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Materials Sciences Division

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December 1996

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RESONANT INELASTIC SCATTERING IN DILUTE MAGNETIC SEMICONDUCTORS BY SOFT X-RAY FLUORESCENCE SPECTROSCOPY

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Abstract

Soft x-ray fluorescence (SXF) provides a means of measuring the element and angular momentum selective valence band density of states in complex materials. Recent studies have demonstrated that SXF excited near the absorption threshold generates an array of spectral features that depend on the nature of the material, particularly on the localization of excited states in s and d -band solids. The current interest in dilute magnetic semiconductors (DMS) remains highly motivated by recent prospective applications, especially in optoelectronics. The Mn and S -L resonant x-ray emission spectra of $Zn_{1-x}Mn_xS$ (where x=0.2) and MnS were measured as the energy of the exciting radiation was tuned across the S and Mn -$L_{3,2}$ absorption edges of these compounds. Strong resonance peaks in Mn -L emission spectra and the systematic appearance of new spectral features in S -L emission spectra were observed. Partial substitution of Zn by a magnetic Mn ion results in strong hybridization of the Mn 3d orbitals with the sp band of the host semiconductor. A detailed study of resonant inelastic scattering in the vicinity of the S and Mn -$L_{2,3}$ absorption edges of these DMS is presented.

Introduction

As modern, technologically important materials have become more complex, element specific techniques have become invaluable in studying the electronic structure of individual components from the bulk system. Soft x-ray fluorescence (SXF) and absorption (SXA) spectroscopies provide a unique means of measuring element and angular momentum selective density of states for the valence and conducting bands in complex materials. SXF spectra reflect the partial density of states of the *occupied* valence band due to the dipole selection rule. The configurational interaction in the core excited state is particularly important in the transition and rare-earth metals compounds where the unfilled localized d or f orbitals take part in the screening of the core hole potential through hybridization with the valence bands [2] and lead to considerable narrowing of the observed spectra [3].

SXA spectra reflect the partial density of states of an *unoccupied* band due to the dipole selection rule. X-ray absorption and the decay of the excited state through x-ray emission are generally assumed to be two independent single-photon processes. Recent studies, however, have demonstrated that SXF excited near the absorption threshold generates an array of spectral features that depend on the nature of the materials, particularly on the localization of excited

states in s and d -band solids and that these two processes can not be treated independently [4-6].

In this paper we present the Mn and S -L resonant emission spectra of $Zn_{1-x}Mn_xS$ (where x=0.2) and MnS as the energy of the exciting radiation is tuned across the Mn and S -$L_{2,3}$ absorption edges, along with the resonant excited spectra from elemental Mn as a reference. The $Zn_{1-x}Mn_xS$ compounds belong to the class of so called dilute magnetic semiconductors (DMS). The current interest in DMS remains high due to recent and prospective applications, especially in optoelectronics. The partial substitution of Zn by a magnetic ion of Mn results in strong hybridization of the 3d Mn states with the sp band states of the host semiconductor. This inevitably leads to modification in the crystal, electronic, and magnetic structure. Direct evidence of modification in the crystal structure has been shown by EXAFS (extended x-ray-absorption fine structure) studies which found different bond lengths between each type of cation and the anion [7-9]. Evidence of modification in the electronic structure has been reported by photoelectron, reflectivity, and XANES (x-ray-absorption near-edge structure) measurements [10-13] . In recent studies of Mn and S -L absorption edges [14], strong evidence of Mn 3d antibonding states participating in the formation of a metal-S bond was reported. A sharp resonance at the Mn $L_{2,3}$ emission in MnS and $Zn_{1-x}Mn_xS$ compounds is observed, indicating the existence of well-localized 3d antibonding states while only systematic appearance of new structure is detected in the spectra of elemental Mn and in the S L-emission of $Zn_{1-x}Mn_xS$ compounds.

Experimental

High resolution x-ray emission spectra were recorded on the Advanced Light Source (ALS) Beamline 8.0, a 5.0 cm period undulator beamline with a spherical grating monochromator operating between 70 eV and 1200 eV. The energy resolution of the monochromator was set to be about 0.3 eV during these measurements. The soft x-ray fluorescence endstation includes a Rowland circle grating spectrometer coupled to a photon-counting area detector [15]. All the SXF measurements reported in this work were made with a 100 μm entrance slit for the spectrometer and using the 1500 lines/mm, 10 meter radius grating. At the Mn L region, the resolution of the spectrometer is approximately 1.0 eV.

The high resolution x-ray absorption spectra at the $L_{3,2}$ edges of manganese and sulfur in $Zn_{1-x}Mn_xS$, MnS and Mn were measured at ALS Beamline 6.3.2, a bend magnet beamline [16] operating in the 50 - 1000 eV region. This beamline is equipped with a Hettrick-Underwood type varied line space (VLS) grating monochromator and various novel mechanical design features resulting in high performance in energy resolution, throughput, stability, and ease of operation. The resolving power of the monochromator, $E/\Delta E$, was 1700 and 1000 at the $L_{3,2}$ edges of S and Mn, respectively. This energy resolution was sufficient to distinguish the fine changes in the spectra as a function of Mn content. Increasing the resolving power up to ~4000 did not result in resolving new structures in the absorption spectra and significantly decreased the signal intensity.

Results and Discussion

The Mn -L_3 absorption spectra of Mn, MnS, and $Zn_{1-x}Mn_xS$ (where x=0.33) are shown in Figure 1. The L_3 absorption edge of all the spectra are similar, each having at least three resolved features. For elemental Mn, the main peak occurs at 639.5 eV and the smaller features at 1.5 eV and 3.5 eV above the main peak. In spite of the natural width of the 2p level which

considerably broadens the absorption spectrum and smears the sharp features the of conduction band, the Mn L edge from the ternary alloy is much narrower than for elemental Mn. This suggests that the Mn 3d conduction states exhibit much more localized character in the ternary alloys than for elemental Mn.

The Mn $L_{2,3}$ - emission spectra from elemental Mn are presented in Figure 2. The excitation energy was tuned from 629 eV to 669 eV. This energy range can be divided into resonant and non-resonant regimes. In the resonant energy regime, core electrons are excited by photons to unoccupied states just above the Fermi level, E_f. The absorption and emission events are coupled in this regime, and this coupling manifests itself, depending in part on the degree of localization of the states above E_f in the material. Selective excitations to these states provide new opportunities for studying localized systems. In the non-resonant regime, the energy of the radiation incident on the sample is far above E_f and the processes of absorption and emission are independent. The emission spectra in this region no longer depend on the energy of the exciting radiation.

Upon examination of the intensity and structure of Mn emission spectra as a function of the photon excitation energy close to the L_3 edge (Figure 2), a systematic increase of intensity is observed up to 638 eV excitation energy. The intensity of the L_3 emission peak then slowly decreases until a rapid increase appears at 642 eV (incident energy). The next minimum occurs at 643 eV excitation energy, which is above the L_2 absorption edge. The resonance of the L_2 is stronger than for the L_3, reaches a maximum when the excitation energy is 648 eV, and then slowly loses intensity with increasing excitation energy. At an incident energy of 654 eV, the L_2 to L_3 ratio is already close to 1:2 and resembles the emission spectrum characteristic for the non-resonant regime where the exciting energy is far above E_f. The observed changes in intensity in the resonant regime do not indicate strong coupling between absorption and emission processes. Therefore, the final states in Mn have rather delocalized character, similar to graphite or diamond [4, 5].

The series of emission spectra from MnS is presented in Figure 3. The excitation energy was again tuned from 629 eV to 669 eV, as in the case of elemental Mn. In addition, spectra were also recorded with excitation energies of 679 eV and 689 eV. The shape of the spectra in the resonant regime differ considerably as compared to the spectra of elemental Mn. At an energy of 637 eV, the well resolved two peak structure of the L_3 spectrum is easily distinguishable. The maximum intensity at the L_3 emission was again observed at 638 eV. The double peak structure disappears after increasing the excitation energy by 1 eV and the overall intensity of the resonant spectra start to decrease. Similar to elemental Mn, the intensity then increases to a maximum at an excitation energy about 3 eV above the resonant maximum. The intensity of the L_3 emission then decreases considerably as the excitation energy increases above the energy of the L_2 absorption threshold. At 648 eV (incident energy), a strong resonance on the L_2 emission was observed. With the further increase of the exciting radiation energy the intensity of the L_2 emission considerably decreases, reaching a minimum at 654 eV. The appearance of the two peaks at the resonant excitation of L_3 spectra in MnS indicates a very localized character of the Mn 3d states in the conduction band of MnS.

Upon examination of the structure of the resonant emission spectra from $Zn_{1-x}Mn_xS$ DMS compounds (where x=0.2, 0.3), a very unusual and interesting behaviour of the spectral shape is observed. For the compound with a smaller amount of Mn (x=0.2), the resonant emission with the maximum intensity appears at an excitation energy of 636 eV while, at 635 eV, no emission intensity was detected (Figure 4). The resonant spectrum, with three well-resolved peaks, is significantly different from the spectrum obtained for "normal" emission

(excitation energy of 685 eV). Increasing the energy of the excitation radiation to 637 eV results in a decrease in the intensity of the third peak, and an increase in intensity of the second peak. At the excitation energy of 639 eV, the three peak structure has disappeared, the intensity of the L_3 spectra is decreased, and the L_2 emission has appeared. Similar to both the Mn and MnS spectra, the L_2 resonance appears at 648 eV, but is not as pronounced for $Zn_{0.8}Mn_{0.2}S$. A similar dependence of Mn emission spectra on excitation energy was observed for x = 0.3 (data not shown).

ZnS is a semiconductor with a wide gap. The substitution of Mn for Zn adds well-localized 3d states which have character similar to the well-localized excitonic states observed in an insulator. Therefore, we suspect coupling between the hole and the excited electron. These measurements of Mn L emission, obtained as a function of excitation energy, provide evidence that for Mn bound to S the Mn 3d conduction states exhibit much more localized character than in the case of elemental Mn. As described above, the absorption spectra support this trend. The significant modification of the resonant emission spectra occurs in a very narrow range of excitation energy (3 eV), indicating that the coupling between emission and absorption events takes place only for states close to the bottom of the conduction band. These states are reached only by direct transition from the core level. We do not find any indication of population of these states for higher energies due to shake-up processes as is observed for materials which do not have well localized conduction states [17]. When the excitation energy is increased to 639 eV, the spectra exhibit a single peak characteristic for a 3d transition metal and, with further increasing of the excitation energy, the structure of the L_2 emission appears. A very sharp resonance occured at the L_2 emission of MnS presented in figure 3. No additional structure was observed, except for a pronounced increase of the L_2 emission line intensity. This increase was also found for elemental Mn at the excitation energy of 648 eV where the intensity of the L_2 emission is two times stronger than the L_3 emision feature. In the case of MnS, the intensity of the L_2 emision feature is more than three times higher than the intensity of L_3 emision. The intensity ratio of these two lines is related to the probability of core hole decay *via* different channels. The strong resonance at the L_2 emision indicates that decay of the core hole *via* non-radiative transitions such as Auger and Coster- Kronig is less probable at the resonant energy. When the excitation energy increases, the L_2 line intensity decreases, indicating a successive opening of the Auger decay channel.

The lack of additional emission features at the L_2 resonance indicates that there is very little coupling between the absorption and emission processes for the L_2 resonant region. Since Raman scattering processes conserve the crystal momentum, the spin of the empty 3d states must be the same as the spin of the electrons from the $2p_{3/2}$ shell. For the L_3 resonant emission, the spectator electron strongly couples to the valence hole whereas, for a $2p_{1/2}$ electron with opposite spin, there is no coupling. The 3d levels of Mn(II) are half filled and all of the electrons have parallel spin. The lack of the coupling between emission and absorption of the L_2 resonant region yields direct evidence of the importance of spin direction for hole - spectator electron interactions.

In Figure 5, the sulfur $L_{2,3}$ soft x-ray emission spectra of $Zn_{1-x}Mn_xS$ (where x=0.05, 0.2, 0.3) are shown for three excitation energies: 162 eV (below the resonance), 164 eV (at the resonance), and 168.4 eV (above the resonance). Additionally, the S -L absorption edge for these compounds and ZnS are presented in Figure 6. The shape of the S -L absorption, suggest a lack of well-localized states in the conduction band of sulfur. Tuning the energy of excitation along the S absorption edge therefore results in only the successive appearance of the S -L emission spectrum. No coupling between emission and absorption processes is observed. In the

case of ternary alloys, the sulfur atoms are bound to the Zn and Mn atoms. The increase of Mn content results in a smearing of the peaks at 151 eV and 152.5 eV in the emission spectra, thus indicating the difference in the valence state distribution of sulfur depending on the cation. With the increase of Mn content, the probability of finding two Mn atoms around S increases and leads to an increase of asymmetry in the electron state distribution which manifests in the smearing of the spectral structure.

Conclusion

The results of the Mn and the S -L resonant emission investigation of $Zn_{1-x}Mn_xS$ (where x=0.2) and MnS were presented together with the resonant excited spectra from elemental Mn. The emission spectra were recorded as the excitation energy was tuned across the Mn and S -$L_{2,3}$ absorption edges. The sharp resonance at the Mn $L_{2,3}$ line in MnS and $Zn_{1-x}Mn_xS$ compounds indicates the existence of well-localized Mn 3d antibonding states. Systematic appearance of new x-ray emission features were observed when the excitation energy was tuned across the Mn and S -L absorption edges. Additionally, a strong resonance at the Mn L_2 line was observed for all materials investigated. This resonance indicates that the Auger decay channel is closed at resonant excitation. With the increase of excitation energy, the Auger decay channel is successively opened, causing the decrease of L_2 line intensity. The lack of coupling between absorption and emission processes for the L_2 line indicates the importance of parallel spin between valence hole and spectator electron in order to observe the coupling process.

Acknowledgements

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Figure Captions

Figure 1 : The absorption spectra at the Mn L_3 -edge for Mn (dotted line), MnS (thin line) and for $Zn_{1-x}Mn_xS$, x=0.33 (bold line).

Figure 2 : Resonant excited Mn $L_{3,2}$ - emission spectra of elemental Mn. The exciting radiation energy was tuned from 629 eV to 669 eV, as indicated in the figure.

Figure 3 : Resonant excited Mn $L_{3,2}$ - emission spectra of MnS. The exciting radiation energy was tuned from 629 eV to 689 eV, as indicated in the figure. The intensities of the spectra on the left side of Figure 3 were arbitrarily divided by 1.6. The spectra with excitation energies fo 644 eV and 645 eV are shown twice for comparison of the different y scales.

Figure 4 : Resonant excited Mn $L_{3,2}$ - emission spectra of $Zn_{0.8}Mn_{0.2}S$. The exciting radiation energy was tuned from 630 eV to 685 eV, as indicated in the figure.

Figure 5 : Sulfur $L_{3,2}$ soft x-ray emission spectra of $Zn_{1-x}Mn_xS$ (where x=0.05, 0.2 and 0.3) for three energies of excitation radiation a) 162 eV (before the resonance); b) 164 eV (at the resonance) and c) 168.4 eV (after the resonance).

Figure 6 : Sulfur $L_{3,2}$ absorption spectra for $Zn_{1-x}Mn_xS$ (where x=0.0, 0.05, 0.2, 0.3).

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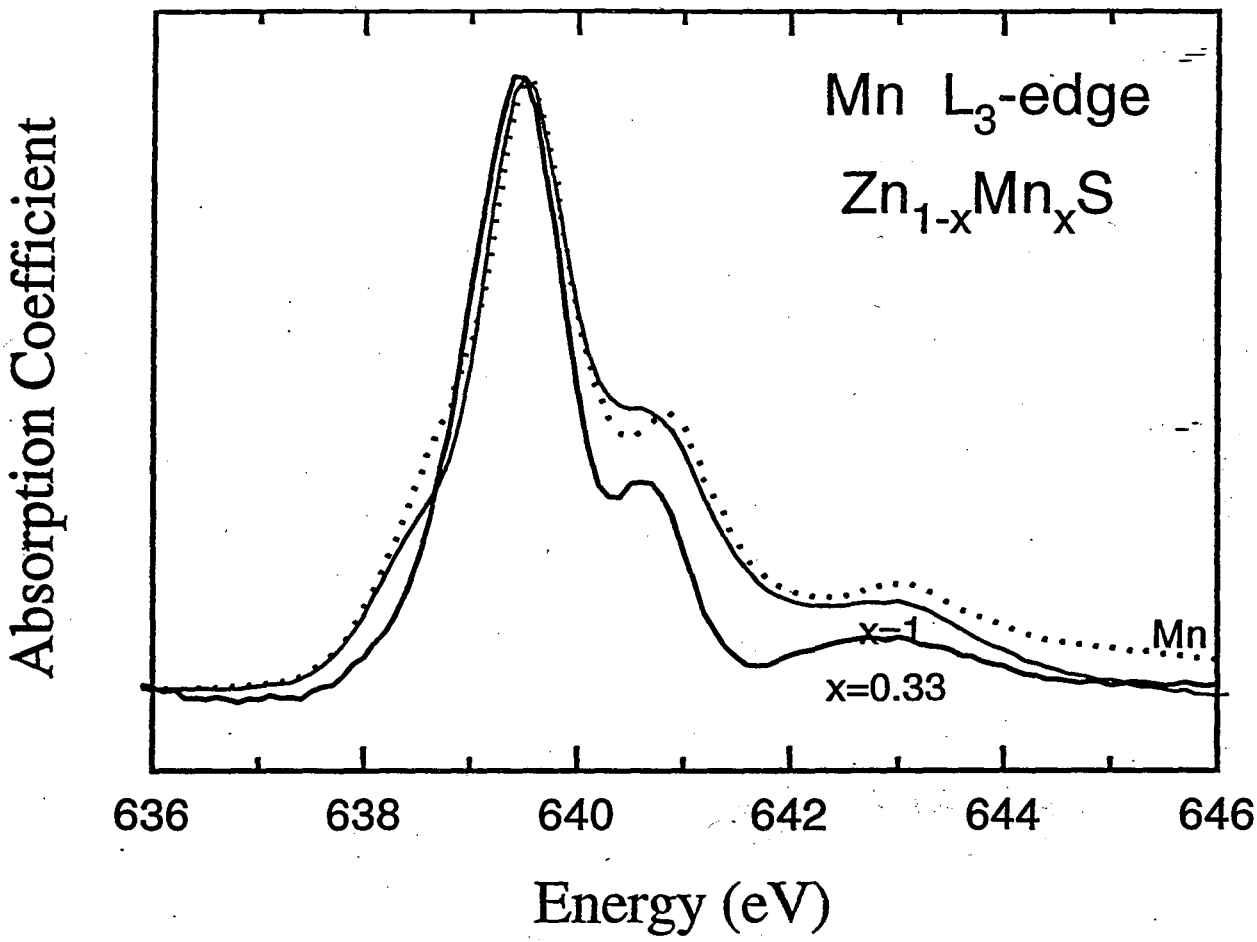
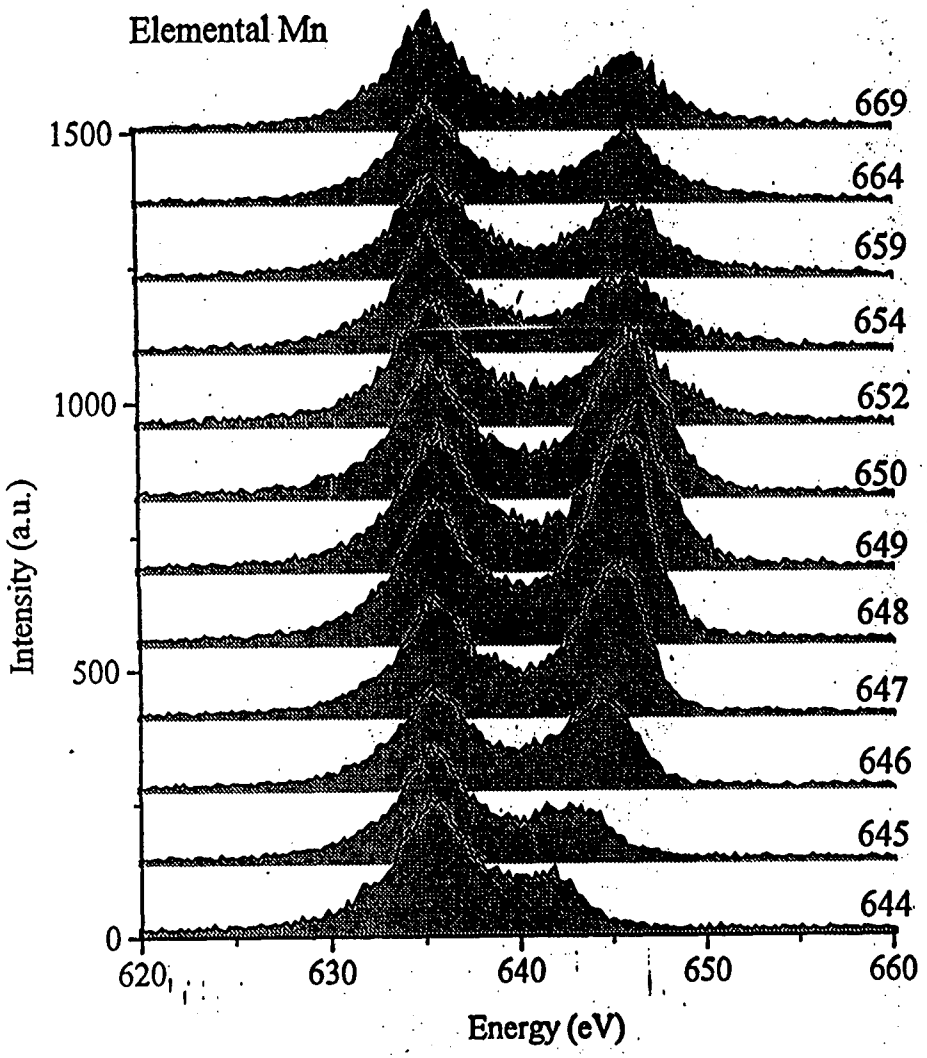

Mn L3-edge
Zn1-xMnxS
Absorption Coefficient
x=1
Mn
x=0.33
636
638
640
642
644
646
Energy (eV)

FIGURE 1


Elemental Mn
1500
1000
500
0
Intensity (a.u.)
620
630
640
650
660
Energy (eV)
669
664
659
654
652
650
649
648
647
646
645
644

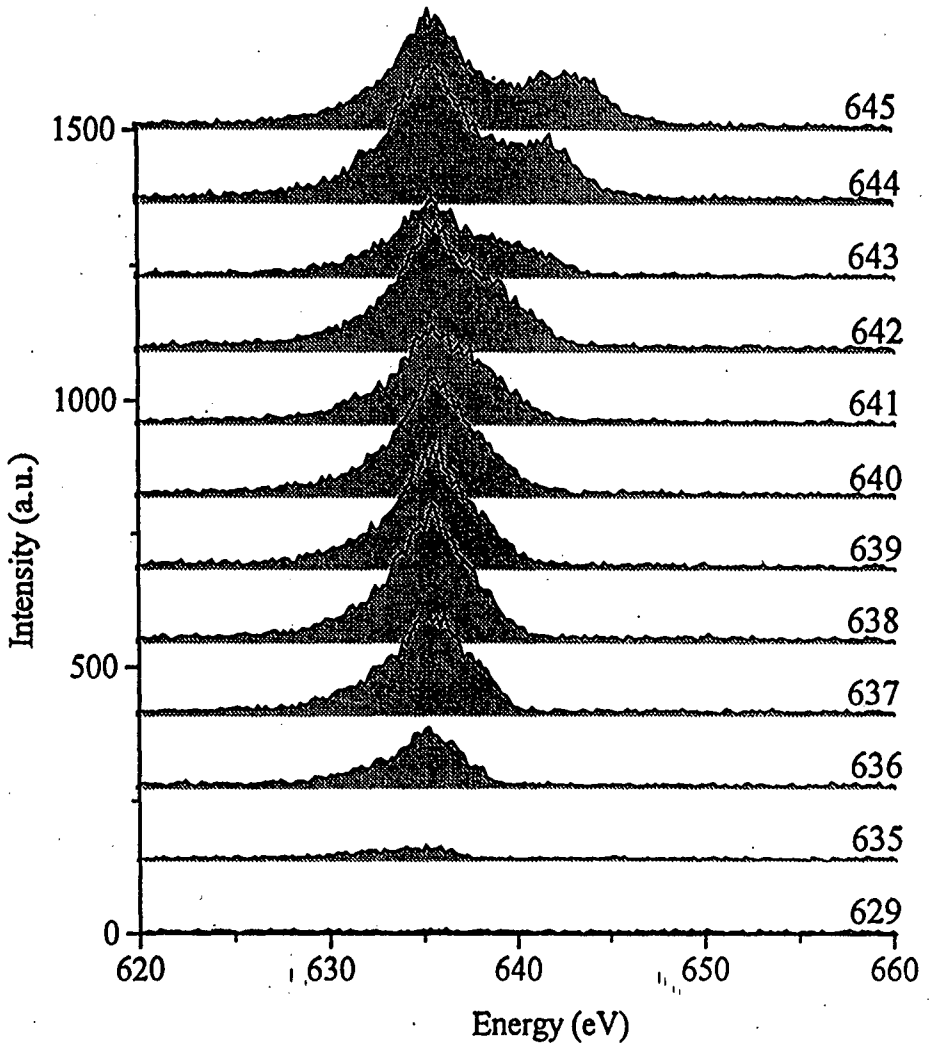
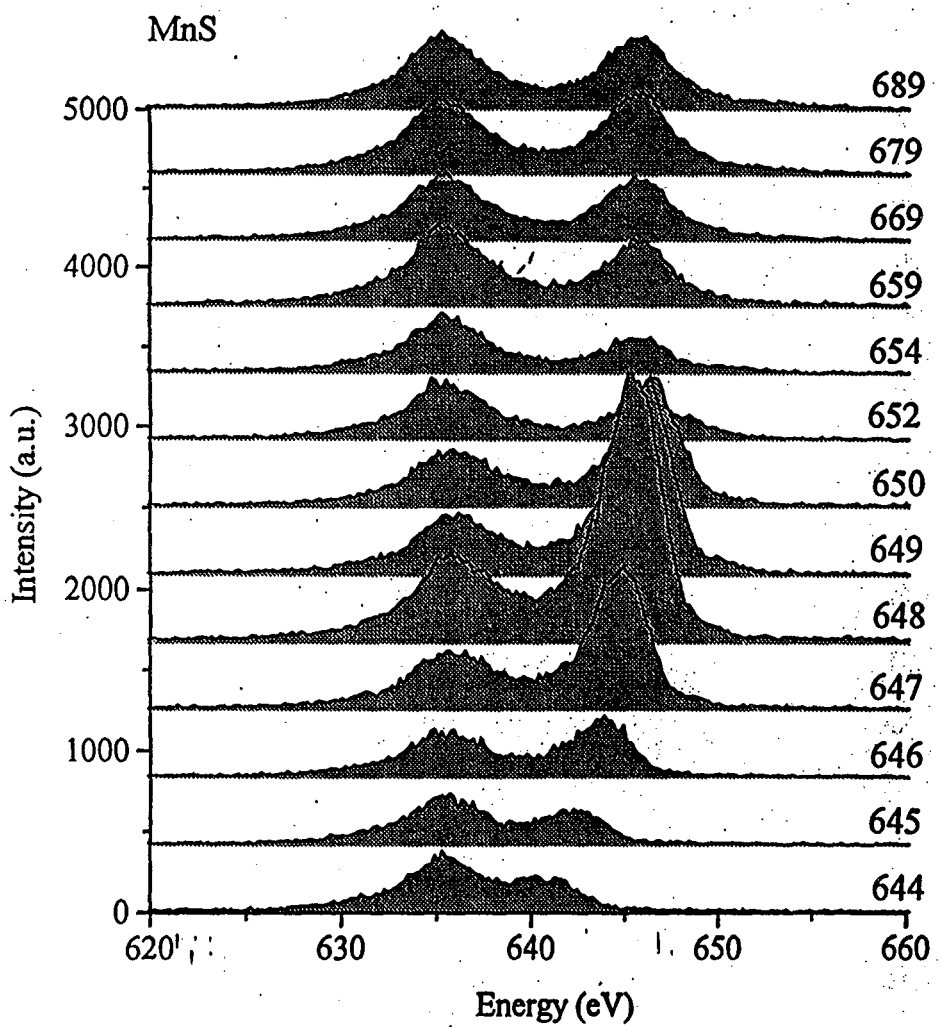

1500
1000
500
0
Intensity (a.u.)
620
630
640
650
660
Energy (eV)
645
644
643
642
641
640
639
638
637
636
635
629

FIGURE 2


MnS
Intensity (a.u.)
Energy (eV)
0
1000
2000
3000
4000
5000
620
630
640
650
660
689
679
669
659
654
652
650
649
648
647
646
645
644

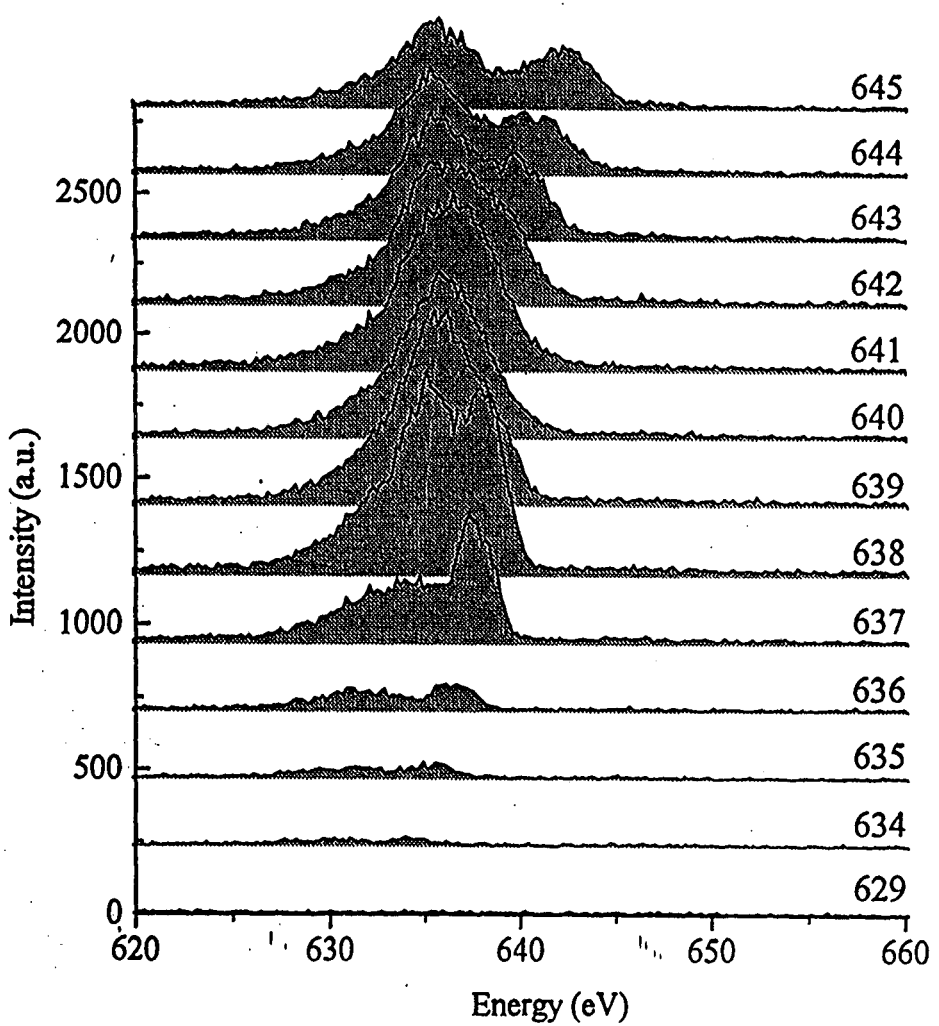

Intensity (a.u.)
Energy (eV)
0
500
1000
1500
2000
2500
620
630
640
650
660
645
644
643
642
641
640
639
638
637
636
635
634
629

FIGURE 3

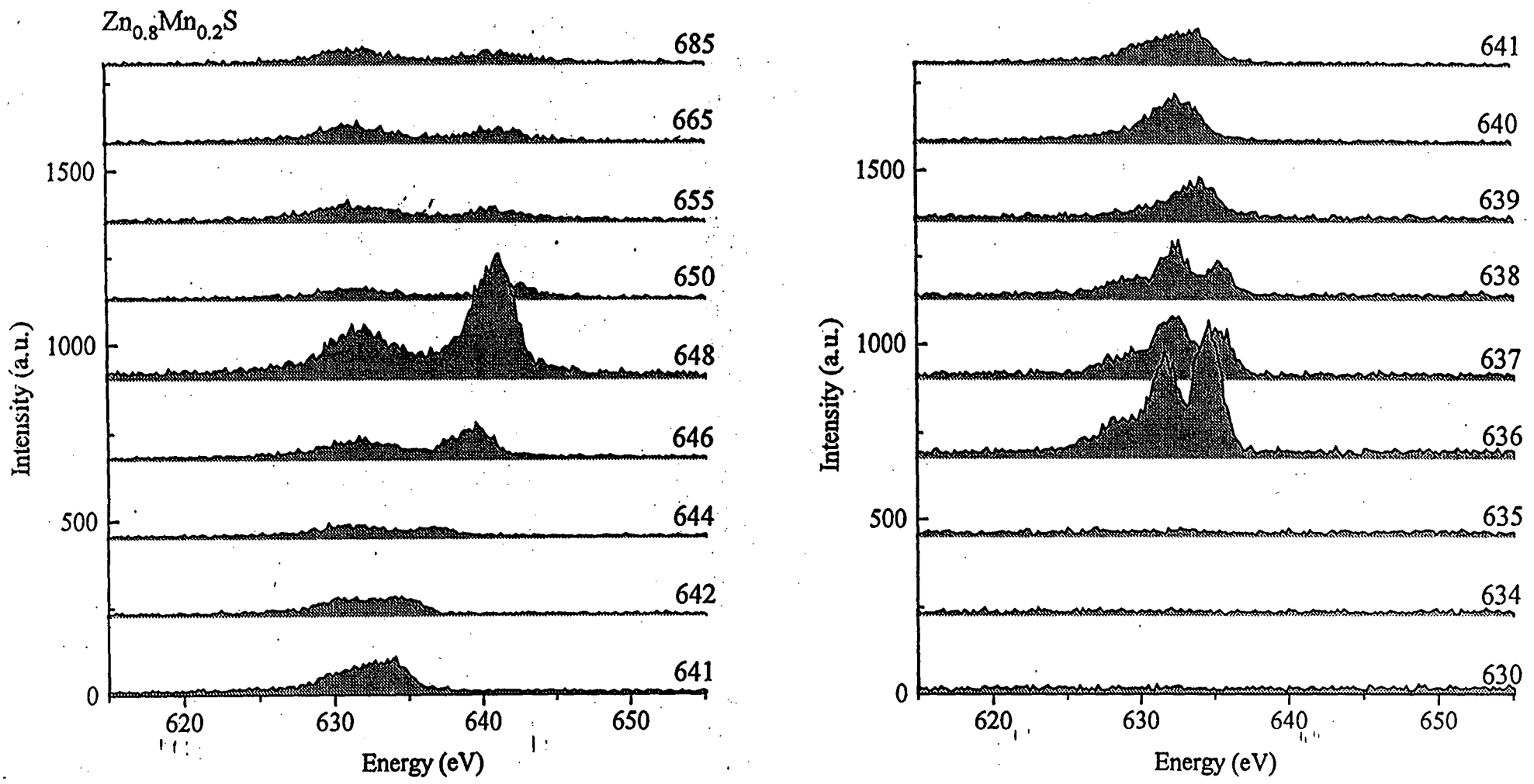

$Zn_{0.8}Mn_{0.2}S$
685
665
655
650
648
646
644
642
641
1500
1000
500
0
Intensity (a.u.)
620
630
640
650
Energy (eV)
641
640
639
638
637
636
635
634
630
1500
1000
500
0
Intensity (a.u.)
620
630
640
650
Energy (eV)

FIGURE 4

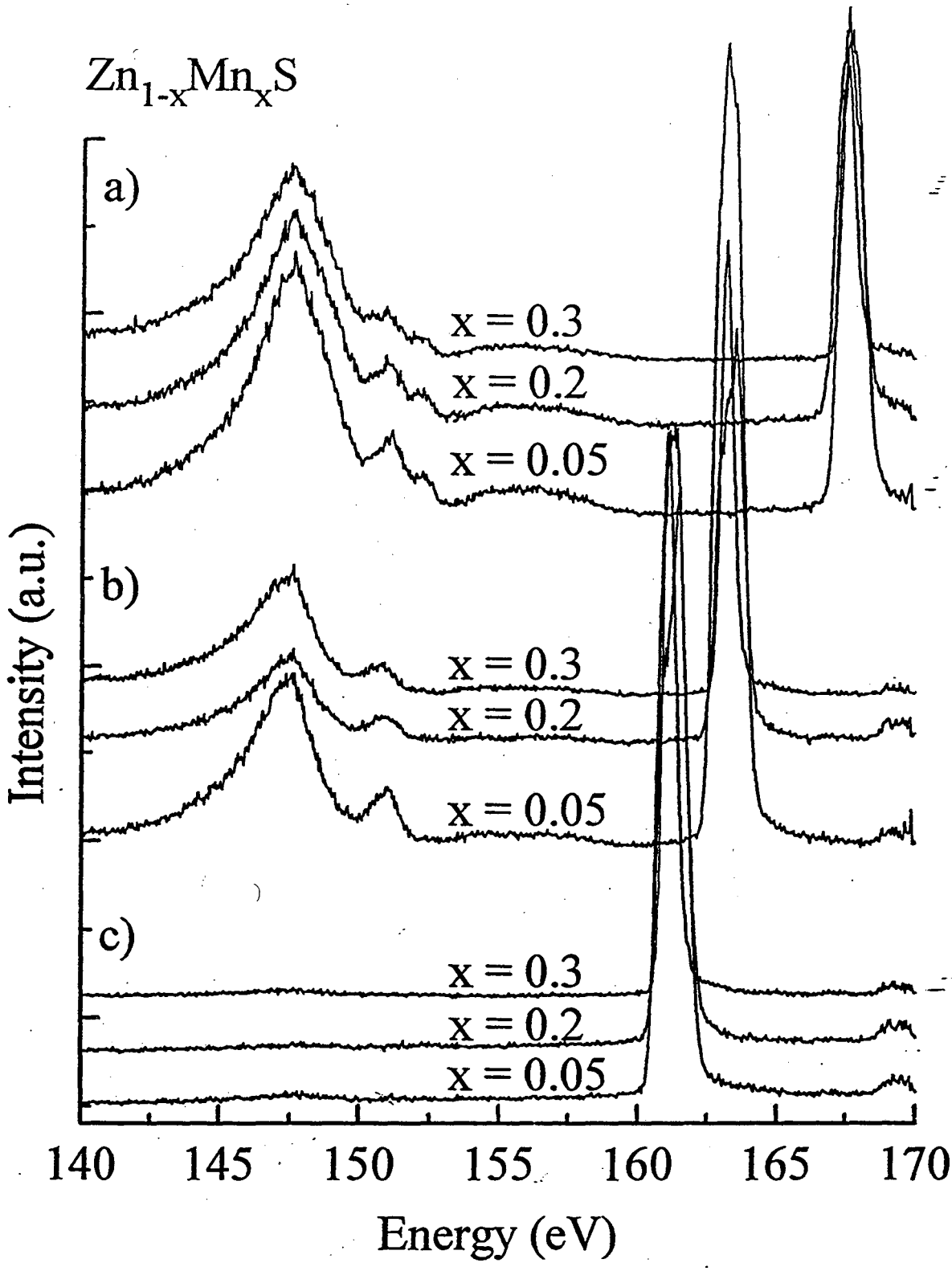

$Zn_{1-x}Mn_xS$
a)
x = 0.3
x = 0.2
x = 0.05
b)
x = 0.3
x = 0.2
x = 0.05
c)
x = 0.3
x = 0.2
x = 0.05
Intensity (a.u.)
140
145
150
155
160
165
170
Energy (eV)

FIGURE 5

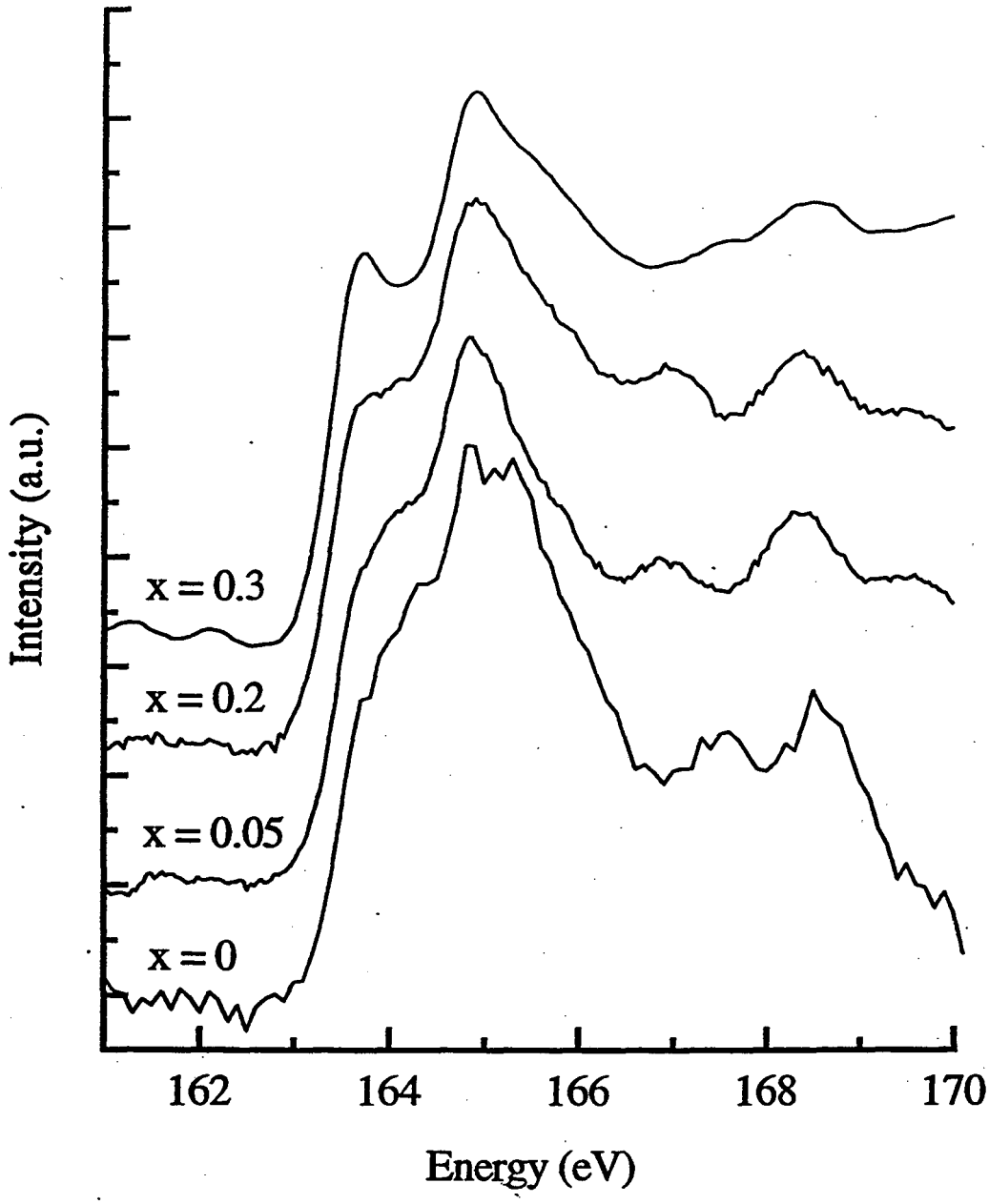


FIGURE 6

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