Solid State Communications, Vol. 7, pp. 1439–1441, 1969. Pergamon Press. Printed in Great Britain

BAND CALCULATIONS FOR VANADIUM

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(*Received* 19 *July* 1969 *by J.A. Krumhansl*)

The band structure of vanadium is calculated by the augmented plane wave method. The computations were made for two different coefficients of the exchange term of the crystal potential i.e., 1. and $\frac{2}{3}$. In addition calculations were made for three different lattice spacings, normal, reduced 5 per cent and expanded 5 per cent. The results seem to favor Slater Exchange.

RECENTLY there has been speculation about the proper form that should be taken by the exchange term in the one-electron Hamiltonian used for band calculations. In early calculations the normal $\rho^{1/3}$ Slater exchange form[1] was used, where ρ is the charge density, but in 1965 Kohn and Sham[2] suggested that this expression should be reduced by multiplication by a factor of $\frac{2}{3}$. In line with this suggestion several recent calculations[3] have been made with the coefficient of the exchange term α as a parameter which could be varied to obtain agreement with experiment.

In order to investigate this we have determined the energy bands of bcc vanadium on a mesh of 128 points in the Brillouin zone using the augmented plane wave method for different exchange potentials. The muffin-tin potential was obtained from a superposition to third nearest neighbors of the Herman–Skillman[4] free atom (configuration $3d^3\,4s^2$) charge densities using the Löwdin[5] alpha expansion as outlined by Mattheiss.[6]

The resulting energy bands are shown in Fig. 1 for the N–Γ–H symmetry lines for $\alpha = \frac{2}{3}$ and 1. As expected, the effect of exchange on the d-like bands is drastic. For example, if one considers the $3d$ band width w_D as defined by the difference in energy between the H_{12} and N_3 levels, one finds w_D equals 11.7 eV for $\alpha = \frac{2}{3}$ and w_D equals ~~11.7~~ for $\alpha = 1$. Although there is a paucity of experimental information about the electronic structure of vanadium, soft X-ray emission and absorption spectra[7] suggest a d-band width of from 4 to 7 eV. In addition the photoemission data of Eastman[8] indicate a d-band width below the Fermi level of about 3 eV. This is compared with our values of 2.9 eV calculated for $\alpha = 1$ and 4.4 eV for $\alpha = \frac{2}{3}$. Thus it appears as if the full Slater exchange gives better agreement with experiments.

It is interesting to note that the p-like point N_1' falls below the Fermi level for $\frac{2}{3}$ exchange and lies above it for the full exchange potential. Thus the resulting Fermi surfaces for the two cases should be observably different. In fact, preliminary pulsed field de Haas–van Alphen effect

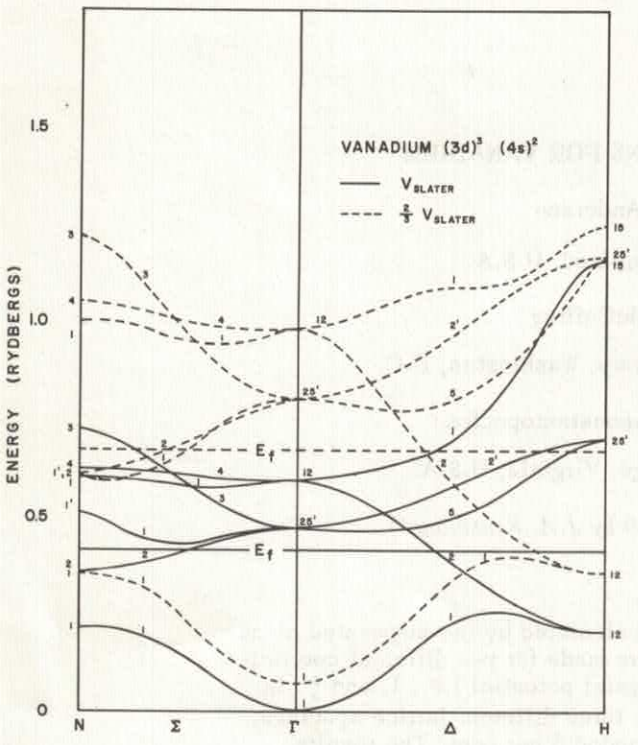

FIG. 1. Energy bands of vanadium along the symmetry direction N–Γ–H. Solid line for full Slater exchange and dotted line for Kohn–Sham exchange.

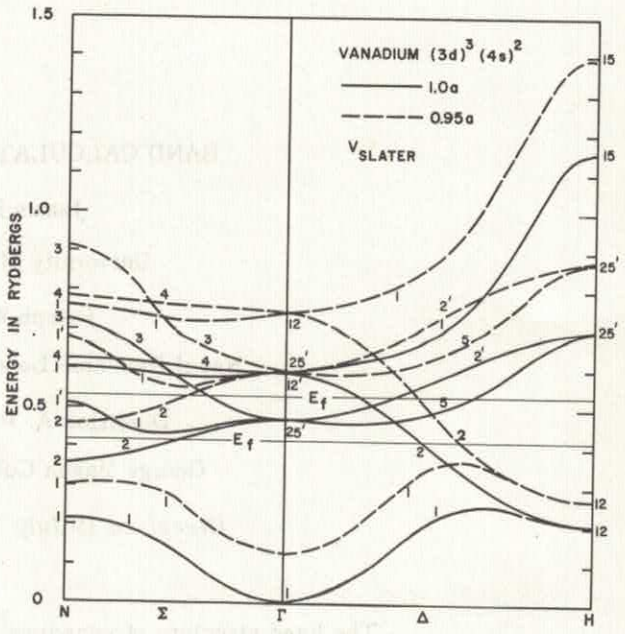

FIG. 2. Energy bands of vanadium along the symmetry directions N–Γ–H. Solid line for normal lattice spacing and dotted line for reduced lattice spacing.

experiments by Phillips[9] give oscillations which have been tentatively attributed to hole ellipsoids at N. Only minor modification of the potential would be necessary to obtain such ellipsoids from the full exchange calculation; drastic changes would be required for $\frac{2}{3}$ exchange. Finally, however, we wish to point out that our results for $\frac{2}{3}$ exchange are qualitatively the same as those of Mattheiss[10] using full exchange and a $3d^4\ 4s^1$ atomic configuration.

In Fig. 2 are plotted the energy bands of vanadium again along N–Γ–H using full Slater exchange for two values of lattice constant, a = 5.72 a.u. (normal pressure) and 0.95a (240 kbar pressure). We see that w_D increases by about 1.5 eV for reduced lattice spacing. In addition if we take the energy difference $\Gamma_1 - H_{15}$ as a measure of the sp-band width, this width increases also by about 1.5 eV at high pressures. The ordering of levels remains unchanged as the lattice spacing is changed from a to $0.95a$, but but similar calculations for $1.05a$ revealed an interchange of levels H_{15} and H_{25}. Since the position of the Fermi level has been calculated for each of these lattice spacings, it is possible to calculate changes of the Fermi surface with pressure. For example, we have estimated that the hole surface centered at Γ changes in cross-sectional area normal to [100] by less than 0.01 per cent/kbar.

In order to determine the optimum form of the exchange potential, it is necessary to carry out the band calculations to self-consistency and to compare the results with suitable experiments. We have begun the self-consistent calculations and plan to compare them with dHvA measurements.

Acknowledgements – We are indebted to Dr. A. Switendick and Dr. J. Wood for the use of their computer programs and for many helpful discussions on this problem.

J.R.A. would like to thank the Advanced Research Projects Agency, and D.A.P. the National Science Foundation.

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Die Bandstruktur von Vanadium wird mit Hilfe der 'augmented plane wave' – Methode berechnet. Für den Koeffizienten des Austauschgliedes des Kristallpotentials werden hierbei die Werte 1 und $\frac{2}{3}$ benutzt. Zusätzlich wird die Gitterkonstante variiert. Wir nahmen den normalen, dem um 5 Prozent verkleinerten und den um 5 Prozent vergrößerten Wert. Auf Grund der Ergebnisse scheint die Slater–Austauswechselwirkung bevorzugt zu sein.