Lawrence Berkeley National Laboratory
LBL Publications

Title

PSEUDOPOTENTIAL CALCULATION OF THE ELECTRONIC STRUCTURE OF A TRANSITION METAL?NIOBIUM

Permalink
https://escholarship.org/uc/item/15182879

Author

Fong, C.Y.

Publication Date

1971-12-01

eScholarship.org Powered by the California Digital Library
University of California

Submitted to
Solid State Communications

RECEIVED
LAWRENCE
RADIATION LABORATORY

LBL-485
Preprint c.2

LIBRARY AND
DOCUMENTS SECTION

PSEUDOPOTENTIAL CALCULATION OF THE ELECTRONIC STRUCTURE OF A TRANSITION METAL--NIOBIUM

C. Y. Fong and Marvin L. Cohen

December 1971

AEC Contract No. W-7405-eng-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY

25

LBL-485
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Subject Index 44.1

Pseudopotential Calculation of the Electronic Structure of a Transition Metal--Niobium*

C. Y. Fong

Department of Physics, University of California, Davis, California 95616†

and

Department of Physics, University of California, Berkeley, California 94720

and

Marvin L. Cohen

Department of Physics, University of California

and

Inorganic Materials Research Division, Lawrence Berkeley Laboratory

Berkeley, California 94720

Abstract

The electronic band structure and density of states is calculated for niobium using the Empirical Pseudopotential Method with a non-local d-potential. The results are in good agreement with APW calculations for states near and below E_F indicating that the niobium pseudopotential derived here can now be used for pseudopotential calculations of niobium compounds.

---

*Work supported in part by the National Science Foundation Grant GP 13632

†Permanent address

In this letter we report the first application of the Empirical Pseudopotential Method (EPM)[1] (with a nonlocal potential) to a calculation of the electronic structure of a transition metal. We believe that this extension of the EPM is important not only because this simple method can now be applied to this interesting class of metals, but also because of the calculations which are now possible for transition metal compounds. The pseudopotential method is particularly suited to calculations for compounds[2] once the pseudopotentials for the constituent atoms are known. In particular, the results of the work presented here indicates that similar calculations can be done for compounds of Nb like NbN which is a high temperature superconductor and layer compound superconductors like $NbSe_2$.

Following the calculation for the noble metals[1,3] the nonlocal part of the pseudopotential is chosen to determine the main features of the d-bands, while the local part is used for the s and p states and for the s-d interaction. Since the electronic configuration of Nb is similar to Ag,[3] we expect these potentials to be similar. For Ag accurate wavelength modulation spectra are available[3] while this is not the case for Nb; hence the Ag potential provides a good starting point for the Nb calculation. The lack of data for Nb forces us to refer to other band calculations[4,5] for the principle energy splittings to fix the Nb potential. Hopefully, accurate optical data will become available and our calculations can be refined further.

The crystal structure of Nb is bcc with a lattice constant a = 3.30A.[6] We choose the origin of our coordinate system at a Nb atom. The pseudopotential Hamiltonian has the form

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V_L(\vec{r}) + V_{NL}(\vec{r}) \qquad (1)$$

where $V_L(\vec{r})$ and $V_{NL}(\vec{r})$ are the local and nonlocal parts of the pseudopotential. The local potential is expanded in the reciprocal lattice

$$V_L(\vec{r}) = \sum_{\vec{G}} V(|\vec{G}|)\, e^{i\vec{G}\cdot\vec{r}} \qquad (2)$$

where $\vec{G}$ is a reciprocal lattice vector and $V(|\vec{G}|)$ is the local pseudopotential form factor. We have truncated $V(|\vec{G}|)$ for $|\vec{G}|^2 \geq 8$; this gives the same number of form factors for the Nb(bcc) case as for the Cu(fcc) case.

The form for the nonlocal part of the pseudopotential is given in reference 1. To assure convergence to within 0.1 eV for the important energy gaps at the Γ, H, and N points of the Brillouin zone, we choose a cutoff energy for our matrix, $E_1 = 14.1$, in units of $(2\pi/a)^2$. The size of the matrix is of the order of 110 × 110. Because of the large number of plane waves, we don't use the Löwdin[7,2] perturbation scheme.

The numerical values for the parameters are: $V(110) = -0.0410$ Ry, $V(200) = -0.0200$ Ry, $V(211) = -0.0090$ Ry, $V(220) = 0.070$ Ry, $A_2 = -3.8840$ Ry, $R_s = 1.136$ Å, $\alpha = 0.206$ and $\kappa = 1.668$ $(2\pi/a)$. The value of R_s is smaller than the APW sphere radius which is 1.43 Å used by Mattheiss.[4] In Fig. 1, we plot the resulting band structure along the important symmetry lines. A density of states curve resulting from setting a mesh of 91 points in $\frac{1}{48}$th of the Brillouin zone is shown in Fig. 2. The comparison between the important energy gaps obtained from the APW method and the present calculations is shown in Table IA. We remark here that the APW results are considered to be quite good. In particular, selected areas of the Fermi surface are within 10% of the measured results.[4]

The maximum discrepancy for bands not far from the Fermi energy is at $\Gamma_{25'} \rightarrow \Gamma_{12}$ for which our calculated value is lower than Mattheiss's result by 0.32 eV. The shapes of the band structure for the two calculations agree very well for energies below the $\Gamma_{25'}$ bands. One can see this in Table IB where a comparison of the positions for the peaks in the density of states between the two different calculations is given. Two main differences occur for the bands with energies higher than $\Gamma_{25'}$: First, the Δ_1 band coming from Γ_{12} in the APW results has the shape of a free electron band, but as shown in Fig. 1, the present results clearly show an s-d hybridization between the two Δ_1 bands. The lower one being the Δ_1 band derived from Γ_1 which has strong s-like character near Γ, but because of the hybridization flattens and turns down halfway to H. Second, the s-like higher bands, like P_1, have lower energies in the EPM calculation than the corresponding ones in Ref. 4. We believe this results from our truncation of the $V(|\vec{G}|)$'s which also causes the local pseudopotential form factor, V(220), to be quite large. This results from the fact that the differences in the lengths of the $\vec{G}$-vectors are small around $|\vec{G}|^2 = 8$; it is likely that the large V(220) is compensating for the lack of higher $V(|\vec{G}|)$'s, i.e. the sharp cutoff. We can adjust this with a more gentle (and more realistic) cutoff. We have not done this at this time in order to limit the set of parameters to the smallest possible set until optical or other measurements become available to fit more parameters.

In summary we have presented a calculation of the band structure of Nb using the EPM and we have shown that the results are consistent with the APW results for energies near and below E_F. The resulting pseudopotential for Nb should then be a good approximation for this atom and it can be used as a starting point to calculate the band structure of the compounds with Nb as a constituent atom.

Acknowledgements

One of us (CYF) would like to thank Professor C. Kittel and Professor M. L. Cohen for their hospitality during his stay at Berkeley in the summer of 1971. Part of this work was done under the auspices of the United States Atomic Energy Commission.

References

1. C. Y. Fong and M. L. Cohen, Phys. Rev. Letters 24, 306 (1970).
2. M. L. Cohen and V. Heine, Solid state physics 24 (Academic Press, Inc., New York, N. Y., 1970), p. 37.
3. J. Stokes, Y. R. Shen, C. Y. Fong and M. L. Cohen (to be published).
4. L. F. Mattheiss, Phys. Rev. B1, 373 (1970).
5. R. A. Deegan and W. D. Twose, Phys. Rev. 164, 993 (1967).
6. R. W. G. Wyckoff, Crystal structures, 2nd edition, vol. 1, p. 16, John Wiley and Sons, Inc., New York (1963).
7. P. Löwdin, J. Chem. Phys. 19, 1396 (1951).

Figure Captions

Figure 1 Band structure of Niobium. The Fermi level was chosen to coincide with the Fermi level of reference 4.

Figure 2 The Niobium density of states derived from the band structure. The Fermi level was chosen to coincide with the Fermi level of reference 4.

Table Captions

Table IA Comparison of important energy gaps between the present results and APW calculations.

Table IB Comparison of the positions of the prominent peaks in the density of states N(E) of Nb between the present results and APW calculations. Energy is measured relative to the Γ_1 state which is the lowest band at Γ.

Table IA

Symmetry	APW[4]	present calculation
$\Gamma_1 \rightarrow \Gamma_{25'}$	5.89 (eV)	5.71 (eV)
$\Gamma_{25'} \rightarrow \Gamma_{12}$	2.4	2.08
$\Gamma_1 \rightarrow H_{12}$	1.5	1.72
$H_{12} \rightarrow H_{25'}$	9.19	9.38
$\Gamma_1 \rightarrow N_1$	1.84	1.99
$\Gamma_1 \rightarrow N_{1'}$	7.63	7.38 (s → p)
$N_1 \rightarrow N_2$	2.06	1.87
$\Gamma_1 \rightarrow P_4$	4.35	4.31

Table IB

peak label	APW[4]	present calculation
a	2.76 (eV)	2.75 (eV)
b	3.86	3.95
c	5.19	5.05
d	8.6	7.95

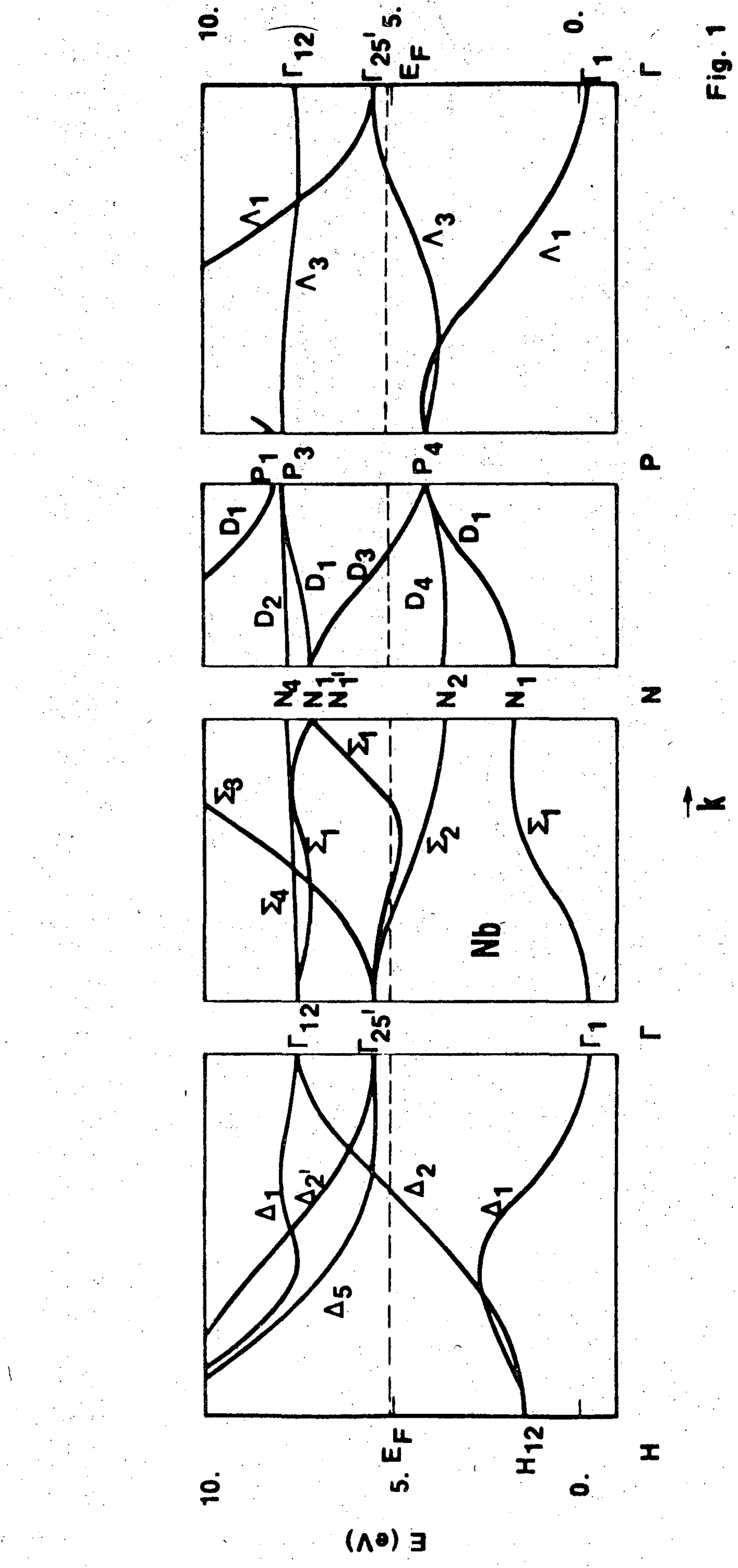
E (eV)
10.
5. E_F
0.
H_{12}
H
Γ
N
P
Γ
k
Nb
Γ_{12}
Γ_{25}'
Γ_1
Δ_1
Δ_2'
Δ_2
Δ_5
Δ_1
Σ_3
Σ_4
Σ_1
Σ_1
Σ_2
Σ_1
N_4
N_1
N_1'
N_2
N_1
D_1
D_2
D_1
D_3
D_4
D_1
P_1
P_3
P_4
Λ_1
Λ_3
Λ_3
Λ_1
Γ_{12}
Γ_{25}'
E_F
Γ_1

Fig. 1

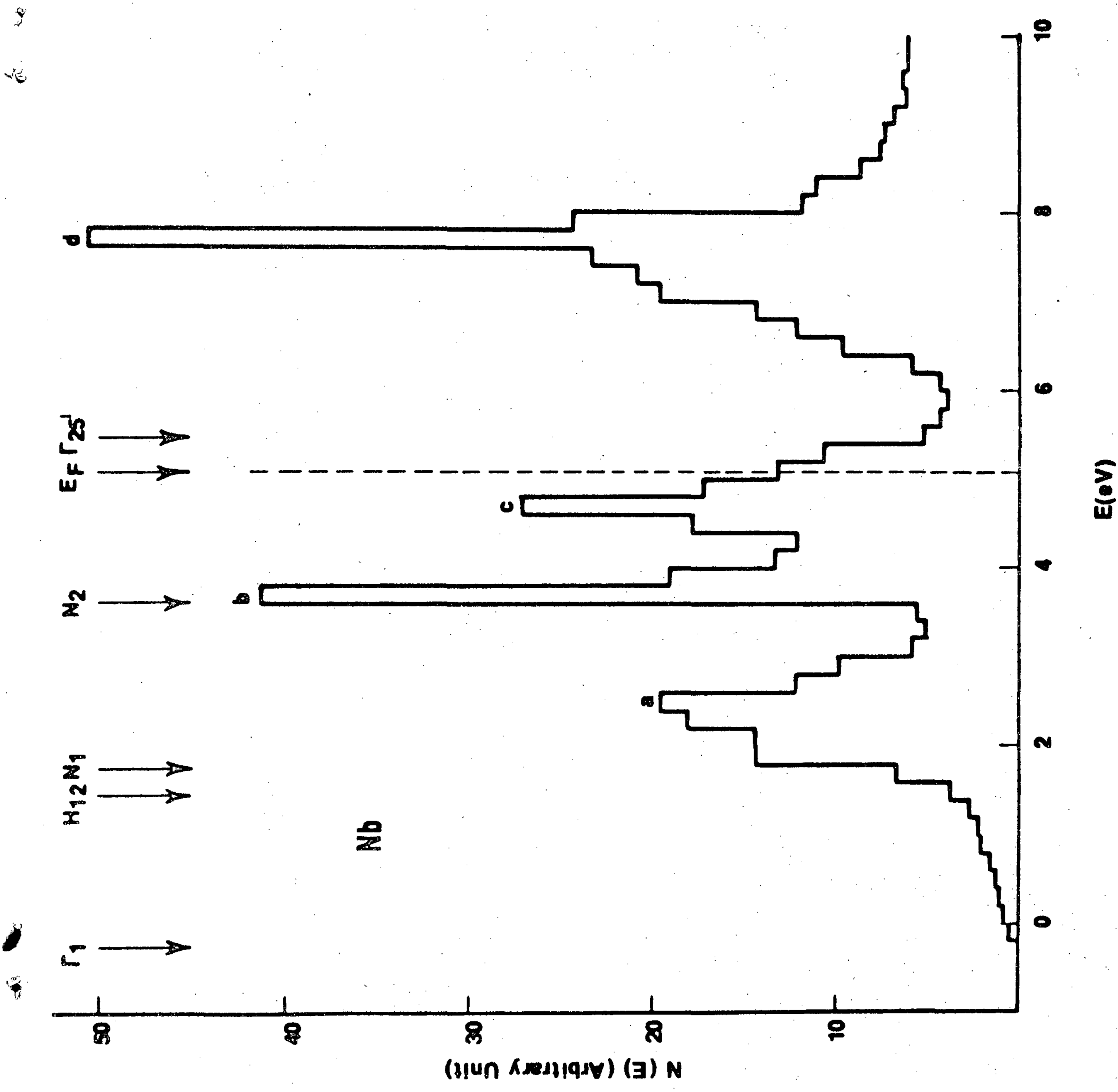
Γ_1
H_{12}
N_1
N_2
E_F
$\Gamma_{25'}$
Nb
a
b
c
d
N (E) (Arbitrary Unit)
50
40
30
20
10
E(eV)
0
2
4
6
8
10

Fig. 2

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720