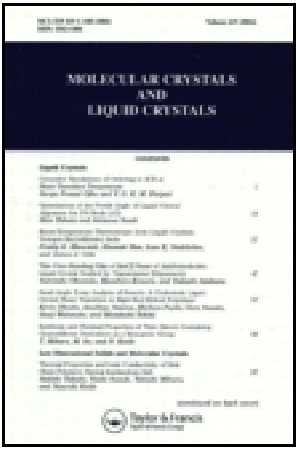

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Valence Band Photoemission Study of Cs Intercalated VSe_2

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VALENCE BAND PHOTOEMISSION STUDY OF Cs INTERCALATED VSe_2

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Abstract We have used photoemission spectroscopy to study the valence band structure of clean and *in situ* Cs intercalated VSe_2. The results show that the valence band structure of VSe_2 is transformed, from initially being of 3D character, to become essential 2D, as Cs is intercalated. The changes in the electronic structure are to a large extent understandable as caused by intercalation-induced de-coupling of the VSe_2 layers, and electronic charge transfer from Cs to the host material. Comparison with band structure calculations supports this picture. Our findings indicate that the Cs/VSe_2 system may be of great value in studies of "reduced dimensionality" phenomena.

INTRODUCTION

The layered transition metal dichalcogenides (TMDC's) exhibit a rich variety of physically interesting phenomena, such as periodic lattice distortions, charge density waves, and phonon anomalies.[1] Many of these phenomena arise as a result of the high degree of anisotropy found in these materials, but referring to them as "two-dimensional" (2D) is not fully appropriate, as e.g. in many cases the electronic energy bands have dispersion perpendicular to the layers comparable to the parallel dispersion.[2,3]

The possibility to modify these materials in a controllable way by intercalation with donor species adds significantly to the usefulness of TMDC's as model systems in the study of various phenomena. Many of the changes occurring upon intercalation can be understood in terms of charge transfer from the introduced species to the host lattice, which alters the band filling of the host material. In this context, the rigid band model is often a useful approximation for reaching a qualitative understanding of the resulting effects. Another important effect of intercalation is the increased spacing between layers necessary to accommodate the intercalated species. This will affect the degree of anisotropy, and may produce changes not compatible with the rigid band model. In addition to these principal effects there may also occur charge-transfer induced structural changes within the layers, or changes in layer stacking because of modified interlayer interactions.

Of the intercalation induced effects, the de-coupling of individual layers by increased interlayer spacing is very interesting as a tool to study the importance of "reduced dimensionality". Intercalation of TMDC's with large organic molecules has been used for this purpose, but intercalation complexes of this kind are not suitable for angle-resolved photoelectron spectroscopy (ARPES) or other techniques requiring ultra-high vacuum (UHV). Of the mono-atomic species that can be intercalated, Cs is an interesting choice, since its large ionic radius (1.69 Å)[4] by necessity must lead to significantly increased interlayer separation. An attractive feature of several alkali metal/TMDC systems, e.g. Cs/$TaSe_2$ (Ref. 5), is the possibility to form intercalates *in situ* by deposition of the metal on the TMDC surface, from where it spontanously 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_2 with Cs. VSe_2 adopts the 1T - CdI_2 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 4p and V 3d 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.[6-10] These measurements have been in fair agreement with band structure calculations, although some significant deviations have been noticed.[7]

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 $CsVSe_2$. The linear augmented plane wave (LAPW) method was used for this, together with the local density approximation of the density functional theory. Our LAPW bands for VSe_2 are in excellent agreement with extensive ARPES measurements using He I radiation.[11]

A more detailed account of the measurements will appear elsewhere.[11]

EXPERIMENTAL DETAILS

The photoemission spectra reported here were measured using synchrotron radiation from the storage ring at MAX-lab, Lund, Sweden. A toroidal grating 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.*

Cs was deposited from carefully outgassed SAES getter sources. The sample was held at room temperature during the deposition. The Cs deposition and intercalation was monitored by recording of Cs 4d and Se 4p core level spectra. Figure 1 shows the Cs 4d spectrum

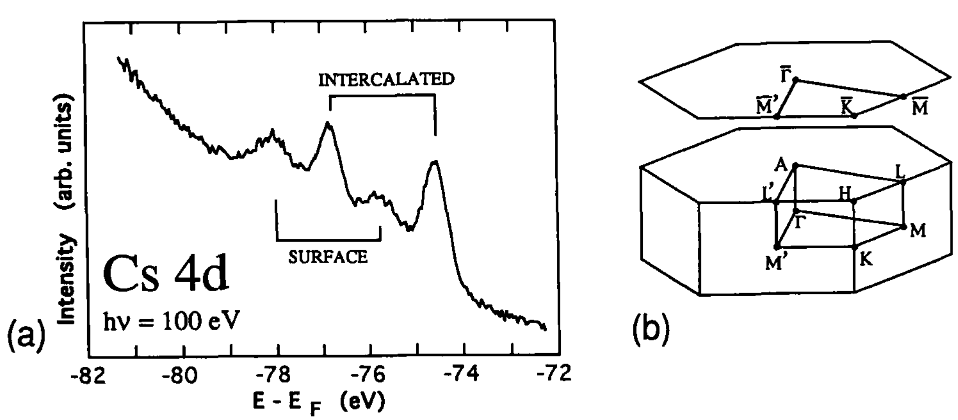

FIGURE 1 (a) Cs 4d core level spectrum recorded with hν = 100 eV, after five minutes of Cs evaporation. Two pairs of peaks, corresponding to different Cs sites, are indicated. (b) The bulk and surface Brillouin zones of VSe_2.

recorded after five minutes of Cs evaporation, with the SAES getter source operating at 5.0 A, and positioned about 20 mm from the sample. The amount of Cs deposited by this should be far more than required to obtain monolayer coverage. The spectrum clearly shows the presence of Cs in two different forms, with a 1.2 eV difference in binding energy. Comparing with the study of the Cs/TaSe$_2$ system by Pettenkofer *et al.*[5], we associate the sharp and more intense pair of peaks at higher energy (lower binding energy) with intercalated Cs, while the weaker and broader pair at lower energy (higher binding energy) are probably due to Cs remaining at the surface, and perhaps trapped by impurities. Repeated Cs depositions induced only minor changes in the spectra. This indicates that deposited Cs atoms are rapidly intercalated into the interior of the substrate, and that once the intercalation has begun, continued Cs deposition mainly increases the intercalation depth, without changing the near-surface composition. The LEED pattern remained sharp after Cs deposition, with no extra spots appearing.

The clean VSe$_2$ surface is known to be very inert due to the absence of dangling bonds, but also the Cs dosed surface turned out to be remarkably inert. Even 14 hours after the initial Cs evaporation, core and valence band spectra indicated only moderate surface contamination, despite a pressure of about 1×10^{-9} Torr in the UHV chamber. This inertness can be understood from the fact that no metallic Cs overlayer is formed at room temperature.

RESULTS

Normal emission energy distribution curves (EDC's) for a range of photon energies provide detailed information about the valence band disperison along the ΓA symmetry direction, which is perpendicular to the layers. Figure 2 shows such data for the VSe$_2$, before and after Cs intercalation, for photon energies in the range 24 - 40 eV. In the EDC's from the clean

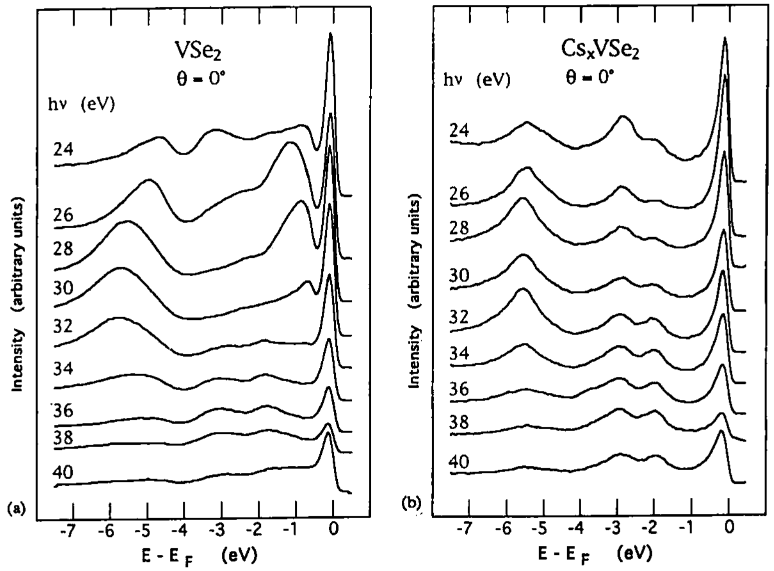

FIGURE 2 Normal emission EDC's, measured from clean (left side), and Cs intercalated (right side) VSe$_2$, with light incident at $\psi = 45°$ in the $\overline{\Gamma M}$ azimuthal direction, and hν ranging from 24 to 40 eV.

VSe_2 surface [Fig. 2(a)] most structures are seen to disperse as the photon energy is changed. The dispersion of the peaks agrees fairly well with that expected from the calculated valence bands along ΓA.[11] 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 3 shows room temperature EDC's for the same two surfaces as in Figure 2, but measured with hν = 24 eV, and polar emission angles θ ranging from -10° to 60° in the $\overline{\Gamma M}$' azimuthal direction. Measurements in this mode probes the band dispersion along the layer planes, and in both cases strong dispersion is observed as θ is varied.

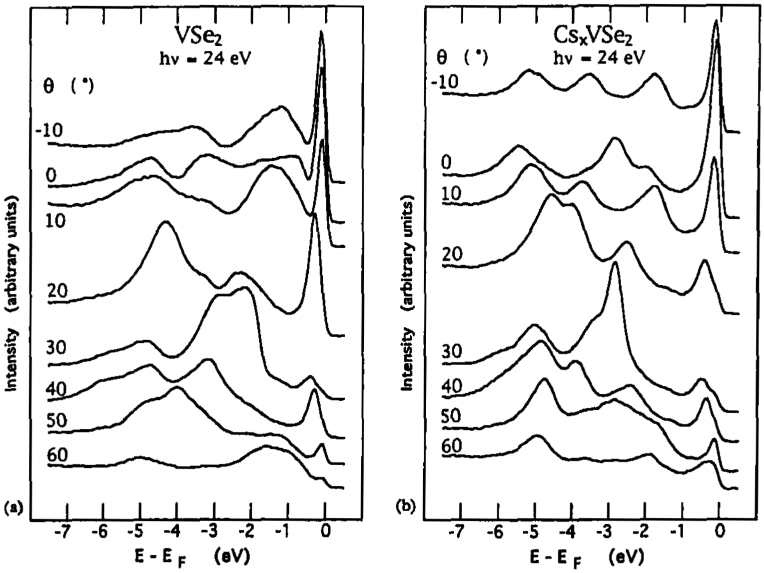

FIGURE 3 EDC's measured from clean (left side), and Cs intercalated (right side) VSe_2, with hν = 24 eV, ψ = 45°, and θ ranging from -10° to 60° in the $\overline{\Gamma M}$' azimuthal direction.

DISCUSSION

The observed energy band dispersion, both perpendicular to, and parallel with the layers, for pure VSe_2, illustrates the 3D character of this compound. The remarkable absence of perpendicular dispersion after Cs intercalation, together with the continued (but different) strong dispersion parallel to the layers, is clear evidence for an intercalation induced transition from 3D to 2D behaviour of the valence electrons.

By using the relationship $k_{//} = 0.512\sqrt{E_{\mathrm{kin}}}\sin\theta$, with $k_{//}$ and E_{kin} in units of Å^{-1} and eV, respectively, one may plot the initial energy as a function of $k_{//}$, the wave-vector component parallel to the surface.[12] Figure 4(a) shows such a structure plot for the clean surface, together with the corresponding LAPW bands for the ΓM (full lines) and AL (dashed lines) symmetry lines. These two sets of calculated bands corresponds 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.

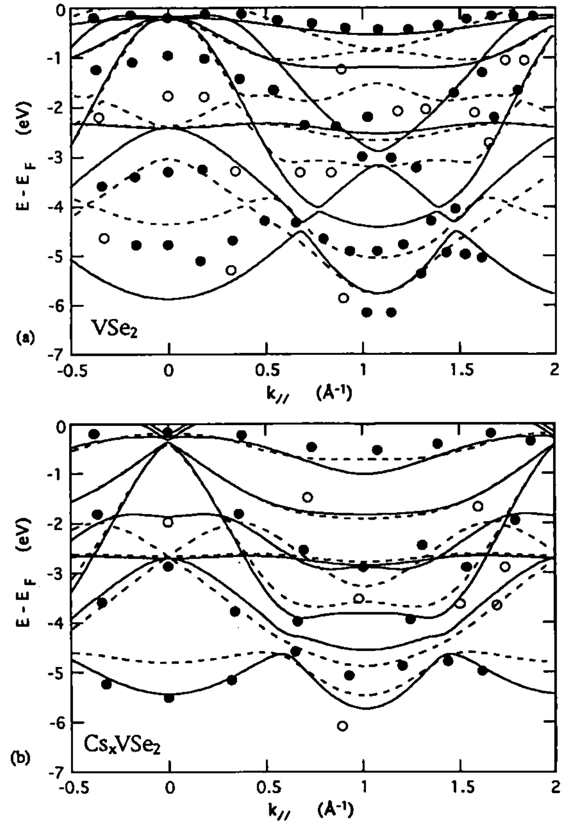

FIGURE 4 Structure plots for clean (upper panel), and Cs intercalated (lower panel) VSe$_2$ along the $\overline{\Gamma M}$' symmetry line. Filled circles refer to conspicuos spectral peaks, unfilled to weak structures. Comparison are made with the ΓM (full lines) and AL (dashed lines) bands, calculated by the LAPW method for VSe$_2$ and CsVSe$_2$.

Figure 4(b) shows the corresponding structure plot for the Cs intercalated VSe$_2$. The experimental points are compared with LAPW bands calculated for the hypothetical compound CsVSe$_2$. In the calculations, the Cs atoms were assumed to occupy octahedral sites between the layers, the in-plane lattice parameter was set to 3.58 Å (as compared to 3.35 Å for VSe$_2$), and the repeat distance perpendicular to the layers was chosen to be 8.7 Å (6.12 Å for VSe$_2$). These estimates for the structural parameters were based on ionic radii considerations and comparison with other alkali-metal intercalates. Bearing in mind the uncertainties regarding Cs concentration and exact lattice parameters, one finds an agreement between the experimental data and the calculated CsVSe$_2$ bands which is truly exceptional. 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 reduced (pulling the band entirely below E$_F$ along AL), the increased band filling does not result in a significant downward shift of the corresponding spectral peak, however. 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 planes could not be made consistent with the experimental structure plot. Obviously the intercalated Cs atoms has to be included in any realistic calculation.

To what extent is the transition to 2D behaviour reflected by the LAPW calculation? As can be seen in Figure 4, the calculated $CsVSe_2$ bands have much less perpendicular dispersion (difference between full and dashed lines) than the VSe_2 bands, but it is not completely zero. This is in conflict with our measurements, as the corresponding peaks seen in Figure 2(b) definitely not show any remaining dispersion of the magnitude seen for some of the calculated bands. We do not have a ready explanation for this at this stage, but one may speculate whether the interlayer coupling may be further weakened by many-body effects. Another possibility, worth further study, is whether the absence of perpendicular dispersion could be due to intercalation induced stacking disorder.

Anyhow, the striking agreement found in Figure 4(b) for the dispersion along the layers strongly indicates that the real structure of the intercalation compound is very close to that used in the LAPW calculations.

CONCLUSIONS

We have demonstrated that the valence band structure of VSe_2 is transformed, from initially being of 3D character, to become essential 2D, as Cs is intercalated. The change of the electronic structure goes far beyond the rigid band model, but may to a large extent be understood in terms of intercalation induced de-coupling of the VSe_2 layers, and electronic charge transfer from Cs to the host material. Band structure calculations must include the Cs atoms between the layers in order to reproduce the experimental result.

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 "reduced dimensionality" phenomena.

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