

### 3D-to-2D Transition by Cs Intercalation of VSe<sub>2</sub>

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Angle-resolved photoemission spectroscopy has been employed to study *in situ* intercalation of the layered compound VSe<sub>2</sub> with Cs. The results show that the valence band structure of VSe<sub>2</sub>, which initially is of 3D character, is transformed to become essentially 2D upon Cs intercalation. The changes, which go far beyond the rigid-band model, are successfully reproduced by self-consistent linear-augmented-plane-wave calculations. This is the first report of a UHV compatible system where the dimensionality of the electronic structure can be controlled *in situ*.

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Layered transition-metal dichalcogenides (TMDC's) are often referred to as "two-dimensional" (2D), but this description is not fully appropriate, despite the highly anisotropic properties of these materials. In many cases band dispersion perpendicular to the layers is comparable to the parallel dispersion [1,2].

One particularly interesting property of TMDC's is the possibility of forming intercalation complexes by introducing foreign atoms or molecules between the layers [3]. This can be used to modify the physical properties in a controllable way, e.g., to turn a semiconducting compound into a metallic one.

Many of the changes occurring upon intercalation can be understood in terms of charge transfer from the introduced species to the host lattice, and indeed this charge transfer process is actually considered to be the driving force for the intercalation process. The charge transfer alters the band filling of the host material, and the rigid-band model is often a useful approximation for reaching a qualitative understanding of the resulting effects. The charge transfer may also strengthen the interlayer bonding by giving it an ionic character.

Another important effect of intercalation is the increased spacing between layers necessary to accommodate intercalated species larger than the available interstitial sites. It is, for example, possible to achieve interlayer separations about 10 times larger than the single layer thickness by intercalation with large organic molecules, and it is in this way possible to study the physical properties of effectively isolated layers.

In addition to these principal effects there may also occur charge-transfer-induced structural changes (of bond lengths, coordinations, and superstructures) within the layers, or changes in layer stacking because of modified interlayer interactions.

Of these effects, the decoupling of individual layers by increased interlayer spacing is very interesting as a tool to

study the importance of "reduced dimensionality" for various physical phenomena. It is, for instance, generally believed that the quasi-2D character of the bands near the Fermi level in high- $T_c$  cuprates is essential for the mechanism of superconductivity in these materials [4-6]. To have available a material that can be made more or less "2D" in a controllable way is therefore of great potential value in studies of reduced dimensionality phenomena.

As is mentioned above, intercalation of large organic molecules in TMDC's has been used to separate the individual layers, but this kind of intercalation complex is not suitable for angle-resolved photoelectron spectroscopy (ARPES) or other techniques requiring ultrahigh vacuum (UHV) conditions. Of the monoatomic species that can be intercalated, Cs is an interesting choice, since its large ionic radius (1.69 Å) [7] by necessity must lead to significantly increased interlayer separation. An attractive feature of alkali metals, in general, is their strong tendency to donate their single valence electron to the host layers [3], which will limit the hybridization between alkali metal and host valence bands. An intercalated atom or molecule which hybridizes strongly with the substrate will act to couple the layers together, contrary to our present objective. For several alkali-metal/TMDC systems, e.g., Cs/TaSe<sub>2</sub> (Ref. [8]), intercalates can be formed *in situ* by deposition of the metal on the TMDC surface, from where it spontaneously intercalates. This method is particularly useful for producing high-quality surfaces of intercalates under UHV conditions.

In this paper we report on *in situ* intercalation of VSe<sub>2</sub>, which is one of the most widely studied TMDC's. VSe<sub>2</sub> adopts the 1T-CdI<sub>2</sub> structure, characterized by octahedrally coordinated metal atoms and the layers stacked without lateral displacements. The valence and conduction bands are primarily derived from the Se 4*p* and V 3*d* orbitals, respectively. The former give rise to six bands,

which are almost completely filled, leaving one electron per unit cell to occupy the lowest band of V  $3d$  character. Because of this half-filled V  $3d$  band,  $VSe_2$  is a metallic compound. The occupied and unoccupied bands of  $VSe_2$  have been extensively studied by ARPES, inverse photoemission, and other techniques [9–13]. These measurements have been in fair agreement with band structure calculations, although some significant deviations have been noticed [10]. In order to facilitate the analysis of our results, we have carried out self-consistent band structure calculations for  $VSe_2$ , as well as for the hypothetical compound  $CsVSe_2$ . These bands were obtained by applying the linear-augmented-plane-wave (LAPW) method, within the local density approximation (LDA) of density functional theory (DFT). In the calculations 65  $k$  points in the irreducible part of the Brillouin zone (BZ) were used and 400 LAPW basis functions. The parametrized [14] Ceperley-Alder [15] form of the exchange-correlation potential was used. Our LAPW bands for  $VSe_2$  are in excellent agreement with extensive ARPES measurements using He I radiation [16].

The experiments reported here were performed using a VSW spectrometer and synchrotron radiation from the storage ring at MAX-lab, Lund, Sweden. The spherical-sector electron energy analyzer had  $\pm 2^\circ$  angular acceptance and typically 0.1 eV energy resolution. A toroidal grating (TGM) monochromator provided photons with energies in the range 10–200 eV.

The  $VSe_2$  single crystal was attached to the sample holder by silver filled epoxy resin, and a clean mirrorlike surface was obtained by cleavage *in situ*. The sample was azimuthally oriented by LEED, and the inequivalent  $\bar{\Gamma}\bar{M}$  and  $\bar{\Gamma}\bar{M}'$  crystallographic directions were identified as described by Law, Andrews, and Hughes [12].

Cs was deposited from carefully outgassed SAES getter sources. The sample was held at room temperature during the deposition. In order to monitor the Cs deposition and intercalation we recorded Cs  $4d$  and Se  $4p$  core level spectra.

The pressure in the UHV chamber was about  $1 \times 10^{-9}$  Torr, which was higher than desired, but quite sufficient for measurements on the clean  $VSe_2$  surface, which is very inert, due to the absence of dangling bonds. The surface also turned out to remain remarkably inert during and after Cs evaporation. Even 14 h after the initial Cs evaporation, core and valence band spectra indicated only slight surface contamination. One clue about the inertness was provided by the Cs  $4d$  core level spectra, whose intensities increased only slowly as more Cs was deposited. This indicates that the deposited Cs atoms were rapidly ionized and intercalated into the interior of the substrate. We therefore find reason to believe that once the intercalation has begun, continued Cs deposition chiefly increases the intercalation depth, without major compositional changes in the surface region. This is in good agreement with the findings of Pettenkofer *et al.* [8], who

studied Cs deposition onto, and subsequent intercalation into,  $2H-TaSe_2$ . As repeated Cs depositions induced only minor changes in the ARPES results, we report here only the data collected before and after the initial Cs evaporation, which lasted for 5 min, with the SAES getter source operating at 5.0 A, and positioned about 20 mm from the sample. The LEED pattern remained sharp after Cs deposition, with no extra spots appearing. The threefold symmetry of the LEED pattern was less apparent after the deposition, however. A more detailed account of the measurements will appear elsewhere [16].

Normal-emission EDC's for a range of photon energies provide detailed information about the valence band dispersion along the  $\Gamma A$  symmetry direction, which is perpendicular to the layers. Figure 1 shows such data for the  $VSe_2$ , before and after Cs intercalation, for  $h\nu$  in the range 24–40 eV. The synchrotron radiation was incident at  $\psi = 45^\circ$  in the  $\bar{\Gamma}\bar{M}$  azimuth and polarized in the plane of incidence. In the EDC's from the clean  $VSe_2$  surface [Fig. 1(a)] most structures are seen to disperse as  $h\nu$  is changed. The dispersion of the peaks agrees fairly well with that expected from the calculated valence bands along  $\Gamma A$  [16]. In contrast, the EDC's from the Cs-intercalated  $VSe_2$  show four peaks which, within experimental error limits, do not disperse at all with photon energy, i.e., the valence band dispersion perpendicular to the layers has vanished.

Figure 2 shows room temperature EDC's for the same two surfaces as in Fig. 1, but measured with  $h\nu = 24$  eV, and polar emission angles  $\theta$  ranging from  $-10^\circ$  to  $60^\circ$  in the  $\bar{\Gamma}\bar{M}'$  azimuthal direction. Measurements in this mode provide information about the band dispersion along the layer planes, and in both cases strong dispersion is observed as  $\theta$  is varied.

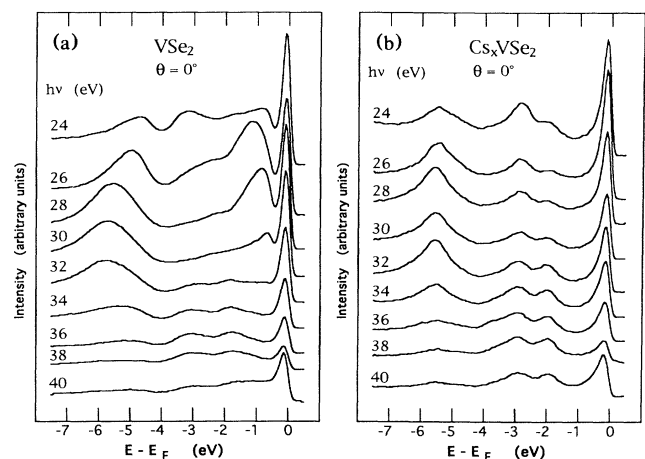


FIG. 1. Normal-emission EDC's, measured from clean (left side) and Cs-intercalated (right side)  $VSe_2$ , with light incident at  $\psi = 45^\circ$  in the  $\bar{\Gamma}\bar{M}$  azimuthal direction, and  $h\nu$  ranging from 24 to 40 eV.

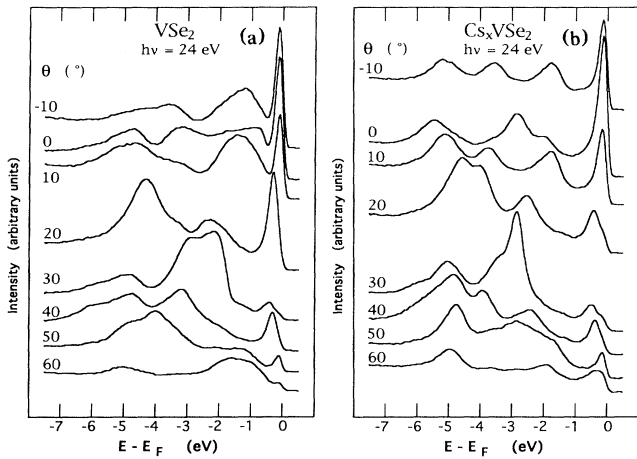


FIG. 2. EDC's measured from clean (left side) and Cs-intercalated (right side)  $\text{VSe}_2$ , with  $h\nu=24$  eV,  $\psi=45^\circ$ , and  $\theta$  ranging from  $-10^\circ$  to  $60^\circ$  in the  $\bar{\Gamma}\bar{M}'$  azimuthal direction.

By using the relationship

$$k_{\parallel} = 0.512E_{\text{kin}}^{1/2} \sin\theta,$$

with  $k_{\parallel}$  and  $E_{\text{kin}}$  in units of  $\text{\AA}^{-1}$  and eV, respectively, one may plot the initial energy as a function of  $k_{\parallel}$ , the wave-vector component parallel to the surface [17]. Figure 3(a) shows such a structure plot for the clean surface, together with the corresponding LAPW bands for the  $\bar{\Gamma}\bar{M}$  (full lines) and  $\bar{A}\bar{L}$  (dashed lines) symmetry lines. These two sets of calculated bands correspond to zero and maximum value, respectively, of the perpendicular wave-vector component  $k_{\perp}$  in the BZ, but as  $k_{\perp}$  is undetermined in the measurements, experimental points appearing in between connected pairs of full and dashed lines are also consistent with the calculations. Considering this, the agreement is generally very good, and most spectral structures are readily identified in terms of the calculated bands.

Figure 3(b) shows the corresponding structure plot for the Cs-intercalated  $\text{VSe}_2$ . The experimental points are compared with LAPW bands calculated for the hypothetical compound  $\text{Cs}_x\text{VSe}_2$ . In the calculations, the Cs atoms were assumed to occupy octahedral sites between the layers, and the in-plane lattice parameter was increased to  $3.58 \text{ \AA}$  (as compared to  $3.35 \text{ \AA}$  for  $\text{VSe}_2$ ), which is the experimentally determined value for  $\text{LiVSe}_2$  (Ref. [3]). It is likely that the in-plane expansion is controlled by the degree of charge transfer to the host layers, and as this should be about the same for both compounds, it appeared reasonable to assume the same value also for the in-plane expansion. Using ionic radii considerations we also could estimate the repeat distance perpendicular to the layers to be  $8.7 \text{ \AA}$  for the  $\text{CsVSe}_2$  ( $6.12 \text{ \AA}$  for  $\text{VSe}_2$ ). The agreement between the experimental data and the calculated  $\text{CsVSe}_2$  bands is exceptional, considering that

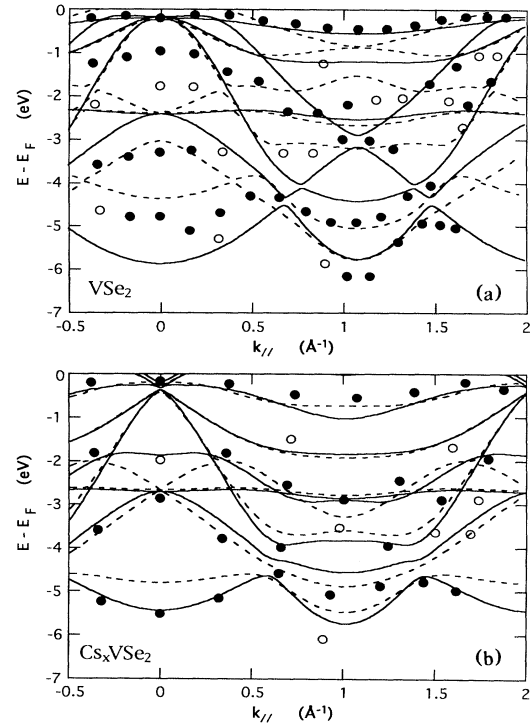


FIG. 3. Structure plots for clean (upper panel) and Cs-intercalated (lower panel)  $\text{VSe}_2$  along the  $\bar{\Gamma}\bar{M}$  symmetry line. Filled circles refer to conspicuous spectral peaks, unfilled to weak structures. Comparison is made with the  $\bar{\Gamma}\bar{M}$  (full lines) and  $\bar{A}\bar{L}$  (dashed lines) bands calculated by the LAPW method for  $\text{VSe}_2$  and  $\text{CsVSe}_2$ , respectively.

both the Cs concentration and the exact lattice parameters of our sample have yet to be determined. The addition of one valence electron per unit cell is reflected in the calculated bands by the increased filling of the lowest V  $3d$  band. Since the perpendicular dispersion of this band simultaneously is greatly reduced (pulling the band entirely below  $E_F$  along  $\bar{A}\bar{L}$ ), the increased band filling does not result in a significant downward shift of the corresponding spectral peak, however. The fact that reasonable agreement was found between experiment and calculation, without having to shift the calculated bands in energy, indicates that the charge transfer was close to the assumption. It should be mentioned that attempts also were made to simulate the effects of Cs intercalation by simply increasing the layer separation in the calculations. As expected, this reduced the band dispersion perpendicular to the layers, but the resulting band dispersions along the layer could not be made to fit the experimental structure plot. Obviously the intercalated Cs atoms have to be included in any realistic calculation.

One interesting question is now to what extent the experimentally found transition to 2D behavior is reflected by the LAPW calculation. As is reflected in Fig. 3 by the reduced difference between  $\bar{\Gamma}\bar{M}$  (full lines) and  $\bar{A}\bar{L}$

(dashed lines) bands, the calculated CsVSe<sub>2</sub> bands have much less perpendicular dispersion than the VSe<sub>2</sub> bands, but it is not zero. In particular, there are two bands, along the  $\Gamma A$  symmetry line ( $\mathbf{k}_{\parallel}=0$ ), that have 0.6 and 0.8 eV dispersion, respectively. This is in conflict with our measurements, as the corresponding peaks seen in Fig. 1(b) definitely do not show any dispersion of this magnitude. We do not have a ready explanation for this at this stage, but one may speculate whether the inter-layer coupling may be further weakened by many-body effects. There is of course also the more trivial possibility that the discrepancy reflects a difference between the real and the hypothetical structure of the intercalate, but the impressive agreement found in Fig. 3(b) for the dispersion parallel to the layers does indeed suggest that the real structure is very close to that used in the calculations. Another possibility, worth further study, is whether the absence of perpendicular dispersion could be due to intercalation-induced stacking disorder.

In conclusion, we have demonstrated, using ARPES, that the valence band structure of VSe<sub>2</sub> is transformed, from initially being of 3D character, to become essentially 2D, as Cs is intercalated. The intercalation was achieved by room temperature deposition of Cs onto the surface, which remained remarkably inert. The observed changes in the electronic structure, which go far beyond the rigid-band model, are to a large extent understandable as caused by intercalation-induced decoupling of the VSe<sub>2</sub> layers, and electronic charge transfer from Cs to the host material. Band structure calculations must include the Cs atoms between the layers, however, in order to qualitatively reproduce the experimental band structure of the intercalate.

To our knowledge, there are no previous reports of any UHV compatible systems where the dimensionality of the electronic structure can be controlled *in situ*. Systems of this kind should be interesting for the investigation of re-

duced dimensionality phenomena.

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