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Conduction-band effects in the appearance-potential spectra of transition-metal dichalcogenides

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The $L_{3,2}$ appearance potential spectra (APS) of titanium or vanadium in TiS_2, $TiSe_2$, and VSe_2 show a doubly peaked L_3 threshold quite different from the single peak observed for the pure transition metals or for the same levels in the compounds using x-ray photoelectron spectroscopy. We show that this is a consequence of the crystal-field splitting of the d-like conduction band in these materials and that the APS threshold shape may be interpreted in terms of the derivative of the self-convolution of the conduction-band density of states. Determination of the latter by deconvolution of the threshold function gives excellent agreement with data from x-ray and synchrotron absorption studies.

I. INTRODUCTION

In the most usual form of appearance potential spectroscopy (APS),[1] a solid surface is bombarded with electrons, and the total soft-x-ray yield is detected as a function of the incident-electron energy (SXAPS). When this energy is in excess of the binding energy of a core electron, there is the possibility of exciting this electron to an empty state above the Fermi level. It is normally assumed that the deexcitation process leads to a contribution to the observed x-ray intensity which is directly proportional to the rate of production of core holes; since two electrons may be accommodated in states above the Fermi level, the shape of the APS threshold may then be interpreted in terms of a self-convolution of the conduction-band density of states.[2] This process is shown schematically in Fig. 1.

In a previous attempt[3] to demonstrate this relationship, Park and Houston found only a systematic trend in the APS peak widths for the $3d$ transition metals, the spectra implying essentially structureless d bands. We have therefore obtained the appearance potential spectra of titanium and vanadium in the metallic layered dichalcogenides TiS_2, $TiSe_2$, and VSe_2 in which the crystal-field environment of the transition-metal atom is known to be distinctly different from that in the pure metal. Within this environment, the empty d-like conduction-band density of states is modified and the data presented below provide direct evidence to support an interpretation of the APS threshold shape in terms of the self-convolution model. The conduction-band density of states derived by numerical deconvolution of the threshold function is shown to give qualitative agreement with the calculations of Myron and Freeman[4] for the titanium compounds; in addition, excellent quantitative agreement is found with Fischer's x-ray absorption data[5] and the Sonntag-Brown synchrotron absorption data[6] for TiS_2.

II. LAYER TRANSITION-METAL DICHALCOGENIDES

The compounds studied are members of the group of layered transition metal dichalcogenides which have aroused considerable interest during recent years; reviews of their properties have been given by Wilson and Yoffe[7] and more recently by Yoffe.[8] That the crystals are made up of layers is of significance experimentally because of the ease with which they may be cleaved. This makes them particularly amenable to surface studies, since flat, chemically unreactive surfaces may be prepared freshly in vacuum. Each layer comprises hexagonal sheets of metal atoms sandwiched between sheets of chalcogen atoms; in the materials of interest in the present investigation, the metal is octahedrally coordinated by the chalcogen, as shown in Fig. 2. In this crystal-field environment the metal d band is expected to be split into two narrow subbands, where the lower of these is associated with orbitals of d_{z^2}, d_{xy}, and $d_{x^2-y^2}$ symmetry.[9] Band-structure calculations for TiS_2 and[4] $TiSe_2$ predict such a splitting between subbands of about 1.3 eV for each compound, with a further gap between these d and the chalcogen p-like bands. In the stoichiometric titanium compounds, transfer of electrons from the Ti (s^2d^2) to the S (s^2p^4) should lead to both of the d subbands being completely empty and thus to semiconducting behavior. In fact photoemission measurements[10] suggest metallic behavior for the crystals used in this investigation in that both compounds show a finite density of states at the Fermi level—the latter is fixed with reference to the sharp band edge in nickel under similar experimental conditions. A distinct narrow d band (containing 0.05 electrons per titanium atom) is observed in TiS_2. In VSe_2 (group V) the metal is now in a d^1 configuration,

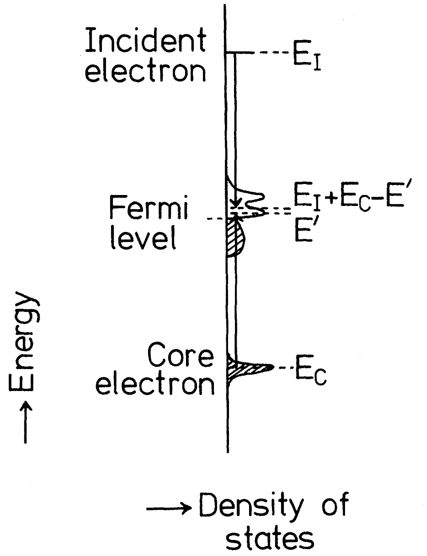

FIG. 1. The excitation process in appearance potential spectroscopy in which both the incident and the excited core electron must be accommodated in states just above the Fermi level. This leads to the model for the threshold shape in terms of the self-convolution of the conduction-band density of states.

but as there is still only one electron in the lower d band, the empty conduction-band density of states should closely resemble that in the titanium compounds.

On the basis of the APS model outlined in the Introduction and shown in Fig. 1, if we assume constant matrix elements for the transitions and sharp core levels, the measured threshold is given by the derivative of the self-convolution of the conduction-band density of states, i.e.,

$$\frac{d}{dE}\int_0^E N(E')N(E-E')dE' , \qquad (1)$$

where $N(E')$ is the density of states at E' ($E' > E_F$), E is the energy of the incident electron less the binding energy of the core electron (i.e., $E=E_I+E_c$, Fig. 1); the zero of energy is taken to be at the Fermi level E_F. The implication for a material with a doubly peaked conduction-band density of states, as outlined above, is that each core level is expected to give rise to a triply peaked APS threshold. The three peaks correspond to the possibilities: (i) both electrons being scattered to the lower subband, (ii) one electron to each subband, or (iii) both electrons being scattered to the upper subband.

III. RESULTS AND EXPERIMENTAL

APS spectra were recorded digitally for single crystals (grown by vapor-phase transport) cleaved at 10^{-8} Torr; x-ray photoemission spectra (XPS) were recorded at 10^{-9} Torr using Mg $K\alpha$ radiation from similar crystals following cleaving in an ancillary chamber of the electron spectrometer (Messrs. Vacuum Generators Ltd., Model ESCA 3) at 10^{-7} Torr. APS spectra were recorded within ten minutes of cleaving, XPS over a similar period. No deterioration in the spectra could be observed during this time but prolonged observation in APS (approximately one hour) resulted in a deterioration in the resolution of sharp structure in the spectra.

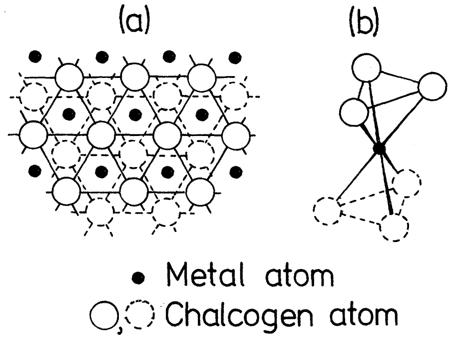

FIG. 2. (a) The projection of a single layer of the CdI_2 structure ($P\overline{3}m$) adopted by the Ti and V chalcogenides. (b) Each metal atom in the structure is octahedrally coordinated by six chalcogens, leading to a pronounced crystal-field splitting in the transition metal d states.

The APS spectra so obtained of the Ti (or V) $L_{3,2}$ levels in VSe_2, $TiSe_2$, and TiS_2 are shown in Fig. 3. In none of the cases could sulphur or selenium thresholds be positively identified, but this is in accord with a previously noted insensitivity of APS to sulphur.[11] The L_3 peaks all show a prominent splitting which is not found in the APS spectra of metallic titanium or vanadium.[3] Derivative XPS spectra for both the titanium compounds are superimposed on the APS thresholds in Fig. 3. The binding-energy scale for the XPS spectra is fixed with reference to nickel as outlined in the previous section and that for APS includes the usual correction (4.5 eV) for the work function of the tungsten emitter. The L_3 and L_2 levels in XPS are both seen to give rise to sharp single peaks, in contrast to the APS observation, but as we showed to be the case for Fe and Ni in a recent investigation,[12] there is very close agreement over the low energy rise at the L_3 threshold between XPS and APS. This strongly reinforces our earlier argument that identical *initial* states are involved in both XPS and APS when soft x-ray (Mg or Al $K\alpha$) excitation is used in the former. Comparison of the sulphide with the selenide reveals a shift in the initial state of 0.4 eV to higher binding energy in the sulphide; this may reflect a greater degree of ionicity in the bonding in the latter relative to the selenide, as might be antici-

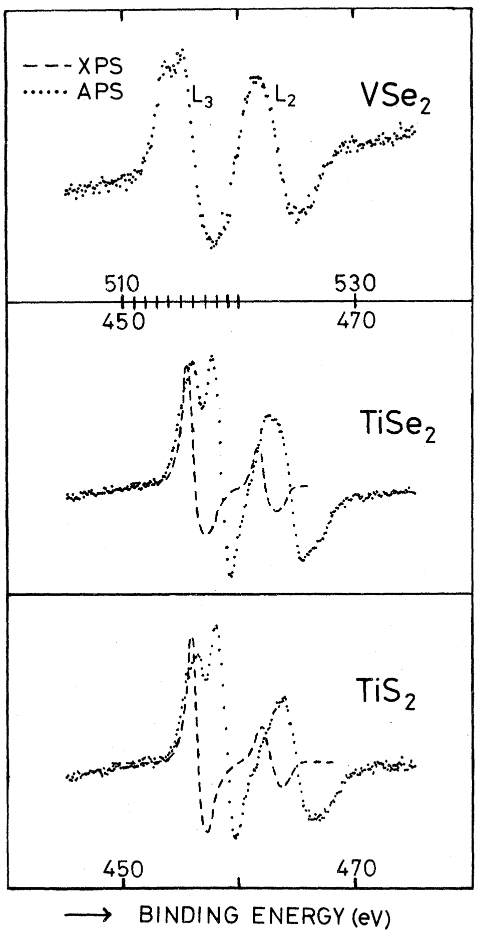

FIG. 3. APS spectra of the Ti $L_{3,2}$ core levels in TiS_2 and $TiSe_2$, and of the V $L_{3,2}$ levels in VSe_2. The derivatives of the XPS spectra of both TiS_2 and $TiSe_2$ are superimposed after correction for the work function of the W emitter in APS.

pated.

The pronounced difference between APS and XPS spectra at the high binding energy side of the threshold suggests that it is final-state effects which are responsible for the splitting seen in APS, and this proposal is examined in detail below. The alternative interpretations in terms of either nonstoichiometry or oxidation of the samples can be discounted on the basis of the XPS data recorded under similar vacuum conditions. Either effect, if present to any significant degree, should result in a splitting in the XPS as well as the APS spectra, contrary to observation.

IV. DISCUSSION

We conclude, therefore, that the doublet structure of the L_3 peak in APS is a consequence of scattering into a crystal-field-split d-like conduction band as described earlier. An iterative deconvolution routine was accordingly arranged to fit the conduction-band density of states, $N(E')$ assuming Eq. (1) to apply strictly. Because of the overlap between the L_3 and L_2 thresholds, only the positive part (the region between the arrows in Fig. 4) of the L_3 threshold can be regarded as known unambiguously. Hence the routine did not match beyond this region, thereby only allowing $N(E')$ to be determined for a similar energy range above the Fermi level. The accuracy of the final matching can be seen in Fig. 4 where the original spectrum is compared with the numerical fit on the basis of the density of states $N(E')$ for $TiSe_2$ shown in Fig. 5. That part of the computed threshold at energies higher than the arrowed region, where overlap with the L_2 occurs, is, of course not significant since no allowance has been made for the possibility that electrons may be scattered to states higher in energy than the upper d subband. Such a consideration would lead to a closer fit in the region above $\mathcal{E}$, including the third peak, but would have no effect on the closeness of the fit below $\mathcal{E}$.

The conduction-band densities of states so derived for TiS_2 and $TiSe_2$ shown in Fig. 5, together with the calculated histograms of Myron and Freeman,[4] and Fischer's x-ray absorption band (Fig. 2, Ref. 5) for TiS_2. Since no account has been taken of core level and instrumental broadening effects (probably of the order of 1 eV) in the APS results,

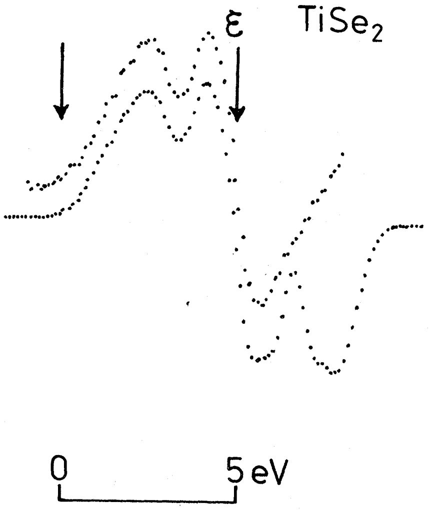

FIG. 4. The lower trace shows the calculated derivative of the self-convolution of the conduction-band density of states shown in Fig. 5 for $TiSe_2$. This is compared with an expanded portion of the L_3 threshold in the upper trace. Fitting was only carried out for the region between the arrows, so that deviations between experimental and fitted data above $\mathcal{E}$ have no significance.

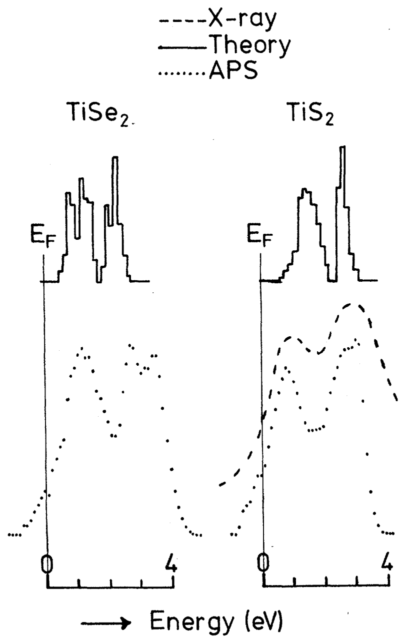

FIG. 5. The conduction-band densities of states TiS_2 and $TiSe_2$ deconvoluted from the thresholds in Fig. 3; these are compared with the calculated histograms of Myron and Freeman (Ref. 4), and with the x-ray absorption band (Ti L_{III}) for TiS_2 obtained by Fischer (Ref. 5). The Fermi level has been approximately located for the purposes of comparison by assuming a broadening of 1 eV (due to instrumental and core-level contributions) in APS.

detailed agreement with theory cannot be expected; furthermore, broadening processes inherent in the excitation mechanism in both APS and XPS due to coupling of the excited core-hole with the conduction electrons[13,14] may invalidate any purely empirical adjustment for linewidth effects. Nevertheless, the qualitative agreement between the deconvolved and the theoretical $N(E')$ is fair and is in agreement with the simple predictions of the crystal-field model. However, the actual magnitude of the splitting, for which reasonable agreement might be expected, is different. For both the sulphide and the selenide, the Myron-Freeman results suggest a separation of about 1.3 eV between the centers of gravity of the two subbands compared with the 2.1 eV implied by the APS measurements. But there is excellent agreement between the APS value and the 2.2 eV obtained from x-ray absorption in TiS_2 by Fischer[5] and a similar value obtained by synchrotron absorption.[6] A value of 2.1–2.2 eV for the crystal-field splitting in TiS_2 would therefore seem to be well established experimentally, with the APS measurements suggesting a similar value for $TiSe_2$.

No deconvolution attempt was made for the VSe_2 spectrum because of the poorer signal to noise ratio and less marked splitting. The latter indicates a narrower energy separation between the subbands in VSe_2 than in the titanium compounds, and the threshold as a whole is narrower as is expected on a rigid band approach when there is one electron per atom in the lower subband. Comparison of the splitting of about 1.3 eV for the VSe_2 APS spectrum with the results for TiS_2 and $TiSe_2$, where the experimental spectra show a splitting of 1.7 eV suggests a value of about 1.6 eV for the separation of the subbands in the vanadium compound. In this case, core-level and instrumental broadening effects would be expected to degrade the resolution in the APS spectrum as compared with the titanium materials.

Similarly, the absence of any appreciable structure in the L_2 peak in the TiS_2 and $TiSe_2$ APS spectra may imply a broadening in the L_2 core level relative to the L_3. The XPS spectra do show the Ti L_2 level to be some 10% broader than the L_3, possibly as a result of a decreased core-hole lifetime due to Coster-Kronig transitions,[15] which is consistent with this assertion. In addition, the overlap between the high-energy side of the L_3 and the low-energy side of the L_2 threshold distorts the latter so that useful information regarding the conduction-band density of states may only be deduced from the positive part of the L_3, as discussed previously.

Finally, we note that the above self-convolution approach to an interpretation of the APS threshold has been questioned recently following measurements on rare-earth elements by Harte, Szczepanek, and Leyendecker.[16] These elements give particularly intense APS thresholds which are associated with a subthreshold resonance in the bremsstrahlung background, such as has been observed by Liefeld, Burr, and Chamberlain[17] in the M-series x-ray spectra of La. Harte *et al.* suggest that a similar phenomenon may occur in the $3d$ transition elements on the basis of similar trends for both the $4f$ and $3d$ elements in the difference between tabulated binding energies[18] and those determined by APS. However, this would seem to be a dangerous extrapolation in view of our earlier observation of identical initial-state binding energies in APS and XPS for Fe and Ni,[12] and the present close correlations for TiS_2 and $TiSe_2$. Furthermore, we observe no subthreshold effects in any of these materials and discount a resonance interpretation of the splitting in the present data.

V. CONCLUSIONS

We have shown for the layer transition-metal dichalcogenides studied here that appearance potential spectroscopy can be employed as an effective probe of the conduction-band densities of states. Values for the octahedral crystal-field splitting of the empty *d* states in TiS_2 and $TiSe_2$ (2.1 eV) have been obtained by deconvolution of the APS threshold function, and the splitting in TiS_2 has been shown to be in good agreement with that determined by x-ray and synchrotron absorption.

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