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ENERGY LEVEL POSITION OF Ni AND BAND OFFSETS IN $Zn_{1-x}Cd_xSe:Ni$ AND $ZnS_xSe_{1-x}:Ni^*$

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Absorption and reflectivity measurements have been carried out for $Zn_{1-x}Cd_xSe:Ni$ and $ZnS_xSe_{1-x}:Ni$ solid solutions. Energy level positions of nickel $2+ / 1+$ charge state have been used for estimation of band offsets for the valence and conduction bands of $ZnCdSe/ZnSe$ and $ZnSSe/ZnSe$. Intra-shell transitions of Ni^{2+} were also studied.

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1. Introduction

It was pointed out [1, 2] that the energy levels of transition metal (TM) ions are pinned to a certain universal reference level of semiconductor. It was also shown that for two isovalent semiconductors the difference in the valence band-referred TM energy levels is equal to the valence band offsets of a given heterojunction, i.e., the band offsets can be estimated if the energy level positions of TM ions are known for given compounds. In this paper we positively verify the theory for Ni ion in solid solutions $Zn_{1-x}Cd_xSe$ and ZnS_xSe_{1-x} for the wide range of Cd and S fractions. The values of the band offsets which were extrapolated from the optical absorption data are very close to the theoretical ones predicted by the above-mentioned theory. We point out, however, that a relatively good agreement is also obtained from a simple model which takes into account differences in electron affinities.

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2. Experimental

The single crystals of $\text{Zn}_{1-x}\text{Cd}_x\text{Se}:\text{Ni}$ and $\text{ZnS}_x\text{Se}_{1-x}:\text{Ni}$ with Cd or S fractions from $x = 0.0$ to 0.5 were grown by the chemical transport method. All samples were doped with nickel to the level of about 10^{17} cm^{-3} . Absorption and reflection spectra were recorded by a BOMEM DA.13 Fourier transform spectrometer and DFS-12 monochromator. The samples were mounted in a gas flow liquid helium cryostat working in the temperature range of 2–300 K. Exciton reflectivity measurements were done to establish band gap energies, in which the position of maximum of a line was taken as a free exciton energy. The observation of broad, relatively strong absorption band in the range 1.7–2.2 eV allowed us to estimate energy level positions of nickel $2+ / 1+$ charge state. These results are presented in Table.

TABLE
Composition x , position of a free exciton reflection maximum E_{FE} and a threshold energy $h\nu_{\text{th}}$ for the Ni photoionization ($2+ \rightarrow 1+$) in $\text{Zn}_{1-x}\text{Cd}_x\text{Se}:\text{Ni}$ and $\text{ZnS}_x\text{Se}_{1-x}:\text{Ni}$ alloys at 2 K.

| Compound | x | E_{FE} [eV] | $h\nu_{\text{th}}$ [eV] |
|-------------------------------------------------|-------|----------------------|-------------------------|
| ZnSe:Ni | 0.0 | 2.80 | 1.85 |
| $\text{Zn}_{1-x}\text{Cd}_x\text{Se}:\text{Ni}$ | 0.001 | 2.80 | 1.85 |
| | 0.01 | 2.78 | 1.85 |
| | 0.1 | 2.69 | 1.85 |
| | 0.2 | 2.52 | 1.85 |
| | 0.3 | 2.44 | 1.81 |
| | 0.5 | 2.26* | 1.82 |
| $\text{ZnS}_x\text{Se}_{1-x}:\text{Ni}$ | 0.001 | 2.80 | 1.85 |
| | 0.01 | 2.81 | 1.85 |
| | 0.1 | 2.86 | 1.90 |
| | 0.2 | 2.93 | 1.95 |
| | 0.5 | 3.2* | 2.07 |

*These values are calculated from the $E_{\text{FE}}(x)$ dependence.

3. Discussion

The threshold energies were determined from $\alpha^{2/3}$ versus $h\nu$ plot, which should be a straight line for the photoionization process [3], cutting the energy axis at the impurity ionization energy. The value $h\nu = 1.85$ eV for ZnSe:Ni crystal is in agreement with some previous estimations [3]. For ZnCdSe:Ni this energy does not change to $x = 0.2$, and then decreases by *ca.* 30 meV for a larger Cd content. The energy level position of Ni in ZnSSe:Ni increases monotonously by about 200 meV for the range of S fraction varied between 0.01 and 0.5. Taking the Ni acceptor level as a reference level we estimated valence and conduction band edges in the whole composition range studied (Fig. 1). The values of the

determined band offsets are very close to the theoretical ones [2]. A zero valence band offset and a large conduction band offset were predicted by the common anion rule for the ZnCdSe/ZnSe heterojunction [4]. The weak shift of the valence band edge for $x > 0.2$ (Cd) can be connected with a structural transition of a crystal from a zinc-blend to a wurzite phase, which takes place in this composition range. Our data for the ZnSSe/ZnSe show almost equal valence and conduction band offsets. They are relatively close to those obtained from a simple electron affinity rule [5], but differ from a number of experimental data for ZnSSe/ZnSe superlattices, which give for the conduction band offset values in the range of 0.01–0.0688 eV [5]. We can suggest that in solid solutions with anion substitution the ionization energy of a TM impurity can depend on a composition, because in this case the nearest-neighbor impurity surrounding and, thus hybridization of the impurity d -shell and of the valence band p -states, changes strongly.

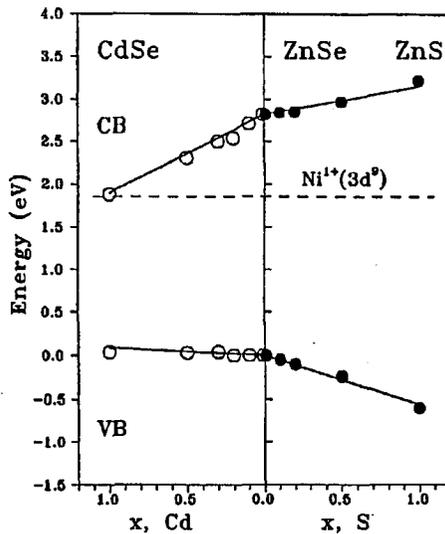


Fig. 1. The valence and conduction band offsets of ZnCdSe/ZnSe and ZnSSe/ZnSe measured relative to the Ni acceptor level. Solid line is extrapolated from the TM averaging procedure for the corresponding binary compounds (after Ref. [2]).

Intra-shell transitions of Ni^{2+} ($3d^8$) are also modified with the change of x composition. The disorder of the alloys produces qualitatively similar broadening of the absorption lines in compounds with substitution in the anion and cation sublattices, but in ZnSSe:Ni this broadening is more pronounced. Absorption lines also shift with increasing x composition. The magnitude and sign of the shifts are different for each transition. For example, for the ${}^3T_1(F) \rightarrow {}^1T_2(F)$ transition the line shifts slightly to the lower energy in ZnCdSe:Ni (by about 40 cm^{-1} for $x = 0.1$) and to the higher energy in ZnSSe:Ni (by about 15 cm^{-1} for $x = 0.1$). The temperature induced modification of the spectra was also studied.

Concluding, we have determined energy level positions of Ni $2+/1+$ charge state for the wide range of Cd and S content in ZnCdSe and ZnSSe. The estimated band offsets for the valence and conduction bands of ZnCdSe/ZnSe and ZnSSe/ZnSe are in good agreement with the theory [1, 2], but in the latter case they differ from some experimental data obtained for superlattices.

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