RESONANT PHOTOEMISSION AND ABSORPTION
SPECTROSCOPY STUDY OF THE Cr_xTi_{1-x}Se_2

ELECTRONIC STRUCTURE

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Solid solutions of 1T-Cr_xTi_{1-x}Se_2 (x = 0-0.83) were synthesized for the first time. To study the electronic structure of Cr_xTi_{1-x}Se_2 monocrystals, photoemission spectra of core levels, resonance spectra of valence bands, and absorption spectra of Ti and Cr were obtained. Titanium and chromium atoms were found to have the oxidation state 4+ and 3+, which is supported by atomic multiplet calculations for Ti and Cr in the octahedral environment. According to calculation of the local density of chromium electronic states, the Cr_3d electrons are spin-polarized, and the density of chromium states is of half-metal nature. The calculation agrees well with the experimental data.

Keywords: resonance photoemission, photoelectron and absorption spectroscopy.

INTRODUCTION

The state of half-metal magnetic was predicted for CrSe_2 compound [1]. However, pure CrSe_2 cannot be obtained in a stable state due to instability of Cr^{4+} ion. This problem is commonly solved by intercalation of additional donor atoms into the lattice. The scientific literature provides no information on experimental studies of the electronic structure of chromium diselenides, except for very limited data on X-ray photoemission and ultraviolet photoemission with the angular resolution for NaCrS_2 compound reported in [2].

Earlier we examined the chromium intercalated titanium diselenide Cr_{0.1}TiSe_2, which has a localized magnetic moment equal to 3μ_0 on chromium atoms [3]. The localization state degrades after attaining a threshold value in sublattice of titanium atoms coordinated by chromium at its concentration about 25% [4].

Intercalation of acceptor admixtures is impossible due to strong Coulomb repulsion between intercalant layer and the nearest layer of chalcogen; thus, substitution of titanium atoms by chromium is the only way to provide acceptor doping of TiSe_2 in solid solutions of Cr_xTi_{1-x}Se_2 [5]. Investigation of the electronic structure of Cr_xTi_{1-x}Se_2 system upon variation of chromium content can provide data on the formation of electronic structure and spin polarization of states near the Fermi level.

To examine the electronic structure of Cr_xTi_{1-x}Se_2, we obtained spectra of X-ray photoemission (XPS), resonance X-ray photoemission (RXPS), and X-ray absorption (XAS), performed model band calculation and calculation of multiplet atomic spectra for titanium and chromium absorption in the crystal field.
EXPERIMENT AND THEORY

Spectral studies were carried out only with monocrystal samples of Cr$_x$Ti$_{1-x}$Se$_2$. The Cr$_x$Ti$_{1-x}$Se$_2$ monocrystals were grown by the gas transport method with direct evaporation in evacuated ampoules from polycrystalline phase of a specified composition. The crystals were used as thin plates of size $2\times2\times10^{-3}$ mm. Their chemical composition was determined by X-ray fluorescence analysis on a JEOL-733 spectrometer. The crystal structure was revealed by X-ray diffraction of polycrystals and, for a chosen composition, the monocrystal was examined using an X-calibur 3 (Oxford Diffraction) X-ray monocrystal diffractometer.

X-ray photoelectron spectra and absorption spectra were recorded on a BESSY II synchrotron in the Russian-German laboratory. Measurements were performed at a MUSTANG (Multi User STage for ANGular resolved photoemission) experimental station with a PHOIBOS HSA3500 150 analyzer. The core-level spectra were taken at the excitation energy of 800 eV. The spectra were calibrated against the Pt4f$_{7/2}$ line ($E_b = 71.2$ eV). All the samples were oriented at a 45° angle between incident radiation and surface of a sample. The analyzer axis was parallel with the normal to the sample surface. The analyzer spot was $0.5\times0.5$ mm in size. To obtain a fresh surface, the crystals were cleaved in the working chamber at a pressure of $\sim 1\times10^{-9}$ mbar. All measurements were performed at room temperature.

Atomic multiplet calculation of the $L_{2.3}$ absorption spectra of Ti$^{4+}$ and Cr$^{3+}$ in the octahedral environment was made using a software package [6]. The best agreement with experiment was observed when Ti$L_{2.3}$ absorption spectrum was calculated with the following parameters: Slater integrals were decreased to 70% of the value calculated by the Hartree–Fock method, the crystal field splitting parameter $10D_q$ was equal to 2 eV, the charge transfer parameter $\Delta$ was 3 eV. The following parameters were used to calculate the Cr$L_{2.3}$ absorption spectrum: Slater integrals were decreased to 40% of the value calculated by the Hartree–Fock method, the crystal field splitting parameter $10D_q$ was equal to 1.6 eV, the charge transfer parameter $\Delta$ was 3 eV. Calculation was made for the $O_h$ symmetry.

The band structure was calculated using a full-potential method of linearized augmented plane waves (FP-LAPW) implemented with the Wien2k software package [7]. Integration over the Brillouin zone in reciprocal space was made using a mesh of $12\times12\times6$ special $k$ points. The calculation was performed with experimentally obtained parameters of the crystal structure: $a = 3.54$ Å and $c = 6.008$ Å, and the space group $P-3m1$ (164). To simulate the effect of Ti $\rightarrow$ Cr substitution on the electronic structure, we devised a supercell containing 8 formula units of TiSe$_2$. This cell was used to make a structure with substitution of one titanium atom by chromium (Cr$_{1/8}$Ti$_{7/8}$Se$_2$). The resulting unit cell has the same symmetry as the initial one. The radii of atomic spheres $R_{Cr}$ 2.5 au, $R_{Ti}$ 2.5 au and $R_{Se}$ 2.24 au were chosen for the calculation. Within the same model we calculated the electronic structure of a hypothetical pure compound CrSe$_2$ in the absence of stabilizing titanium in van der Waals gap. For this reason, due to deficit of electrons, the Fermi level was 0.5 eV lower than pseudogap for the projection of down-spin density of states.

RESULTS AND DISCUSSION

Earlier it was shown [8] that at small concentrations of chromium (up to $x = 0.25$), unit cell parameters are virtually independent of the composition. This circumstance, taking into account approximately equal atomic radii of chromium and titanium, is indicative of the substitution. The space group $P-3m1$ is retained, similar to initial titanium diselenide. An increase in the chromium concentration is accompanied by ordering of chromium atoms with the formation of a superstructure and by transition from hexagonal to trigonal-prismatic structure. This conclusion is based on the analysis of monocrystal diffractometry data for Cr$_{0.83}$Ti$_{0.26}$Se$_2$ sample. The sample has a hexagonal symmetry with space group $P3$, which testifies the absence of chromium ordering in titanium positions.

Figure 1 shows a typical fragment of the crystal structure. Similar to the initial 1T-TiSe$_2$ structure, it is layered and consists of alternating CrSe$_2$ layers and titanium atoms in van der Waals gap. Titanium atoms occupy two