Photoemission study of $\text{Ge}_{1-x-y}\text{Mn}_x\text{Eu}_y\text{Te}$ at Mn 3p–3d and Eu 4d–4f resonances

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Abstract

The electronic structure of $\text{Ge}_{0.4}\text{Mn}_{0.5}\text{Eu}_{0.1}\text{Te}$ has been investigated by means of resonant photoemission spectroscopy. The spectra were acquired for the photon energy ranges of 130–155 and 40–60 eV corresponding to the Eu 4d $\rightarrow$ 4f and Mn 3p $\rightarrow$ 3d resonances, respectively. The features related to Eu 4f and Mn 3d states were revealed in the emission from the valence band. It was shown that europium ions occur as Eu^{2+} . The Mn^{2+} 3d states contribute to the whole valence band with a maximum of the Mn 3d distribution at 3.9 eV.

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1. Introduction

Narrow-gap IV–VI semiconductors attract large interest as suitable materials for infrared radiation sources, detectors or thermoelectric generators. Diluted magnetic semiconductors (DMS), formed of those compounds by doping with transition metals or rare earth elements, exhibit further properties that are also very interesting from the point of view of basic research as well as of applications. One of the most important is the ferromagnetic order appearing in such compounds as $\text{Pb}_{1-x-y}\text{Sn}_x\text{Mn}_y\text{Te}$ [1], $\text{Sn}_{1-x}\text{Mn}_x\text{Te}$ [2] or $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$ [3]. It is governed by the Ruderman–Kittel–Kasuya–Yoshida (RKKY) interaction mediated by charge carriers. In IV–VI based DMS, contents of magnetic ions and carrier concentration can be controlled independently. This allows us to modify their transport and magnetic properties to our needs.

In $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$, the Curie temperature strongly depends on Mn concentration and it can reach 140 K [4]. Such properties

of this material inspired its extensive investigations in view of future spintronic applications [4,5]. GeTe doped with other transition metals are also studied [6].

In this paper, we report on studies of $\text{Ge}_{0.4}\text{Mn}_{0.5}\text{Eu}_{0.1}\text{Te}$. Introduction of Eu ions into the system markedly influences its magnetic properties. The Curie temperature becomes relatively high at markedly lower Mn contents, e.g. T_C of $\text{Ge}_{0.89}\text{Mn}_{0.07}\text{Eu}_{0.04}\text{Te}$ is higher than that of $\text{Ge}_{0.6}\text{Mn}_{0.4}\text{Te}$. Since contribution of Mn 3d and Eu 4f states to the electronic structure of the system plays an important role in magnetic interactions, we have undertaken an attempt to reveal them by means of photoelectron spectroscopy. In particular, the resonant photoemission spectroscopy was used as a tool enabling us to identify emission from open shells against a background of the valence-band-related emission. In such experiments, the photon energy is tuned to the energy of an intra-ion transition to unoccupied states in the partly filled shell, like 3p $\rightarrow$ 3d excitation in transition metal ions or 4d $\rightarrow$ 4f—in rare earth ions. Under such conditions two processes leading to different final states of the same energy may occur. The first one is the direct photoemission from the open shell to the continuum of free electron states. The second one is a process of the discrete intra-ion excitation.

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For Mn and Eu-containing crystals one considers the following transitions:

$$\text{Mn } 3d^5 + h\nu \rightarrow \text{Mn } 3d^4 + e^- \quad \text{and} \quad \text{Mn } 3p^6 3d^5 + h\nu \rightarrow \text{Mn } 3p^5 3d^6 \quad (1)$$

or, for Eu ions,

$$\text{Eu } 4f^7 + h\nu \rightarrow \text{Eu } 4f^6 + e^- \quad \text{and} \quad \text{Eu } 4d^{10} 4f^7 + h\nu \rightarrow \text{Eu } 4d^9 4f^8 \quad (2)$$

Due to quantum interference between these processes, and the autoionization of Mn $3p^5 3d^6$ (or Eu $4d^9 4f^8$) to Mn $3d^4 + e^-$ (or Eu $4f^6 + e^-$) (via a super Coster–Kronig process) a Fano resonance [7] occurs and a Fano-type line appears in the absorption spectra at the energy corresponding to the intra-ion transition. Therefore, the photoemission from the open shell is resonantly increased and the resonant photoemission can be used for identification of the spectral features which can be ascribed to the emission from partly filled shells.

By this method, we revealed the Eu 4f and Mn 3d contribution to the valence band of $\text{Ge}_{0.4}\text{Mn}_{0.5}\text{Eu}_{0.1}\text{Te}$. The europium ions occur as Eu^{2+} and the corresponding maximum appears at the valence band edge. The Mn^{2+} 3d states also contribute to the valence band. We detected this contribution (with maximum at 3.9 eV) in the spectra measured at photon energies close to the Mn $3p \rightarrow 3d$ resonance (about 50 eV) as well as in those obtained for the energies of 140–150 eV (corresponding to non-resonant enhancement of d-related emission).

2. Experimental details

The $\text{Ge}_{1-x-y}\text{Mn}_x\text{Eu}_y\text{Te}$ ($x = 0.5$, $y = 0.1$) polycrystalline samples were grown by a Bridgman method in the Institute for Problems of Materials Science, National Academy of Sciences of Ukraine. The clean crystal surfaces for photoemission experiments were prepared *in situ* by scraping the sample with a diamond file under UHV conditions. The resonant photoemission experiments were performed in the synchrotron radiation laboratory HASYLAB, Hamburg (Germany). Synchrotron radiation obtained from the storage ring DORIS III was monochromatized with the FLIPPER II plane grating vacuum monochromator designed for the photon energy range of 15–200 eV. The spectrometer was equipped with a CMA electron energy analyzer. The total energy resolution was kept at 250 meV. The origin of the energy axis was set at the Fermi energy as measured for a reference metallic sample.

3. Results and discussion

A typical set of photoemission spectra of $\text{Ge}_{0.4}\text{Mn}_{0.5}\text{Eu}_{0.1}\text{Te}$ for the photon energy range covering the energy of the Eu $4d \rightarrow 4f$ transition is shown in Fig. 1a. The spectra were normalized with respect to the photon beam intensity. The background of secondary electrons was subtracted by means of the Shirley method. The binding energy range of the spectra covers the valence band as well as some of the core levels. The peaks at 31.3, 41–42.3 and 48.8 eV correspond to Ge 3d, Te

Fig. 1. (a) Photoemission spectra of $\text{Ge}_{0.4}\text{Mn}_{0.5}\text{Eu}_{0.1}\text{Te}$ taken the photon energy range from 130 to 155 eV. The inset: the CIS spectrum measured for the initial state energy (E_i) equal to 2.2 eV. (b) The resonance–antiresonance difference spectrum shown together with the curves obtained for $h\nu = 132$ and 141 eV.

Fig. 2. (a) Photoemission spectra of the $\text{Ge}_{0.4}\text{Mn}_{0.5}\text{Eu}_{0.1}\text{Te}$ valence band taken the photon energy range from 40 to 60 eV. The inset: the CIS spectrum measured for $E_i = 3.8$ eV. (b) The resonance ($h\nu = 50$ eV) and antiresonance ($h\nu = 47.5$ eV) spectra shown together with the difference spectrum obtained by subtraction of the latter from the former one.

4d and Mn 5p, respectively. The valence band (0–15 eV) has two distinct maxima: at 2.1 and 4 eV. The former corresponds to emission from the Eu^{2+} 4f states. Its intensity changes as a function of photon energy in accordance with the Fano-like resonance profile (see the inset of Fig. 1a). The resonance energy ($h\nu = 141$ eV) and the binding energy of this peak correspond well to those reported for Eu^{2+} in other IV–VI compounds [8,9].

In order to reveal the energy distribution of the Eu^{2+} 4f related emission, a difference spectrum was derived by subtraction of the spectrum taken for anti-resonance energy ($h\nu = 132$ eV) from that recorded for the resonance energy ($h\nu = 141$ eV). The obtained curve is presented in Fig. 1b. The Eu^{2+} 4f emission manifests itself as a single peak at 2 eV. The negative part of the spectrum, starting from the sharp minimum at 3.5 eV and spreading to 10 eV, occurs due to dependence of the valence-band-related emission on photon energy. We believe that Mn 3d states markedly contribute to this part of the electronic structure of the system (as shown below on the basis of studies carried out at photon energies close to the Mn 3p $\rightarrow$ 3d resonance). In IV–VI crystals, substitutional europium ions occur usually as Eu^{2+} , however, some other Eu ions may have the Eu^{3+} charge state, like on the surface of $\text{Pb}_{1-x}\text{Eu}_x\text{Te}$ cleaned by sputtering [8]. The Eu^{3+} 4f emission appears as a broad feature in the binding energy range of 5–12 eV (in $\text{Pb}_{1-x}\text{Eu}_x\text{Te}$ [8] or in purely trivalent europium compounds [10]). Such a feature does not occur in our spectra. It was also confirmed by constant-initial-state (CIS) photoemission measurements - no Fano-like feature was detected for initial state binding energy of 7–8 eV.

In order to determine the contribution of the Mn 3d states to the valence band, photoemission spectra of $\text{Ge}_{0.4}\text{Mn}_{0.5}\text{Eu}_{0.1}\text{Te}$ were measured also for photon energies close to the Mn 3p $\rightarrow$ 3d resonance (Fig. 2a). The broad feature spreading from the Fermi energy to 11 eV (with shoulders appearing at 1.2, 6.7, and 10.2 eV) corresponds to the valence band formed of Ge 4p and Te 5p orbitals. However, this part of the spectrum of $\text{Ge}_{0.4}\text{Mn}_{0.5}\text{Eu}_{0.1}\text{Te}$ is markedly broadened and the features are less discernible, with respect to the spectra of pure GeTe [11]. The maximum at 13.3 eV corresponds to Te 5s. A CIS photoemission spectrum measured for a shoulder at 3.8 eV (the inset in Fig. 2a) clearly shows a Fano-like profile at the photon energy of about 50 eV. This energy corresponds well to the Mn 3p $\rightarrow$ 3d transition. The overall shape of the Mn 3d states contribution to the valence band of the investigated system was determined by subtraction of the antiresonance spectrum ($h\nu = 47.5$ eV) from the resonance ($h\nu = 50$ eV) one (Fig. 2b). The difference spectrum reproduces the partial density of Mn 3d states. It is similar to that reported for $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$ [12].

4. Summary

The contributions of the Mn 3d and Eu 4f states to the electronic structure of $\text{Ge}_{0.4}\text{Mn}_{0.5}\text{Eu}_{0.1}\text{Te}$ were determined by means of resonant photoemission spectroscopy in the photon energy ranges corresponding to Mn 3p $\rightarrow$ 3d and Eu 4d $\rightarrow$ 4f resonances. Mn 3d contribution spreads from the Fermi energy to 12 eV with a maximum at 3.9 eV. Europium ions occur in

the system as Eu^{2+} . The Eu^{2+} 4f emission manifests itself as a single peak at 2 eV.

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