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Total electron yield XANES of zinc-blende MnTe

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ABSTRACT

The electronic structure and chemical bond of zinc-blende (zb) MnTe have been studied by using total-electron-yield (TEY) X-ray absorption near-edge structure (XANES) spectroscopy. Close resemblances of the shape of Mn K-edge XANES in zb-MnTe and in $Zn_{1-x}Mn_xTe$ [A. Titov, X. Biquard, D. Halley, S. Kuroda, E. Bellet-Amalric, H. Mariette, J. Cibert, A.E. Merad, G. Merad, M.B. Kanoun, E. Kulatov, Yu.A. Uspenskii, Phys. Rev. B 72 (2005) 115209] indicated predominant influence of the 1st coordination shell. In particular, identical single-peak pre-edge structure for both cases was mainly ascribed to the Mn 1s-3d/4p weakly allowed dipole transitions. The quantitative analysis of XANES in zb-MnTe concerned the observed chemical shift of Mn K-edge threshold energy and a magnitude of the relevant cation–anion charge transfer (or effective cation charge), q(Mn–Te) [calculated after M. Kitamura, H. Chen, J. Phys. Chem. Solids 52 (1991) 731]. It also provided a comparison with our earlier X-ray absorption studies of $Zn_{1-x}Mn_xB$ alloys (B = S, Se). The estimated charge transfer within the chemical bond of zb-MnTe enabled us to complete the q(Mn–B) versus chalcogen ligand (B = S, Se, Te) dependence and to interpret it in terms of p-d hybridization and a contribution of Mn 3d electrons to the overall charge transfer.

1. Introduction

Manganese telluride (MnTe), grown by the equilibrium methods, crystallizes in the hexagonal NiAs-type structure [1]. Until late 1980s, the cubic zinc-blende (zb) MnTe had been only considered as a hypothetical endpoint compound for the series of ternary magnetic alloys of zinc-blende structure (namely, $Zn_{1-x}Mn_xTe$, $Cd_{1-x}Mn_xTe$, and $Hg_{1-x}Mn_xTe$), which belong to the so-called diluted magnetic semiconductors (DMSs) [2].

MnTe in a cubic phase (zb-MnTe) has been obtained for the first time in 1989 by molecular beam epitaxy (MBE) [3]. Since then, remarkable progress in the crystal growth of zb-MnTe by the nonequilibrium methods was reached (e.g. [4–7]).

Numerous reports contained the experimental results concerning structural properties of zb-MnTe, performed by X-ray diffraction (XRD) (see e.g. [4–7]) or by both the XRD and neutron diffraction ([8,9] and references therein). Among the latter ones, of special importance seems the evidence of complex investigations of MBE-grown 'semibulk' zb-MnTe and $Zn_{1-x}Mn_xTe$ ($0.695 < x < 1$) as well as the MnTe/ZnTe superlattices carried out with use of neutron- and X-ray diffraction [8], which led to determine the effect of strain and Mn dilution on the antiferromagnetic properties of zb-MnTe and its derivative compounds.

On the contrary, the literature related to X-ray spectroscopy studies remains relatively poor. In fact, it is limited to the X-ray photoelectron spectroscopy (XPS) experiments [4,10,11], and particularly to the investigations of electronic structure of the principal core-levels, i.e. Mn 2p and Te 3d [10,11].

Lack of X-ray absorption spectroscopy (XAS) data for cubic mangenese telluride has motivated us to measure its X-ray absorption near-edge structure (XANES) spectrum at the K-edge of Mn, in order to study partial density of states (DOS) in the conduction band and in the energy gap of zb-MnTe.

At this point we felt additionally encouraged by the earlier results of our group, which included the XANES data for K-edge of Mn in the $Zn_{1-x}Mn_xB$ (B = S, Se) diluted magnetic semiconductors (DMSs) [12–15]—namely, the respective XANES spectrum of zb-MnTe could provide a completion of the experimental XAS evidence for the case of Mn bound to chalcogen atom (S, Se, Te) in a tetrahedral coordination of zinc-blende (and/or wurzite) structure.

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Similarly as in our earlier XPS investigations of zb-MnTe [10,11] we used here single-crystalline epilayers grown by MBE technique [6]. This obviously implied a choice of the total-electron-yield (TEY) as the only possible detection mode in the present experiment (see [16–18]).

TEY detection is somewhat surface sensitive, since it involves nonradiative decay of the core holes by emission of Auger electrons. In consequence, it has much shorter probing depth than the fluorescence detection method and therefore has been mainly used for thin-film and surface XAS experiments (see [17] and references therein). Nevertheless, TEY avoids the usual corrections for self-absorption necessary when using fluorescence detection for thick concentrated samples.

2. Experimental

In the present experiment, standard single-crystalline zb-MnTe (0 0 1) epilayers (5 μm thick), grown on GaAs (1 0 0) substrate with a thick (4.5 μm) CdTe buffer layer [6], were used.

The room-temperature XANES measurements at the Mn K-edge of zb-MnTe were carried out in the A1 beamline station of the HASYLAB (Hamburg, Germany). Double-crystal Si(1 1 1) monochromator was applied. The absorption spectrum was acquired by the total electron yield technique using drain current detection mode [18]. The measurement chamber was evacuated to less than 10^{-6} Torr during the experiment. The sample was electrically isolated from the spectrometer and its drain current, induced by X-ray beam (normal incidence to the crystal surface), was measured by Keithley 617 electrometer. Additionally, the reference XANES spectrum of elemental Mn has been recorded in the transmission mode with use of metallic Mn foil.

It is noteworthy that in the case of K-edge absorption measurements of selected transition metals (i.e. Cr, Fe, Ni) the estimated sampling depth of the TEY method equaled approximately 1000 Å [16] (see also [18]). The probing depth for the TEY detection is determined primarily by the penetration ranges of Auger electrons emitted from the absorbing atoms—in the case of KLL Auger electrons (corresponding to the K-edge absorption) this range is of order of thousands of angstroms [17]. Therefore we could anticipate a comparable magnitude of the TEY sampling depth (as in Refs. [16,18]) in our experiment.

3. Results and discussion

Fig. 1 presents the Mn K-edge XANES spectrum of zb-MnTe, acquired by the TEY technique. Also, the respective X-ray absorption spectrum of the p-type $Zn_{1-x}Mn_xTe$ ($x = 0.038$) DMS compound (taken from [19]) was included for comparison.

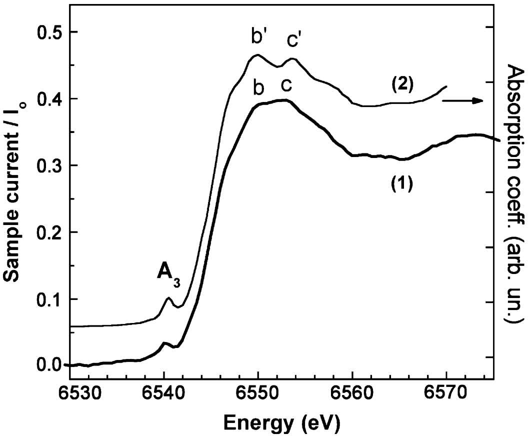

Fig. 1. Mn K-edge X-ray absorption spectra of: (1) zinc-blende MnTe (p-type)—this work, (2) $Zn_{1-x}Mn_xTe$ (p-type, $x = 0.038$)—from Ref. [19].

First examination of the above plot indicates a close resemblance of the XANES spectra of zb-MnTe and of $Zn_{1-x}Mn_xTe$ ($x = 0.038$), despite the fact that the latter one was acquired in the fluorescence mode [19] which has higher penetration depth than TEY detection (see, e.g. [20]). Both the above XANES spectra refer to the case of Mn^{2+} ion (d^5 configuration) tetrahedrally coordinated by Te ligands in zinc-blende-type lattice, with the same value of Mn–Te bond length (see [21] and references therein).

In particular, there is a noticeable pre-edge peak (marked here by A_3, following the notation of Ref. [19]) centered at about 6540.5 eV (Fig. 1).

Analogous pre-edge structure in the Mn K-edge absorption spectrum is typical for a large number of Mn compounds (see, e.g. [19,22] and references therein). More generally, the pre-edge structure for the Mn K-edge of these compounds comprises one, two or three small peaks labeled by A_1–A_3, which have Mn 3d character. These features are also observed in XANES spectra of the other transition metals (TM) in different TM compounds, and are usually ascribed to mixtures of 1s-3d quadrupole and 1s-3d dipole transitions (weakly allowed by a hybridization between 3d states and 4p states of TM), with prevailing contribution of the latter ones (see [19,22]).

Identical pre-edge feature (as in Fig. 1), containing only single peak (A_3), has been found earlier in the Mn K-edge XANES of $Zn_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xSe$ DMSs [13] as well as in $Ga_{1-x}Mn_xAs$ [19] and $Ga_{1-x}Mn_xN$ [23] ferromagnetic DMSs.

Complex analysis of the Mn K-edge XANES in $Ga_{1-x}Mn_xN$, $Ga_{1-x}Mn_xAs$ and $Zn_{1-x}Mn_xTe$, performed by Titov et al. [19], enabled us an unanimous identification of the A_3 pre-edge peak in the Mn XANES spectrum of zb-MnTe (Fig. 1) as mainly due to the dipole transitions from Mn(1s) to Mn(3d) states. These are not forbidden, since the Mn(4p) orbitals have the t_2 symmetry in the tetrahedral coordination of Te ligands, and therefore a hybridization between the Mn($4p_{t2}$) and Mn($3d_{t2}$: spin down) states can occur [19].

Taking into account the above mentioned results [19], supported by calculations of the total and partial (i.e. referred to Mn 3d states) DOS for ZnTe: Mn [24], it becomes clear that in our case of p-type zb-MnTe the Mn($4p_{t2}$) and Mn($3d_{t2}$: spin down) states are located above the Fermi level within an energy gap (E_g).

Qualitative similarity between the presented XANES spectrum of zb-MnTe and the analogous one of $Zn_{1-x}Mn_xTe$ [19] (Fig. 1) also concerns their main peak, located above the energy of K-absorption threshold. In $Zn_{1-x}Mn_xTe$ it consists of two well-resolved peaks, centered at about 6550 eV and 6553.5 eV [19], and denoted here by b′ and c′. On the other hand, the main peak of the Mn K-edge spectrum of zb-MnTe exhibits a broad top spread between 6550 eV and 6553 eV (Fig. 1). Nevertheless, its shape suggests existence of two constituent and partially overlapping peaks (see the features labeled by b and c in Fig. 1), which seem to correspond directly to those of $Zn_{1-x}Mn_xTe$ spectrum (marked by b′,c′).

The above mentioned resemblances between the cases of zb-MnTe and $Zn_{1-x}Mn_xTe$ [19] directly suggest that the shape of their Mn K-edge XANES spectra is mainly influenced by the first coordination shell (i.e. Te ligands).

Direct information about the electronic state of an atom in a solid can be obtained from XANES spectrum, due to its sensitivity to the valence state of absorber. For manganese in different Mn compounds, a relationship between the position of Mn K-absorption edge and the valence of Mn ion was demonstrated, e.g. in Refs. [19,22,23,25,26].

Besides a capability to verify a valence of Mn (or the other transition metal) ion in a solid matrix, measurement of the exact