XANES Analysis of L3,2 Edges of Zinc Selenides with Transition Metals

M. Zimnal-Starnawska, E. Czarnecka-Such, A. Kisiel, W. Frentrop, W. Giriat

► To cite this version:

M. Zimnal-Starnawska, E. Czarnecka-Such, A. Kisiel, W. Frentrop, W. Giriat. XANES Analysis of L3,2 Edges of Zinc Selenides with Transition Metals. Journal de Physique IV Proceedings, 1997, 7 (C2), pp.C2-1201-C2-1202. 10.1051/jp4:19972193 . jpa-00255264

HAL Id: jpa-00255264

<https://hal.science/jpa-00255264>

Submitted on 1 Jan 1997

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

XANES Analysis of $L_{3,2}$ Edges of Zinc Selenides with Transition Metals

M. Zimnal-Starnawska, E. Czarnecka-Such, A. Kisiel, W. Frentrop* and W. Giriat**

Institute of Physics, Jagellonian University, Reymonta 4, 30-059 Kraków, Poland

** Humboldt-Universität zu Berlin, Institut für Physik, EES, Invalidenstr. 110, 10115 Berlin, Germany*

*** Instituto Venezolano de Investigaciones Científicas, Centro de Física, Apartado 827, Caracas 1010A, Venezuela*

Abstract. X-ray Absorption Near Edge Structure (XANES) for ternary compounds $Zn_{1-x}TM_xSe$ ($TM=Cr, Mn, Fe, Co$, and Ni) with different concentration x of transition metals (TM) has been studied with the use of synchrotron radiation. XANES measurements were carried out in the fluorescence detection mode using synchrotron radiation from the HE-PGM2 plane grating monochromator at BESSY. The $L_{3,2}$ edges for Se, Zn and different transition metals (Cr, Mn, Fe, Co, and Ni) in $Zn_{1-x}TM_xSe$ compounds have been analyzed. Moreover, the analysis of $L_{3,2}$ edges for different transition metals in binary TMSe has also been made. The characteristic feature of $L_{3,2}$ edges for transition metals containing two white lines was observed. The energy positions of these maxima are in good agreement with the theoretical results. The studies of $L_{3,2}$ edges of Se in ternary compounds in comparison to the same edge of host crystal (ZnSe) allowed us to obtain information about the influence of additional 3d-states of TM on the density of states of ternary compounds.

X-ray Absorption Near Edge Structure (XANES) for ternary compounds $Zn_{1-x}TM_xSe$ ($TM=Cr, Mn, Fe, Co$, and Ni) with different concentration x of transition metals (TM), crystallizing in zinc blende structure, has been studied with the use of synchrotron radiation. The investigated compounds belong to a class of materials often referred to as diluted magnetic semiconductors (DMS's). As a result of alloying transition metals and II-VI semiconducting compounds, DMS's exhibit unique electrical, magnetic, and optical properties, many of which can be attributed to the short range exchange interactions between the spins of the magnetic ions and between the magnetic ions and group-VI anion sp-band electrons [1]. The XANES analysis allows to obtain information about the partial density of unoccupied states. For X-ray energies in the XANES region, the excited photoelectron undergoes transitions from the core states to an unoccupied state just above the Fermi level, the final state being determined in relation to the initial state by the dipole selection rule [2]. In DMS's, XANES involves photoelectrons undergoing transitions to unoccupied localized and delocalized states, some of which may be involved in the magnetic cation 3d, 4s- and anion p-orbital hybridization.

XANES measurements were carried out in the fluorescence detection mode using synchrotron radiation from the HE-PGM2 plane grating monochromator at BESSY and utilizing the fluorescence chamber with high purity germanium detector.

The $L_{3,2}$ edges for Se, Zn and different transition metals (Cr, Mn, Fe, Co, and Ni) in $Zn_{1-x}TM_xSe$ compounds have been analyzed. Moreover, the analysis of $L_{3,2}$ edges for different transition metals in binary TMSe, crystallizing mainly in NiAs structure has also been made. The $L_{3,2}$ edges XANES spectra have been normalized after background subtraction and the zero energy scale has been chosen for each spectrum at the first inflection point. In Fig. 1 the $L_{3,2}$ edges XANES spectra of Se in different $Zn_{1-x}TM_xSe$ compounds are shown. The energy position of the first inflection point as well as the shape of these spectra, compared with pure ZnSe, are very similar. In Fig. 2 we present the TM $L_{3,2}$ edges XANES spectra for binary TMSe mixed crystals. Our experimental data are in good agreement with the theoretical results calculated for 3d transition metals by Müller et al. [3]. The spectra are dominated by the large peaks, the so-called white lines, which are due to transitions from $2p_{3/2}$ and $2p_{1/2}$ core levels into the unfilled 3d states in the conduction bands. The relative size of the L_3 and L_2 white lines follows the multiplicity ratio 2 to 1 of the $2p_{3/2}$ and $2p_{1/2}$ core states within the single-particle approximation used in the calculations [3]. The spin-orbit splitting of these levels is very small in 3d transition metals and it becomes larger while the number of 3d electrons increases. This effect one can see in Fig. 2 as the increasing energy distance between the white lines while the atomic number Z rises. The energy positions of white lines in our experimental spectra are in good agreement with the theoretical results [3], in spite of various crystalline structures of pure 3d transition metals,

Figure 1: Se $L_{3,2}$ absorption edges for pure ZnSe and ternary compounds $Zn_{1-x}TM_xSe$ ($TM=Ti, Cr, Mn, Fe$, and Ni).

but their relative intensities are different. The additional structure between the L_3 and L_2 edges is observed.

The $L_{3,2}$ edges XANES spectra for transition metals (Mn, Fe, Co, and Ni) in ternary compounds were analyzed. The results for one of them (Mn) are presented in Fig. 3. The magnitude of absorption at higher energy part of spectra is responsible for the concentration of manganese in the investigated materials (Fig. 3). In the case of other TM $L_{3,2}$ spectra the white lines in ternary compounds are sharper and better distinguished than the same lines in pure materials. Moreover, their relative intensities are in good agreement with theoretical predictions. It seems to be reasonable when one assumes the more atomic-like character of TM electronic states in ternary compounds than in pure TMSe.

In Fig. 4 the $L_{3,2}$ edges for Zn in ZnSe and ternary compounds are shown. The main features of ternary compounds spectra are very similar to binary ones and there is no evidence of transition metals influence, maybe due to small concentration of TM. However, the exchange of anion in binary and ternary compounds causes the significant modification of the shape of spectra (Fig. 5).

The further analysis of $L_{3,2}$ edge XANES spectra for ternary compounds containing transition metals are going to be performed.

Figure 2: Experimental TM $L_{3,2}$ absorption edges for binary compounds TMSe (TM=Cr, Mn, Fe, Co, and Ni).

Figure 3: Mn $L_{3,2}$ absorption edges for pure MnSe and ternary compounds $Zn_{1-x}Mn_xSe$.

Figure 4: Zn $L_{3,2}$ absorption edges for pure ZnSe and ternary compounds $Zn_{1-x}TM_xSe$.

Figure 5: Zn $L_{3,2}$ absorption edges for pure ZnTe and ternary compounds $Zn_{1-x}TM_xTe$.

Aknowledgments

This work is in part supported by programme No PB-I 147/P3/94/06 of the Polish Committee for Scientific Resarch. We wish to thank Dr. W. Braun and the BESSY technical staff for their interest and hospitality.

References

- [1] *Diluted Magnetic Semiconductors*, edited by J.K. Furdyna and J. Kossut, Semiconductors and Semimetals vol. 25, (Academic, New York, 1988)
- [2] A. Kisiel, G. Dalba, P. Fornasini, M. Podgórný, J. Oleszkiewicz, F. Rocca, and E. Burattini, *Phys.Rev.B*, **39**, (1989), 7895.
- [3] J.E. Müller, O. Jepsen, and J.W.Wilkins, *Solid state Commun.* **42**, (1982), 365.