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RESONANT PHOTOEMISSION STUDY OF Gd $4f$ STATES IN IV-VI CRYSTALS

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Resonant photoemission experiments were performed in order to reveal the contributions of half-filled Gd $4f^7$ shell to the electronic structures of $\text{Sn}_{0.95}\text{Gd}_{0.05}\text{Te}$ and $\text{Pb}_{0.95}\text{Gd}_{0.05}\text{S}$ crystals. The influences of the Gd $4f^6$ final-state multiplet splitting and f -ligand hybridization on the shapes of the spectra are discussed.

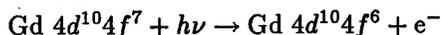
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1. Introduction

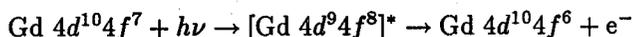
In 1956, Tombulian and Hartman used synchrotron radiation to measure the optical transmission through Be and Al foils [1]. In the course of the forty years which have passed since that famous experiment, the range of applications of synchrotron radiation to scientific research has been widened immensely. Thanks to the wide spectral range and the high brilliance of synchrotron radiation sources many experimental methods gained new aspects. Many experiments would not be performed at all, if synchrotron radiation was not available. Resonant photoemission measurements belong to them. The possibility to tune the photon energy to the energy of a particular intra-ion transition is crucial for selective stimulation of electron emission from the states derived from partly filled shells of transition metal (TM) or rare-earth (RE) atoms. The advantages of the method were discovered when it was applied to investigations of TM or RE containing solids [2-4].

In this paper we present results of the experiments which consist in applications of resonant photoemission spectroscopy to the study of $\text{Sn}_{1-x}\text{Gd}_x\text{Te}$ and

$\text{Pb}_{1-x}\text{Gd}_x\text{S}$. The measurements were carried out in order to identify the partial contribution of Gd $4f^7$ shells to the valence bands of these solid solutions. Energy distribution curves (EDC's) were measured for the photon energy range covering the Gd $4d-4f$ absorption edge (140–160 eV). Then the interference between the processes [5]:



and



selectively stimulated emission from Gd $4f$ states. The resonant enhancement of some features observed in the spectra enabled us to reveal the partial contribution of f states to the emission derived from the valence band. Complementary data were obtained by a constant-initial-state (CIS) technique.

Solid solutions of RE chalcogenides and IV–VI compounds form an interesting and fast growing group of diluted magnetic semiconductors (DMS). They combine properties of narrow-gap semiconductors with optical characteristics of the atoms which have partly-filled shells of f -electrons. Moreover, the interaction between the RE ion system and band electrons of the host crystal leads to interesting magneto-optical and magneto-transport phenomena. Some of the properties of these mixed crystals turned out to be very useful in fabrication of optoelectronic devices [6, 7]. The interesting physical properties and the possible applications stimulate the strong interest focused on many questions concerning the electronic band structure of these solids. In particular, information about the f states energy distribution, which can be obtained from the resonant photoemission spectroscopy results, is crucial for the analysis of the interaction between f -shells and band electrons.

2. Experimental conditions

The experiments were carried out at the E1 beamline of the storage ring DORIS II in the synchrotron radiation laboratory (HASYLAB) in Hamburg, Germany. The FLIPPER II experimental setup is designed for sample preparation and extended characterization of solids by means of electron spectroscopies (photoemission, low-energy electron diffraction (LEED)). The system is attached to the beamline via a plane grating monochromator operating over the photon energy range of 15–200 eV.

The samples of $\text{Sn}_{0.95}\text{Gd}_{0.05}\text{Te}$ and $\text{Pb}_{0.95}\text{Gd}_{0.05}\text{S}$ were grown by the Bridgman method in the Institute of Physics, Polish Academy of Sciences. The crystal composition was determined by electron microprobe analysis. The crystal structure and homogeneity of the samples were tested by X-ray diffraction experiments. Clean surfaces for photoemission measurements were prepared *in situ* by cleavage ($\text{Sn}_{0.95}\text{Gd}_{0.05}\text{Te}$) or by scraping of the samples with a diamond file ($\text{Pb}_{0.95}\text{Gd}_{0.05}\text{S}$).

3. Experimental results and discussion

Figure 1 shows the sets of EDC's taken for $\text{Sn}_{0.96}\text{Gd}_{0.04}\text{Te}$ and $\text{Pb}_{0.95}\text{Gd}_{0.05}\text{S}$. The curves were measured for photon energy near to the energy of the intra-ion Gd $4d-4f$ transition. It was determined by comparison of these EDC's and analysis of

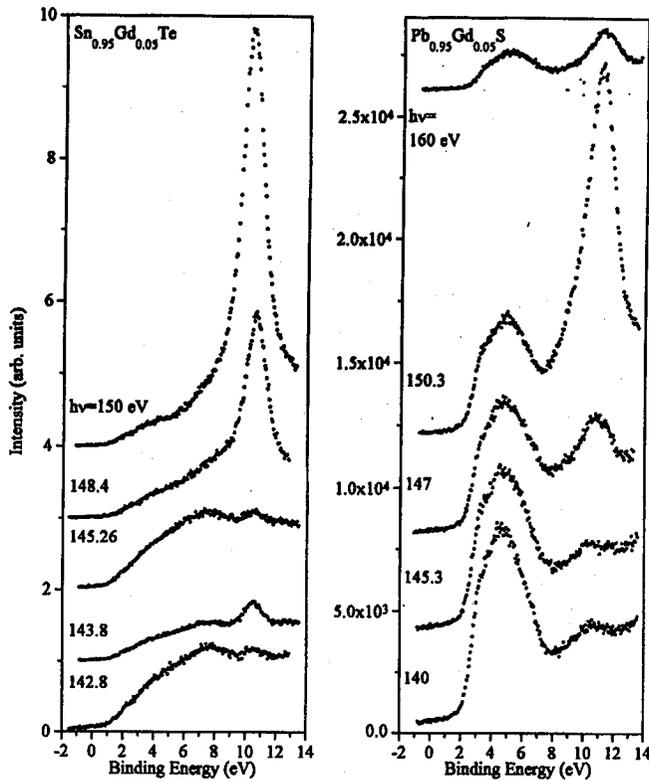


Fig. 1. Sets of energy distribution curves of $\text{Sn}_{0.95}\text{Gd}_{0.05}\text{Te}$ and $\text{Pb}_{0.95}\text{Gd}_{0.05}\text{S}$. Zero binding energy is set at the Fermi level.

the CIS curves that the energy of 150.5 eV corresponds to the maximum enhancement of the resonant photoemission for both $\text{Sn}_{0.95}\text{Gd}_{0.05}\text{Te}$ and $\text{Pb}_{0.95}\text{Gd}_{0.05}\text{S}$.

In order to visualise the Gd 4f derived contributions to the spectra, we took differences between the curves measured on and off resonance (Fig. 2). In the obtained difference spectra the single maxima were found at energies of 10.3 and 11.1 eV for $\text{Sn}_{0.96}\text{Gd}_{0.04}\text{Te}$ and $\text{Pb}_{0.95}\text{Gd}_{0.05}\text{S}$, respectively. The shapes of the maxima are similar and correspond well to the shape of the Gd 4f photoemission spectrum calculated by Gerken [8]. Thus, we can assume that the shape of the difference spectra is determined mainly by the Gd 4f⁶ final-state multiplet splitting. The energy position of its lowest component ($J = 0$) can be used as a measure of the Gd 4f shell binding energy. A least squares fit of the theoretically obtained multiplet [8] (convolved with Gaussian or Lorentzian line shapes) to our experimental data enabled us to estimate the Gd 4f shell binding energies. The values obtained were 9.8 eV and 10.4 eV for $\text{Sn}_{0.96}\text{Gd}_{0.04}\text{Te}$ and $\text{Pb}_{0.95}\text{Gd}_{0.05}\text{S}$, respectively. Further analysis with application of asymmetric Doniach-Sunjić [9] or Mahan [10] line shapes (characteristic of the spectra measured for rare-earth metals) is under progress.

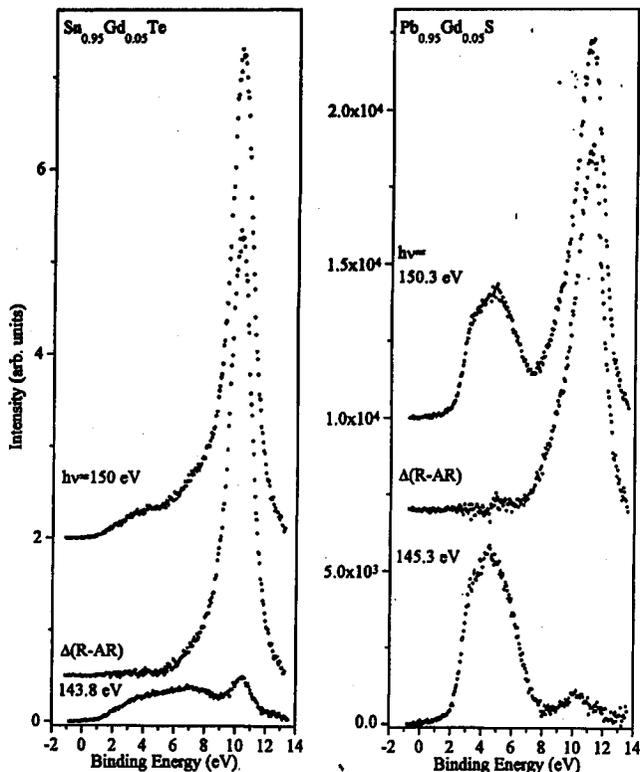


Fig. 2. Difference spectra ($\Delta(R-AR)$) obtained from the curves taken on and off resonance for $\text{Sn}_{0.95}\text{Gd}_{0.05}\text{Te}$ and $\text{Pb}_{0.95}\text{Gd}_{0.05}\text{S}$. For $\text{Pb}_{0.95}\text{Gd}_{0.05}\text{S}$, in order to correct the difference spectrum for the photon energy dependence of the valence band photoemission cross-section, the EDC's were additionally normalised to match the heights of the maxima corresponding to the valence band.

The correspondence between the spectra calculated by Gerken for the rare-earth metals and our experimental spectra, taken for Gd ions in $\text{Sn}_{0.96}\text{Gd}_{0.04}\text{Te}$ and $\text{Pb}_{0.95}\text{Gd}_{0.05}\text{S}$, shows that interaction between the f shell and ligand orbitals is negligible in both materials. It is in contrast with the results obtained for Ce, Pr and Nd halides [11]. In those compounds hybridization of RE $4f$ states with ligand orbitals leads to the occurrence of a satellite close to the main $4f^n \rightarrow 4f^{n-1}$ maximum.

4. Summary

The $4f$ derived contributions to the electronic structure of $\text{Sn}_{0.95}\text{Gd}_{0.05}\text{S}$ and $\text{Pb}_{0.95}\text{Gd}_{0.05}\text{S}$ were revealed by means of resonant photoemission. They are well localised in energy and located at binding energies of 9.8 and 10.4 eV for $\text{Sn}_{0.96}\text{Gd}_{0.04}\text{Te}$ and $\text{Pb}_{0.95}\text{Gd}_{0.05}\text{S}$, respectively. The strength of the resonant enhancement of the emission is similar in both materials.

The shape of the maxima is determined mainly by the $4f^6$ final-state multiplet splitting and no manifestation of the hybridization between the f shell and ligand orbitals was observed in the spectra.

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