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# Surface-structure determination of the layered compounds $MoS_2$ and $NbSe_2$ by low-energy electron diffraction

B. J. Mrstik, R. Kaplan, and T. L. Reinecke*
*Naval Research Laboratory, Washington, D. C. 20375*

M. Van Hove and S. Y. Tong†
*Department of Physics, Universtity of Wisconsin, Milwaukee, Wisconsin 53201*

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The stacking sequence and interplane and interlayer separation of $2H$-$MoS_2$ and $2H$-$NbSe_2$ are determined by the dynamical low-energy-electron diffraction approach. Although lateral reconstructions corresponding to alteration in the bulk stacking sequence at the surface are physically reasonable, we find that such reconstructions do not in fact occur for these two compounds.

The unusual properties resulting from the highly anisotropic crystal structures of the layered transition-metal dichalcogenide compounds have been the subject of many experimental and theoretical studies.[1] Although most of these studies have been concerned with bulk properties, there has recently been considerable interest in the surface properties of these compounds, notably in measurements of angular-dependent photoemission[2] and of anisotropic surface-vibration modes.[3] In some cases data obtained from surface-sensitive techniques (such as ultraviolet photoemission[4,5]) have been compared to results of bulk band-structure calculations.[6-8] There has been no detailed determination of the surface structure of these compounds. Information obtained from such a study is clearly important for a full understanding of their surface properties.

In this paper we report the first detailed determination of the surface crystallography of two of the layered compounds $2H$-$MoS_2$ and $2H$-$NbSe_2$ by the dynamical low-energy-electron-diffraction (LEED) method. We show that the surface planes of $NbSe_2$ have the same spacing as the bulk planes, and that the surface interplanar spacing of $MoS_2$ is contracted by about 5%. We point out that because of their unique structures, a lateral translation of certain atomic planes near the surface of these compounds is physically reasonable. Such lateral translations would correspond to crystals having a different polytype and thus significantly different properties[9] at the surface than in the bulk. In understanding the surface properties of these layered materials, it is therefore essential to determine whether such surface reconstructions do in fact occur. We present here results which show conclusively that the compounds $2H$-$MoS_2$ and $2H$-$NbSe_2$ maintain their bulk structure up to the surface.

Structurally, the layered compounds consist of sandwiches of tightly bonded atoms separated from similar sandwiches by large Van der Waals (VdW) gaps (see Fig. 1). The sandwiches are composed of planes of like atoms in hexagonal arrays stacked so that the plane of transition-metal atoms is between the chalcogen atom planes. The coordination of the metal atoms may be either octahedral or trigonal prismatic. Stacking of sandwiches to form the crystal occurs in a number of ways, with a periodicity ranging from between one and six sandwiches. The stacking sequences characteristic of $2H$-$MoS_2$ and $2H$-$NbSe_2$ are shown in Fig. 1(a). Both materials have structures which repeat after two sandwiches, and the metal atoms in each sand-

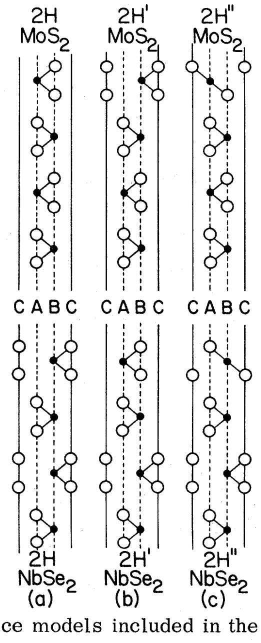

FIG. 1. Surface models included in the structural search (surface at top of diagrams). The atoms of the hexagonal planes have the possible lateral positions A, B, C along the $\tilde{X}$ cut described in the text.

wich have trigonal prismatic coordination. It is important to note that the two structures differ only in the stacking of the sandwiches. In $2H$-NbSe$_2$ the metal atoms of different sandwiches lie along lines perpendicular to the surface, whereas in the $2H$-MoS$_2$ structure alternate sandwiches are shifted parallel to the surface by an amount

$$\vec{X} = \tfrac{2}{3}\vec{a}_1 + \tfrac{1}{3}\vec{a}_2 ,$$

where $\vec{a}_1$ and $\vec{a}_2$ are the primitive lattice vectors parallel to the surface.

Changes in interplanar spacings at surfaces resulting from the abrupt termination of the lattice potential have been predicted from lattice-dynamical calculations, and have been observed experimentally in some materials.[10] In addition, in some materials the change in lattice potential causes surface atoms to reconstruct as observed in LEED studies by the presence of fractional order diffraction patterns. For the layered compounds $2H$-MoS$_2$ (Refs. 11–13) and $2H$-NbSe$_2$ we observe no fractional order beams. In view of the asymmetry of the restoring forces on the surface sandwich and the weak VdW forces between sandwiches in the bulk, however, it seems plausible that the top sandwich may be shifted as a whole. That such a shift requires very little change in lattice potential is suggested by the fact that both the $2H$-MoS$_2$ and $2H$-NbSe$_2$ type structure for trigonal prismatic sandwiches are quite common bulk structures. This type of reconstruction which is apparently unique to the layered compounds would not result in fractional order diffraction beams, and could only be directly detected by a detailed study of LEED intensity-energy ($IV$) spectra.

Specifically, we have studied the following structural changes at the surface of $2H$-MoS$_2$ and $2H$-NbSe$_2$: (i) an expansion or contraction of the top interplanar spacing within the top sandwich, (ii) an expansion or contraction of the top intersandwich spacing (i.e., the first VdW gap distance), (iii) a shift of the top sandwich of $2H$-MoS$_2$ by $\vec{X}$ (structure denoted by $2H'$-MoS$_2$) and of $2H$-NbSe$_2$ by $\vec{X}$ (structure denoted by $2H'$-NbSe$_2$) as shown in Fig. 1(b), and (iv) a shift by $\vec{X}$ of the surface plane [denoted by either $2H''$-MoS$_2$ or $2H''$-NbSe$_2$, as shown in Fig. 1(c)]. All of the shifts suggested lead to surface structures which are identical to known stable bulk structures. The reconstructed structure $2H'$-MoS$_2$, for example, has six surface planes which are identical to the bulk structure of $2H$-NbSe$_2$. Similarly, $2H'$-NbSe$_2$ has six surface planes which are identical to the bulk $2H$-MoS$_2$ structure. In the structures proposed by (iii) the surface intersandwich chalcogen-chalcogen distance is the same as in the bulk, thus the binding energy is changed very little.

The MoS$_2$ crystals used in this study were cut from a piece of natural molybdenite; the NbSe$_2$ crystals were grown by Canadian Thin Films Ltd. by the iodine-vapor transport method. Although the samples were cleaved outside the vacuum system, Auger analysis indicated that the resulting surfaces had less than 3% carbon contamination. LEED intensity-energy spectra of the (10), (01), (11), (20), and (02) beams were measured by the standard spot photometer technique. The measurements reported here were all obtained while the sample temperature was near 95 K in order to reduce thermal effects.

For the calculation of ($IV$) spectra in the energy range from 10 to 200 eV, we used the renormalized-forward-scattering layer iteration method[14–16] employing eight phase shifts and 55 beams. Band-structure potentials[6] of MoS$_2$ and NbSe$_2$ were used to generate the energy dependent phase shifts. Inner potentials of 5 and 2 eV were used for MoS$_2$ and NbSe$_2$, respectively. For simplicity, a constant inelastic damping of 5 eV was used along with our experimentally determined values of the Debye temperature (350 K for MoS$_2$ and 280 K for NbSe$_2$). A more realistic model of the damping and Debye temperature would result in some variation in peak heights, but would have only a small effect on peak positions and widths, and therefore would not affect the conclusions about the surface structure.

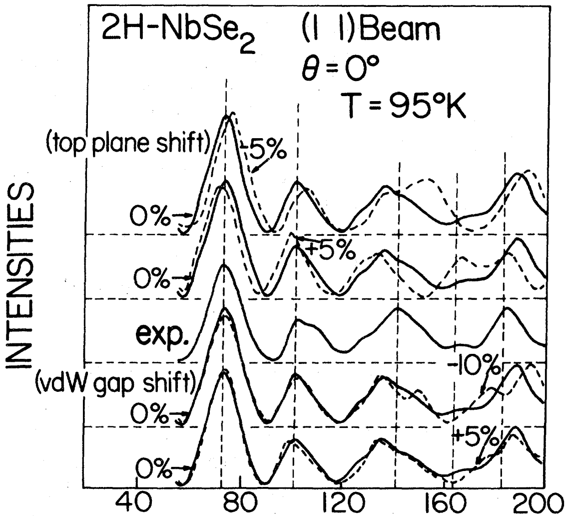

FIG. 2. Normal incidence intensity-energy curves for the (11) diffracted beam from the $2H$-NbSe$_2$ surface. Calculated curves for changes in the topmost interplanar spacing and in the first Van der Waals spacing are shown. The solid curve for 0% change is repeated in each panel for comparison.

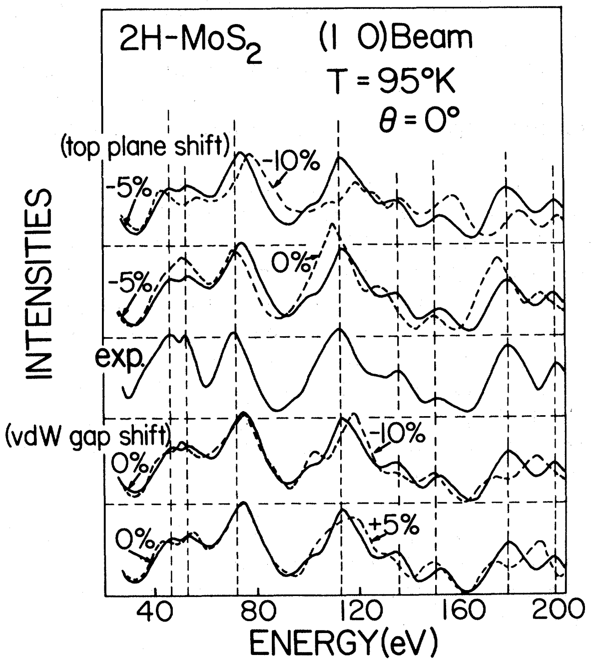

FIG. 3. Same as Fig. 2 for the (10) beam diffracted from $2H$-MoS$_2$. The curve for the optimal structure determined, − 5% change in the topmost interplanar spacing and 0% change in the first Van der Waals spacing is repeated as solid lines for comparison.

We first examine contraction and expansion of the top interplanar spacing and the first VdW gap distance. In Fig. 2 we show the comparisons between theory and experiment for the (11) beam of $2H$-NbSe$_2$ where the top interplanar spacing was varied in steps of ±5%. The best agreement is obtained with no contraction or expansion of the top interplanar spacing. In the lower four curves of Fig. 2 the first VdW spacing is varied. The (*IV*) spectra at low energies are not very sensitive to changes of the top VdW spacing, probably due to the small penetration of the incident electrons. From comparisons of the higher-energy peaks we conclude that there is no evidence that the VdW gap is contracted or expanded in $2H$-NbSe$_2$. Figure 3 shows similar comparisons for the (10) beam of $2H$-MoS$_2$. From the comparison with experiment, we find some evidence (e.g., the peak positions at 113 and 180 eV) for a contraction of up to 5% in the top interplanar spacing. The lower curves of Fig. 3 show that the top VdW gap is unchanged.

Comparisons for lateral rearrangements are shown in Fig. 4. The upper panel compares calculations for the $2H$, $2H'$, and $2H''$ structures with experimental results for the (01) beam of NbSe$_2$. Here the evidence is strong that the surface of $2H$-NbSe$_2$ is unrearranged. The lower panel shows the effect of the $2H$, $2H'$, and $2H''$ structures on

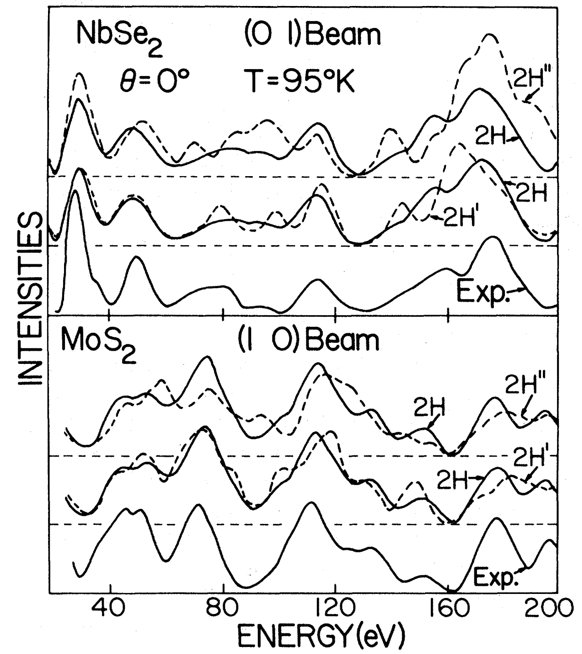

FIG. 4. Intensity-energy curves calculated using the optimal spacings and with the lateral surface structure being varied through the models $2H$, $2H'$, and $2H''$ defined in Fig. 1 are shown. The calculated curves of the $2H$ structures with the optimal spacings are repeated as solid lines for comparison.

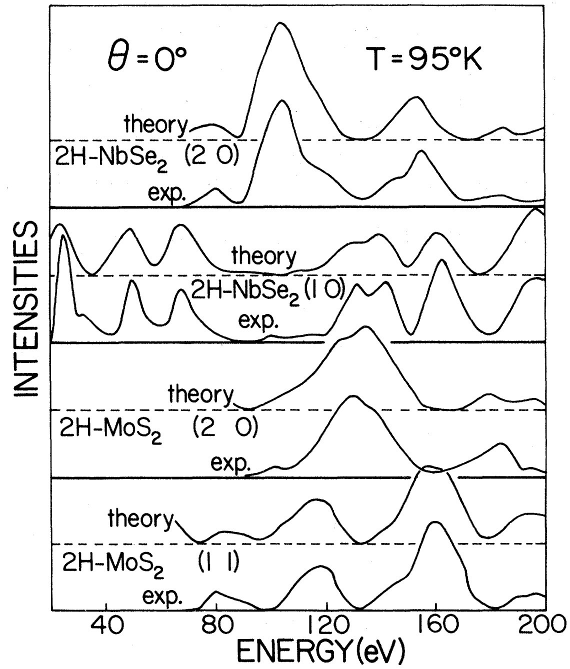

FIG. 5. Comparison of selected experimental intensity-energy spectra with theoretical curves calculated using the optimal spacings and stacking sequences determined.

the (10) beam of $MoS_2$ with the 5% contraction of the top interplanar spacing. Again, there are large differences in the ($IV$) spectra of these structures, and the unrearranged $2H$-$MoS_2$ structure is strongly favored. These conclusions about the interplanar spacings and lateral shifts are given equally well by comparisons with the other diffraction beams. In Fig. 5 we show the close agreement obtained between theory and experiment for other beams, using the optimal structures determined in this work.

In summary, we have determined the surface arrangements of $2H$-$NbSe_2$ and $2H$-$MoS_2$. We find that for $2H$-$NbSe_2$, a metallic compound, the bulk structure is maintained all the way up to the top surface plane. Like the case for other close-packed metal faces [e.g., the (111) faces[10] of Al, Ni, Cu, and Pt], there is no indication of any contraction or expansion of the top interplanar spacing or of the first VdW gap distance. More importantly, we have strong evidence that lateral rearrangements of surface planes do not occur. Thus we expect the surface of $2H$-$NbSe_2$ to exhibit metallic characteristics. The same conclusions about lateral rearrangements are also found to be true for $2H$-$MoS_2$. For $MoS_2$ which has semiconductor properties the bulk structure is maintained all the way up to the top plane, except for a contraction of the top interplanar spacing by about 5% or less. These findings, especially the results on the surface stacking sequence, should provide valuable input information for studies of the electronic, thermal, and chemical properties at the surface region of the layered compounds. We are encouraged by the excellent agreement achieved in the comparison between theory and experiment, and feel that the LEED technique is suitable for determining surface structures of these and other layered compounds.

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[1] For a general review, see J. A. Wilson and A. D. Yoffee, Adv. Phys. 18, 193 (1969).

[2] M. M. Traum, N. V. Smith, and F. J. DiSalvo, Phys. Rev. Lett. 32, 1241 (1974).

[3] S. L. Cunningham (private communication).

[4] J. C. McMenamin and W. E. Spicer, Phys. Rev. Lett. 29, 1501 (1972).

[5] R. M. Williams, J. M. Thomas, M. Barber, and N. Alford, Chem. Phys. Lett. 17, 142 (1973).

[6] L. F. Mattheiss, Phys. Rev. Lett. 30, 784 (1973).

[7] R. V. Kasowski, Phys. Rev. Lett. 30, 1175 (1973).

[8] E. K. Wood and J. B. Pendry, Phys. Rev. Lett. 31, 1400 (1973).

[9] J. A. Wilson, F. J. DiSalvo, and S. Mahajam, Phys. Rev. Lett. 32, 882 (1974).

[10] J. A. Strozier, Jr., D. W. Jepsen, and F. Jona, in *Surface Physics of Crystalline Materials,* edited by J. M. Blakely (Academic, New York, 1975).

[11] B. J. Mrstik, R. Kaplan, A. K. Ganguly, and S. Y. Tong, Solid State Commun. 17, 755 (1975).

[12] G. David, J. Escard, and S. Goldsztaub, C. R. Acad. Sci. (Paris) B 265, 1449 (1967).

[13] S. Ino, S. Ogawa, M. Uchiyama, and Z. Oda, Jpn. J. Appl. Phys. 7, 308 (1968).

[14] J. B. Pendry, Phys. Rev. Lett. 27, 856 (1971).

[15] M. A. Van Hove and S. Y. Tong, J. Vac. Sci. Technol. 12, 231 (1975).

[16] S. Y. Tong, *Progress in Surface Science,* edited by S. G. Davison (Pergamon, Oxford, 1975), Vol. I, Pt. 2.