AN X-RAY SPECTRSCOPY STUDY OF THE

ELECTRONIC STRUCTURE OF TiS₃

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X-ray photoemission and absorption spectra of TiS_3 are studied. The temperature dependence of the magnetic susceptibility is measured and the electron density of states is calculated. Titanium ions in different oxidation states are found to coexist.

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INTRODUCTION

Interest in the investigation of the electronic structure and the features of the chemical bond in TiS_3 is due to the anomalous temperature dependence of the conductivity found in this compound, which suggests the occurrence of the collective electronic state [1]. It turned out that the properties of TiS_3 in this state were similar to the properties of quasi-1D conductors with the moving charge density wave (CDW) [2-4]. Nonlinear conductivity was detected to occur along and across metal chains [2, 5], which has not so far been observed in conductors with CDW. Up to this point, materials with moving CDW have not been found among chalcogenides of group IV transition metals. In [1, 6] the photoelectron spectra of TiS_3 were measured. Data on the studies of the electronic structure of this compound by other methods are unknown.

EXPERIMENT AND CALCULATIONS

Single crystal samples of TiS₃ were grown in quartz ampoules by gas transport reactions using TiS₂ as the initial batch and sulfur excess. Transfer was performed to the cold end on which a temperature of 500 °C was maintained whereas the TiS₂ weighed portion was kept at a temperature of 700 °C. The crystal growth process took from a few days to a week. The samples were faceted wiskers with the dimensions $b \times a \times c$ (500-3000)×(10-200)×(1-20) µm.

Studies with the use of synchrotron radiation were carried out on an Elettra synchrotron, CIPO line[7]. Spectra of the core levels and the valence band spectra were calibrated with respect to the Au4*f* line. The Ti $L_{2,3}$ absorption spectrum was calibrated using the spectrum of pure titanium. All spectra were obtained under the conditions of high vacuum at room temperature. Carbon and oxygen lines are absent in the survey spectra.

For the theoretical description of the density of states of the materials under study the ab initio calculations were

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Fig. 1. Fragment of the crystal structure of TiS₃, ZrSe₃ structure type.

performed. The calculations were carried out within the full-potential linearised augmented-plane wave (FP-LAPW) method implemented in the ELK program package [8]. In the calculations the experimentally found crystal structure parameters were applied (structure type $P2_1/m$:b [9], lattice parameters a = 4.9664 Å, b = 3.4048 Å, c = 8.801 Å, $\beta = 97.38^{\circ}$). A fragment of the crystal structure is shown in Fig. 1.

The multiplet calculation of the absorption spectrum of titanium was performed using the program [10]. The calculation parameters are listed in Table 1.

RESULTS AND DISCUSSION

Fig. 2 depicts the temperature dependence of the magnetic susceptibility of the ceramic sample of TiS_3 , which was obtained from the field dependences of the magnetization of the ceramic TiS_3 sample by linear approximation.

As seen from Fig. 2 the susceptibility reaches almost 9 emu/(mol·Oe), which is close to the value of the diamagnetic susceptibility of the ideal superconductor of $4\pi \approx 12.56$ emu/(mol·Oe). For TiS₃ whose conductivity has a semiconductor type, such a high value of the magnetic susceptibility is anomalous.

The photoelectron spectrum of the S2*p* level of TiS₃ shown in Fig. 3 has an additive character. As a result of its decomposition with regard to the experimental resolution and the width of the respective core levels it is found that this spectrum is a sum of contributions from sulfur atoms in two crystallographically non-equivalent positions. The corresponding spectra are shifted relative to each other by 1.2 eV with the binding energy of 162 eV for S(1)2*p*_{3/2} and 160.8 eV for S(2)2*p*_{3/2}. The ratio of contributions S(1)/S(2) = 2. This is consistent with the structural data. The distances $d_{S(1)Ti} = 2.36$.Å and $d_{S(2)Ti} = 2.42$ Å. Both these facts (the difference in the binding energy and interatomic distances) indicate strong polarization of the chemical bond in the S(1)–Ti–S(2) chain.

In Fig. 4 for comparison the spectra of the Ti2p level of TiS_3 and TiS_2 are given. The spectra of the Ti2p levels have a relative shift of 1 eV. In both cases, titanium is four-valent, however, TiS_3 is characterized by lower ionicity.

Calculation	Slater	10Dq	e_g	t_{2g}	Upd	Δ	Udd
1	0.9	0	1	1	0.8	0	0
2	0.4	0	1		3.2	0	0

TABLE 1. Multiplet Calculation Parameters for Two States of the Titanium Atom



Fig. 2. Temperature dependence of the magnetic susceptibility of TiS_3 .

Fig. 5 depicts the valence band spectra in a resonant excitation mode (eV) (452.4(1), 455.8(2), 457.95(3), 460.7(4), 597.4(5) and far beyond its limits 1486.6(6)).

It is seen that the spectra obtained in the resonant excitation mode beyond its limits (6) in Fig. 5, have a small peak directly on the Fermi level (excitation energies of 456 eV and 458 eV). Moreover, it is possible to distinguish crossover: a transition from the resonant Auger Raman spectrum (RARS) to the normal Auger spectrum. It is seen that the form of the spectrum with a high (6 in Fig. 5) excitation energy differs from the spectra with a lower excitation energy. This is caused by a change in the photoionization cross-section at a significant change in the excitation energy [11]. In order to distinguish the partial contributions from the states of sulfur and titanium atoms to the electronic structure the calculation of the density of states was performed for TiS_3 .

Fig. 6 depicts the partial densities of states for TiS_3 . From the partial densities of states of sulfur it is seen that there are two sulfur positions: two atoms (S2 and S3 in Fig. 6) of one type of sulfur and one position of another type of sulfur (S1 in Fig. 6). The situation is similar to the spectrum of the S2*p* level. It should be noted that the densities of states of sulfur of the S1 type are similar in structure to the density of states of sulfur in TiS_2 . The structure of the density of states for sulfur of the S2 and S3 types differs for both *p* and *s* states. The density of states of titanium occupies the energy range up to 6 eV. Above 6 eV only the states of the sulfur atoms are located. In the experimental spectrum obtained at an energy of 1486.6 eV, the region of 10-15 eV contains two spectral contributions of S3*s* states at different binding energies (left panel in Fig. 6) corresponding to two types of sulfur atoms, as is well seen from the calculation.





Fig. 3. Spectrum of the S2*p* level for TiS_3 . Darkened peaks show the components of the spectrum. The ratio of the sum of the areas of peaks *1* and *2* to the sum of the areas of peaks *3* and *4* is 2.



Fig. 4. Spectrum of the Ti2p level for TiS_3 and TiS_2 .



Fig. 5. Valence band spectra obtained in the resonance Ti2p-3d excitation mode (*1-5*) and far beyond its limits (*6*). The respective excitation energies are given in the text. The RRAS line marks the crossover of the pseudo-Raman peak into the normal Auger peak. The dashed line R denotes the resonance peak.

experimental spectra.

Fig. 7 shows the total densities of states with regard to the photoionization cross-section value at the corresponding excitation energy and concentration.

It is seen that with a change in the energy the intensity ratio of the main peak (0-7 eV) and peaks with the energies ranging from 8 eV to 17 eV is considerably altered.

Fig. 8 depicts the experimental X-ray absorption (XAS) spectrum of $TiL_{2,3}$ along with the results of model calculations. In order to model the real state of the chemical bond we assumed the titanium atom to exhibit two oxidation states. These oxidation states are characterized by some distinction in the iconicity and the interaction force of the Ti2p vacancy and Ti3d electrons. These arguments follow from the above data on strong polarization in the environment of the titanium atom and are taken into account in the selection of the calculation parameters (Table 1). Therefore the model absorption spectrum is a total result of two calculations with different parameters. A combined analysis of the experimental data on the binding energy of the Ti2p level, the spectral features in the valence band near the Fermi energy, and the first peak in the absorption spectrum indicates the presence of the narrow Ti3d band localized in the vicinity of the Fermi level, which is not reproduced by the band calculation of the electron density of states. This feature of the electronic structure of



Fig. 6. Partial densities of states for TiS_3 : *s* sulfur states (*a*), *p* sulfur states (*b*), titanium states (*c*).



Fig. 7. Total densities of states at photoionization cross-sections of 1486.6 eV and 440 eV.



Fig. 8. Absorption spectrum of titanium in TiS_3 and the result of the multiplet calculation for Ti^{4+} . Calculation parameters are listed in Table 1.

 TiS_3 can reflect special states appearing as a result of strong polarization of the chemical bond of titanium atoms in the lattice of the compound.

CONCLUSIONS

The experimental X-ray photoemission spectra and $TiL_{2,3}$ absorption spectra of TiS_3 are studied. A narrow band located near the Fermi level is found. The occurrence of this band is due to the polarization of the chemical bond of titanium atoms with the lattice. The measurement results of the temperature dependence of the magnetic susceptibility give evidence of strong diamagnetism of the compound. The model calculation of the electron density of states does not completely describe the experimental data. The analysis of the experimental data makes it possible to assume the coexistence of titanium ions in different oxidation states.

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