient, V is the molar volume, T is the temperature, α_e is the electronic part of the coefficient of thermal linear expansion, and K is the bulk modulus. We calculate the left-hand side of Eq. (3) to be $+0.43$. By measuring α_e for copper, Carr, McCammon, and White[37] were able to calculate the right-hand side of Eq. (3) from experimental quantities, obtaining $+0.63\pm0.06$ which is to be compared with the ideal free-electron value of $\frac{2}{3}$. The agreement between calculation and experiment is only semiquantitative, but it is gratifying considering the precision required to calculate the γ's and the possibility of errors in interpreting experimental measurements to obtain the value of α_e due to the necessity of separating it from the total coefficient of thermal linear expansion. Also, as mentioned in Ref. 3, the potential corresponding to lattice spacing a overestimates the experimental value of γ by 3%, which might explain some of the discrepancy between the calculated and experimental results for Eq. (3).

In a "Note added in proof" Green[36] has indicated that rigid-band interpretation of specific-heat data on copper-based alloys gives a negative value for the left-hand side of Eq. (3). In an attempt to rescue the rigid-band model, Green mentioned possible changes in $(\partial \ln\gamma/\partial \ln V)_T$ due to electron-phonon enhancement. As discussed in Ref. 3, we do not expect electron-phonon enhancement to affect γ at normal lattice spacing by more than a few percent. The above comparison between calculated and experimental results also seems to indicate that electron-phonon enhancement will not greatly affect $(\partial \ln\gamma/\partial \ln V)_T$, especially enough to change its sign.

Zallen[38] has observed the shift with pressure of the reflectivity edge in copper and put an upper limit on the pressure dependence of (top of d-band)$-$(Fermi energy) separation of 1.0×10^{-6} eV/bar. More recently, Gerhardt, Beaglehole, and Sandrock,[11] using piezo-optical measurements, have obtained $0.80(\pm0.07)\times10^{-6}$ eV/bar for the same quantity. The states X_2, X_5, and $L_3^{(2)}$ are at, or in the immediate vicinity of, the top of the d-band, and the pressure shifts for the separations (E_f-X_2), (E_f-X_5), and $(E_f-L_3^{(2)})$, are calculated to be 0.5 to 0.6×10^{-6} eV/bar. The pressure shift of reflectivity structure near 4.2 eV has also been measured by Zallen who obtained $7.0(\pm1.5)\times10^{-6}$ eV/bar, while Ref. 11 quotes $7.5(\pm1.1)\times10^{-6}$ eV/bar for the same quantity. We calculate the pressure shift of $(L_1^{(\mathrm{up})}-L_{2'})$ to be 6.0×10^{-6} eV/bar, and $(L_1^{(\mathrm{up})}-E_f)$ to be 3.5×10^{-6} eV/bar. Although the potential corresponding to the lattice spacing a gives 5.1 eV for the separation $(L_1^{(\mathrm{up})}-L_{2'})$, we feel the calculated pressure shift for this separation adds support to Beaglehole's[39] assignment of the reflectivity structure at 4.2 eV to the transition $L_{2'}\rightarrow L_1^{(\mathrm{up})}$.

Another possible application of the data of Table II is purely theoretical. Although not attempted by us, from the results of Table II, it is possible to use either of the two recently proposed[40,41] interpolation schemes to obtain an interpolated description of the total band structure. This interpolated band structure could then be used to calculate the same quantities given in Table III. Comparing such results with the numerically exact results in Table III would give an excellent mechanism for judging the size and type of errors which are present in the interpolation schemes.

The above comparison between the results of our calculations and experimental measurements can serve to answer the question asked in Sec. III concerning the accuracy of the potential prescription when used to describe relative effects in band structure with change in lattice spacing. In all, we have found quite excellent agreement between calculational and experimental relative changes with lattice spacings. Large discrepancies appeared between the two only where either the initial potential gave a bad absolute description of copper's band structure or the experimental quantities were uncertain. Thus, we conclude the potential prescription

---

[35] W. J. O'Sullivan and J. E. Schirber (private communication).

[36] B. A. Green, Jr., Phys. Rev. **144**, 528 (1966).

[37] R. H. Carr, R. D. McCammon, and G. K. White, Proc. Roy. Soc. (London) **A280**, 72 (1964).

[38] R. Zallen in *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abelès (North-Holland Publishing Co., Amsterdam, 1966), p. 164.

[39] D. Beaglehole, in *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abelès (North-Holland Publishing Co., Amsterdam, 1966), p. 154.

[40] L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. **152**, 505 (1966).

[41] F. M. Mueller, Phys. Rev. **153**, 659 (1967).

appears to be very promising in its ability to describe relative changes of metallic band structures with change in lattice spacing, especially in the vicinity of the Fermi energy, once a reasonably accurate potential has been found for the uncompressed metal. This conclusion seems to imply that the predominant change in band-theory potentials as the lattice spacing changes is simply due to a superposition of single-atom charge densities, while the change in these charge densities with small changes in lattice spacing is, at most, a second-order effect. Of course, this conclusion is based only on this study of the change of copper's band structure, and we hope to have the opportunity in the near future to perform similar studies on other metals.

ACKNOWLEDGMENTS

We wish to thank Dr. W. J. O'Sullivan and Dr. J. E. Schirber for their permission to quote their unpublished result concerning the relative change of the dog's bone de Haas–van Alphen frequency with pressure. Also, we are indebted to Dr. N. D. Lang for correspondence pointing out the consistency between our calculations and the reflectivity measurements of Ref. 38.

PHYSICAL REVIEW VOLUME 167, NUMBER 3 15 MARCH 1968

Towards a Quantum Many-Body Theory of Lattice Dynamics. II. Collective Fluctuation Approximation

N. S. Gillis and N. R. Werthamer
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received 17 July 1967)

A novel viewpoint towards the lattice dynamics of an anharmonic crystal, put forward in a previous paper of the same title, is enlarged and extended. This viewpoint first focuses attention on the motion of a single atom in a static environment, and develops the collective modes of the crystal as a whole from a superposition of the motions of the individual atoms. It is shown that of the many collective modes for a given wave vector, three are identifiable as one-phonon modes in that only these contribute to the displacement-displacement response, and a simple expression for the eigenfrequencies of these modes is exhibited. The other modes are shown to be associated with single-particle transitions, and their contribution to the neutron structure function $S(\mathbf{k},\omega)$ is derived in the special case of a purely harmonic lattice. The many-body approximation is extended to include collective fluctuations in the equilibrium state. Serious difficulties in principle are encountered, associated with maintaining translational invariance, but are partially overcome by an *ad hoc* procedure. Collective-mode frequencies renormalized in this way are compared with those obtained from an alternative theory which deals exclusively and from the outset with collective coordinates only.

I. INTRODUCTION

In a previous paper[1] of the same title, a novel viewpoint towards the lattice dynamics of a crystal was put forward. This viewpoint first focuses attention on the motion of a single atom in a static environment, and then develops the collective modes of the crystal as a whole from a superposition of the motions of the individual atoms. The philosophy is the same as that of the random phase approximation (RPA) which is also the starting point of the theory of most other many-body systems.

No assumption is made in this theoretical approach about the smallness of the atomic displacements relative to the interatomic spacing. Hence this theory is appropriate for highly anharmonic crystals, a leading example of which is helium. Here the traditional quasiharmonic theory fails, due to the light mass and weak restoring force, and consequent large zero-point motion of the atom. Yet the present picture gives a good account[2,3] of the phonon spectrum and attendant thermodynamic properties.

Despite the success of the RPA approach in giving at least qualitatively correct results for the phonon spectrum, some other aspects of the lattice dynamics are not treated adequately, notably the temperature dependence. This is because the phonon collective modes are only obtained from the response of the crystal to a disturbance. In the absence of any disturbance, i e., at equilibrium, the RPA regards the crystal as an array of nondynamically interacting atoms with a discrete single-particle excitation spectrum. Consequently, there are no Boltzmann factors of the form exp[$-$(phonon energy)/k_BT] as should be expected, only factors exp[$-$(single-particle excitation energy)/k_BT], which

---

[1] D. R. Fredkin and N. R. Werthamer, Phys. Rev. **138**, A1527 (1965), hereafter referred to as I. Similar ideas have also been discussed by W. Brenig, Z. Physik **171**, 60 (1963), and more recently by G. Meissner, *ibid.* **205**, 249 (1967).

[2] L. H. Nosanow and N. R. Werthamer, Phys. Rev. Letters **15**, 618 (1965).

[3] F. W. de Wette, L. H. Nosanow, and N. R. Werthamer, Phys. Rev. **162**, 824 (1967).