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Polarized XANES spectra of titanium dichalcogenides – experiment and theory

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We studied unoccupied electron states of titanium dichalcogenides by means of polarized x-ray absorption spectroscopy. Experimental spectra of TiS₂, TiSe₂, and TiTe₂ at the Ti *K* edge and of TiTe₂ at the Te *L*₁ edge were compared with results of real-space multiple-scattering calculations and, in the case of TiS₂, also with results of selfconsistent band-structure calculations. The Ti *K* edge spectra of all three dichalcogenides are quite similar to each other provided that differences in their lattice constants are suppressed by comparing the spectra in equivalent energy scales. The correspondence between Te *L*₁ edge of TiTe₂ and S *K* edge of TiS₂ is not so unambiguous. The effect of varying cluster sizes on particular spectral features is investigated.

Keywords: titanium dichalcogenides; polarized XANES spectroscopy.

1. Introduction

The crystal structure of titanium dichalcogenides TiS₂, TiSe₂, and TiTe₂ can be regarded as a sandwich consisting of chalcogen-Ti-chalcogen slabs, which are strongly bonded internally but only weakly coupled to each other. This feature allows to create intercalated sub-layers. For this reason, the electronic structure of titanium dichalcogenides has been subject of intensive study lately (Fang *et al* 1997, Bödicker & Schattke 1997, Claessen *et al* 1996). In our study, we concentrate on comparing results for different titanium dichalcogenides which definitely must correlate with each other and thus prove or negate the adopted conclusions.

2. Methods

The experiments were carried out at the beam line E4 (HASYLAB, Hamburg) equipped with an x-ray focusing mirror and a Si (111) double crystal monochromator. For each compound, four to five measurements with different sample-to-radiation orientations were made. That made it possible to separate partial spectral components arising from different symmetry resolved groups (parallel to the titanium layers $p_{x,y}$ and perpendicular to those layers p_z) by solving appropriate systems of linear equations (Dräger *et al* 1988, Heumann *et al* 1995, Bocharov *et al* 1998).

The XANES spectra were calculated within the real-space multiple-scattering (RS-MS) formalism, using a modified ICXANES computer code of Vvedensky *et al* (1986). Non-selfconsistent muffin-tin potentials were generated via the so-called Mattheiss prescription. A relaxed and screened model was used for the core hole potential.

For TiS₂, a selfconsistent pseudopotential band structure calculation (free from muffin-tin constraints) was performed as well. In order to describe *unoccupied* states correctly, an iterative pseudopotential generating technique had to be applied (Šimůnek *et al* 1997, Vackář *et al* 1998).

Theoretical results presented in this paper include broadening by an energy-dependent Lorentzian of full width at half maximum $w + 0.1(E - E_F)$. The constant part w accounts for the core hole lifetime, the energy-dependent term represents inelastic energy losses of the photoelectron of energy E .

All the investigated compounds have identical geometrical structures, apart from a uniform bond-length scaling. Differences in their XANES spectra caused by different lattice constants can be compensated by displaying them in “equivalent energy scales” conforming the relation $(E_{\max} - E_{\min})R^2 = \text{const}$, where R is the characteristic interatomic distance and E_{\min} and E_{\max} define the appropriate energy interval (Bocharov *et al* 1998).

In all the drawings in the next section, the theoretical spectra were horizontally aligned so that the best visual agreement with experiment is reached. The separation between Te *L*₁ and Ti *K* edges in TiTe₂ was fitted so that it would comply with experiment (their relative intensity, however, was correctly provided by the theory itself).

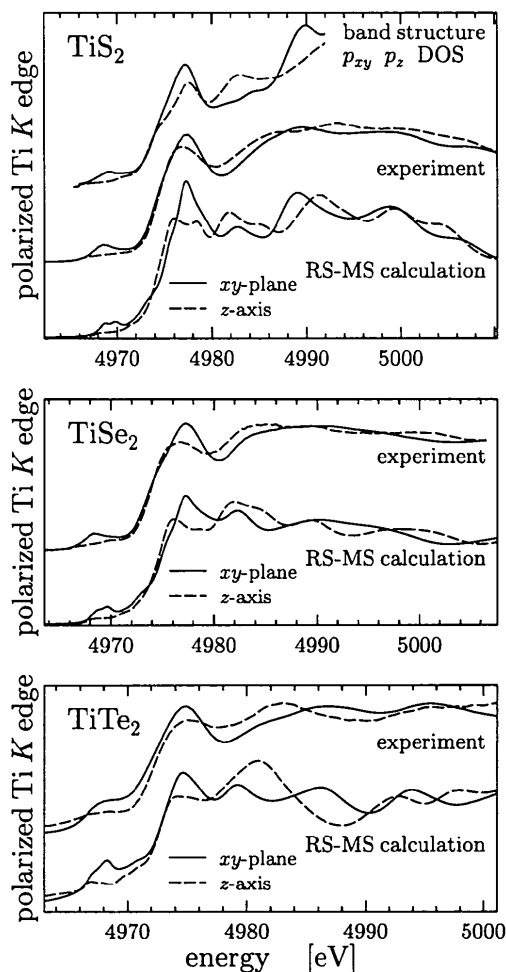
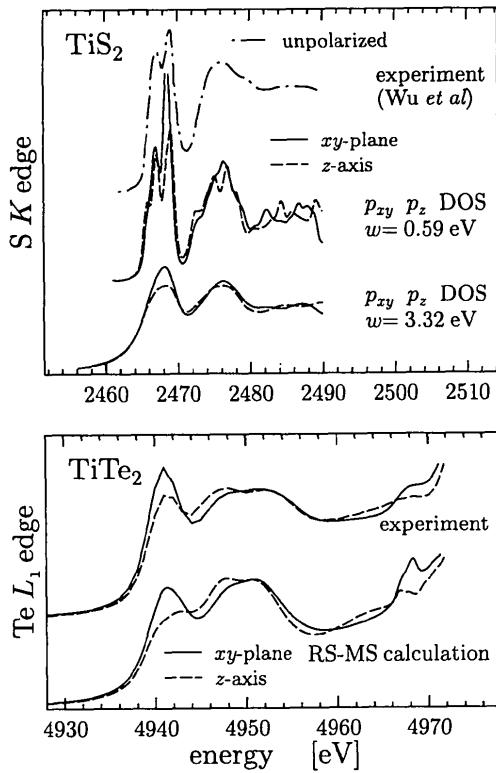


Figure 1
Theoretical and experimental polarized Ti *K* edge spectra of TiS₂, TiSe₂, and TiTe₂. Solid lines represent components parallel to Ti layers, dashed lines stand for components perpendicular to Ti layers.

**Figure 2**

Upper panel displays unpolarized experimental S K edge spectrum of TiS_2 (chain line) as taken from Wu *et al* (1996) together with polarized projected DOS calculated by pseudopotential method and broadened by two different Lorentzians. Lower panel shows polarized Te L_1 edge spectrum of TiTe_2 , both experimental and calculated using the RS-MS method. As in Fig. 1, solid lines represent polarized components parallel to Ti layers, dashed lines stand for components perpendicular to Ti layers.

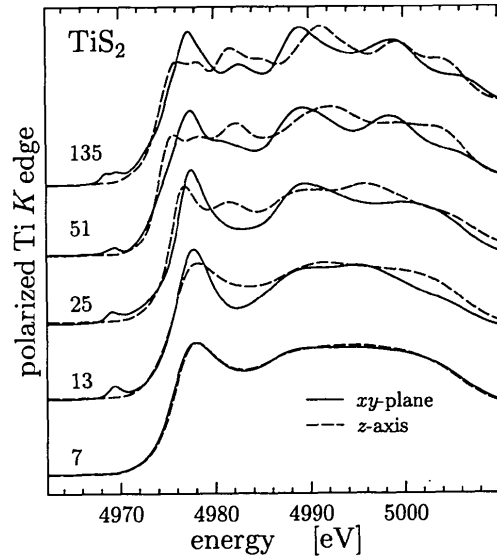
3. Results and discussion

In Fig. 1, theoretical and experimental Ti K edge polarized spectra of TiS_2 , TiSe_2 , and TiTe_2 in equivalent energy scales are presented. There is an apparent correlation between spectral features of the three compounds. The selfconsistent pseudopotential calculation confirms the suitability of non selfconsistent Mattheiss potential for this study. The largest discrepancy between the theoretical and experimental curves occurs in the region above the main peak for all three compounds (4980-4985 eV). The disagreement is most prominent in TiS_2 (see also unpolarized study of Wu *et al* 1997), while the TiSe_2 experimental spectrum is described remarkably better in this region by the theory. Hence we tentatively ascribe this disagreement to multielectron effects — the simple phenomenological linearly energy-dependent Lorentzian broadening probably is not good enough to describe inelastic losses in TiS_2 properly.

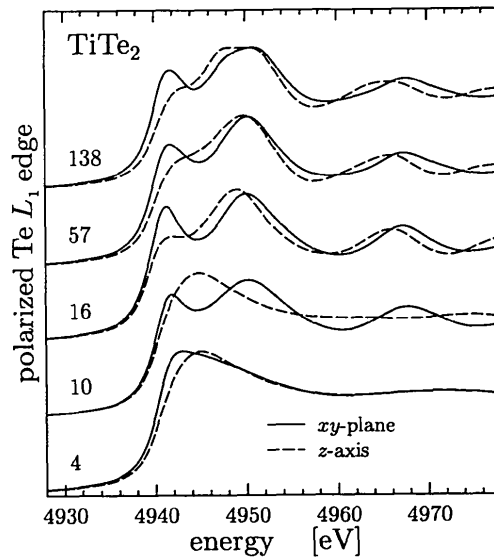
A complementary study of Te L_1 spectrum of TiTe_2 and S K spectrum of TiS_2 is shown in Fig. 2 (again in equivalent energy scales). The TiTe_2 spectrum contains the low-energy tail (pre-peak) of the Ti K edge, too. For TiS_2 , unpolarized experiment of Wu *et al* (1996) is displayed together with polarized density of states (DOS) broadened to account both for the $1s$ core hole lifetime in S (0.59 eV) and for the $2s$ core hole lifetime in Te (3.32 eV). The correspondence between features of TiTe_2 and TiS_2 spectra is a bit

ambiguous: While the polarization dependence of the peaks seems to be similar in both compounds, there is a clear difference between the broad double peak around 4950 eV in TiTe_2 and the unique peak at 2476 eV in TiS_2 .

The influence of the size of the cluster on Ti spectrum of TiS_2 is investigated in Fig. 3. Our results support the conclusion of Wu *et al* (1997) that the anisotropic pre-peak is generated by Ti atoms in the second coordination shell. Most significant features of the spectrum are converged if 51 atoms (eight coordination spheres) are included.

**Figure 3**

Polarized Ti K edge spectra of TiS_2 calculated for varying cluster sizes. The number at each curve indicates number of atoms contained in the corresponding cluster.

**Figure 4**

Polarized Te L_1 edge spectra of TiTe_2 calculated for varying cluster sizes. The number at each curve indicates number of atoms contained in the corresponding cluster.

The cluster size convergence of Ti spectra of TiSe₂ and TiTe₂ exhibits the same pattern as in the case of TiS₂, so we do not display corresponding sets of curves here for brevity.

In Fig. 4, cluster size effect for the Te spectrum of TiTe₂ is examined. The convergence with cluster size is slower than in the case of Ti edge in TiS₂ (or, equivalently, in TiTe₂): Three coordination spheres are needed to reproduce the first peak correctly (at 4941 eV) and even as much as 57 atoms are not enough to describe the double structure of the second peak around 4950 eV (well-resolved in experiment — cf. Fig. 2).

This is similar to the cluster size convergence of *K* spectra of ZnS, which is essentially quicker for the Zn edge than for the S edge (Saintavit *et al* 1987). The explanation proposed by Saintavit *et al* utilizes the fact that the scattering cross section of Zn (as well as Ti) atoms is roughly smaller by half than the cross section of chalcogen atoms in the relevant energy region. Hence it was suggested that the key factor influencing the cluster size convergence is the number of *chalcogen atoms* contained in the cluster rather than the total number of atoms. A more detailed study would be needed to elaborate this conjecture for transition metal dichalcogenides.

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