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Gd $4f$ AND $5d$ ELECTRONS IN $Sn_{0.96}Gd_{0.04}Te$ VALENCE BAND*

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The synchrotron radiation was applied to measure resonant photoemission spectra (Fano-type Gd $4d$–$4f$ resonance), constant initial states and constant final states to study the valence band electronic structure of $Sn_{0.96}Gd_{0.04}Te$ crystal. The resonant energy was found equal to 150.3 eV. The electrons $4f$ were found to contribute to the valence band of the crystal with the maximum located at 9.5 eV below the valence band edge whereas $5d$ electrons contribute at the crystal valence band edge.

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Semimagnetic semiconductor (SMSC) [1] or diluted magnetic semiconductor (DMS) based on IV–VI semiconductor compound was created due to the introduction of the rare earth (RE) Gd cation on the site of Sn cation in SnTe. The introduction of RE cations on the site of group IV cation leads to the contribution of its $5d$ and $4f$ electrons to the valence band of the new ternary alloy, e.g. $Sn_{0.96}Gd_{0.04}Te$ crystal, and it is responsible for magnetic and semimagnetic properties of the crystal. The aim of our work is to determine the contribution of Gd $4f$ and $5d$ electrons to the valence band of $Sn_{1-x}Gd_xTe$ and by this way experimentally verify the model of Gd impurity in SnTe matrix, recently presented in [2, 3].

The Fano-type resonant photoemission spectra were measured on the unique line FLIPPER II of the Synchrotron Ring of HASYLAB, DESY in Hamburg. The vacuum ultraviolet radiation of variable photon energy range between 10 and 200 eV was used. The clean surface of the sample was obtained by the cleavage of the sample in UHV conditions ($p = 3 \times 10^{-10}$ torr) and the spectra were taken

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in situ. The experimental setup allowed us to take energy distribution curves (EDCs), constant initial states (CIS) and constant final states (CFS) spectra.

In the resonant photoemission experiment the photon energy is tuned relatively to the energy of optical absorption edge corresponding to the $4d$–$4f$ transition. For this photon energy the Gd ions are excited selectively and locally. The relaxation of excited Gd ions leads to the additional emission of the Gd electrons. The contribution of the resonant photoemission can be described by the Fano resonance formulas [4, 5]. In the case of Gd the enhancement of the electrons emission occurs due to the coupling of the discrete excitation

$$4d^{10}4f^7 + h\nu = [4d^9 4f^8]^* \qquad (^* \text{ — excited state})$$

with

$$4d^{10}4f^7 + h\nu = 4d^{10}4f^6 + e^- \qquad (e^- \text{ — ordinary emitted photo-electron})$$

continuum channel via the autoionization of the $[4d^9 4f^8]^*$ excited state.

The cross-section for an isolated resonance interacting with several continua is given by a Fano type profile

$$\sigma = \sigma_a + \sigma_b(q+\varepsilon)^2/(1+\varepsilon^2)$$

where σ_a represents the noninteracting part of continuum excitation, σ_b represents the interacting part of continuum excitation. $\varepsilon = (h\nu - h\nu_{\text{res}})/\Gamma$ ($h\nu_{\text{res}}$ — in resonance energy, Γ — full width half maximum). The asymmetry parameter q determines the shape of the resonance. The positive value of the parameter q causes the cross-section changes to go through a minimum (antiresonance) below

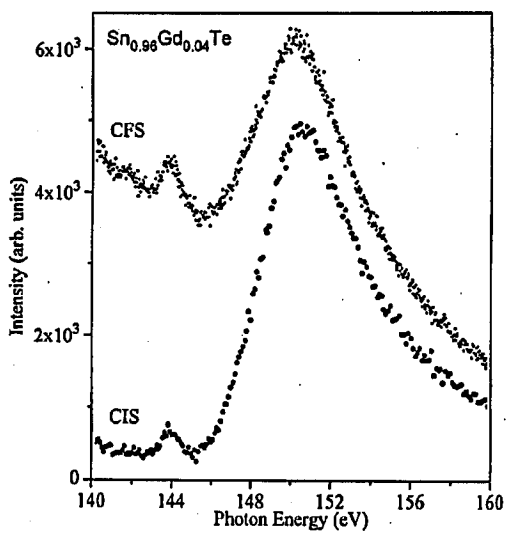

Fig. 1. The spectra CIS (initial energy equal to 9.5 eV) and CFS (final kinetic energy equal to 10 eV) measured for $Sn_{0.96}Gd_{0.04}Te$ crystal.

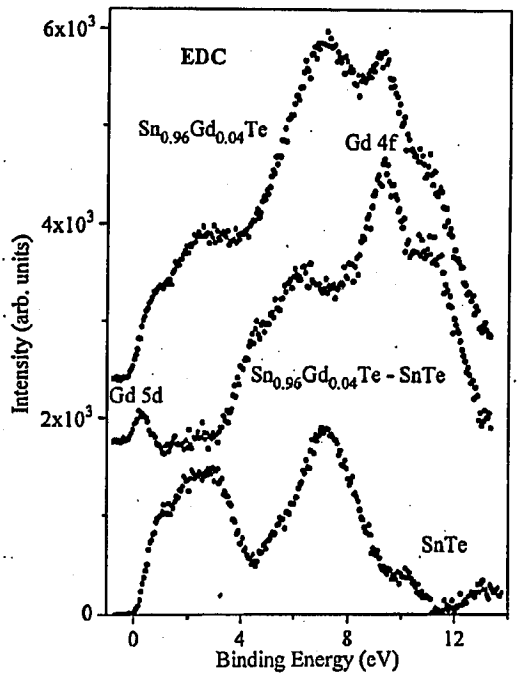

Fig. 2. The EDC's of the $Sn_{0.96}Gd_{0.04}Te$ crystal valence band obtained for $h\nu = 50$ eV (highest curve) and SnTe crystal obtained for $h\nu = 51$ eV (lowest curve). The difference between curves is presented as a curve at the middle.

the resonance maximum. In the energy region close to the resonant energy both of ionization processes (interacting and noninteracting with continuum) contribute to the measured spectrum of the EDC changing its shape and intensity of the peaks. The Fano resonance will result in an enhancement of the photoemission only for EDC's taken for photon energies close to the resonance energy.

The value of Fano type resonant radiation energy was determined from constant initial spectra with initial energy equal to 9.5 eV and from constant final spectra with final kinetic energy equal to 10 eV. The Fano type giant resonance maximum Gd ($4d$–$4f$) was found for energy $h\nu = 150.3$ eV and this maximum almost disappears for the antiresonance minimum found for $h\nu = 145.5$ eV (see Fig. 1).

The highest curve in Fig. 2 presents the EDC of the valence band of $Sn_{0.96}Gd_{0.04}Te$ crystal while the lowest one presents the EDC of the SnTe crystal. The difference between the highest and the lowest one is presented as a middle curve in Fig. 2. The lowest energy peak (middle curve in Fig. 2) corresponds to the Gd $5d$ electrons and it is located at the valence band edge of the $Sn_{0.96}Gd_{0.04}Te$. The peak located at energy 6 eV is of unknown origin. The peak located at energy 9.5 eV corresponds to the Gd $4f$ electrons and its position with giant maximum was measured for near resonant energy $h\nu = 150$ eV [6]. The relative position of

Gd $5d$ and $4f$ electrons obtained in the experiment well corresponds to the relative position obtained for clean gadolinium metal [7, 8].

The Gd $5d$ electrons maximum is located at the valence band edge of $Sn_{0.96}Gd_{0.04}Te$ crystal. The Gd $5d$ electrons position is estimated at 0.19 eV over the valence band edge of the SnTe crystal. This position well corresponds to the position used to explain anomalous magnetic and electric properties of the material [2, 3].

The Gd $(4f)$ electrons contribution to the valence band of the crystal was found with a maximum at a distance 9.5 eV below the valence band edge. $4f$ electrons are responsible for the permanent magnetic moment experimentally observed in $Sn_{1-x}Gd_xTe$ [2, 3], but do not contribute to charge transport.

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