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**COLLABORATIVE RESEARCH AND DEVELOPMENT
(CR&D)**

Delivery Order 0070: Ab-initio Modeling of Slippery Hexagonal Solids

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Universal Technology Corporation

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14. ABSTRACT This research in support of the Air Force Research Laboratory Materials and Manufacturing Directorate was conducted at Wright-Patterson AFB, Ohio from 18 April 2007 through 17 March 2008. This task worked to develop, validate, and explore the models of slippery hexagonal lattice solids using ab initio density function theory (DFT) calculations. The various mechanical, electronic, and other properties of the following hexagonal slippery solids were evaluated: Lattice constants, a, c; Elastic Constants, C11, C12, C33, C44, C13, C66L; Density of States (DOS); Local Density of States (LDOS); Band Structures; Voigt, Reuss, Hill Bulk Moduli, Bv, Br, Bh; Voigt, Reuss, Hill Shear Moduli, Gv, Gr, Gh; Poisson's Ratio σ ; Young's Modulus, E; and Relationships with Coefficient of friction, u. The results are shown in appropriate tables.						
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TO UTC and WPAFB
FROM Sanjay V. Khare
DATE April 18, 2008

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The electronic properties of remaining compounds i.e., MoX_2 , where ($\text{X} = \text{O}, \text{S}, \text{Se}, \text{Te}$) were found in the first two weeks. Their band structures, local density of states and total density of states were plotted and studied. A comparative study of all the four compounds MoO_2 , MoS_2 , MoSe_2 , and MoTe_2 in the group was done.

Meanwhile, literature survey was performed to find a relationship between the elastic constants and the coefficient of friction. Preliminary studies showed that there exists a relationship between coefficient of friction and Young's modulus. Further studies were carried out in that direction.

After completion of the computations for the mechanical and electronic properties of 'Mo' compounds along 16th group of the periodic table, we searched for other materials of interest to the Air Force. We then found published work by Dr. Voevodin of the Wright Patterson Air Force Base (WPAFB) on NbSe_2 which had similar tribological behavior to MoX_2 . We thus began working on NbX_2 by the end of the last week.

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As in case of Mo, we decided to run through the 16th group i.e., O, S, Se, and Te for a systematic comparison of properties. Hence we considered compounds with identical structures such as NbO_2 , NbS_2 , NbSe_2 and NbTe_2 .

The first two weeks were consumed in conducting various convergence tests on the above mentioned compounds of Nb. The same procedure as in case of MoX_2 was followed to find lattice constants 'a' and 'c' i.e., by keeping one of them constant and varying the other. Like in case of NbSe_2 , initially 'c' was fixed and 'a' was varied and then 'a' was fixed (fixed to the value found previously) and 'c' was varied. Similar procedures were followed for NbTe_2 and both showed a consistent pattern in reaching convergence. Repeating this process for NbO_2 and NbS_2 yielded their lattice constants 'a' and 'c'.

After the lattice constants were found, the independent parameter 'u' was taken into consideration. Few more tests were conducted with varying 'u' and fixed 'a' and 'c' to see to it that the independent parameter 'u' was also finalized.

Elastic constants were found for all the four compounds. All the five independent elastic constants for NbO_2 , NbS_2 , NbSe_2 and NbTe_2 were calculated. Bulk modulus was also

found from these elastic constants from the relationship between elastic constants and bulk modulus derived previously.

Simultaneously further studies were made on the relationship between coefficient of friction and elastic constants. This time it was clearly found that the coefficient of friction is directly proportional to shear strength and inversely proportional to effective Young's modulus raised to two third.

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Now since the mechanical properties of the materials were calculated, work was started on calculating the electronic properties of the materials NbO₂, NbS₂, NbSe₂ and NbTe₂. The band structures, local density of states and total density of states of NbX₂ were plotted and the required values were found from these plots. As in case of the 'Mo' series, the first Brillouin zone of a hexagonal lattice was chosen, and the high symmetry k points along this region were marked. These k-points along with other files were used to plot band structures. All the results were plotted and compared. By the end of the month work on NbX₂ was completed.

Literature survey revealed that 'W' was the next material of interest for comparison with 'Mo' and 'Nb' series. Hence, we started working on the WX₂ series next. To start with, the 'a' and 'c' values of all the four materials WO₂, WS₂, WSe₂ and WTe₂ were evaluated.

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We proceeded to compute the elastic constants and other mechanical properties i.e., Bulk modulus, Young's modulus, Poisson's ratio and others. We followed this by finding the electronic properties of the WX₂. The band structures were estimated using the k-points derived from the first Brillouin zone of the hexagonal lattice as in case of other compounds. Also the local density of states and total density of states were plotted and compared.

At last a comparative study of all the compounds researched so far i.e., MoX₂, NbX₂, WX₂ (X = O, S, Se, Te) was done. Also by the end of the grant period an equation was derived for the relationship between elastic constants and coefficient of friction and was checked for authenticity.

RE Beyond the grant period

We are planning to closely compare our theoretical results with experimental results obtained at WPAFB. We are closely collaborating with WPAFB scientists led by Dr. Andrey Voevodin and working on journal publications of these results.

TO UTC and WPAFB
 FROM Sanjay V. Khare
 DATE May 21, 2008

RE Final report for Collaborative Research and Development (CR&D) Task Order 0070

In the course of our effort we evaluated various mechanical, electronic and other properties of several hexagonal slippery solids which were listed below:

1. Lattice constants, a , c .
2. Elastic Constants, C_{11} , C_{12} , C_{33} , C_{44} , C_{13} , C_{66} .
3. Density of States (DOS).
4. Local Density of States (LDOS).
5. Band Structures.
6. Voigt, Reuss, Hill Bulk Moduli, B_v , B_r , B_h .
7. Voigt, Reuss, Hill Shear Moduli, G_v , G_r , G_h .
8. Poisson's Ratio, σ .
9. Young's Modulus, E .
10. Relationship with Coefficient of friction, u .

We also derived a relationship between shear strength, Young's modulus and coefficient of friction. It was found that coefficient of friction is directly proportional to the shear strength and inversely proportional to the effective Young's modulus raised to the power of one third.

Listed in Tables 1-3 are the results of our computations. Table 1 lists properties of MoX_2 ($X = \text{O}, \text{S}, \text{Se}, \text{Te}$).

Table 1a: The five independent elastic constants (C_{11} , C_{12} , C_{33} , C_{44} , C_{13}), Bulk Modulus (B), lattice constants (a and c) and Energy band gap (E_g).

	MoO_2	MoS_2	MoSe_2	MoTe_2
C_{11} (GPa)	494.218	231.006	195.705	140.080
C_{12} (GPa)	184.942	65.374	46.465	38.480
C_{33} (GPa)	44.950	48.342	52.748	53.388
C_{44} (GPa)	6.528	17.439	20.068	25.613
C_{13} (GPa)	12.318	10.235	14.818	15.908
B (GPa)	161.393	75.782	66.262	52.682

a (Å)	2.799	3.123	3.250	3.472
c (Å)	9.856	12.190	12.750	13.762
E_g (eV)	0.514	0.758	0.692	0.659

Table 1b: The Voigt Bulk Modulus (B_v), Voigt Shear Modulus (G_v), Reuss Bulk Modulus (B_r), Reuss Shear Modulus (G_r), Hill Bulk Modulus (B_h), Hill Shear Modulus (G_h), Young's Modulus (E) (all in units of GPa), Poisson's Ratio (σ), and relationship $u = G_h / E^{2/3}$ (in units of $(\text{GPa})^{1/3}$) which is a quantity proportional to the coefficient of friction.

	B_v	G_v	B_r	G_r	B_h	G_h	σ	E	u
MoO₂	161.393	88.459	41.991	14.231	101.692	51.345	0.284	131.846	1.982
MoS₂	75.782	51.840	40.094	29.233	57.938	40.536	0.216	98.611	1.899
MoSe₂	66.262	47.488	42.771	31.507	54.517	39.498	0.208	95.443	1.891
MoTe₂	52.682	37.955	40.716	32.793	46.699	35.374	0.198	84.728	1.834

Table 2 lists the properties of NbX₂ (X = O, S, Se, Te).

Table 2a: Same properties as in Table 1a for NbX₂ (where X = O, S, Se, Te).

Note: ' - ' indicates negative value which is unphysical, i.e. the compound is unstable.

	NbO₂	NbS₂	NbSe₂	NbTe₂
C₁₁ (GPa)	421.003	190.870	155.590	89.290
C₁₂ (GPa)	216.367	62.630	41.510	45.610
C₃₃ (GPa)	53.892	54.360	62.140	74.560
C₄₄ (GPa)	18.960	1.550	-	11.140
C₁₃ (GPa)	35.037	14.260	15.515	14.760
B (GPa)	163.198	68.711	57.600	44.822
a (Å)	2.948	3.285	3.387	3.576

c (Å)	9.179	11.901	12.545	13.583
E_g (eV)	0.453	0.758	0.692	0.494

Table 2b: Same properties as in Table 1b for NbX₂ (where X = O, S, Se, Te).

Note: ' - ' indicates negative value which is unphysical, i.e. the compound is unstable.

	B_v	G_v	B_r	G_r	B_h	G_h	σ	E	u
NbO₂	163.198	68.678	52.717	32.106	107.957	50.392	0.298	130.821	1.955
NbS₂	68.711	36.441	43.822	3.697	56.267	20.069	0.341	53.809	1.408
NbSe₂	57.600	-	45.374	-	51.487	-	-	-	-
NbTe₂	44.822	20.691	42.770	16.719	43.796	18.705	0.313	49.122	1.395

Table 3 lists the properties of WX₂ (X = O, S, Se, Te).

Table 3a: Same properties as in Table 1a for WX₂ (where X = O, S, Se, Te).

	WO₂	WS₂	WSe₂	WTe₂
C₁₁ (GPa)	566.410	259.473	214.172	151.926
C₁₂ (GPa)	190.180	59.057	41.988	28.554
C₃₃ (GPa)	47.840	47.640	54.118	53.984
C₄₄ (GPa)	10.727	18.876	21.415	26.677
C₁₃ (GPa)	11.145	14.337	13.906	15.029
B (GPa)	178.400	82.449	69.118	52.784
a (Å)	2.793	3.123	3.245	3.470
c (Å)	9.890	12.201	12.806	13.825
E_g (eV)	0.923	0.900	0.824	0.791

Table 3b: Same properties as in Table 1b for WX_2 (where $X = O, S, Se, Te$).

	B_v	G_v	B_r	G_r	B_h	G_h	σ	E	u
WO₂	178.400	106.460	44.506	22.041	111.453	64.250	0.258	161.682	2.165
WS₂	82.450	59.516	41.417	31.364	61.934	45.440	0.205	109.532	1.985
WSe₂	69.118	53.295	43.644	33.922	56.381	43.609	0.193	104.010	1.972
WTe₂	52.784	42.956	40.692	35.341	46.738	39.149	0.173	91.811	1.924

We are planning to closely compare our theoretical results with experimental results obtained at WPAFB. We are closely collaborating with WPAFB scientists led by Dr. Andrey Voevodin and working on journal publications of these results.