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INVESTIGATION OF ELECTRONIC STRUCTURE OF $Zn_{1-x}Mg_xSe$ MIXED CRYSTALS BY COMPTON SPECTROSCOPY METHOD

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The first experimental study of the Compton profiles of $Zn_{1-x}Mg_xSe$ for $x = 0.25$, 0.47, 0.56 mixed crystals is presented. The Compton profiles were measured with the use of the ^{241}Am radioactive source with a resolution of 0.57 a.u. The experimentally obtained Compton profiles were compared with the theoretical ones based on the free-atom model. The results are interpreted in terms of outermost electrons of Zn and Mg being promoted to the higher momentum states, and $4p$-electrons of Se becoming more delocalised in a solid, being thus promoted to the lower momentum states.

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The $Zn_{1-x}Mg_xSe$ crystals attract significant interest for their potential applications in technology of blue light-emitters (light emitting diodes and laser diodes) [1–3]. However, there is a little known about the fundamental properties of this material. This paper deals with the study of the Compton profiles of $Zn_{1-x}Mg_xSe$ crystals with x ranging from 0.25 to 0.56. Crystals were grown by the high-pressure Bridgman method. The crystals composition and structure were verified by electron probe microanalysis and X-ray diffractometry. For the Compton investigations the crystals were cut perpendicularly to the crystal growth axis in 1 mm thick plates. Laue patterns show that different ingots of $Zn_{1-x}Mg_xSe$ exhibit a usually different orientation. It was found that for a low concentration of Mg the $Zn_{1-x}Mg_xSe$ crystallises in sphalerite form while for higher Mg concentrations in wurtzite one. The structural phase transition appears at $x = 0.18 \pm 0.03$. For compositions close to the phase transition region a significant amount of stacking faults and of politypes is observed.

Typical photoluminescence spectra of $Zn_{1-x}Mg_xSe$ consist of near-band-edge and deep levels emission which intensity ratio increases with increasing Mg content [4]. All as-grown $Zn_{1-x}Mg_xSe$ crystals with high concentration of Mg exhibit high electrical resistivity [5, 6]. The electronic structure of the mixed crystals and the

mechanism of the observed increase in the energy gap and resistivity with an increase in Mg are still a subject of investigations.

It is known that the Compton spectroscopy offers a useful method to investigate the electronic structure of a material [7–9]. The so-called Compton profile, $J(p_z)$, measured in the experiment is a function given by the integral of the $n(p)$-electron density in momentum space

$$J(p_z) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} n(p) \mathrm{d}p_x \mathrm{d}p_y. \tag{1}$$

The shape of the Compton profile is particularly sensitive to the outer shell electrons responsible for electronic properties of the material under investigation.

The Compton experiment has been performed on a spectrometer working with the ^{241}Am annular source. The experimental data have been analysed using standard procedure described elsewhere [10]. Table shows the most important parameters of the spectrometer and the samples.

TABLE

Parameters of the spectrometer and the samples.

Source ^{241}Am	
Activity	1.85×10^{11} Bq
Primary energy	60 keV
Source-Sample distance	70 mm
Sample-Detector distance	170 mm
Scattering angle	167.8°
Ge detector	GLP-16195/10-P
Resolution	0.57 a.u.
Time of data collection	300 [h]/sample
Counts in maximum of Compton peak	100×10^3
Signal to background ratio	30 : 1
Samples	
Diameter	8.20–8.56 mm
Thickness	1.05–1.09 mm
Density	4.15–4.77 g/cm^3

The measurements have been carried out for three different concentrations of Mg: $x = 0.25$, 0.47 and 0.56 (all samples exhibit the wurtzite type structure). Because there is no available solid state theory of the Compton profile for these crystals, the experimental data were compared with the free-atom theory [11]. Figure 1 presents a difference between such a free-atom calculation for $Zn_{0.75}Mg_{0.25}Se$ and the experiment. A promotion of slow electrons (momentum range below, say, 0.5 a.u.) into the higher momentum (from 0.5 to 1 a.u.) state, when a solid is formed, is well seen. This effect is well known and results from both the bonding and the constrained volume for electrons (mainly outermost electrons of Zn and Mg in our case) in solids. One can also notice a rearrangement in the population of states in the momentum region of 1–4 a.u. With the aid of atomic wave functions one can claim that a partial delocalization of $4p$-electrons of Se is responsible

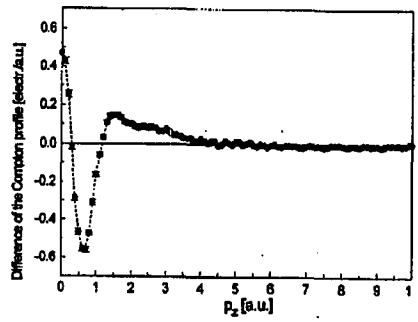

Fig. 1. The difference between the theoretical and experimental Compton profiles for $Zn_{0.75}Mg_{0.25}Se$. The free-atom theoretical Compton profile was calculated on the base of the calculations of Biggs et al. [11] and was convoluted with the Gaussian function with FWHM = 0.57 a.u. which mimics the experimental resolution.

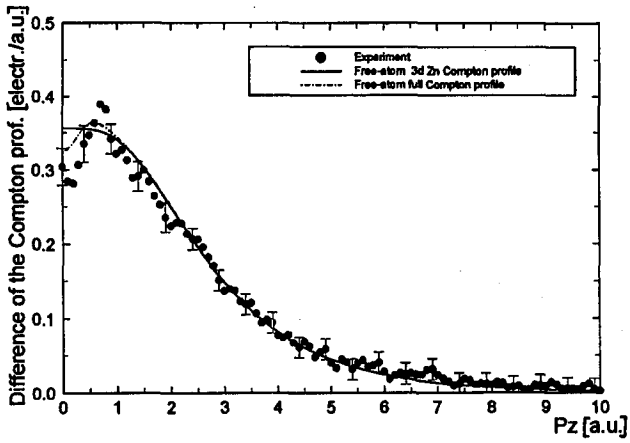

Fig. 2. The difference between the valence Compton profiles of $Zn_{0.75}Mg_{0.25}Se$ and $Zn_{0.53}Mg_{0.47}Se$, obtained after extracting the core contributions from the experimental Compton profiles (for Mg: $1s^22s^22p^6$ for Zn and Se: $1s^22s^22p^63s^23p^6$). The solid line represents $3d$ Zn free-atom theoretical Compton profile (convoluted with the Gaussian resolution function with FWHM = 0.57 a.u.). The dashed line accounts also for the contribution of the outermost s-electrons of Zn and Mg.

for the observed effect. This conclusion finds a strong support in the electronic band structure calculations [12], which show that mainly just these electrons form the top of the valence band. All the d-states which could be of importance here are lying deep below this energy, and are atomic-like. This is also confirmed by an observed difference between the experimental Compton profiles of the valence electrons for $x = 0.25$ and $x = 0.47$, shown in Fig. 2. It indicates an interesting behaviour of the electronic density in the momentum space. The area under the ex-

perimental points (solid circles) is exactly 1.1 electrons, i.e. the difference between the number of the valence electrons per molecule for these two compositions. The solid line shows the contribution of free-atom $3d$-electrons of Zn. The atomic-like character of this contribution is clearly seen. A small dip observed in the momentum range from 0 to 1 a.u. is largely due to a difference of the distributions of $4s$- and $3s$-electrons of Zn and Mg, respectively. Their contribution is accounted for in the dashed curve in Fig. 2. Some unexpected features are seen in the momentum range of 1.5–2.5 a.u. Similar features were also observed in the difference profile of samples with $x = 0.25$ and $x = 0.53$. It is suspected that they may originate from the crystallographic anisotropy of the Compton profiles of the $Zn_{1-x}Mg_xSe$ crystals. The pseudopotential calculations of this effect by Nara et al. [13], which show such anisotropy, concern, however, the ZnSe with the zinc-blende structure only.

In conclusion we may say that our experiment shows that indeed the $3d$ Zn states are much atomic-like, as expected from Ref. [12], and the most essential solid state effects are concerned mainly with promotion of the outermost electrons of Zn and Mg to the high momentum states plus an opposite trend which we associate with a delocalization of the $4p$ states of selenium forming the top of the valence band.

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