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A. Kisiel, E. Czarnecka-Such, P. Lee, E. Burattini, W. Giriat. An Analysis of Zn and Se K Edge XANES Spectra for ZnMeSe (Me = Ni, Cr, V and Ti). Journal de Physique IV Proceedings, 1997, 7 (C2), pp.C2-1199-C2-1200. 10.1051/jp4:19972192 . jpa-00255263

HAL Id: jpa-00255263

<https://hal.science/jpa-00255263>

Submitted on 1 Jan 1997

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An Analysis of Zn and Se K Edge XANES Spectra for ZnMeSe (Me = Ni, Cr, V and Ti)

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Abstract. Experimental studies of X-ray Absorption Near Edge Structure (XANES) have been carried out for Se and Zn K edges in ZnNiSe, ZnCrSe, ZnVSe and ZnTiSe. A comparison is made between the experimental results for a zincblende crystalline ZnMeSe (where Me = Ni, Cr, V, and Ti) with theoretical LMTO calculations of the electron densities of states (DOS) in the conduction band for the ordered ferromagnetic phase of ZnMeSe (with 25% Me content). The agreement between the theoretical x-ray absorption edges and experimental details is not so satisfactory as for ZnMnSe and ZnFeSe, which have been obtained earlier [P.M. Lee et al., J. Phys. Condensed Matter, 6, (1994), 5771], particularly in the intensities and the energy positions of the fine structure of the XANES experimental and theoretical spectra. However, the p-like DOS for ZnMeSe around Se and Zn ions in an energy range close to the Fermi level have been compared with success. From experimental Se and Zn K edges, hybridized contributions of the transition metals in ZnNiSe, ZnCrSe, ZnVSe and ZnTiSe have been extracted and analyzed. The comparison between ternary compounds ZnNiSe, ZnCrSe and ZnVSe and pure ZnSe, taken as standard compounds, presents a characteristic maxima of p-like contribution localized at 0.25, 1.8 and 0.25 eV below ZnSe conduction band minimum (CBM), respectively. A close correlation between theoretical p-like DOS maximum in 0 - 2 eV energy range and features subtracted from experimental data is found. The contribution of Ti in ZnSe is not observed, probably due to small solubility of Ti in ZnSe (less 1%).

Experiment and results

The aim of this communication is to analyze the unoccupied p-like conduction band states of ZnMeSe (where Me = Ni, Cr, V and Ti) around the Se and Zn ions by use of the X-ray Absorption Near Edge Structure (XANES) analysis and a comparison between these experimental data and the theoretical band structure calculations carried out with use of one-electron LMTO method. Some experimental and theoretical results are compared also with the respective data for ZnSe based ternary compounds with other transition metals (Mn, Fe, Co) [1, 2]. X-ray absorption measurements have been carried out with use of synchrotron radiation at the Adone Wiggler facility in Frascati utilizing the Si(111) and Si(220) channel-cut crystal monochromators [3]. The original samples were high purity monocrystalline ZnMeSe (Me = Ni, Cr, V and Ti) produced by a chemical transport method. Because of low solubility of Ni, Cr, and V in pure ZnSe, the content of these transition metals does not exceed 1%, in the case of Ti even less. To obtain thin specimens of the controlled thickness and homogeneity as required by x-ray absorption techniques, the samples were finely powdered and deposited on the polyacetate films. The contribution of each edge to the absorption coefficient has been isolated by extrapolating the pre-edge region to higher energies by a Victoreen-like fit and by subtracting the fitted curves from the remaining experimental spectrum [4]. XAS measurements have been carried out on the Se and Zn K edges, i.e., the transitions of Se and Zn s core state to p-like conduction band have been analyzed. Fig. 1 shows the reduced experimental Se K edges for ZnNiSe, ZnCrSe, ZnVSe and ZnTiSe. Because of space limitation, the complete experimental data for K edges of Se and Zn for these compounds will be presented elsewhere [5]. Se K edges presented in Fig. 1 (a) are very similar, but small differences can be distinct after subtraction of pure ZnSe from ZnMeSe spectrum. Suggested procedure, applied previously with success [6,7], allows to show how much the conduction band DOS of ternary compounds differs from respective DOS of host binary compound. In the case of Se and Zn K edges, we can extract a contribution of 4s and 3d hybridized states of analyzed transition metals in p-like DOS of the conduction band around Se or Zn ions. Fig. 1 (b) shows results of Se K edges extraction. The p-like contributions of Ni, Cr and V in ZnSe host crystal are localized at about 0.25, 1.8 and 0.25 eV below the ZnSe conduction band minimum (CBM). For Ti the result of this

Figure 1: (a) Experimental reduced x-ray absorption Se K edges for ZnMeSe. (b) A contribution of 4s and 3d hybridized states of Ni, Cr, V and Ti in ZnMeSe.

extraction has been found to be negative, likely because of small quantity of Ti in the samples. The calculations of the K edge absorption have been carried out using electron densities of states for the conduction band in an ordered ferromagnetic lattice with 25% Ni, Cr, V and Ti in ZnSe. The details of these calculations based on LMTO band structures have been described before [6,7]. It is worth remembering however that the method uses a local density approximation for exchange and correlation and is therefore susceptible to limitations in describing details of the d states. Also the calculations are for 25% transition metal contribution, which is much larger concentration than could be used in an experiment (1% or even less). Fig. 2 presents the Se K edges calculations for ZnNiSe, ZnCrSe, ZnVSe and ZnTiSe. Also these edges are similar but have richer structure than respective experimental data. A comparison between Figs. 1 (a) and 2 shows that the agreement of the experimental and theoretical data for ZnNiSe, ZnCrSe, ZnVSe and ZnTiSe is not so satisfactory as for ZnMnSe and ZnFeSe [1]. Apart from this comparison result, an analysis of the p-like DOS around Se and Zn ions for ZnSe with various transition metals is of particular interest in the energy range close to the edge since this should reflect the different effective p-s, d hybridization in all these cases. Because we expect much stronger hybridization effect for Se K edges in this paper we limit the analysis only to this case. A comparison of the theoretical p-like contributions of Ni, Cr, V and Ti around Fermi level as well as an analysis respective contributions for Mn, Fe and Co [2] shows that in all cases in 0 - 2 eV energy range are observed distinct peaks in p-like DOS caused by sd-p interaction. The dependence of the energy positions of these peaks in respect to the Fermi level presents Fig.3 (a). A similar dependence of the energy positions of the subtracted contributions for V, Cr and Ni (see Fig.1 (b)) and completed by data for Mn, Fe [1] and Co [2] are in Fig.3 (b). The both dependencies characterize a similar tendencies i.e. a maximum for Mn, a minimum for Cr and increase for V.

Conclusions

A XANES analysis shows small differences in x-ray absorption K edges of ZnMeSe (Me = Ni, Cr, V and Ti). Differences are well seen after extraction of the p-like DOS contribution of 3d and 4s hybridized states in ZnSe conduction band structure. A maximum contribution of Ni, Cr and V to Se K edges is observed at about 0.25 eV, 1.8 eV and 0.25 eV below ZnSe CBM, respectively. A maximum contribution of Ni and Cr to Zn K edges is observed at 0.5 eV and 0.4 eV below CBM, respectively. For V and Ti the extraction gave a negative result. The comparison of experimental data with calculated values based on theoretical LMTO band structures shows no satisfactory agreement, particularly in the position of the maxima of the experimental spectra. But a comparison of the energy positions of theoretical p-like DOS contribution in 0-2 eV energy range for V, Cr, Mn, Fe, Co and Ni with respective energy positions of experimental p-like contributions is satisfactory. Therefore, it has been shown that the interaction s,d states of transition metals has a significant influence on p-like states of ZnSe host crystal.

Aknowledgments

We wish to thank the technical staff of the PWA group of the Laboratori Nazionali di Frascati for their help and hospitality. This work is in part supported by programme No. 1147/P3/06/94 of the Polish Committee for Scientific Research.

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Figure 2: Theoretical x-ray absorption Se K edges.

Figure 3: Energy position of p-like contribution (a)-theoretical data, (b)-extracted from experimental data.