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REFLECTIVITY STUDY OF $Hg_{1-x}Co_xSe$ CRYSTALS

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The reflectivity spectra of $Hg_{1-x}Co_xSe$ ($x = 0.0$, 0.024, 0.031) crystals were measured in the vacuum ultraviolet photon energy range from 4 to 12 eV to find the influence of Co ions on the valence band electronic structure of the HgSe crystal. The structure of the reflectivity spectra was interpreted in terms of the electronic band structure of the binary material (HgSe) assuming direct allowed interband transitions.

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$Hg_{1-x}Co_xSe$ crystals belong to II–VI compounds containing substitutional transition metal cations. The interaction of M (M — transition metal) $3d$ electrons with the valence band electronic structure determines their anomalous magneto-transport and magneto-optical properties due to modification of the energy bands in some points of the Brillouin zone [1–3].

$Hg_{1-x}Fe_xSe$ crystals have been investigated by means of the vacuum ultraviolet reflectivity spectroscopy [3] and photoemission spectroscopy [4]. $Hg_{1-x}M_xSe$ crystals with contribution of the Mn^{2+}, Fe^{2+} and Co^{2+} cations were investigated by means of resonant photoemission spectroscopy [5].

HgSe crystal is a semi-metallic material, which crystallizes in the zinc-blende structure. In $Hg_{1-x}Co_xSe$ crystal Co^{2+} ions occupy sites of Hg^{2+} ions and it leads to crystalline, chemical and magnetic disorder. The crystalline disorder is caused by the local structure (the Hg–Se distance is different from the Co–Se distance). The chemical and magnetic disorder is caused by random distribution of Hg^{2+} or Co^{2+} cations.

The purpose of the experiment was to identify the region of k-space influenced by the Co $3d^7$ electrons.

The crystals used in this study were grown by a modified Bridgman method at the Institute of Physics, Polish Academy of Sciences. The content of Co atoms was carefully measured by means of the electron microprobe and energy dispersive X-ray fluorescence (EDXRF) methods. The X-ray diffraction measurements of the samples did not show any precipitation of Co atoms.

The reflectivity spectra were taken at room temperature for vacuum ultraviolet radiation in the energy range between 4 and 12 eV. A vacuum monochromator based on the Seya–Namioka scheme was used. The source of the ultraviolet radiation was a hydrogen gas discharge lamp connected to the monochromator without any window. The beam exiting from the monochromator was modulated by a rotating modulator. The part of the light transmitted through the modulator was reflected by a sample towards a prism coated with a luminophor and then measured by means of a photomultiplier with a quartz window. The second part of the light went above the sample to another luminophor–photomultiplier set. Modulated signals from the two photomultipliers were measured with lock-in nanovoltmeters. The data were recorded by an IBM XT computer.

The spectra of the reflectance coefficient of $Hg_{1-x}Co_xSe$ ($x = 0.0$, 0.024, 0.031) taken with the setup described above are presented in Fig. 1.

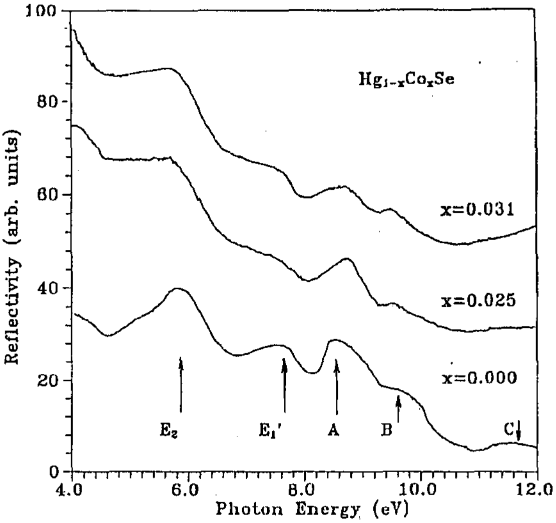

Fig. 1. Reflectivity spectra of $Hg_{1-x}Co_xSe$ crystals recorded at 300 K for $x = 0.0$, 0.024, 0.031.

The measured reflectivity spectra of HgSe ($x = 0.0$) correspond very closely to those obtained earlier [3, 6]. The calculation performed by Bloom and Bergstresser [7], and by Overhof [8] assigned the peaks of the reflectivity spectra of HgSe to the following transitions at some particular points in the Brillouin zone:

— the maximum at 5.75 eV (E_2 maximum) is attributed to transitions at X point (probably X_6^v–X_7^c or X_7^v–X_7^c),

— the maximum at 7.35 eV (E_1' maximum) is attributed to transitions at $L_{4.5}^v$–$L_{4.5}^c$ and W_6^v–W_6^c,

— the maximum at 8.25 eV (A maximum) is attributed to transitions at $L_{4.5}^v$–$L_{4.5}^c$, $L_{4.5}^v$–L_6^c,

— the maximum at 9.35 eV (B maximum) is attributed to transitions at L_6^v (first valence band)–L_6^c (third conduction band),

— the maximum at 11 eV (C maximum) is attributed to transitions at L_6^v (second valence band)–L_6^c (third conduction band).

In $Hg_{1-x}Co_xSe$ crystals the main peak at 5.75 eV broadens and shifts to lower energies (shift of about 0.2 eV), as x increases, but its intensity is the same.

The considerable broadening suggests that there is an influence of Co^{2+} ions at the X point and along the Δ direction of the Brillouin zone.

The E_1' structure has a maximum at the same position for every x, but the peak decreases for crystals containing Co^{2+} ions. We interpreted the decreasing and broadening of this maximum as caused by chemical and structural disorder occurring in ternary crystals. The E_1' structure is expected to be more sensitive to the disorder than other structures as it is a result of transitions at two different points of Brillouin zone (L and W).

The A feature disappears with the increase in the x value, and the position of the maximum shifts to higher energies. In analogy to the A peak behavior in $Hg_{1-x}Fe_xSe$ reflectivity spectra [3] we assume that the decrease and shift of the A peak obtained in our spectra may be connected with hybridization of the L final states ($L_{4.5}^c$ and L_6^c) with the unoccupied Co $3d$ states.

The weak B and C structures do not depend apparently on the x value. Both peaks are due to transitions between L_6^v and L_6^c bands. These transitions were found not to be affected by the presence of Co^{2+} ions.

The presence of the Co^{2+} ions leads to:

— broadening of the HgSe reflectivity peaks obtained for the energy range between 5.75 eV and 8.3 eV (E_2, E_2' and A peaks),

— decrease in the reflectivity peaks between 7.3 eV and 8.3 eV (E_1' and A peaks),

— shifts of certain peaks to the lower (E_2 peak) or higher (A peak) energies.

The addition of Co^{2+} ions considerably affects the electronic band structure of $Hg_{1-x}Co_xSe$ crystal. The broadening and decrease in the reflectivity features was attributed to the crystalline disorder created by introduction of Co^{2+} ions. The shift of the reflectivity peaks can be treated as a result of hybridization of the Co $3d$ states with the valence and conduction bands of the HgSe crystal. This effect

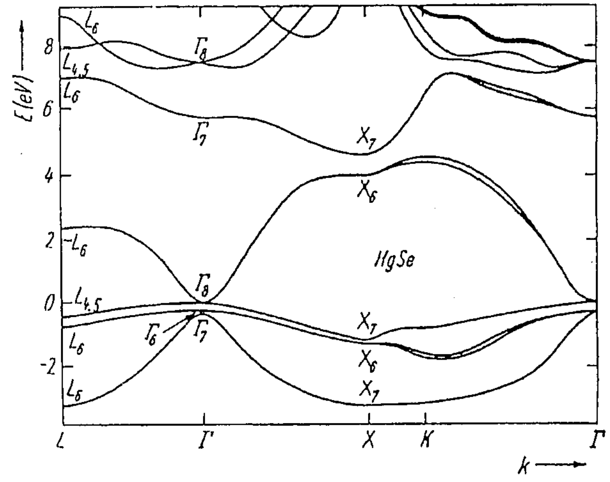

Fig. 2. Electronic band structure of HgSe [7].

was observed in L and X high symmetry points of the Brillouin zone (see Fig. 2). The hybridization of Co $3d$ states with the HgSe valence band was confirmed by the results of resonant photoemission experiment [5].

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