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Authors

Fong, C.Y.

Cohen, Marvin L.

Publication Date

1973-12-01

Submitted to Physical Review Letters

LBL-2554

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C. Y. Fong and Marvin L. Cohen

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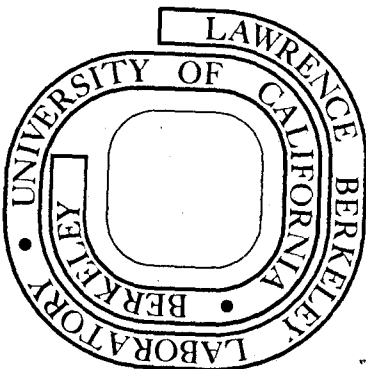
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Band Structure and Charge Densities

of 2H-NbSe₂

C. Y. Fong^{*}

Department of Physics, University of California
Davis, California 95616

and

Marvin L. Cohen[†]

Department of Physics, University of California

and

Inorganic Material Research Division, Lawrence Berkeley Laboratory
Berkeley, California 94720

Abstract

The electronic energy band structure of 2H-NbSe₂ is calculated using the Empirical Pseudopotential Method. The results are compared with other calculations and with experimental data. Charge densities for the completely filled valence bands and the partially filled conduction bands are calculated using a set of special k -points in the Brillouin zone. The relations between the calculated charge densities and the various bonding models are discussed.

The group V transition metal chalcogenides with layered structure and trigonal prism coordination have attracted considerable attention¹ because of their interesting superconducting and magnetic properties. In particular, among these compounds, $2H-NbSe_2$ has been subjected to intensive study. Theoretical studies related to the electronic properties of $NbSe_2$ have involved schematic band models^{1,2,3}, energy band calculations^{4,5}, and models describing bonding properties⁶. In this letter, we present charge density calculations for both the filled bands and the partially filled conduction band states in two different planes of the real space lattice. These results represent the first charge density calculations for a d-band material and they give some insight into the electronic bonding properties of these materials. The charge densities were obtained from a calculated band structure using the nonlocal pseudopotential method. The results of the band structure appears to give better agreement with the experimental data than previous calculations. We start by discussing the band structure and then go on to describe the charge density calculations.

An essential feature of the present calculation is the d-states. Experimental evidence⁷ indicated that the d-states of the transition metal atom play an important role in the electronic properties of compounds containing these atoms. Consequently the usual local pseudopotential scheme was augmented to include a nonlocal d-potential centered at the Nb-atoms to account for the d-states. The pseudopotential method and the form of the nonlocal pseudopotential used have been discussed elsewhere^{8,9}.

For the NbSe₂ case, the unit cell is hexagonal and has two molecules. The corresponding space group is D_{6h}^{10} . The length of the side of the hexagon, a , is 3.45 Å and the lattice constant along the \hat{c} -axis is 12.54 Å. Because the ratio c/a is 3.63, the number of nonvanishing local pseudopotential form factors for each atom is 32 with a cutoff at $|\vec{G}|^2 = 14.5 \left(\frac{2\pi}{\sqrt{2}a}\right)^2$, where \vec{G} is a reciprocal lattice vector. The form factors of Nb and Se atoms were first scaled from Nb¹¹ and ZnSe¹². These form factors and the 4 parameters in the nonlocal pseudopotential were adjusted to obtain a band structure consistent with both the photoemission^{13,14} and the reflectivity data^{15,16}. Because of the large c/a ratio, the resulting matrix size for the pseudopotential Hamiltonian over the plane wave basis states is of the order of 190×190. An additional 300 plane waves were used in the Löwdin-Brust¹⁷ perturbation scheme for the local part of the potential. Even with the present size of the matrix, the c/a ratio still causes convergence problems for energies along Σ to M and results in significant adjustments in the form factors of Nb and Se at large $|\vec{G}|$. The convergence in the energy at M is of the order of 0.1-0.2eV. We also limit our band structure calculations to yield $E(\vec{k})$ only along the symmetry directions.

The band structure results for the 5-th band to the 27-th band are plotted in Fig. 1. The zero of the energy scale is placed at the 17-th band at Γ , and the lowest valence band at Γ (not shown in Fig. 1) is -15.eV. For the filled valence bands, the results here are similar to the ones obtained by Mattheiss⁴. However, the partially filled and the unoccupied conduction bands are different. The main difference is along T; the

present band structure shows no crossing for T_4 and T_1 bands. The gap between d and p states ($\Gamma_2^- \rightarrow M_1^+$) is 0.3 eV which is about half of the value obtained by Mattheiss. Since the 17th and 18th bands are partially filled, the Fermi energy should be at about 0.2-0.3eV above Γ_1^+ . The Fermi surface has both electron and hole surfaces. The minimum for the T_1 band and the bands with energies, E , around -2.4eV should result in maxima in the density of states at 0.6 and 2.6eV below E_F . Comparing these results with the experimental values at -0.4 and -2.2^{13, 14}, the agreement is reasonably good. The calculated width of the partially occupied d bands is 0.9 eV. The corresponding width determined by Williams and Shepherd¹⁴ is 0.7eV and the width determined in Ref. 13 is 1.eV. The smallest interband transition should be 0.6eV near Σ . The bands near $\Sigma_1(18)$, $\Sigma_3(16)$ and $T_4(18)$, $T_5(16)$ are quite parallel with energy differences of about 2.eV. These will contribute to the measured structure at $\hbar\omega \approx 1.9$ eV. We expect that the 2.5eV structure should be due to transitions arising from a large volume inside the zone. It is difficult to make a definite identification at present. We would estimate that the overall agreement between the present band structure and the experimental results is of the order of 0.3eV.

In Fig. 2, we plot the calculated charge densities in two different planes. The plane DEFG in Fig. 2a contains one layer with one Nb and two Se atoms and the plane OABC in Fig. 2b has 4 Nb atoms at the corners of the graph. The actual locations of these two planes are shown at the lower left corner of the figure. The dotted circles in the figures show the core radii. The values of the charge distribution within the core region at Se are not expected to be accurate, because the pseudowave function are not orthogonalized to the core states. These charge distributions were

calculated using the scheme of Chadi and Cohen¹⁸. We used 6 \vec{k} -points. The overlapping charge between one particular lattice point in real space and its nearest neighbors vanishes at least up to 12 shells. The normalization corresponds to 2 electrons per band because spin-orbit interaction is neglected. Fig. 2a shows the total charge distribution of the filled 16 bands. The closed shell type of contours within a layer illustrates clearly the characteristic distribution of the filled bands. The charge is mainly around the chalcogenides and the configuration has a similar shape to that of SnSe_2 ¹⁹. It indicates that the p-lobes of the Se atom point toward the nearest metallic ions. These lobes do not combine with the s-like state to form sp^3 orbitals so that a lone pair will be in the interlayer region and will be cut by this plane. The bonding charges make 40.2° with respect to a line bisecting the distance between the Se ions and passing through the Nb ion. This makes the bonding angle of Se-Nb-Se to be 80.4° . According to the directed valence bond results^{20,6}, the d and s like states of the transition metal ion will hybridize with its unoccupied p like states to form equivalent cylindrical bonds pointing toward the chalcogenides under the trigonal prism symmetry. The mixing of the p-states can be at least 10%. These dsp orbitals and the p-orbitals on the Se ions form the covalently bonding charge of the crystal. We have applied the projection operator of 5p states centered at the Nb-atoms to find the extent of the mixing of the 5p states in the wavefunctions for the 16 occupied bands at Γ , M and K. There is no significant contribution from the 5p states. Therefore, the bonding charges are mainly the p states of the chalcogenides mixing with ~~the~~ d like states of the Nb atom. The maximum density within the 18.5 contours makes an angle of 59° with respect

to the same line described above. These regions of the charge densities are the extended distributions of the other bonding charges intersected by this plane.

In Fig. 2b, the charge densities of the partially filled conduction bands are shown. Although the scheme for calculating charge distributions of the partially filled bands by a few k -points is expected to be only approximate, nevertheless, the qualitative features are likely to be correct. The chalcogenides are directly above and below the center of the triangular contours with magnitude equal to 2. Most of the charge density for these conduction bands are near the Nb ions. We expect that these charges should have d-like character. The shapes of these contours do indicate that they are mixtures of d_{xy} and $d_{x^2-y^2}$ states of Nb. As Mattheiss⁴ pointed out, the presence of these states are due to the d-d hybridization. Our band structure results show this hybridization especially along Σ . The $\Sigma_1(19)$ band derived from Γ_5^+ , which is composed of the degenerate states of d_{xy} and $d_{x^2-y^2}$, would have connected to the 17th band at M, if there was no hybridization of this band with the lower Σ_1 bands which are derived from d_{z^2} states. The maximum value of the contours for these partially filled conduction bands is about 14% of the value for the bonding charge of the filled bands. However, because of the d-character of these states, the distribution is not as uniform as in simple metals, e.g. Al²¹. These nonuniform charge densities, especially near the Nb ion, illustrate the characteristic feature of the d-band metals.

In conclusion, the charge densities of NbSe₂ obtained from a band structure which agrees with the experimental data to the order of 0.3 eV, show similar distribution of the charges for the filled bands near the Se ions as in the case of SnSe₂ and show a linear combination of d_{xy} and

$d_{x^2-y^2}$ for the partially filled bands. The insignificant contribution of the 5p states of Nb atom to the bonding charge found by applying the projection operator favors the simple bonding picture! The bonding charge between the metallic and chalcogen ions are composed of the p-like states of the Se atoms mixing with the s and d-like states of the Nb atom. However, this result does not imply the bonding nature of the crystal is purely ionic. The tightly bound atomic d states of the Nb atom and the resonance between the d-states and the p-states of the chalcogenides can result significant charge distributions between the atoms as we have obtained here.

Acknowledgment

One of us (CYF) would like to thank D. J. Chadi for discussions. Part of the research was under the auspices of the U.S. Atomic Energy Commission.

*Supported in part by the Air Force Office of Scientific Research (AFSC) under grant No. AFOSR-72-2353.

†Supported in part by National Science Foundation Grant GH 35688.

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Figure Captions

- Fig. 1 The electronic band structure of NbSe₂ along symmetry lines in the Brillouin zone starting with the fifth valence band.
- Fig. 2a The charge distributions for the filled 16 bands in plane DEFG.
- Fig. 2b The charge distributions for the partially filled conduction bands in plane OABC.

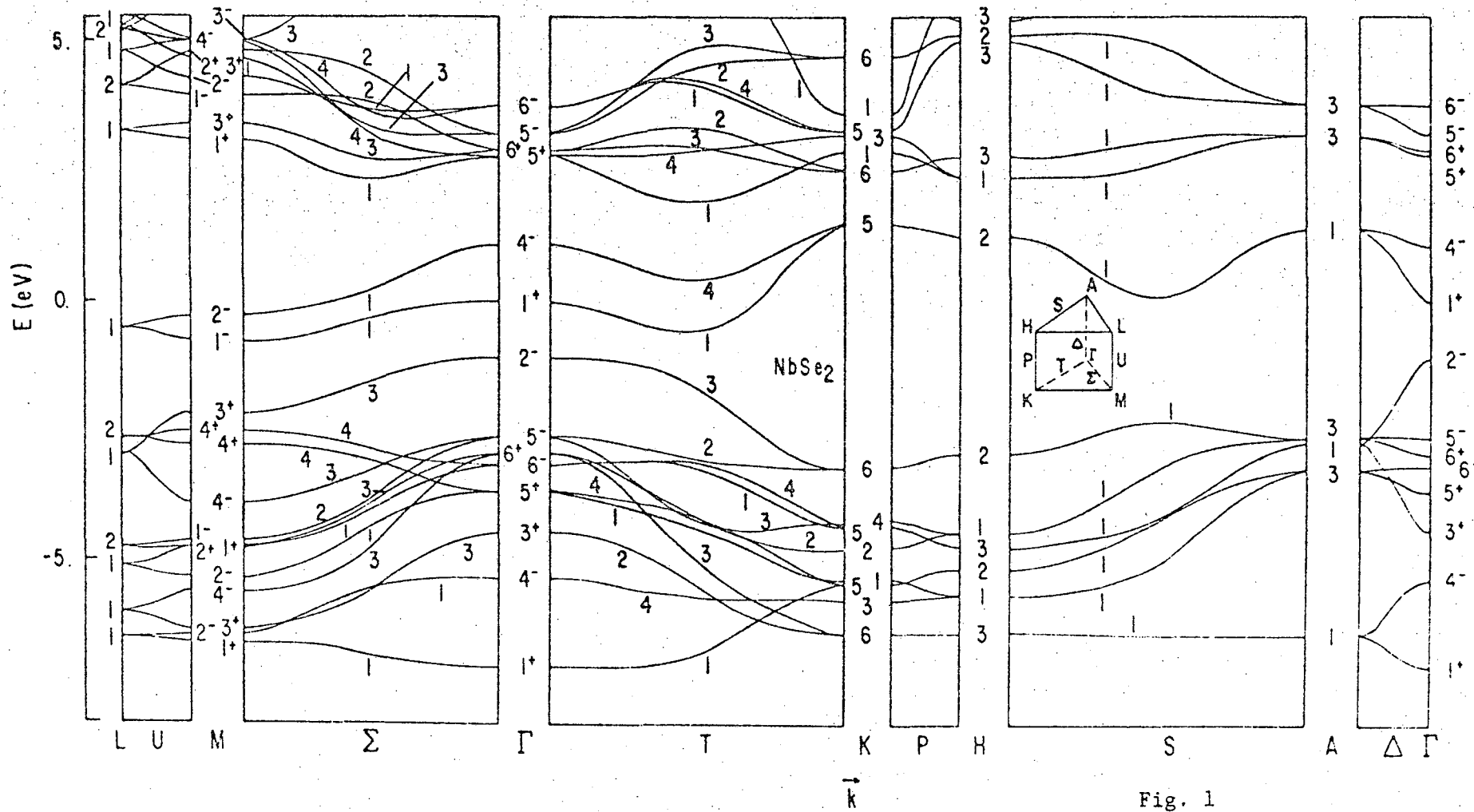


Fig. 1

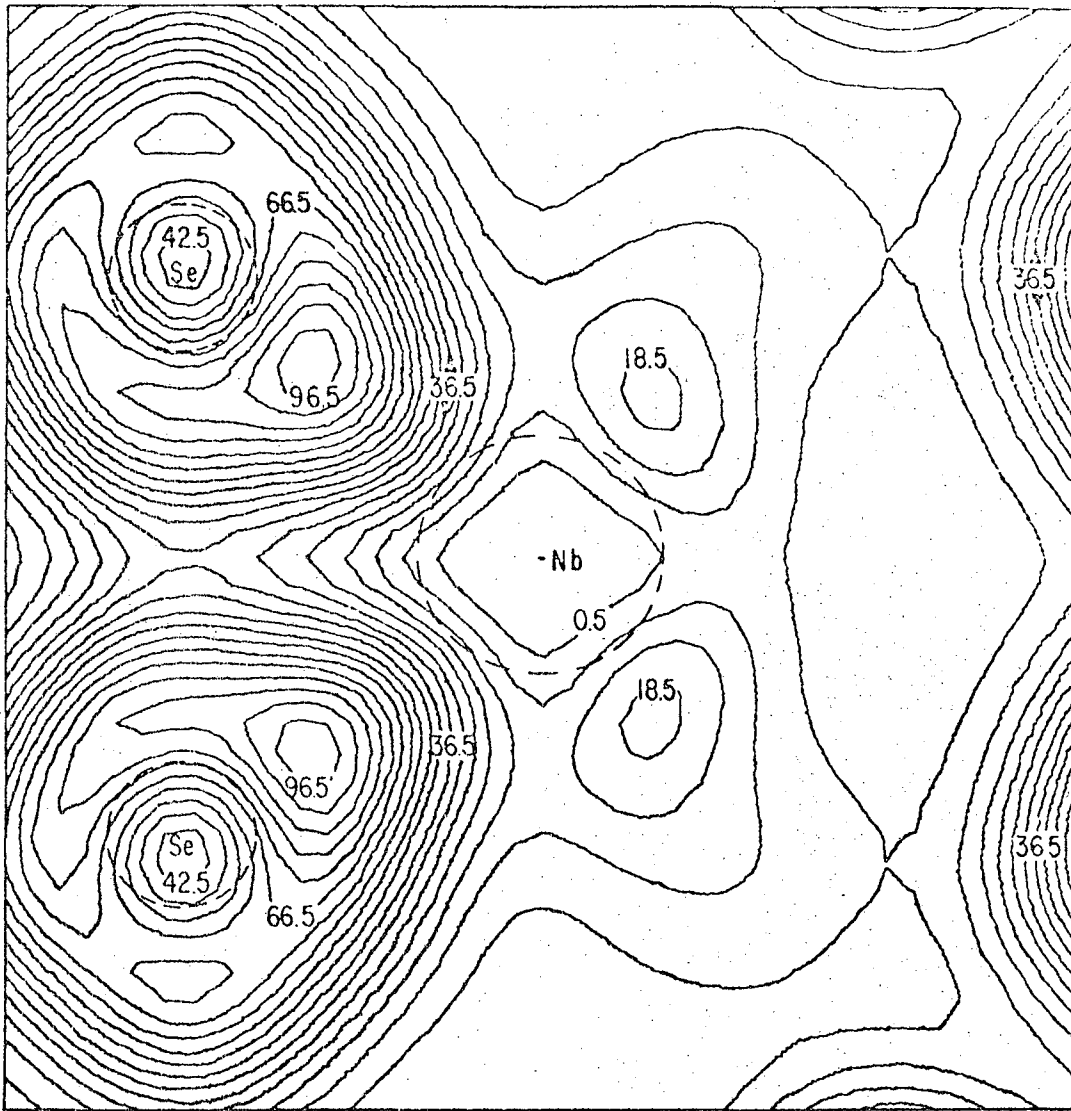


Fig. 2a

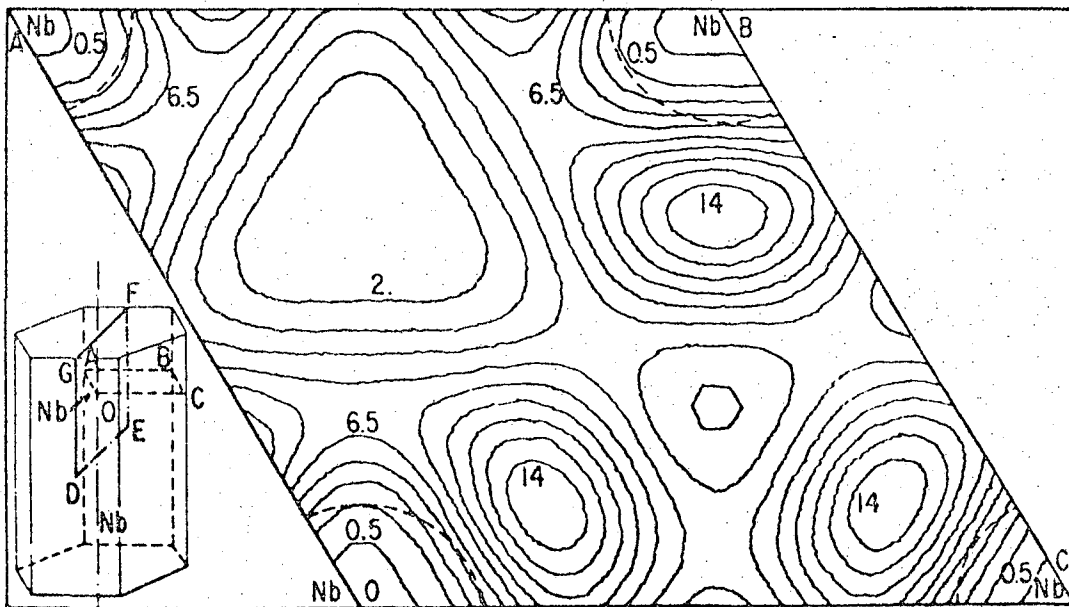


Fig. 2b

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