Journal of Optoelectronics and Advanced Materials Vol. 7, No. 5, October 2005, p. 2655 - 2660

TEMPERATURE DEPENDENT CHANGE OF THE MnS K-EDGE

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The x-ray absorption near-edge structure (XANES) of Mn K-edge in MnS have been investigated. The full multiple scattering approach has been applied to the calculation of Mn K edge XANES spectra of MnS. The calculations are based on different choices of one electron potentials according to Manganese coordinations by using the real space multiple scattering method FEFF 8 code. The crystallographic and electronic structure of the MnS are tested at various temperature ranges from 300 to 573 K. We have found prominent changes in the XANES spectra of MnS by the change of the temperature. Such observed changes are explained by considering the structural, electronic and spectroscopic properties. The results are consistent with experimental spectra.

(Received July 4, 2005; accepted September 22, 2005)

Keywords: MnS Thin Film, Electronic Properties, Chalcogenide, XANES

1. Introduction

Recently diluted magnetic semiconductors (DMS) have attracted considerable attention both for their important semiconducting as well as for magnetic properties [1-4]. In DMS, the band electrons and holes strongly interact with the localized magnetic moments and cause a variety of interesting phenomena [5,6]. Manganese sulfide (MnS) is a dilute magnetic semiconductor material (E_g = 3.1 eV) that is of potential interest in short wavelength optoelectronic applications such as in solar selective coatings, solar cells, sensors, photoconductors, optical mass memories [7-9]. MnS thin films or powders can be found in several polymorphic forms: the rock salt type structure (α–MnS) which is the most common form, by low temperature growing techniques it crystallizes into the zincblende (β–MnS) or wurtzite (γ-MnS) structure [10,11]. It has been found that β and γ type MnS can transform irreversibly to the stable α type MnS at 373-673 ^{o}K [12-16].

One of the most useful methods serving the electronic structure of materials is the near edge X-ray absorption fine structure (NEXAFS) spectroscopy [17]. The method NEXAFS, especially over the last two decades, became an important way for electronic structure calculations, bondings, valency properties, catalytic properties, orbital and atomic configurations [18]. Near-edge structure, observed in x-ray absorption of inner-shell ionization process, can be sensitive to interatomic distances, local coordination, and local electronic structure. The shape of absorption spectrum in this region is related to the electronic structure of the material, while the oscillation observed in the high energy part of the spectrum, called as the extended X-ray absorption fine structure (EXAFS) region, is associated with the arrangement of the atoms. It contains signals of interference of outgoing electron wave functions and scattered electron wave functions, gives information about the neighboring atoms, their regional configurations, atomic distances, coordination numbers etc. The amplitudes of the fine structure is related the number of atoms that surround the absorbing atom. It is known that these amplitudes exhibit a dependence on temperature which is caused by thermal vibrations of absorbing and scattering atoms. To understand the origins of various features it is necessary to calculate the observed fine structures from a suitable theoretical model.

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The valence band electronic structure of MnS has been investigated in the literature by x-ray and ultraviolet photoemission spectroscopy [19-21]. However, Mn K-edge electronic structure of MnS has not yet been revealed sufficiently [22-26]. The purpose of this study is to calculate Mn K-edge XANES spectra for different types of MnS crystals as a function of temperature. Our attention was mainly focused on the effect of temperature on the electronic states and location of the atoms. With this purpose we have performed full multiple scattering calculations. Theoretical calculations have been compared with the experimental results and they are consistent.

2. Materials and methods

Mn K-edge x-ray absorption fine structure calculations were performed using FEFF 8 code, which is based on real space multiple scattering approach [27]. In the calculations Hedin-Lundqvist exchange correlation potential was used and the FEFF input file was generated by the ATOMS package [28]. The full multiple scattering calculation for 624 atoms cluster was performed with self-consistent potential. We have calculated backscattering and phase shift functions for MnS thin film with single and multiple scattering paths to obtain X-ray absorption spectrum. We applied wurtzite (distorted hexagonal) γ-MnS structure as a model for manganese sulfide. Calculations were performed for 15 Å thick MnS cluster in wurtzite structure, containing 624 atoms (Mn, S) and one Mn atom selected as an x-ray absorber is also a photoelectron emitter at 300, 373, 473 and 573 K temperatures. Mainly, thermal effects on γ-MnS structure are investigated, for this purpose σ^2 Debye Waller factors calculated for related temperatures.

3. Results and discussion

Fig. 1 shows Mn K edge XANES structure calculation of γ-MnS, α-MnS, and metallic Mn spectra as a reference material. The characteristic features are marked from A to C. Energy calibration was performed using metallic Mn foil. Mn K-edge absorption peak begins to increase at photon energy 6538.3 eV, and is the binding energy of Mn K-shell that corresponds to the transition of 1s core electrons to an unoccupied state above the Fermi level.

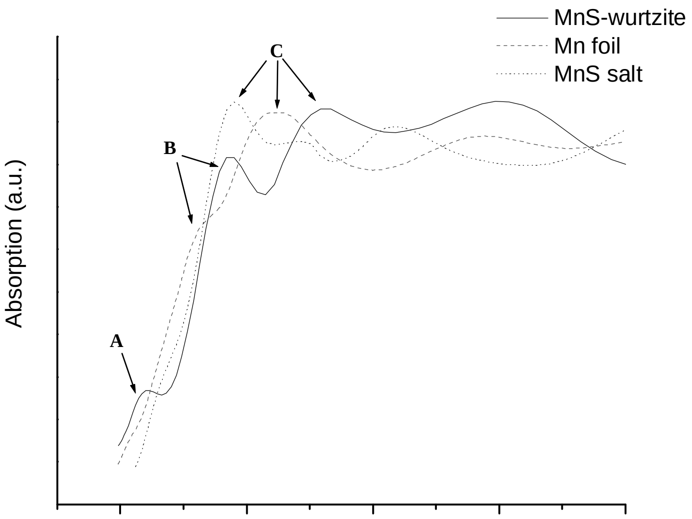

Fig. 1. Mn K-edge XANES calculated spectra for Mn foil, α-MnS and γ-MnS (wurtzite) structure at 300 K.

The pre-edge peak A observed only from wurtzite MnS structure and it has been associated with direct quadrupole transition from 1s to empty Mn 3d states [29]. Pre-edge structure of XANES region has an important role to investigate the electronic and bonding properties of the interested material. Previous studies have showed that structural properties of materials influence the pre edge region [30]. The higher the symmetry of the Mn nearest neighborhood, the weaker is the pre-edge structure observed in absorption spectrum of Mn compounds [23]. Due to asymmetry in the wurtzite structure, short distances between Mn 3d and S 3p orbitals cause to a strong coupling and overlapping. This effect corresponds to a shoulder like shape at the pre-edge (peak A) region in Fig. 1. The intensity of A is weak because it is due to the 1s → 3d transition which is forbidden by the atomic selection rules in the electric dipole approximation. Peak B observed just after the pre edge peak A is due to atomic-like transitions from 1s core to empty lover level of 4p states. Atomic-like transitions from 1s core to empty 4p states produce multi peaks in the near-edge energy region [31]. The main absorption edge C also corresponds to the transition from 1s state to 4p state and exhibits large chemical shift to higher energies. As a result of bonding with sulphur, main absorption edges of Mn, α-MnS and γ-MnS are calculated as 6538.3 eV, 6543.7, 6551.6 eV, respectively. Energy shifts to higher energies of these edges are calculated as 0, 5.4 and 13.3 eV, respectively. The energy shifts in γ-MnS and α-MnS spectra are correlated with the length of Mn-S bond. The shorter it is the greater is the overlap between electron wave functions originating from Mn and S. The asymmetry in wurtzite MnS structure also causes shorter S bond lengths than α-MnS. The spectral differences beyond the absorption edge indicate that there are small changes in the local structure among the samples.

Fig. 2 shows Mn K-edge XANES calculated spectra of γ-MnS (wurtzite) structure at 300, 373, 473 and 573 K. Heating of γ-MnS from 300 to 573 K cause thermal distortions which is calculated by XAFS Debye-Waller factor σ^2. When the temperature is raised the atoms begin to vibrate strongly around their equilibrium lattice sites, they slightly alter the interference pattern [32].

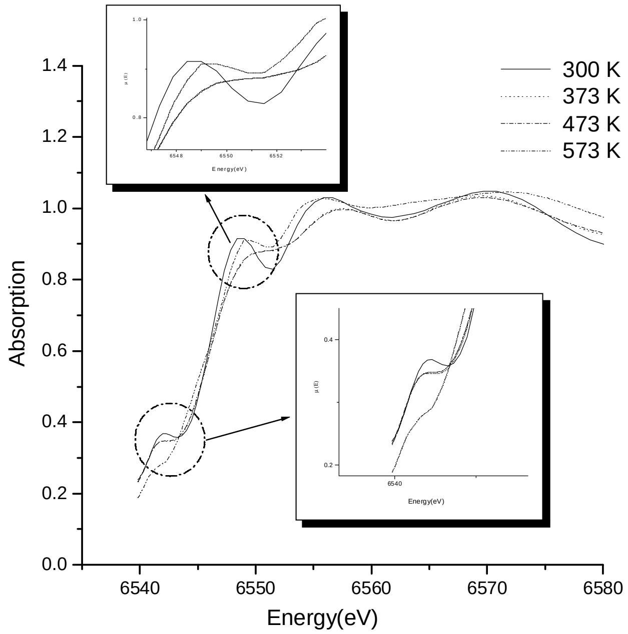

Fig. 2. Thermal disorder effects on γ-MnS wurtzite structure.

The oscillatory part of the absorption coefficient above K-edge is described by chi equation:

$$\chi(k) = \sum_j \frac{N_j}{kr_j^2} F_j(k) e^{-2\sigma^2 k^2} Sin\,(2kr_j + \delta_j(k)) \tag{1}$$

where N_j, coordination numbers of neighboring atoms, r_j , distance to neighboring atoms, σ^2, mean-square disorder in distances between neighboring atoms, $F_j(k)$, scattering amplitude, δ_j phase shifts. Contributions from thermal effects in the chi equation is given by the factor $e^{-2\sigma^2k^2}$, where σ^2 value is called the "Debye-Waller" factor and indicates the thermal oscillations caused by thermal effects [33]. The calculated σ^2 values are: 7.42×10^{-3}, 8.98×10^{-3}, 1.12×10^{-2}, and 1.34×10^{-2} Å^2 for 300, 373, 473 and 573 K temperatures, respectively. Increasing temperature lead to distortions in the structure and overlapping, hybridization in atomic orbitals of γ-MnS structure also tends to change atomic configuration from asymmetry to stable symmetric configurations. This will result a weak smoothing in pre-edge position as seen in Fig. 2. The changes of pre-edge peak with the increasing temperature are plotted in the inset of the Fig. 2. As the temperature is raised, the pre-edge peaks become weaker, which is a signs of asymmetry in the structure. Thus the Mn K edge spectra calculated at 573 K in Fig. 2, indicate that high temperature begins to distort the wurtzite structure which means that the asymmetric structure (wurtzite) tends to change to a symmetric form (rock salt). This result is consistent with the previous reports [12-16].

In order to demonstrate the effect of high temperature on γ-MnS structure, EXAFS calculations of scattering intensities at 300, 373, 473 and 573 K temperatures are given in Fig. 3. The damping of χ(*k*) at large *k* values is apparent in the spectrum. As a characteristic of thermal effects, intensity peaks became weaker and gaussian shaped.

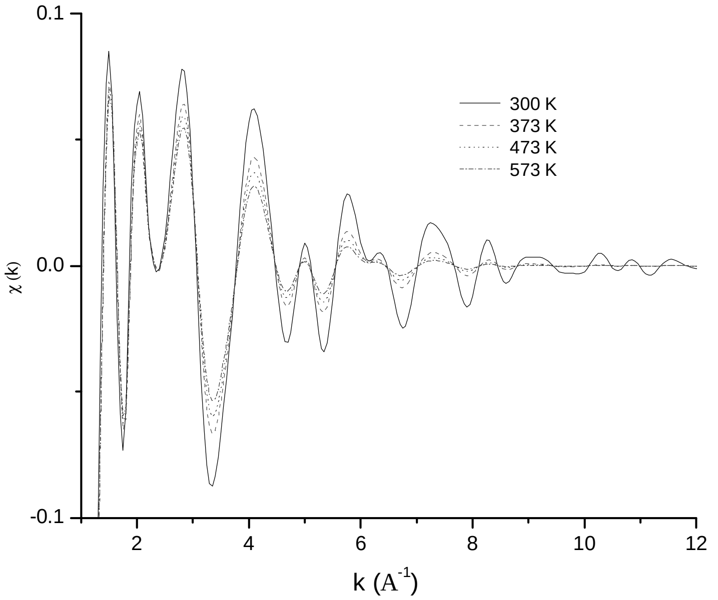

Fig. 3. EXAFS chi signal of γ-MnS at the different temperatures.

The EXAFS intensity in Fig. 3 is correlated with Debye Waller factor in chi equation (1) and represent a superposition of contributions from different scattering shells so that detailed information on temperature dependence could not be extracted from the spectrum. We have calculated a Fourier transform to real space to separate the contribution from each shell. The Fourier transform of the scattering intensities, the radial distribution function (RDF), is given in Fig. 4. In this figure the first five peaks can be attributed to the first five nearest neighbor shells surrounding the absorbing Mn atom. The first peak in the RDF picture of EXAFS calculation of γ-MnS at 300 K corresponds to bonding distance of Mn-S calculated as 2.435 Å, and the second peak corresponds to the bonding distance between Mn-Mn, as calculated 3.224 Å. The damping of photoelectron wave by inelastic scattering process observed from more distant shells. The damping of intensity at high temperature is strong and originates from the atomic vibrations. The large intensity difference between the high and low temperature at the first and the second peaks reflects the thermal disorder. Due to the asymmetry in wurtzite structure, shorter bonded S atoms remain at the same position and we could not observe any shift to asymmetry in their atomic positions despite damping in their intensity. However beyond the third peak, signals from long and weak bonded S atoms disappear, i.e. change their coordination. This points out that the structural modification to a stable and symmetrical configuration (i.e. to rocksalt α-MnS type) begins with increasing temperature. Our result supports the result of previous studies which showed that γ-MnS can exist only in low temperature range, and will transform irreversibly to stable α type at 373-673 ^{o}K [12-16].

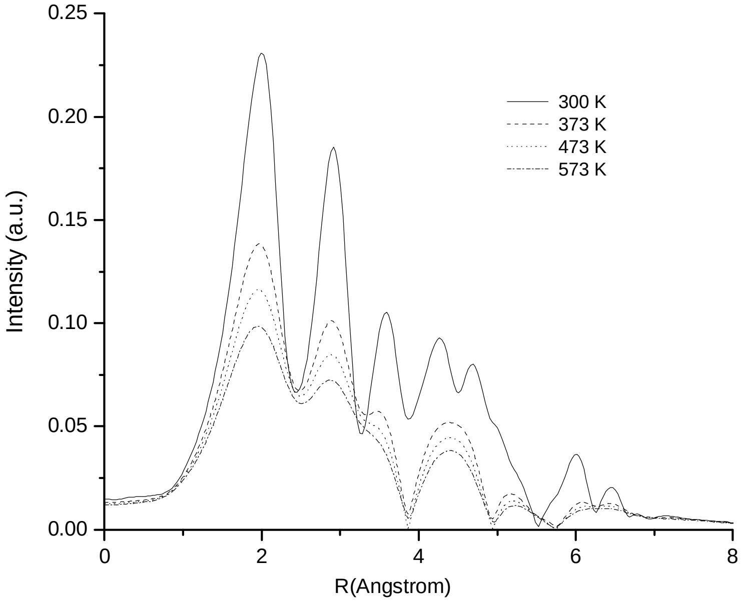

Fig. 4. RDF form of temperature dependence of γ-MnS.

4. Conclusion

In this study, we focused on thermal effects in the EXAFS calculations of Mn K-edge of γ-MnS structure. As the temperature increase, thermal distortions and damping of EXAFS oscillations were observed due to atomic vibrations and static structural disorder. The pre-edge part of the spectra is sensitive to the morphology of MnS. We found a stable structure up to 473 K. However, beyond this temperature, asymmetric wurtzite structure slightly begins to change to a symmetrical coordination. Out of phase situations fasten the structural distortion of γ-MnS, due to asymmetry in the structure, rigid short bonded S anions protect the structure from a total distortion.

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