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Self-Consistent Energy Bands in Vanadium at Normal and Reduced Lattice Spacings

Dimitrios A. Papaconstantopoulos[*]
George Mason College, Fairfax, Virginia 22030

and

James R. Anderson[†]
University of Maryland, College Park, Maryland 20740

and

Joseph W. McCaffrey
Naval Research Laboratory, Washington, D. C. 20390

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Self-consistent energy-band calculations for vanadium were performed by the augmented-plane-wave (APW) method, for different values of the statistical exchange parameter α, at normal and reduced lattice constants. Comparisons have been made, with Fermi-surface, soft-x-ray, photoemission, and electronic specific-heat experiments, and reasonable agreement was found.

I. INTRODUCTION

Only in the last few years has good-quality vanadium become available for meaningful experimental measurement. There now exist Fermi-surface,[1] soft-x-ray,[2] and photoemission[3] measurements for vanadium. As a result enough experimental information is available to warrant a self-consistent fully convergent band calculation for comparison.

Non-self-consistent calculations on the band structure of vanadium were made by Mattheiss,[4] Snow and Waber,[5] Bolemon,[6] and Anderson *et al.*,[7] all using the augmented-plane-wave (APW) method. Mattheiss[4] calculated the energies for full Slater exchange[8] and two different atomic configurations. Snow and Waber[5] also determined the density of states for full Slater exchange but their agreement with the experimental results was poor. Bolemon[6] calculated the bands for three different exchange coefficients, and finally, Anderson *et al.*[7] discussed the effects on the band structure of varying both the exchange potential and the lattice constant. In the present work, having carried the calculations to self-consistency, we wish to compare the calculated band structure with experiment and to consider in greater detail, the effects of varying the exchange potential and lattice constant.

While the present work was in progress a self-consistent calculation was published by Yasui *et al.*,[9] who used a combined tight-binding and orthogonalized-plane-wave (OPW) method. Also, Hattox[10] is performing APW calculations to study the magnetic state of vanadium for lattice constants greater than the normal value.

II. DETAILS OF THE CALCULATION

The calculations have been carried out on a mesh of 1024 points in the Brillouin zone, using the APW method as programmed by Switendick and Wood with the necessary modifications for use with a Univac 1108 Computer.

The starting crystal potential $V(r)$ was obtained from a superposition to fifth-nearest neighbors of the Herman-Skillman[11] free-atom (configuration $3d^3\,4s^2$) charge densities using the Löwdin α expansion.[12]

The starting values $P_l(r)$ for the numerical integration of the radial Schrödinger equation were found from the expression given by Greissen[13]:

$$P_l(r) \sim r^{l+1} e^{-r^2 V(r)/2(l+1)}, \tag{1}$$

where $l = 0, 1, 2, \ldots, 12$.

The quantity r^{l+1} is the usual limiting form of the radial wave function for $1/r$ potential, and the exponential term noticeably affects only the s-like points as is shown on Table I.

We performed calculations with $l_{\max} = 12$ and $l_{\max} = 7$, and observed that the difference in the eigenvalues did not exceed 0.0005 Ry; however, only the charge densities for l up to 5 were used in the self-consistent calculation.

Three complete self-consistent calculations were performed. The first one using the full-Slater-exchange potential ($\alpha = 1$); the second one using the Gaspar-Kohn-Sham[14] ($\alpha = \frac{2}{3}$) exchange potential, and the third for a reduced lattice constant $a = 0.95a_0$ ($a_0 = 5.713$ a.u.)[15] with $\alpha = \frac{2}{3}$ exchange. This reduced lattice spacing corresponds to a pressure of about 240 kbar. (The compressibility K_T at 4.2 °K is 6.26×10^{-4} kbar^{-1}.[16])

In performing the self-consistent calculations the "frozen-core" approximation[17] was used. That is, the spherically averaged radial charge density $\rho(r) = (4\pi r^2)^{-1}\sigma(r)$ was found from the expression

TABLE I. Comparison of eigenvalues for the two different choices of the starting values for the integration of the radial equation with an initial mesh size of $h = 0.005$.

States	$P_l(r) \sim r^{l+1}$	$P_l(r) \sim r^{l+1} \times e^{-r^2 V(r)/2(l+1)}$
Γ_1	0.331	0.269
Γ'_{25}	0.812	0.812
Γ_{12}	0.949	0.949
$\Delta_1(400)$	0.557	0.531
$\Delta_2(400)$	0.711	0.711
H_{12}	0.525	0.525
N_1	0.538	0.523
N_2	0.692	0.692
P_4	0.680	0.680

$$\sigma(r) = \sum_{n,l}^{\text{core}} P_{nl}{}^2(r) + \sum_{n,k} \sigma_{n,k}(r), \qquad (2)$$

where the first term on the right-hand side, representing the charge density of the core electrons as given by the atomic calculation, was kept constant. The second sum is the charge density over the occupied conduction-band states ($3d$ and $4s$) and was recomputed at each cycle of the calculation. This second term was found from the wave functions of a sample of seven points in $\frac{1}{48}$th of the Brillouin zone (see Table II) properly weighted in order to take the symmetry within the zone into account.

The resulting charge density $\rho(r)$ was used to find the potential V^{new} from Poisson's equation

$$\nabla^2 V^{\text{new}} = -8\pi\rho .$$

V^{new} was then averaged with the potential V^{old} of the previous cycle using the formula

$$V(r) = 0.75 V^{\text{old}}(r) + 0.25\, V^{\text{new}}(r). \qquad (3)$$

In Table II we show the convergence of the seven points as a function of iteration. We achieved a convergence to within 0.002 Ry after eight iterations for the $\alpha = \frac{2}{3}$ and after six iterations for the Slater exchange. However, we observed that in the $\alpha = \frac{2}{3}$ case the same convergence was achieved after five iterations if the averaging was done instead with the new and old charge densities and the same weighting as for the potential [Eq. (3)].

We have also noticed that our results after the first iteration with Slater exchange are very close to the results of the last iteration with $\alpha = \frac{2}{3}$ exchange. This cancellation of the effects of self-consistency and exchange was also pointed out by Connolly[18] and Snow and Waber[19] for nickel and copper, respectively.

Finally, the Fermi level E_F was found by integrating the density of states to a value of five electrons per atom, and the Fermi surface was calculated by solving the equation $E(\vec{k}) = E_F$ graphically.

III. WAVE FUNCTIONS AND CHARGE DISTRIBUTION

By solving the radial Schrödinger equation using the self-consistent potential and a mesh of 128 points in the Brillouin zone we found the radial probability density $r^2 u_l^2$ for the occupied conduction-band states, for $\alpha = \frac{2}{3}$. This is plotted in Fig. 1 together with the corresponding atomic orbitals. We note a spreading out of the valence electron charge density in going from the atom to the solid.

In Table III we list the self-consistent electronic charge resolved into s, p, d, and f components, as well as that outside the muffin tin. We found these charges using the calculated radial wave functions and the following expressions[17]:

$$Q_l = \frac{\Omega}{N} \sum_i \sum_j v^*(\vec{k}_i) v(\vec{k}_j)\, C_{ijl} \int_0^{R_s} \left(\frac{r u_l(r, E)}{R_s u_l(R_s, E)} \right)^2 dr ,$$

$$Q_{\text{out}} = (\Omega/N) \sum_i \sum_j v^*(\vec{k}_i) v(\vec{k}_j) A_{ij} \; .$$

In the above equations, Ω is the volume of the unit cell, N is a normalization constant, C_{ijl} and A_{ij} are the probabilities of finding an electron within and outside the APW sphere, respectively; $v(\vec{k}_i)$ is an eigenvector of the APW secular equation, u_l is the radial wave function, and R_s the radius of the APW sphere.

Comparing the two calculations (Table III) at normal lattice spacing we note that for $\alpha = \frac{2}{3}$ all charges except Q_d are greater than for $\alpha = 1$. Thus the d character is more pronounced for the full

TABLE II. Convergence of energy bands of vanadium for $\alpha = \frac{2}{3}$ exchange. Energies are expressed in rydbergs.

	1st	2nd	3rd	4th	5th	6th	7th	8th
V_c	−1.16638	−1.35271	−1.45446	−1.50572	−1.53034	−1.54189	−1.54728	−1.54981
Γ_1	0.36617	0.31890	0.29316	0.28009	0.27375	0.27073	0.26930	0.26861
$\Delta_1(400)$	0.66870	0.60458	0.56812	0.54879	0.53918	0.53457	0.53241	0.53139
$\Delta_2(400)$	0.97296	0.86241	0.78918	0.74828	0.72774	0.71800	0.71350	0.71146
H_{12}	0.73059	0.64340	0.58593	0.55377	0.53757	0.52988	0.52634	0.52475
N_1	0.70887	0.62944	0.57789	0.54904	0.53447	0.52752	0.52431	0.52285
N_2	0.99983	0.86407	0.77883	0.73257	0.70964	0.69883	0.69386	0.69162
P_4	0.91492	0.81401	0.74928	0.71321	0.69502	0.68635	0.68233	0.68049

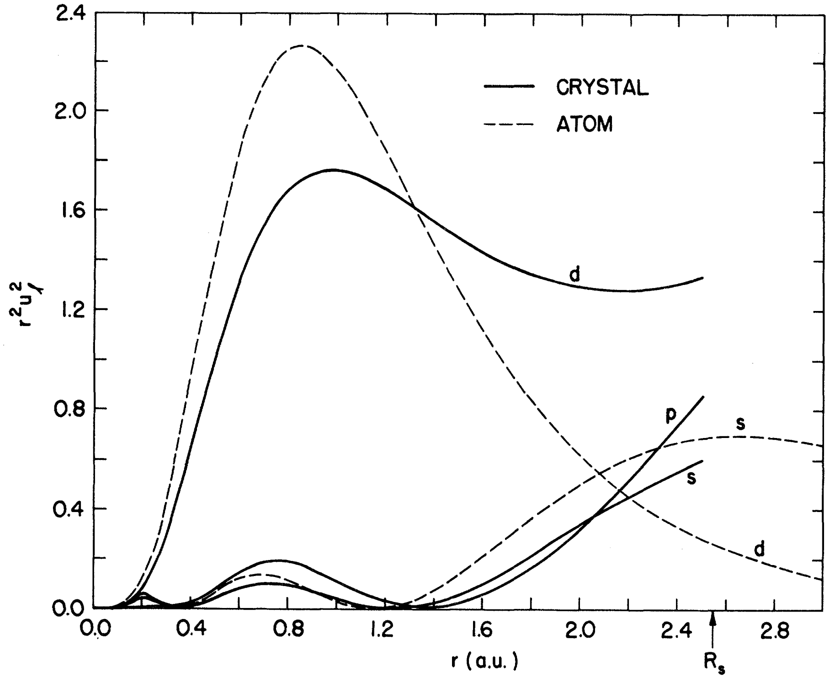

FIG. 1. Radial probability densities for both the crystal and the atom.

Slater exchange.

Looking at the two $\alpha = \frac{2}{3}$ calculations, we observe that for the reduced lattice spacing, the amount of charge Q_{out} outside the APW sphere is greater, while the charge contribution inside the sphere is smaller. Kmetko[20] has performed calculations of this type for several metals. He generally finds that the effect of compression in simple metals is to reduce the s- and p-like charges and increase the d and f components (Pb is shown in Table III as an example.) However, for the transition metals, where the d character is very strong, this rule does not seem to hold. From Table III we see that Kmetko's results for W agree with ours in that Q_d decreases with pressure.

IV. ENERGY BANDS

A. Comparison with Previous Calculations

Figures 2–4 show the self-consistent (SC) bands for the three different calculations performed. They all have the same general shape characteristic of the transition metals with the body-centered structure, similar, for example, to Cr and Fe.[4] The main difference is the width and position of the d band as is shown in Table IV. We observe that the s-d separation and the d and s-p widths are all increased as we go from the Slater to the Kohn-Sham exchange. A further increase is noted when a reduced lattice spacing is used. From Table II it is evident that extensive changes in the band structure occur upon carrying the calculation to self-consistency. In particular, the d-band widths and the s-d separation are reduced at each iteration. The only change in level ordering occurs for the N_1' state which falls below N_4 and N_1 when the exchange is reduced.

Comparing with Yasui *et al.*,[9] we note a major difference in the position of the Fermi level for

TABLE III. Self-consistent charges.

	Compression	Q_{out}	Q_s	Q_p	Q_d	Q_f	
V $\alpha = 1$	0	0.915	0.389	0.246	3.429	0.032	
V $\alpha = \frac{2}{3}$	0	1.139	0.445	0.307	3.076	0.049	Present results
V $\alpha = \frac{2}{3}$	5%	1.191	0.411	0.305	3.056	0.028	
Pb $\alpha = 0.70$	0	0.705	1.428	1.550	0.224	0.063	
	5%	0.795	1.351	1.513	0.256	0.076	Kmetko[a]
W $\alpha = 0.70$	0	1.364	0.350	0.352	3.914	0.069	
	5%	1.460	0.306	0.322	3.783	0.106	

[a] Reference 20.

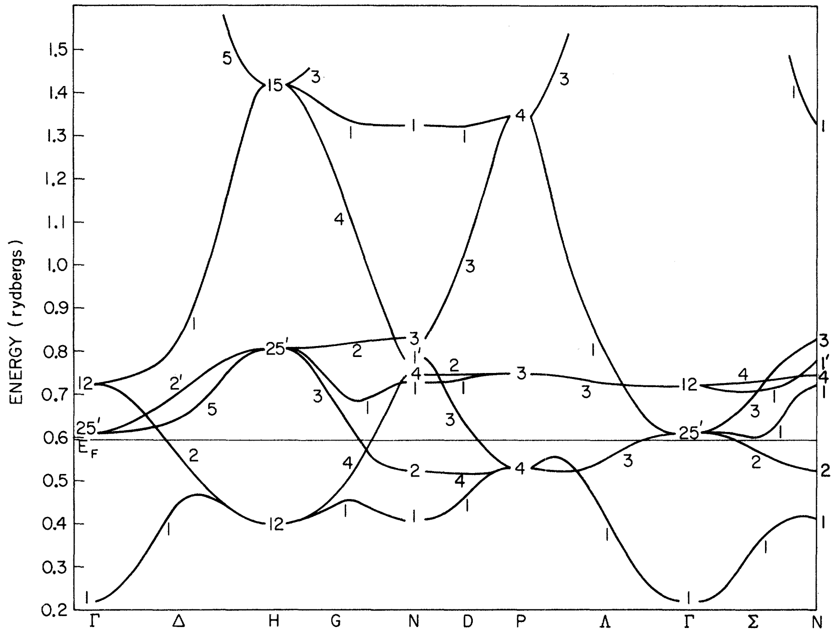

FIG. 2. Energy bands of vanadium for $\alpha = 1$ at normal lattice constant a_0.

$\alpha = 1$. In our calculation E_F is below the state Γ_{25}' while in theirs, E_F is above Γ_{25}'. As shown in Table IV for $\alpha = 1$, we have found larger band widths and s-d separation than Yasui *et al.* Comparison between the reduced exchange calculations cannot be made directly since they used $\alpha = 0.725$. However, qualitatively these calculations seem to agree, except that their energy band Δ_5 appears to dip down and touch the Fermi level. Table IV also shows the widths for the non-self-consistent calculation (NSC) with Slater exchange and $4s^1$ configuration which are in agreement with the previous calculation by Mattheiss,[4] and, as we pointed out in Sec. III, are close to those of the $\alpha = \frac{2}{3}$ self-consistent results.

B. Comparison with Experimental Band Widths

If we consider the separations E_F-H_{12} and E_F-Γ_1 to be a measure of the occupied d-band and s-d band widths respectively, then as is shown in Table

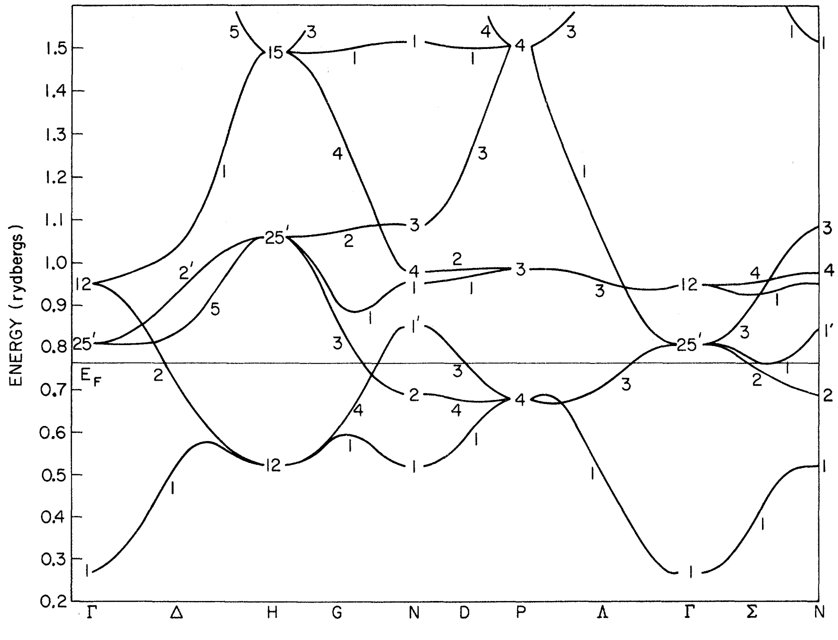

FIG. 3. Energy bands of vanadium for $\alpha = \frac{2}{3}$ at normal lattice constant a_0.

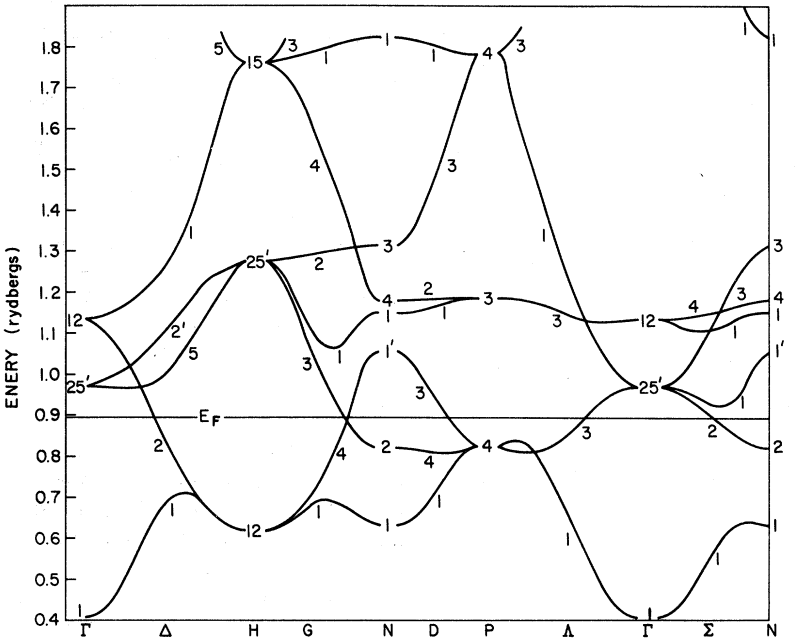

FIG. 4. Energy bands of vanadium for $\alpha=\frac{2}{3}$ at a lattice constant $a=0.95a_0$.

IV, our values for E_F-H_{12} (SC $\alpha=\frac{2}{3}$) are in good agreement with photoemission measurements by Eastman.[3] Also, our values for E_f-Γ_1, the occupied portion of the $3d\,4s$ band, agree well with soft-x-ray emission measurements by Fischer.[2] We must point out, however, that our NSC $\alpha=1$ calculation is in a slightly better agreement with experiment than the SC $\alpha=\frac{2}{3}$.

V. FERMI SURFACES

The Fermi surfaces at normal and reduced lattice spacings for $\alpha=\frac{2}{3}$ are shown in Fig. 5 for (100) and (110) planes. The surface at normal spacing is very similar to that for niobium,[21] consisting of a second-zone octahedral-hole region centered at Γ, a set of third-zone hole ellipsoids centered at

TABLE IV. Energy band widths in rydbergs.

	s-d separation		*d* width	Occupied *d* width	Occupied *s-d* width	*s-p* width
	$\Gamma'_{25}-\Gamma_1$	$H'_{25}-\Gamma_1$	$H'_{25}-H_{12}$	E_F-H_{12}	$E_F-\Gamma_1$	$N'_1-\Gamma_1$
			Present calc.			
$\alpha=1$	0.393	0.587	0.404	0.192	0.375	0.564
$\alpha=\frac{2}{3}$	0.543	0.791	0.535	0.241	0.497	0.583
$\alpha=\frac{2}{3}$, $a=0.95a_0$	0.564	0.869	0.657	0.276	0.488	0.647
NSC $\alpha=1$	0.527	0.754	0.495	0.212	0.471	0.569
			Other calc.			
Mattheiss (APW)						
$\alpha=1$	0.53	0.75	0.49	0.23	0.50	
Yasui *et al.*						
MTB-OPW						
$\alpha=1$	0.334	0.586	0.395	0.166	0.357	0.587
$\alpha=0.725$	0.454	0.758	0.476	0.159	0.441	0.594
			Expt.			
Eastman						
photoemission				0.22		
Fischer						
x ray					0.47	

the zone face (N), and a third-zone hole sheet of multiply connected (100) arms extending from Γ to H, the so-called jungle gym.

In the case of the 5% reduced lattice spacing, the ellipsoids at N have merged with the jungle gym, and thus the multiply connected hole surface is considerably more complicated. From a very crude estimate, assuming a linear variation, with pressure of the energy levels along $\Gamma - N$, we predict that the ellipsoids will connect with the jungle gym at 135 kbars. Unfortunately, this is still beyond the range of low-temperature high-pressure experiments, but it would be interesting to determine whether there is any change in the superconducting properties of vanadium at these pressures.

The main experimental data relating directly to the Fermi surface are the pulsed-magnetic-field de Haas-van Alphen (dHvA) results of Phillips,[1] for the hole ellipsoids at N. Our Fermi-surface areas $\mathfrak{a}$ for $\alpha = \frac{2}{3}$ have been converted to dHvA frequencies F[22] and compared with Phillips's measurements in Table V. Although there is qualitative agreement, our calculated frequencies are about 15% smaller. This discrepancy should be reduced if, following the results of recent self-consistent atomic calculations,[23] we use an exchange multiplier $\alpha = 0.715$ instead of $\frac{2}{3}$. For example, using our self-consistent $\alpha = 1$ and $\alpha = \frac{2}{3}$ results, we have estimated by linear interpolation the dHvA frequency for an ellipsoidal cross section in the HNP plane normal to [110] for $\alpha = 0.715$ to be 52×10^6 G which differs from Phillips's value by only about 8%.

We have also calculated the cyclotron masses for the ellipsoidal sections from

$$\frac{m^*}{m_0} = \frac{\hbar^2}{2\pi m_0}\left(\frac{d\mathfrak{a}}{dE}\right)_F$$

as shown in Table V.

These calculated values must be multiplied by an enhancement factor $1+\lambda$ to compare with experiment. McMillan[24] has used superconducting properties to estimate the enhancement factor for vanadium and gives a value of $1+\lambda = 1.6$. The experimental cyclotron mass value of Phillips is in good agreement with our value multiplied by the above factor.

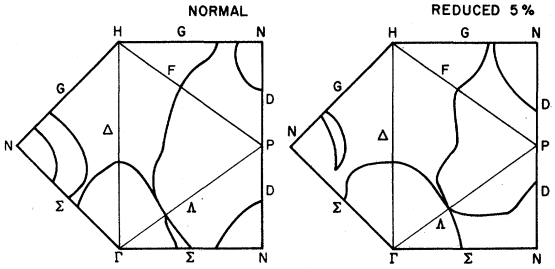

FIG. 5. Fermi surfaces of vanadium at normal and reduced lattice constants for $\alpha = \frac{2}{3}$.

TABLE V. Ellipsoids.

Orbit plane	Normal direction	dHvA frequency (MG) Expt.[a]	dHvA frequency (MG) Calc.	$\frac{d \ln F}{dp}$ (kbar^{-1}) Calc.	$\frac{m^*}{m_0}$ Calc.	$\frac{m^*}{m_0}$ Expt.[a]
HNP	[110]	55.7	46.5	0.0029	0.92	
ΓNP	[001]	52.6	44.9	0.0024	0.86	
ΓNP	[110]	67.1	59.5	0.0023	1.3	1.7–2.1
	[100]	60.2	51.8	0.0027		
	[110]	52.6	48.0	0.0025		

[a] R. A. Phillips, Ref. 1.

From the Fermi-surface areas at normal and reduced lattice spacings we have calculated the logarithmic pressure derivatives of the dHvA frequencies (Table V). We note a change of about 0.25% kbar^{-1} in the ellipsoid cross sections, a rather large effect especially for a transition metal. By way of comparison, from the scaling due to compressibility, $\frac{2}{3} K_T$, one would predict ~0.04% kbar^{-1} increase in area. There are no data yet on the pressure dependence of the Fermi surface of vanadium, but some preliminary experiments by Anderson and Schirber[25] on Nb give values for the changes of cross sections in the ellipsoids in this metal of about 0.1% kbar^{-1}, in good agreement with our self-consistent band calculations for Nb.[26] Thus we predict a bigger effect in vanadium than in niobium.

VI. DENSITY OF STATES

In order to find the density of states we interpolated the APW energies using a Monte Carlo method and a formula suggested by Mattheiss.[27] The results, which involve 48 000 points in the Brillouin zone, are shown in Fig. 6. It is interesting to note that for $\alpha = \frac{2}{3}$, the Fermi level falls at a peak of the density of states as might naively be expected for a high-T_c superconducting material.[28]

In the one-electron approximation, the low-temperature electronic specific-heat coefficient is $\gamma = \frac{1}{3}\pi^2 k^2 N(E_F)$, where $N(E_F)$ is the density of states at the Fermi level. The experimental value of γ is 8.86 mJ mole^{-1} deg^{-2}.[29] To compare with experiment our calculated value of $N(E_F) = 26.6$ states atom^{-1} Ry^{-1} was multiplied by the enhancement factor $1+\lambda = 1.6$.[24] The result for γ was 7.24 mJ mole^{-1} deg^{-2}, which is reasonable in view of the uncertainty in λ and the limited accuracy of our density-of-states calculation.

As is shown in Fig. 6, for the reduced lattice constant, the density of states is similar, but $N(E_F) = 21.6$ states atom^{-1} Ry^{-1} is smaller. We, therefore, expect that at this pressure the transition temperature may be less than the normal value.

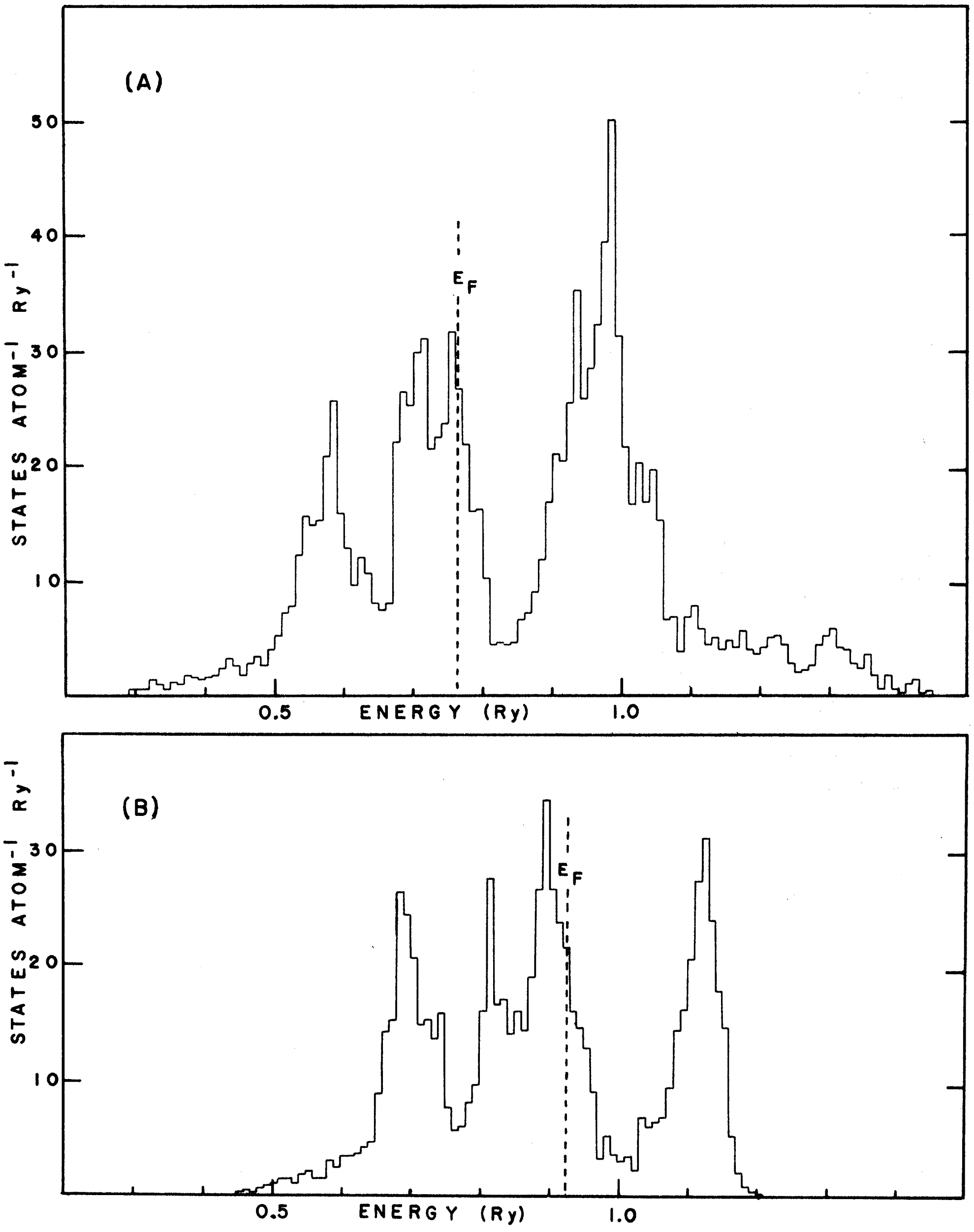

FIG. 6. Density of states of vanadium for $\alpha = \frac{2}{3}$ at normal (A) and reduced (B) lattice constant. (A) corresponds to an interpolation of the lowest six bands while (B) corresponds to the lowest four bands.

However, at much smaller pressures, Gardner and Smith[30] found the pressure derivative of T_c to be positive.

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[1] R. A. Phillips, Phys. Letters <u>36A</u>, 361 (1971).

[2] D. W. J. Fischer, J. Appl. Phys. 40, 4151 (1969).

[3] D. W. Eastman, Solid State Commun. 7, 1697 (1969).

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

[5] E. C. Snow and J. T. Waber, Acta Met. 71, 623 (1969).

[6] J. S. Bolemon and C. P. Poole, Bull. Am. Phys. Soc. 14, 612 (1969).

[7] J. R. Anderson, J. W. McCaffrey, and D. A. Papaconstantopoulos, Solid State Commun. 7, 1439 (1969).

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

[9] M. Yasui, E. Hayashi, and M. J. Shimizu, Phys. Soc. Japan 29, 1446 (1970).

[10] T. M. Hattox (private communication).

[11] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

[12] P.-O. Löwdin, Advan. Phys. 5, 1 (1956); see also F. S. Ham and B. Segall, Phys. Rev. 124, 1786 (1961), Appendix II; and L. F. Mattheiss, Phys. Rev. 133, A1399 (1964).

[13] F. C. Greissen, Phys. Status Solidi 25, 753 (1968).

[14] R. Gaspar, Acta Phys. Acad. Sci. Hung. 3, 263 (1954); W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[15] W. B. Pearson, *Lattice Spacings and Structures of Metals and Alloys* (Pergamon, New York, 1967).

[16] D. I. Bolef, R. E. Smith, and J. G. Miller, Phys. Rev. B 3, 4100 (1971).

[17] L. F. Mattheiss, J. H. Wood, and A. C. Switendick, Methods Comput. Phys. 8, 63 (1968).

[18] J. W. D. Connolly, Phys. Rev. 159, 415 (1967).

[19] E. C. Snow and J. T. Waber, Phys. Rev. 157, 570 (1967).

[20] E. A. Kmetko, Natl. Bur. Std. (U.S.) Spec. Publ. 323 (U.S. GPO, Washington, D.C., 1970).

[21] L. F. Mattheiss, Phys. Rev. B 1, 373 (1970).

[22] Frequency (in gauss) $= 4.517 \times 10^8 \times$ area [in units of $(2\pi/a)^2$].

[23] E. A. Kmetko, Phys. Rev. A 1, 37 (1970); J. H. Wood, Intern. J. Quantum Chem. 3S, 747 (1970); K. Schwarz, *ibid.* (to be published).

[24] W. L. McMillan, Phys. Rev. 167, 331 (1968).

[25] J. R. Anderson and J. E. Schirber (unpublished).

[26] J. R. Anderson, J. W. McCaffrey, and D. A. Papaconstantopoulos, Bull. Am. Phys. Soc. 16, 637 (1971).

[27] L. F. Mattheiss, Phys. Rev. 139, A1893 (1965).

[28] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 106, 162 (1957); 108, 1175 (1957); J. R. Schrieffer, Naval Research Laboratory Report No. 6986, 1969, p. 36 (unpublished).

[29] C. H. Cheng, K. P. Gupta, E. C. van Reuth, and P. A. Beck, Phys. Rev. 126, 2030 (1962).

[30] W. E. Gardner and T. F. Smith, Phys. Rev. 144, 233 (1966).

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Exchange Approximations Used in the Energy-Band Calculations of Metals[*]

Michael Boring and E. C. Snow
University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544

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The use of different exchange approximations in the self-consistent energy-band calculations for a metal (Cu) is shown to yield different one-electron eigenvalue spectra. Specifically, when an energy-dependent exchange potential proposed by Liberman was used, the resulting bandwidths (s-p, d) were much wider than those obtained with the $\rho^{1/3}$ exchange operator. Also it is shown that when the energy-dependent exchange operator is screened, as in the Bohm-Pines theory, the resulting bandwidths were considerably narrowed. Although the "$\rho^{1/3}$" operator and the screened-exchange operator yielded similar results, the variation of the screening parameter did not correspond to a variation of the α parameter of the "$\rho^{1/3}$" method. Use of the screened-exchange operator appears to yield a reasonable band structure.

I. INTRODUCTION

This paper concerns, in a pragmatic way, the role of various exchange approximations used in energy-band calculations of transition metals, and the one-electron eigenvalue spectra generated by these exchange operators are considered for three regimes: the isolated atom, the metallic crystal, and the electron gas. Copper was chosen for the energy-band calculations because it typifies the sensistivity of the d bands of the first-row transition metals to the exchange approximation. Since none of the exchange approximations used here in the band calculations has a rigorous theoretical basis, they are compared solely on the basis of the one-electron eigenvalue spectrum which each generated in self-consistent-field calculations. The calculations are relevant mainly to those energy-band-calculational methods in which the choice of the crystal potential is independent of the self-consistency criterion.

II. THEORY

Since Slater[1] derived the local-electron-gas-exchange approximation ($\rho^{1/3}$ or $X\alpha$ method), it has been used successfully in many atomic calculations[2] and in most energy-band calculations. This exchange operator is

$$V_{xs}(r) = -6[(3/8\pi)\rho(r)]^{1/3}, \qquad (1)$$

where $\rho(r)$ is the (nonuniform) electronic-charge density. From the considerations of Kohn and