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ANGULAR RESOLVED PHOTOEMISSION AND BAND STRUCTURE OF LAYERED TRANSITION METAL DICHALCOGENIDES

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The polar and azimuthal dependence of the energy distribution of photoelectrons has been studied for $TiSe_2$- and VSe_2-single crystals using various rare gas resonance lines for excitation. The results are compared with recent valence band structure calculations. Structure close to the Fermi level is particularly sensitive to the preparation of the surface.

I. Introduction

$TiSe_2$,VSe_2, and their mixed crystals, layered compounds crystallizing in the 1T-structure (space group D_{3d}^3), show interesting transport and optical properties associated with phase transitions at about 200 K and 100 K respectively where superlattices appear in diffraction experiments [1,2]. These properties are related to the detailed band structure of the materials, especially to its behavior close to the Fermi energy, for example the critical overlap of p and d bands at the Γ and L points in the Brillouin zone in $TiSe_2$. In order to understand the observed properties a number of band structure calculations appeared recently for these materials differing by methods and results [3-5]. We have performed new angle resolved photoemission experiments on various 1T-$TiSe_2$ and VSe_2 crystals with the aim to test the new proposed band structures in detail and to compare our results with previous photoemission measurements [6-9] which differed in several respects.

II. Experimental

We have studied the polar and azimuthal dependence of the energy distribution of photoelectrons originating from ultrahigh vacuum cleaved single crystals excited by He I (21.2 eV), Ne I (16.8 eV), Ar I (11.8 eV) and Kr I (10.0 eV) resonance lines using a cylindrical mirror analyser with apertures. The energy resolution was between 0.1 and 0.3 eV, the angular resolution $\pm$ 3°. Several photon energies were useful to test the influence of final states and three dimensional effects. A photon energy as low as 10.0 eV provided improved $K_{\parallel}$-resolution in deriving the experimental bands. A number of different crystals of various origins was investigated. Orientation and cleanness of the crystal surfaces were checked by Laue-, LEED- and Auger method, the latter two in situ.

III. Results and Discussion

As a typical experimental result for $TiSe_2$ the He I energy distribution curves for the ΓM direction in the hexagonal Brillouin zone are presented in Fig.(1). Parameter is the polar angle ϑ with

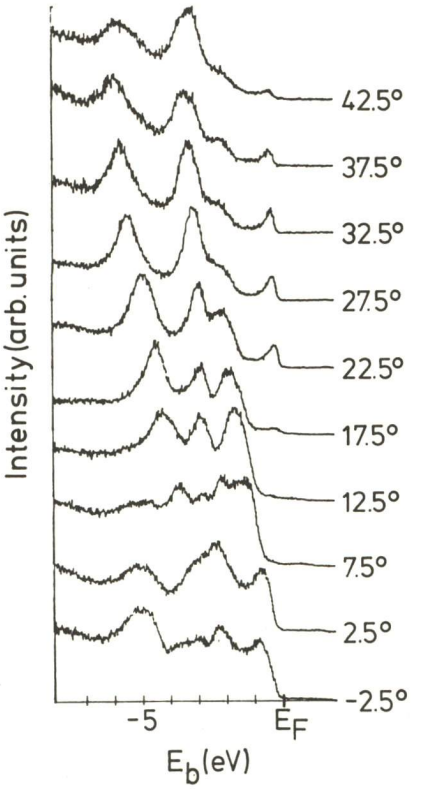

Fig.1 Polar angle dependence of HeI-excited EDCs from $TiSe_2$ in ΓM-direction

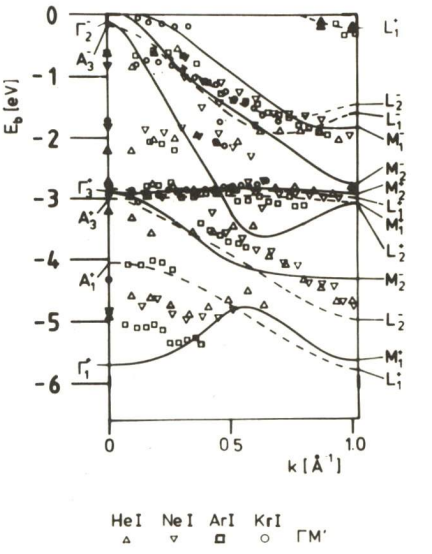

Fig.2 Comparison between measured and calculated band structure [3] of $TiSe_2$

respect to the surface normal. The binding energy referring to the Fermi level is plotted on the x-axis. The main maxima can be attributed to Se 4p-derived bonding states while the maximum appearing at the Fermi energy only at higher angles, i.e. around the zone boundary, is associated with Ti 3d electron pockets predicted at the L point by band structure calculations [3]. From the observed peaks we can derive an experimental band structure referred to the wavevector component parallel to the surface ($k_{\parallel} = \sqrt{2m}/\hbar\sqrt{E}\sin\vartheta$). The results for the ΓM'-direction are compiled in Fig.(2) for different photon energies together with self consistent local density band structure calculations [3] (solid line: Γ-M line from the center of the Brillouin zone to the zone boundary in the middle plane; dashed line: A-L line parallel to ΓM at the top of the Brillouin zone).

The experimental bands confirm several aspects of the calculated bands. At the Fermi level the typical overlap between p and d bands (-0.2 eV) is observed around the center of the Brillouin zone Γ and L at the zone boundary ($K \approx 1 Å^{-1}$) which is responsible for the semimetallic behavior of $TiSe_2$. The visibility of the overlap depends critically on the photon energy used. The upper parts of the Se p-bands can be best seen using the 10.0 eV Kr line while d-like electron pockets at the zone boundary show up best for the Ar and He lines. This is believed to be due to final state effects and transition matrix elements. The general trend of the lower lying calculated bands is also reproduced experimentally. We see the major part of the dispersive band originating from the top of the valence band at Γ dropping to about 2 eV at L(M). There is also a flat band at 3 eV and another dispersive band underneath between 3 and 4 eV. In the 4-6 eV range

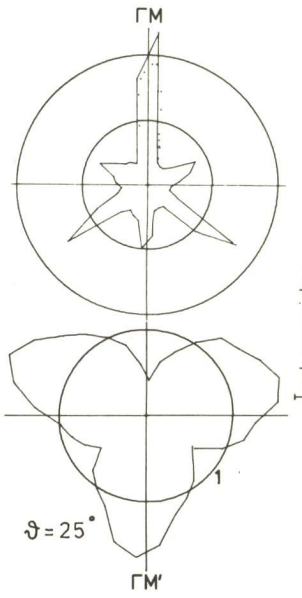

Fig.3 Azimuthal dependence of d-peak intensity and p-peaks intensity-ratio

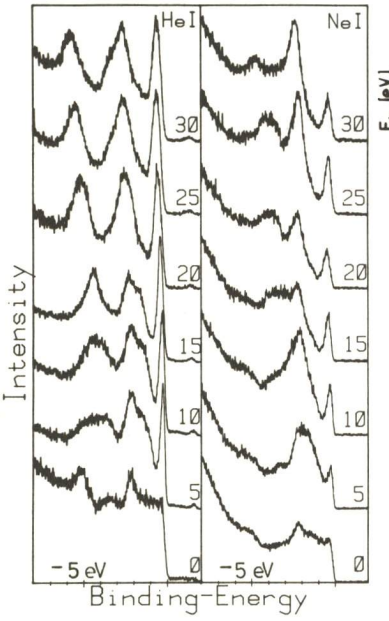

Fig.4 Polar angle dependence of VSe_2 EDCs (ΓM)

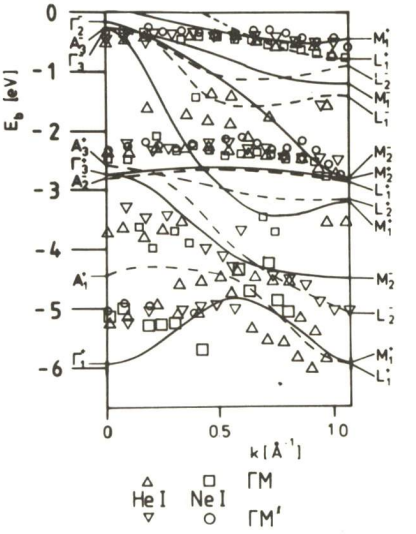

Fig.5 Comparison between measured and calculated band structure [3] of VSe_2

the experimental points lie between the calculated extrema. The only feature which is hard to correlate to any calculated band is a number of points without much dispersion around 2 eV.

A closer inspection of Fig.(2) shows that in certain regions the experimental points vary more or less with photon energy. This indicates that it seems to be necessary to include three dimensional and final state effects to further improve our simple two-dimensional analysis in which the component of the wavevector perpendicular to the surface $K_\perp$ has been completely neglected. For direct transitions and under the crude assumption of parabolic final state bands we can understand for example the photon energy sequence of the two dimensional experimental bands between 4 and 6 eV in the first half of the Brillouin zone by calculating $K_\perp$ using an inner potential of 14eV. The latter value was derived from the peaks in the I(U)-curves of the LEED (0,0) beam. Obvious changes in the visibility of the peaks can be related to changes of the unknown transition matrix elements.- Our experimental bands agree to some extent with previous work in this field [6-8]. However, our results are obtained with more low lying excitation lines on a number of samples of different growth origin. They also appear to be taken with higher resolution which is particularly demonstrated in the near normal emission spectra where we observe a much steeper threshold at the Fermi level and also additional well resolved structure.

The strong variation of the spectra with azimuth gives information on the electron distribution when final states are properly taken into account. Figure (3) shows a radial plot for the intensity as a function of azimuth at a polar emission angle of 25° close to the zone boundary taken with He I for the d-emission peak (upper half) and the intensity ratio of the p-emission peaks at 2 and 3 eV (lower half). Both plots show a characteristic threefold-symmetry related

to the space group symmetry (D_{3d}^3).- Slight shifts of the positions of a few peaks have been observed between measurements in the high symmetry direction ΓM and those taken at an azimuth differing by 60°. This may be also attributable to a three dimensional $K_\perp$ effect since in two dimensions both directions should be strictly equivalent by symmetry.

Figure (4) presents the energy distribution of VSe_2 for two photon energies in ΓM direction with polar angle ϑ as parameter. As compared to $TiSe_2$ there is a very strong emission close to the Fermi energy at all polar angles except at $\vartheta = 0$. This peak is due to V 3d electrons as can be inferred from a comparison with the $TiSe_2$ results and the calculated band structures [3-5]. It has also been identified recently for HeI excitation [9]. The two dimensional experimental bands are shown together with calculated bands [3] in Fig.(5). The behavior of the bands well below the Fermi energy and the agreement between experiment and theory is similar to the case of $TiSe_2$. But the strong d-emission covers almost the entire Brillouin zone as predicted theoretically. A crossing of the Fermi level close to $\vartheta = 0$ does not seem totally excludable, but this would need a more sophisticated analysis of the experimental data around $\vartheta = 0$. As compared to other band structures [4,5] that used for comparison with the experiment seems to yield the best overall agreement in particular concerning absolute energy values. The radial azimuthal plot of the d-emission near the zone boundary shows a threefold symmetry with maxima in the ΓM direction like that of $TiSe_2$ (Fig.3), but the intensity variations are not as prominent.

In the course of our experiments we have investigated the spectra of many samples differing in origin, growth temperature and transport properties down to liquid N_2 temperature, especially in the case of $TiSe_2$. Changes in the spectra, sometimes significant, have been observed predominantly close to the Fermi energy. A prominent peak even larger than the d-emission of VSe_2 has been observed in $TiSe_2$, but was not yet intentionally reproducible. Comparing all the data we feel that the quality of the surface after cleaving and exposure to residual gases should not be neglected as compared to effects due to doping and possible phase transitions in explaining the action at the Fermi level, even though the v.d.Waals surfaces of layered materials are considered as relatively inactive.

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