مجلة جامعة تشرين للدراسات والبحوث العلمية - سلسلة العلوم الاساسية المجلد (21) العدد (8) 1999
Tishreen University Journal for Studies and Scientific Research –Basic Science Series Vol. (21) No (8) 1999

Photoemission Yield Spectroscopy of $Cd_{1-x}Fe_xSe$ Crystals

Dr. Ammar SAREM[*]

(Received 11/2/1999, Accepted 21/4/1999)

❒ ABSTRACT ❒

The electronic structure of $Cd_{1-x}Fe_xSe$ *crystals with concentrations of* $x=0.0$ *and* $x=0.1$ *has been investigated by photoemission yield spectroscopy (PYS) in the photon energy range from 5 to 12 eV. The surfaces* $(11\bar{2}0)$ *were obtained by cleavage in ultrahigh vacuum conditions at pressure* 5.10^{-9} *Torr. The photoemission spectra are characterized by a main edge corresponding to the valence band edge of CdSe (ionization energy* E_T*) and the lower energy edge* E_S *corresponding to the contribution of the Fe3d to the valence band of* $Cd_{1-x}Fe_xSe$*. Valence band photoemission spectra of* $Cd_{0.9}Fe_{0.1}Se$ *exhibit Fe-derived peak at 0.58 eV above the valence band edge of CdSe. Annealing of the surface (room temperature* 5.10^{-9} *Torr) leads to a partial washing out of the structure close to ionization energy edge region and to decrease of the ionization energy* E_T*, energy threshold* E_S *and the crystal affinity* χ*. Also, it found that, the surfaces freshly cleaved with Fe3d atoms are easily interacted with ambient atmosphere rather than for CdSe surfaces crystal.*

---

[*] Associate professor, Department of Physics, Faculty of Science,Tishreen University, Lattakia, Syria.

مجلة جامعة تشرين للدراسات والبحوث العلمية - سلسلة العلوم الأساسية المجلد (21) العدد (8) 1999
Tishreen University Journal for Studies and Scientific Research –Basic Science Series Vol. (21) No (8) 1999

مردود الإصدار الكهرضوئي للبلورات $Cd_{1-x}Fe_xSe$

الدكتور عمّار صارم*

(ورد إلى المجلة في 1999/2/11، قبل للنشر في 1999/4/21)

☐ الملخّص ☐

دُرست البنية الإلكترونية للبلورات $Cd_{1-x}Fe_xSe$ بتراكيز $x=0.0$ و $x=0.1$، بوساطة مردود الإصدار الكهرضوئي (PYS)، في مجال طاقة فوتون (5-12 eV). وقد تم الحصول على السطوح النظيفة $(11\bar{2}0)$ بوساطة قص البلورات، في شروط الخلاء العالي، وتحت الضغط 5.10^{-9} Torr. لقد تميزت منحنيات أطياف الإصدار الكهرضوئي بحد رئيسي مطابق لحد عصابة تكافؤ البلورة CdSe (طاقة التأين E_T)، وحد طاقة أدنى E_S مطابق إلى مشاركة سويات الحديد Fe3d في عصابة تكافؤ البلورة $Cd_{1-x}Fe_xSe$. وقد أظهرت أطياف الإصدار الكهرضوئي من عصابة التكافؤ للبلورة $Cd_{0.9}Fe_{0.1}Se$ وجود قمة فوق حد عصابة تكافؤ البلورة CdSe بحوالي 0. 58 eV. إن إخضاع السطح للتغيرات مع الزمن (في درجة حرارة الغرفة وتحت الضغط 5.10^{-9} Torr) أدت، جزئيا، إلى تعريض البنية بالقرب من منطقة حد طاقة التأين، وإلى تناقص قيم طاقة التأين E_T وعتبة الطاقة E_S والألفة البلورية χ. كما لوحظ –أيضا– أن سطوح البلورات النظيفة والمصقولة حديثا بوجود ذرات الحديد Fe3d، تتفاعل مع الوسط المحيط بشكل أسهل مما تفعله سطوح البلورات النظيفة والمصقولة حديثا بدون وجود ذرات الحديد.

تم إجراء القياسات التجريبية في معهد الفيزياء في أكاديمية العلوم البولونية عام 1998.

---

* أستاذ مساعد في قسم الفيزياء – كلية العلوم – جامعة تشرين – اللاذقية – سورية.

1. Introduction

Semimagnetic semiconductor (*SMSC*) or diluted magnetic semiconductor (*DMS*) based on *II-VI* or *IV-VI* semiconductor compound was created due to the introduction of transition metal (*TM*) like *Mn, Fe* or *Co* on the site of *Hg, Cd* or *Zn* cation in *HgS, CdSe* or *ZnTe* [1]. The introduction of transition metal on the site of group *II* or *IV* cation leads to the new electronic properties appear to be a result of the *Mn* ($3d^5$), *Fe* ($3d^6$) or *Co*($3d^7$) electron contribution to the electronic structure of the valence band in the volume as well as in the surface, and it is responsible for disorders: crystalline (local structure), magnetic (introduction of magnetic ions) and chemical (a foreign ion with valence electrons), and brings a strong interaction between the (*d*) electrons and the valence electrons of *II-VI* or *IV-VI* semiconductor crystals [2]. These materials have attracted a great deal of attention as a new group of semiconductors, mainly from the point of applications in infrared detectors, lasers and other optical devices [2,3].

The present work is strongly stimulated by the recent efforts done to obtain and understand the electronic properties of the surface and the region close to the surface with semimagnetic semiconductors $Cd_{1-x}Fe_xSe$. Investigation of the electronic structure on $Cd_{1-x}Fe_xSe$ $(11\bar{2}0)$ surfaces freshly cleaved in *UHV* conditions, and of changes of this structure under annealing at room temperature ($p=5.10^{-9}$ Torr) are presented.

2. Experimental conditions

The photoemission yield spectroscopy measurements were carried out on $Cd_{1-x}Fe_xSe$ crystals grown by the modified Bridgman method in the Institute of Physics, Polish Academy of Sciences. Samples with *Fe* concentrations of x=0.0 and x=0.10 were studied. *X-ray* diffraction measurements confirmed that the crystal structure of the samples used were hexagonal wurtzite, and showed that the Fe^{2+} atoms substitute for Cd^{2+} atoms [4,5]. The $Cd_{1-x}Fe_xSe$ crystals are n-type [5]. The clean surface of the parallelepipedic sample was obtained by cleavage under *UHV* conditions ($p=5.10^{-9}$ Torr), directly in the photoemission chamber. It gave a clean and smooth surface, and generates a lot of defects (e.g. small density of steps). The crystals have been cleaved in the $(11\bar{2}0)$ plane with dimensions 4x4 mm^2, and investigated *in situ* at room temperature.

Figure(1) illustrates the wurtzite structure together with the surface geometrical structure of the $(11\bar{2}0)$ surface of the $Cd_{1-x}Fe_xSe$ crystals [6].

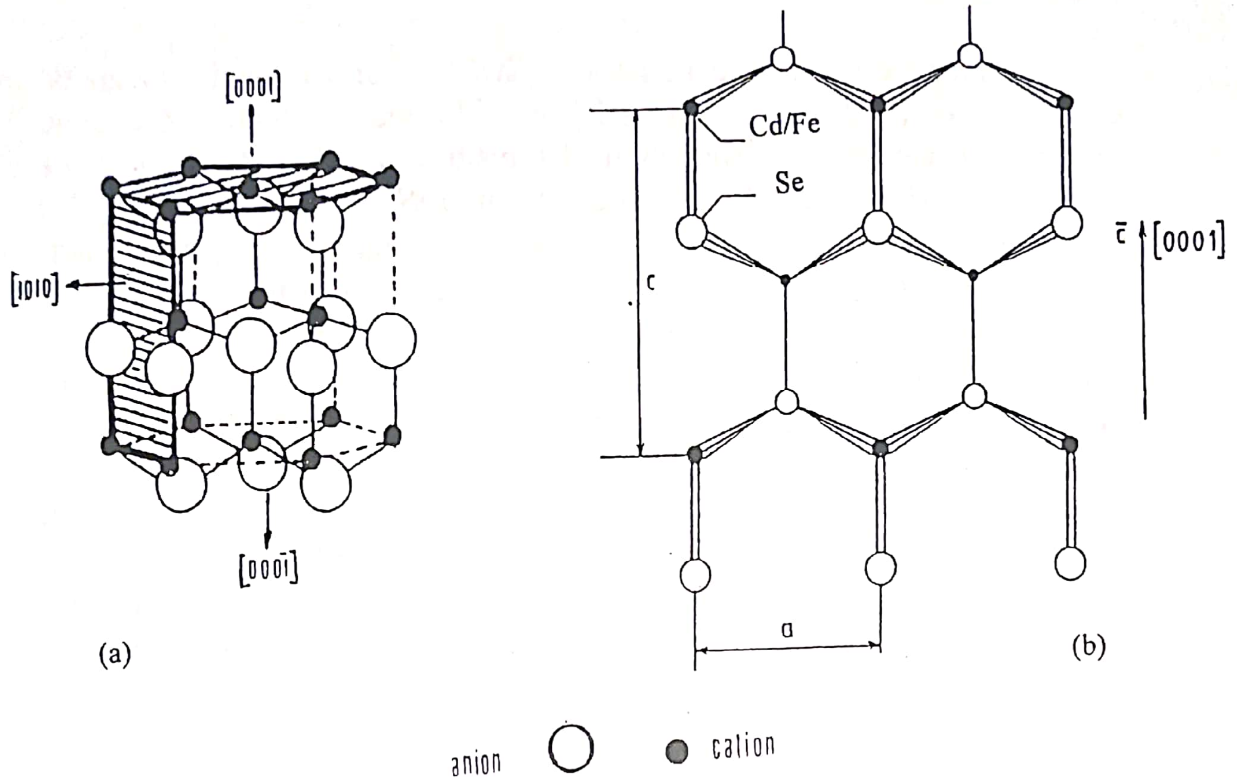

Fig (1). (a) Wurtzite structure of the $Cd_{1-x}Fe_xSe$ crystals, (b) The surface geometrical structure of the $Cd_{1-x}Fe_xSe$ (11$\bar{2}$0) surface.

The experiment was performed using vacuum ultraviolet radiation with available photon energy in the range 5-12 eV, obtained from the Seya-Namioka type monochromator, with a flowing hydrogen low-pressure discharge lamp ($p= 10^{-2}$ Torr) as a light source. A *LiF* window separates the monochromator from the stainless steel *UHV* chamber. A photomultipliers with luminophor (sodium salicylate deposited on a glass plate) was used as a light detector. The photoemission current was measured by an *ECCO* vibrating reed electrometer (sensitivity 10^{-15} *A*). The energy width of the incident light was less than 0.05 eV [7]. The experimental set-up described enables us to measure the photoemission yield for a wide energy range. However, since our work reported in this paper was devoted to investigate the electronic states in the ionization energy edge region, the described procedure of differentiation was applied to the relatively small part of the spectrum experimentally observed (about 1.5 eV just above the valence band edge).

3. Results and discussion

Figure (2) presents the typical photoemission yield spectra obtained for $Cd_{1-x}Fe_xSe$ crystals in the range energy 5-12 eV. The lowest curves (*Nr.1*) correspond to the freshly cleaved $(11\bar{2}0)$ surfaces, and the following curves (*Nr.2* and *Nr.3*) concern the same surfaces, which undergo for annealing process.

With replacement the cadmium atoms by iron atoms in the crystals, it was observed from curves comparison $Y(h\nu)$, that the photoemission yield from $Cd_{0.9}Fe_{0.1}Se$ is, almost, about two orders less yield from obtained for *CdSe*. The spectra are characterized by a main edge corresponding to the valence band density of states of *CdSe*. At photon energies above 6.5 eV dips in the spectral dependence of the photoemission yield (*Fig.2*) correspond well to the positions of the peaks of the reflectivity spectra (for *CdSe* at 7.4, 8.7, 9.75 and 10.60 eV, whereas for $Cd_{0.9}Fe_{0.1}Se$ at 7.30, 8.40, 9.45 and 10.60 eV) measured for these samples [8].

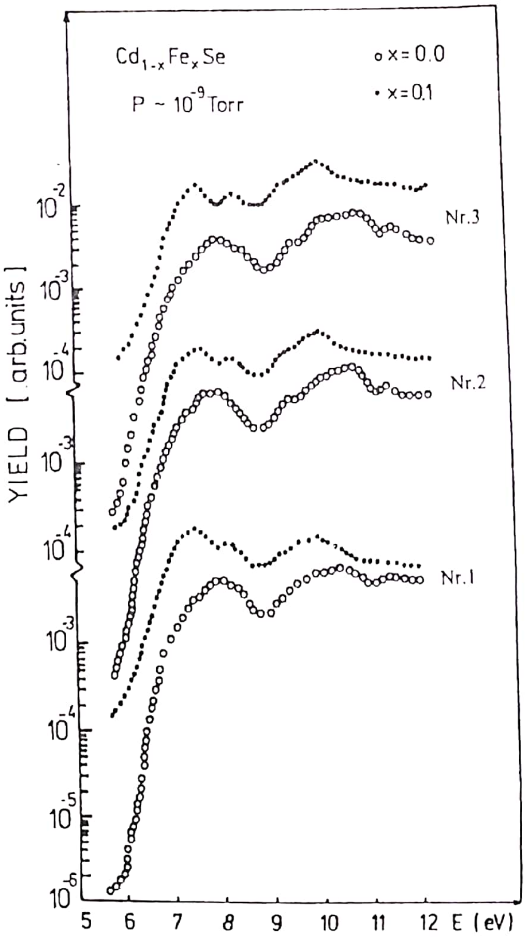

Fig (2). Semilogarithmic plots of the photoemission yield spectra $Y(h\nu)$ for *CdSe* and $Cd_{0.9}Fe_{0.1}Se$ $(11\bar{2}0)$ surface cleaved in *UHV* conditions and annealed at room temperature for various times at a pressure 10^{-9} Torr: curve (*Nr.1*) - 45 min; (*Nr.2*) – 4 days; (*Nr.3*) – 8 days.

The contribution of *Fe* electrons into the crystal lead to appearance of an additional maximum (7.9 eV) below the edge of the valence band and to disappearance yield minimum corresponding to energy about (11eV). The room temperature annealing of the freshly cleaved surface in $p=5.10^{-9}$ Torr leads to: a change of the photoemission yield spectra in the whole range of $h\nu$ energies; a shift of the main edge (E_T) to lower energies, also, an increase of the maximum corresponding to energy (7.9 eV) with time.

Figure (3) presents the photoemission yield spectra $Y^{1/2}$ for *CdSe* and $Cd_{0.9}Fe_{0.1}Se$ crystals in the range of $h\nu$ energies close to threshold energy region. For *CdSe* crystal, the spectra are characterized by a one edge corresponding to the ionization energy (E_T). While for $Cd_{0.9}Fe_{0.1}Se$ crystal, the contribution of the iron ions lead to the appearance two edges. The first one (E_S) corresponds to contribution of the *Fe* states in the *CdSe* crystal, whereas the second edge corresponds to the ionization energy (E_T) [6] and it is shifted to lower energies (for freshly cleaved surfaces E_T=6.10 eV for *CdSe,* while E_T= 5.70 eV for $Cd_{0.9}Fe_{0.1}Se$).

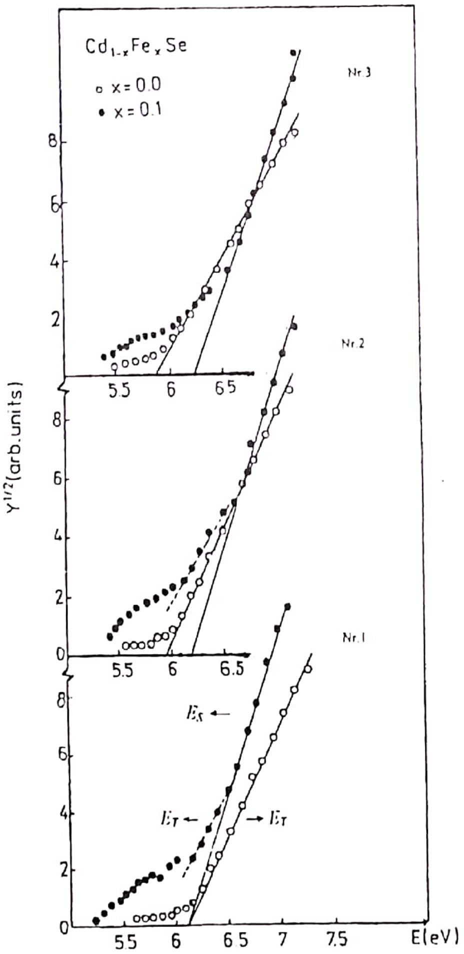

Fig (3). Energy photoemission threshold curves calculated from expression $Y(h\nu) = (h\nu - E_T)^2$

As is apparent (*Fig.3*), in the threshold energy region all of the measured curves have the same character and can be approximated by the equation: $Y(h\nu) = (h\nu - E_T)^2$. This kind of dependence corresponds well to the theory introduced by Kane [9] and Ballantyne [10] for the case when the photoemitted electrons originate from the valence band states in the volume and are due to indirect optical transitions. If the energy gap E_g is taken as 1.80 eV for *CdSe* and 1.92 eV for $Cd_{0.9}Fe_{0.1}Se$ [8], it gives an electron affinity ($\chi = E_T - Eg$) [11]. The table presents values of the energy threshold E_T, E_S and χ for both crystals.

Table of the values of energy photoemission threshold E_T, E_S and χ for CdSe and $Cd_{0.9}Fe_{0.1}Se$ crystals.

Crystal	Nr. Curve	Time	$E_T(eV)$	$E_S(eV)$	χ (eV)
CdSe	1	*45 min*	*6.10*	-	*4.30*
	2	*4 days*	*5.95*	-	*4.15*
	3	*8 days*	*5.90*	-	*4.10*
$Cd_{0.9}Fe_{0.1}Se$	1	*45 min*	*5.70*	*6.10*	*3.78*
	2	*4 days*	*5.60*	*6.17*	*3.68*
	3	*8 days*	*5.55*	*6.22*	*3.63*

The energy in figure (4) is measured from the top of the valence band, that is, for each sample the experimental curve is shifted to overlap at high yields with the curves for other samples. For the sample $Cd_{0.9}Fe_{0.1}Se$, the lower energy threshold is about 0.58 eV below the higher one. The lower part of figure (4) shows schematically the position of the additional density of states given by $Fe^{2+}(3d^6)$ which is responsible for the lower energy photoemission threshold. This fact indicates that the $Fe^{2+}(3d^6)$ appears as an additional density of states, which is localised higher than the top of the valence band. Therefor, the $Fe^{2+}(3d^6)$ states must be locates over the top of the valence band, that is, the $Fe^{2+}(3d^6)$ states locate in the forbidden energy gap (*see figure* 5). This agrees well with the results published previously, Baranowski and Langer [12] placed the $Fe^{2+}(3d)$ level in doped *CdSe* with *Fe* concentration of 1.5×10^{19} cm^{-3} at 0.63±0.02 eV above top of the valence bands from their optical-absorption measurements. For *Fe*-doped *CdSe* sample with concentration up to x=15 %(5×10^{21} cm^{-3}), Mycielski *et al.* [13] reported the $Fe^{2+}(3d)$ level at 0.58±0.03 eV above the valence-band maximum from the analysis of the optical-absorption spectra.

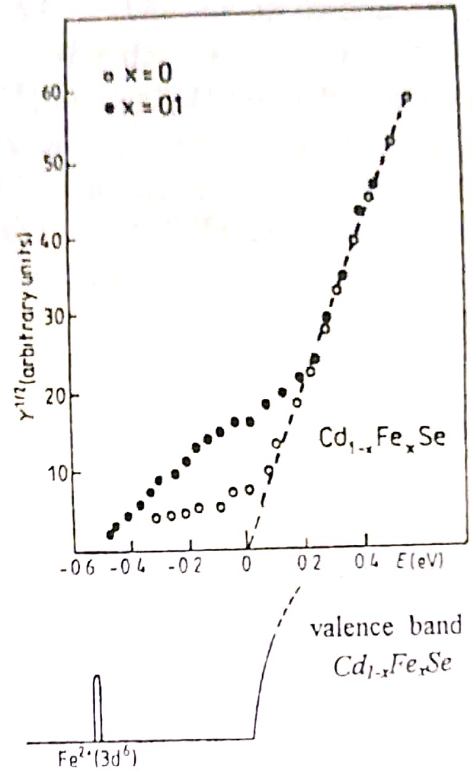

Fig (4). Experimental curves of the photoemission yield for *CdSe* and $Cd_{0.9}Fe_{0.1}Se$ crystals ($T=300$ k). The lower part shows schematically the position of the additional density of states given by $Fe^{2+}(3d^6)$.

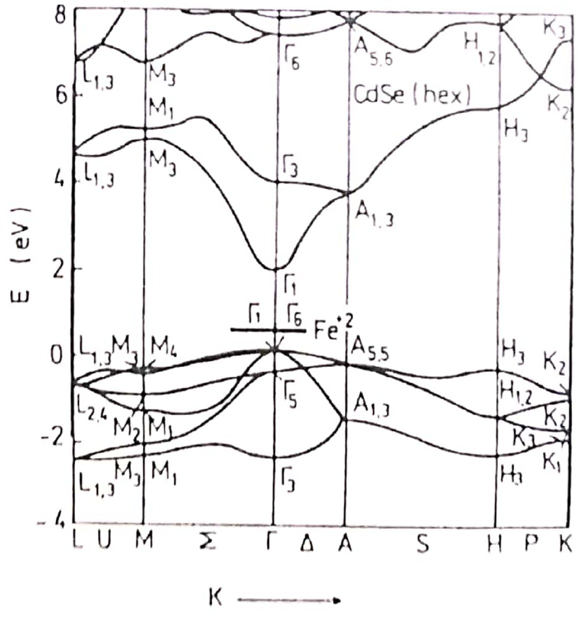

Fig (5). Band structure of the wide-gap wurtzite $Cd_{1-x}Fe_xSe$ crystals near the Γ point, showing the position of the $Fe^{2+}(3d^6)$ state.

According to the electronic band structure diagram (*Fig.5*) [14], in the energy photoemission threshold region, the ionization energy (E_T) may be corresponding to the transitions from the Γ point. The $<11\bar{2}0>$ direction in the reciprocal lattice (/Γ-M/ line in Brillouin zone) corresponds to the momentum of the electrons perpendicular to the cleavage surface $(11\bar{2}0)$ [6]. Thus, the electrons situated on the /Γ-M/ line states can escape easily into the vacuum [9,10].

When the scattering mechanism appears, it is possible that more electrons can reach the best $<11\bar{2}0>$ direction [15]. This mechanism changes the shape of the photoemission yield curves and changes the threshold position [15,16,17]. In our experiments, the scattering effect can be induced by gradual changes of the crystal surfaces and this process will be responsible for the different behavior of the two thresholds. These facts enable us to ascribe, in the case $Cd_{0.9}Fe_{0.1}Se$ crystal, the additional threshold E_S to the optical direct transitions H-H, whereas the threshold E_T in both *CdSe* and $Cd_{0.9}Fe_{0.1}Se$ crystals, to the optical indirect transitions from the Γ point [14]. Therefor, the threshold energy E_S (for x=0.1) corresponds to the density of states below the edge of the valence band in the H point in Brillouin zone.

The collision effect is expected to be similar for the all samples. Thus, the differences between the stabilized photoemission curves from the different $Cd_{1-x}Fe_xSe$ samples are due to the presence of the Fe electrons. The differences between thresholds E_S and E_T increase during the annealing process from 400 meV energy for curve *Nr.1* to energy 670meV for curve *Nr.3* (*see table*).

Figure (6) illustrates the evolution of the distribution of states density observed for $Cd_{1-x}Fe_xSe$ $(11\bar{2}0)$ surfaces with x=0.0 and x=0.1; the derivative of the photoemission yield curves presented in *Fig (2)* . Since Photoemission Yield Spectroscopy (*PYS*) consists in measuring the total photoemission current as a function of photon energy, the number of electrons recorded at a particular energy of light integrates the contribution of all transitions from the occupied states from the Fermi level energy down to $E_F - h\nu - \varphi$ (φ is the work function of the sample). If we assume that the transition matrix elements and the escape function of electrons do not depend on the energy of light, it is possible to consider the first derivative of the photoemission yield versus energy ($dY/d\,(h\nu)$) as an effective density of states. If we consider a small energy this approach usually turns out to be reasonable [18,19]. Thus, the structure of the effective density of states shown in *Fig (6)* appears in the edge E_T region. This structure is partly washed out during the annealing process.

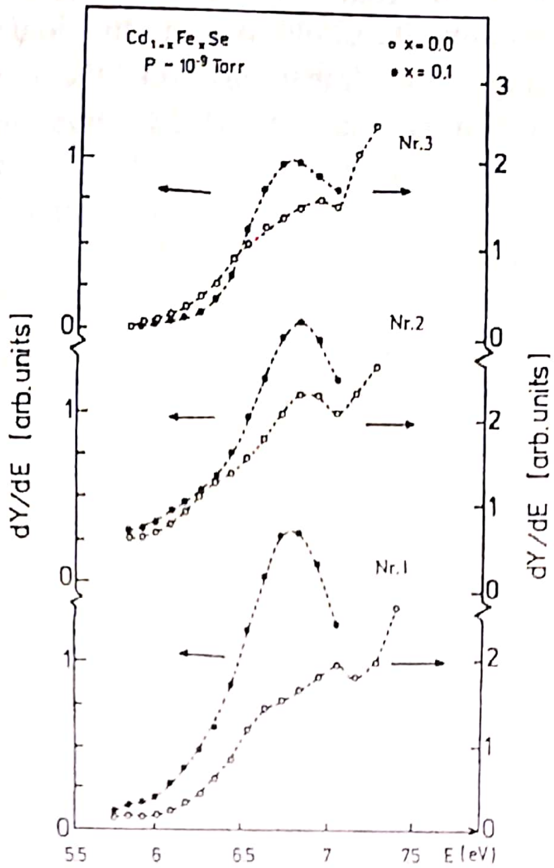

Fig (6). Linear plots of the effective density of states; the derivative of the photoemission yield curves presented in *Fig (2)* in the ionization energy edge region for $Cd_xFe_{1-x}Se$ $(11\bar{2}0)$ (with x=0.0 and x=0.1) surface cleaved in *UHV* and annealed at room temperature at 5.10^{-9} Torr

As a result of the annealing process, the change of the effective density of states distribution is observed. This change of the yield photoemission spectra may be caused by a change of the crystalline structure of the reconstruction surface as well as by a change of the chemical composition of the crystal surface region due to adsorbed atoms during annealing. Interaction with the ambient atmosphere ($p=5.10^{-9}$ Torr) was the phenomenon that enabled us to distinguish the surface related features in the spectra. It was already shown that H_2O, CO_2 , CO, N_2 and O_2 molecules occur on the real surface of the *II-VI* compounds. This set of compounds corresponds well to the low-pressure atmosphere in the *UHV* chamber [20,21]. Thus we can expect that the adsorption of these gases occur during the annealing of the cleaved sample at room temperature at 5.10^{-9} Torr. This, together with the surface electronic structure of the crystals determines the shape of the spectra.

For the freshly cleaved *CdSe* and $Cd_{0.9}Fe_{0.1}Se$ crystals (the lowest curves in *Fig (6)*) the valence band with an ionization energy and band of states sensitive to the gas adsorption (see the other curves in *Fig (6)*) are observed. In the *CdSe* $(11\bar{2}0)$ sample, appears two maxima corresponding to the 6.6 and 7.05 eV energies. The *CdSe* $(11\bar{2}0)$ has been investigated by both experimental and theoretical methods [15] and showed that, in the valence band region at $h\nu$ above E_T no evidence has been found for the presence of surface states on the clean surface. Thus, the broad band in the distribution of the density of states observed in the energy region from 6.2 to 7.1 eV must be connected mainly with the defect induced surface states. The influence of the ambient atmosphere leads easily to a shift of the spectrum towards the lower energies. A change of the relative heights of the maxima is observed, too. It may be that the adsorbed atoms interact with the electrons close to the surface, leading to the formation of new band electronic surface states. Further adsorption causes independent changes in the position of the valence band edge with respect to the other states. For $Cd_{0.9}Fe_{0.1}Se$ crystal the contribution of the Fe3d electrons leads to appearance of a structure at the ionization energy region (see the highest curves in *Fig (6)*), and to different behavior upon annealing than was the case for *CdSe* crystal. The additional peak of the effective density of states appears at energy of $h\nu=6.70$ eV due to the presence of iron [22,23]. The reaction of the adsorbed atoms with the states on the surface, appearing during surface annealing, can lead to a filling up of the states above the edge of the valence band [23,24], and to a decrease of the energy threshold E_S. Also, a change of the relative height of the additional peak is observed and may be expecting of *FeO* dipole layer formation [20]. The shift of the main edge (E_T) to lower energies corresponds to a change of the *CdSe* affinity.

4. Conclusion

Photoemission yield spectroscopy (*PYS*) studies of the $Cd_xFe_{1-x}Se$ $(11\bar{2}0)$ (with x=0.0 and x=0.1) surface cleaved in *UHV* and annealed at room temperature at 5.10^{-9} Torr were found to be very useful for evaluating the electronic properties of this surface. They made possible the determination of the surface band structure parameters: ionization energy E_T, energy threshold E_S and surface electron affinity χ. Moreover they confirmed the existence on this surface of occupied electronic states. These states are sensitive to adsorption of gases on the surface in the case of the $Cd_{0.9}Fe_{0.1}Se$ crystal rather than *CdSe* crystal. The changes of the valence band edge and energy threshold E_S positions on the surface were observed during the adsorption, too.

REFERENCES المراجع

[1]- J.K. Furdyna, 1988, *J. Appl. Phys.* Vol 64, pp. R64.

[2]- J.K. Furdyna and J. Kossut, Diluted Magnetic Semiconductors (*DMS*), Vol 25, 1988, in the series *Semiconductor and Semimetals*, Eds. R.K. Willardson, A.C. Beer, Academic Press, Boston (MA).

[3]- J. Kossut and W. Dobrowolski, in: *Handbook of Magnetic Materials*, Ed. K.H.J. Buschow, Vol 7, 1993,North-Holland, Amsterdam.

[4]- K. Smith, J. Marsella, R. Kershaw, K. Dwight, A. Wold, 1988, Mater. Res.Bull. Vol 23, pp. 1423.

[5]- E.Dynowska, A.Sarem, B.A.Orlowski, A.Mycielski, 1990, Mater. Res. Bull. Vol.25, pp.1109.

[6]- Kjell Magnusson, 1987, *Ph.D. Thesis* Lund, Sweden.

[7]- A. Sarem, B.J. Kowalski, B.A. Orlowski, 1988,*Surface.Sci* Vol.213, pp.277.

[8]- A. Sarem, B.J. Kowalski, B.A. Orlowski, 1990, *J. Phys.:Condens. Matter* Vol 2, pp. 8173.

[9]- E.O.Kane, 1962,*Phys.Rev.* Vol. 127, pp.131.

[10]- J.M. Ballantyne, 1972,*Phys.Rev.* Vol.6, pp.1436.

[11]- B.A. Orlowski, J.P. Lachrme, S.Bensalah and C.A. Sebenne, 1988, *Surface.Sci lett.*Vol.200, pp. L460.

[12]- J.M.Baranowski and J.M.Langer, 1971, *Phys. Status Solidi* Vol. B 48, pp. 863.

[13]- A.Mycielski, 1988, *J. Appl. Phys.* Vol.63, pp. 3279.

[14]- T.K.Bergstresser,M.L.Cohen, 1967, *Phys.Rev.* Vol. 164, pp.1069.

[15]- Y.R.Wang, C.B,Duke, K.Stevens, A.Kahn, K.O.Magnusson, S.A. Flodstrom, 1988, *Surface. Sci,* Vol.206, pp. L 817.

[16]- O.Mhamedi, F.Proix, and C.A. Sebenne, 1988, J.Vac.Sci. Technol. Vol. A6 (2), pp.193.

[17]- F.Proix, O.Mhamedi, and C.A. Sebenne, 1988, J.Vac.Sci. Technol. Vol. A (2), pp.199.

[18]- C.A.Sebenne, 1977, *IL Nuovo Cimento* Vol.39B, pp.768.

[19]- J.Szuber. 1983, *Surface. Sci,* Vol. 33.

[20]- I.A.Kirovskaya, 1989, *Inorg,Mater,* Vol.25, pp.1246.

[21]- I. Adriamanantenasoa, J.P. Lachrme, C.A. Sebenne, 1986 J.Vac.Sci. Technol.Vol.A5 (4), pp. 902.

[22]- Y. Ueda, M.Taniguchi, T. Mizokawa, A. Fujimori, I. Souma, Y.Oka 1994, *Phys.Rev B.* Vol.49, pp.2167.

[23]- B.A. Orlowski, B.J. Kowalski, N.Barrett, D.Martinotti. C.Guillot, J.P.Lachrme, C.A.Sebenne, 1996, *Appl. Surf.Sci* Vol.104/105, 282.

[24]- B.J. Kowalski, B.A. Orlowski, W. Szuszkiewicz, B.Witkowska, and R.L.Johnson, 1995, Acta Phys.Pol. Vol 88, pp. 791.