$4f$ SHELL OF Gd^{2+} AND Gd^{3+} IONS IN $Sn_{1-x}Gd_xTe$ — RESONANT PHOTOEMISSION STUDY

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Resonant photoemission spectra of $Sn_{1-x}Gd_xTe$ ($x = 0.02$ and 0.08) measured for the photon energy range 142 to 151 eV show the valence band density of states distribution and the Gd $4f$ derived maximum. The energy position of the $J = 0$ component of the Gd $4f$ maximum was determined and used as a measure of the Gd $4f$ shell binding energy. The electrostatic model of core level shifts was used to interpret the difference in the Gd $4f$ binding energies observed for $x = 0.02$ and $x = 0.08$.

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1. Introduction

Like many other diluted magnetic semiconductors (DMSs), $Sn_{1-x}Gd_xTe$ attracts persistent interest because of its magnetic, optical and electric properties. It is well known that the basic properties of DMSs are determined by interaction between magnetic ions and band electrons of the host crystal. Thus, the energy distribution of the d states of a transition metal or the f states of a rare-earth (RE) element with respect to the band structure of the crystal is an important factor which influences its properties.

However, the properties of $Sn_{1-x}Gd_xTe$ differ markedly from those of many other DMSs. The recently proposed model [1, 2] predicts that the $f-f$ coupling proceeds via $f-d$ intra-ion and $d-d$ inter-ion interaction. So, the energy positions of the $4f$ and $5d$ shells as well as the number of bound electrons are the crucial elements which characterize the system. For $Sn_{1-x}Gd_xTe$, it is exceptionally difficult to give an experimental answer whether the Gd $5d$ shell is occupied or empty. This is because in $Sn_{1-x}Gd_xTe$ the high optical absorption on free carriers obscures results of optical experiments.

In this paper we present the resonant photoemission spectra which were obtained for the $Sn_{1-x}Gd_xTe$ crystals with different Gd content ($x = 0.02$ and 0.08).

They show the energy position and the configuration of Gd $4f$ shell and they can also be used to discriminate between Gd^{2+} ($4f^7 5d^1$) and Gd^{3+} ($4f^7 5d^0$) charge states. We propose an interpretation which is consistent with the assumption that in $Sn_{0.98}Gd_{0.02}Te$ gadolinium occurs as Gd^{2+} while in $Sn_{0.92}Gd_{0.08}Te$ as Gd^{3+}.
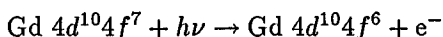
2. Experimental conditions

The experiments were carried out at the E1 beam line of the storage ring DORIS III in the synchrotron radiation laboratory HASYLAB in Hamburg, Germany. The FLIPPER II experimental set-up, designed for sample preparation and extended characterization of solids by means of electron spectroscopies, was attached to the beam line via a plane grating monochromator which operated within the photon energy range of 15–200 eV [3].
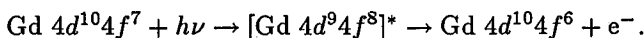
The $Sn_{1-x}Gd_x Te$ samples were grown by the Bridgman method in the Institute of Physics, Polish Academy of Sciences. The crystal composition was determined by the electron microprobe technique. The crystal structure and homogeneity of the samples were tested by X-ray diffraction experiments. Clean surfaces for photoemission measurements were prepared *in situ* by scraping the samples with a diamond file.

3. Experimental results and discussion

The resonant photoemission technique is based on the interference between two processes which lead to the same final state [4]

$$Gd\ 4d^{10}4f^7 + h\nu \rightarrow Gd\ 4d^{10}4f^6 + e^-$$

and

$$Gd\ 4d^{10}4f^7 + h\nu \rightarrow [Gd\ 4d^9 4f^8]^* \rightarrow Gd\ 4d^{10}4f^6 + e^-.$$

As the result the emission from the rare-earth $4f$ states is selectively enhanced if the photon energy was tuned to the energy of the intra-ion $4d \rightarrow 4f$ transition. In the photoemission spectra, which were measured in a constant-final-state (CFS) regime, the resonance manifests itself as a Fano-type shape (Fig. 1).

In photoelectron energy distribution curves (EDC) (Fig. 2) taken at the photon energies marked with arrows at the CFS spectrum, we can follow the strong resonant enhancement of the peak with the binding energy of about 9.4 eV (with maximum intensity at $h\nu = 149$ eV). This enabled us to ascribe it to the emission from Gd $4f$ shell. Due to the very strong resonant enhancement the RE $4f$ derived contribution can be clearly distinguished from the emission from the valence band, even for the systems which contain only a few percent of RE atoms.

The shape of a RE $4f$ derived contribution in photoemission spectra is strongly dependent on the $4f^{n-1}$ final-state multiplet splitting. In order to compare our experimental results with the calculated Gd $4f^7 \rightarrow 4f^6$ photoemission spectra [5], the calculated multiplet lines which correspond to the different values of the quantum number J, were convoluted with the Voigt line shape. It was assumed that the broadening of the lines was equal for both systems. The correspondence, which exists between the experimental spectra and the results of the calculations, was satisfactory and the energy position of the $J = 0$ component
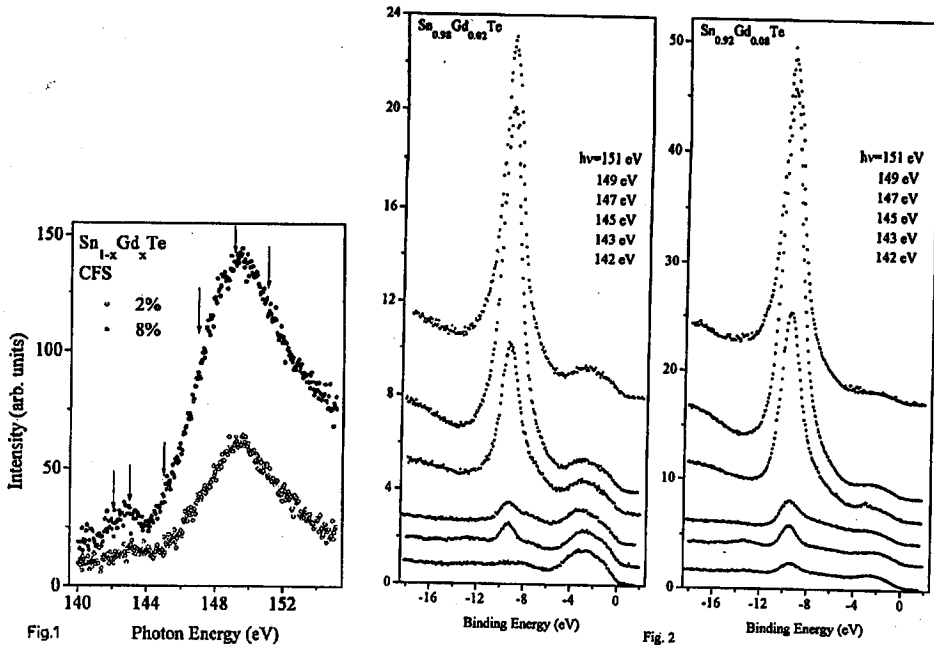
Fig. 1.

Photon Energy (eV)

Fig. 2.   Binding Energy (eV)

Fig. 1.   Constant-final-state photoemission spectra taken from $Sn_{0.98}Gd_{0.02}Te$ and $Sn_{0.92}Gd_{0.08}Te$ in the photon energy region of the Gd $4d \rightarrow 4f$ excitation (a non-resonant background subtracted). They show the spectral dependence of total photoemission yield. Arrows mark the photon energies at which the EDCs were taken (see Fig. 2).

Fig. 2.   Photoemission spectra of $Sn_{0.98}Gd_{0.02}Te$ (left) and $Sn_{0.92}Gd_{0.08}Te$ (right) crystals taken for photon energies near the Gd $4d \rightarrow 4f$ excitation.

could be used as a measure of the binding energy of Gd $4f$ shell. It was equal to -8.88 eV and to -9.04 eV for $Sn_{0.98}Gd_{0.02}Te$ and $Sn_{0.92}Gd_{0.08}Te$, respectively.

A comparison of the binding energies of the Te $4d$, Sn $4d$ and Gd $4f$ core levels in $Sn_{0.98}Gd_{0.02}Te$ and $Sn_{0.92}Gd_{0.08}Te$ enabled us to reveal a net shift of the Gd $4f$ shell (0.1 eV) which cannot be ascribed to the shift of the Fermi level or to changes of the neighboring ions influence on the cation core levels. Thus, the increase in the binding energy of $4f$ electrons should be connected with the lack of the $5d$ electron in the Gd ion.

Applying the electrostatic model of the core level chemical shifts [6] we can estimate changes in the binding energies of Gd $4f$ electrons due to the $Gd^{2+} \rightarrow Gd^{3+}$ transition. The model is based on the idea that the potential of valence electrons felt by the core electrons can be represented by the potential of a charged, hollow sphere. It was successfully used to predict the core level shifts which were caused by alteration in the chemical environment of atoms. It accounts for energy shifts of the f shell in free rare-earth ions which can amount to several electronvolts [7]. However, if the core level shifts in an atom embedded in semiconductor with a high free carrier concentration are considered, then we have to take into account a screening of Coulomb potential. By substituting the term $q \exp(-r/r_{TF})/(4\pi\varepsilon_0 r)$

for $q/(4\pi\varepsilon_0 r)$ we can reproduce the observed Gd $4f$ shell energy shift with reasonable values for the radii of the shells involved and for r_{TF} (the Thomas–Fermi screening radius).

The electrostatic model is obviously too simple to predict credibly the core level shifts which can amount to tenths of an electronvolt. Nevertheless, it shows that the core level screening by free carriers can be efficient enough to reduce the shifts by almost two orders of magnitude.

4. Summary

The Gd $4f$ derived contributions to the electronic structure of $Sn_{0.98}Gd_{0.02}Te$ and $Sn_{0.92}Gd_{0.08}Te$ crystals. They are well localized in the energy scale and correspond to the Gd $4f^7$ binding energies of -8.88 and -9.04 eV, for $x = 0.02$ and 0.08, respectively.

Shapes of the maxima are determined by the $4f^{n-1}$ final-state multiplet splitting and no effect of the hybridization between the f shell and the ligand orbitals was found.

The observed difference in Gd $4f^7$ binding energy can be interpreted as a result of ionization of Gd ions, from Gd^{2+} to Gd^{3+} in $Sn_{0.92}Gd_{0.08}Te$. Then the strong screening of Coulomb potential due to the high concentration of free carriers has to be taken into consideration.

The acquired data suggest that the resonant photoemission spectroscopy of RE $4f$ shell can be used efficiently as a tool for RE ion charge state identification in semiconductors. The method would be particularly useful for investigation of the materials in which high free carrier absorption makes the optical measurements difficult.

Acknowledgments

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