

論文内容の要旨

論文題目 Soft X-ray Spectroscopic Study of Oxide- and Telluride-Based Diluted Magnetic Semiconductors

(酸化物およびテルル化物希薄磁性半導体の軟X線分光による研究)

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Diluted magnetic semiconductors (DMS's), which are semiconductors doped with magnetic ions dilutely, have been studied intensively since the discovery of ferromagnetism in the III-V DMS $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ [1] because the ferromagnetic interaction between the Mn ions mediated by hole carriers enables us to manipulate both the charge and spin degrees of freedom of electrons. Ever since the theoretical prediction that wide-gap semiconductors-based DMS's should show ferromagnetism above room temperature, DMS's based on wide-gap semiconductors such as GaN and ZnO have been investigated and, in fact, there have been many reports on room temperature ferromagnetism in wide-gap semiconductor-based DMS's.

One of the most important properties of DMS is the interaction between the local magnetic moment of doped ions and the spins of *sp*-band electrons of the host semiconductor. In order to obtain a fundamental understanding of the interaction, investigation of the electronic structure of the doped magnetic ions and the host semiconductor is necessary.

Soft x-ray spectroscopy enables us to extract the electronic structure element-specifically. In particular, x-ray magnetic circular dichroism (XMCD), which is defined as the difference between the core-level x-ray absorption spectroscopy (XAS) spectra taken with right- and left-handed circularly polarized x rays, is very efficient to extract important information about the magnetic properties of the doped magnetic ions because XMCD is sensitive only to magnetically active species. *2p-3d* resonant photoemission spectroscopy (RPES) enables us to extract the *3d* partial density of states (PDOS) in the valence band.

In the present thesis, we have employed the soft x-ray spectroscopic techniques for the investigation of ferromagnetic DMS's having Curie temperatures (T_C 's) above room temperature in order to address their magnetic properties. In Chapter 3, we discuss the relationship between local electronic structure of $Zn_{1-x}Cr_xTe$ and the ferromagnetic properties. In Chapter 4, we investigate the origin of the paramagnetic behavior of $Zn_{1-x}Co_xO$ by means of the magnetic-field and temperature dependence of XMCD signal. In Chapter 5, we investigate the hole-concentration dependence of electronic structure of Li-doped $Ni_{1-x}Fe_xO$ by XAS and RPES, and discuss the possible origin of the ferromagnetism. In Chapter 6, effects of V-ion doping on the electronic structure of the host semiconductor In_2O_3 have been studied by XAS and RPES. Based on the findings, we discuss hybridization between the host band and the $3d$ orbitals. In Chapter 7, we study the band structure of the host semiconductor ZnO by soft x-ray angle-resolved photoemission spectroscopy (SX-ARPES).

Soft x-ray magnetic circular dichroism and photoemission studies of $Zn_{1-x}Cr_xTe$

$Zn_{1-x}Cr_xTe$ thin films show ferromagnetism at room temperature and their magnetic circular dichroism signals observed at the absorption edge of $ZnTe$ follow the magnetic behavior of magnetization [2]. Therefore, $Zn_{1-x}Cr_xTe$ has attracted much attention as an intrinsic DMS with strong $s,p-d$ interaction. Recently, spatially inhomogeneous distributions of the Cr ions, that is, spinodal decomposition have been pointed out to influence the magnetic properties. We performed XMCD and RPES measurements on ferromagnetic $Zn_{1-x}Cr_xTe$ ($x=0.03$ and 0.15) thin films. The line

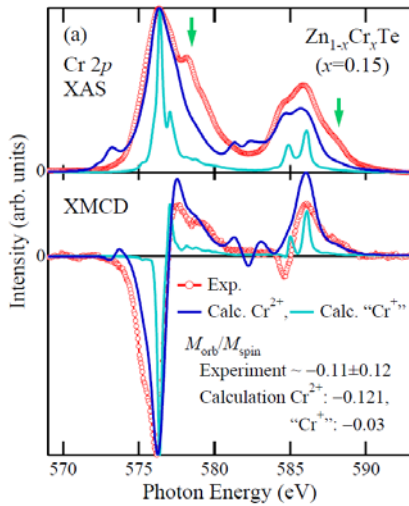


Fig.1 Configuration-interaction cluster-model analysis for the Cr 2p XAS and XMCD spectra of $Zn_{1-x}Cr_xTe$.

shape of the Cr 2p XMCD spectra is independent of magnetic field (H), temperature (T), incident photon angle, and Cr concentration, indicating a spatially isotropic ferromagnetic component. The analysis using configuration-interaction cluster-model calculation suggests that the ferromagnetic XMCD signal is caused by the Cr ions substituting the Zn site. The Co $3d$ PDOS did not show a finite intensity at the Fermi level, indicating that carrier-induced ferromagnetism appears difficult in $Zn_{1-x}Cr_xTe$. Based on these findings, we conclude that $Zn_{1-x}Cr_xTe$ has short-range strong $s,p-d$ interaction and the inhomogeneous distribution of the Cr ions should be taken into account although the Cr ions are substituted for the cation sites.

Soft x-ray magnetic circular dichroism and photoemission studies of $Zn_{1-x}Co_xO$

$Zn_{1-x}Co_xO$ has been investigated intensively since the discovery of ferromagnetism at room temperature because ZnO has potential for optical applications. In the previous XMCD measurements on ferromagnetic $Zn_{1-x}Co_xO$ [3], we have concluded that the ferromagnetism comes from Co ions substituting for the Zn site, and proposed that most of the Co ions are strongly coupled antiferromagnetically with each other. In this work, we have measured H and T dependences of XMCD of other $Zn_{1-x}Co_xO$ thin films, which show both paramagnetism and ferromagnetism. Figure 2 shows the H and T dependences of magnetization estimated from XMCD spectra. The

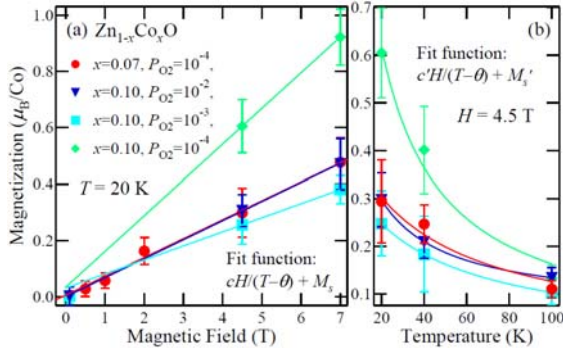


Fig.2 Magnetization of the $Zn_{1-x}Co_xO$ thin films estimated from the XMCD spectra by applying the XMCD sum rules. Solid curves are Curie-Weiss fits.

observations suggest that in the present $Zn_{1-x}Co_xO$ films paramagnetic signals are dominant and the ferromagnetic ones are very weak, consistent with the magnetization measurements. The fit of the magnetic behavior to the Curie-Weiss law have revealed that there is antiferromagnetic interaction between the Co ions. The results support a model that the ferromagnetism can be caused by inhomogeneous Co distribution in $Zn_{1-x}Co_xO$.

Photoemission and x-ray absorption studies of $Li_yNi_{1-x-y}Fe_xO$

$Ni_{1-x}Fe_xO$ has been reported to show ferromagnetism with T_C exceeding room temperature. In addition, recently, Lin *et al.* [4] have shown that the magnetization and electrical conductivity of $Ni_{1-x}Fe_xO$ can be enhanced by Li co-doping, where Li ions substituting the Ni sites act as acceptor. We have measured RPES and XAS on $Li_yNi_{1-x-y}Fe_xO$ thin films having different Li concentrations. The Ni $2p$ core-level photoemission spectroscopy (PES) and XAS spectra did not change with Li doping. In contrast, the Fe $2p$ XAS spectra showed systematic changes with Li content, that is, the Fe^{3+} intensity increased with Li doping compared with the Fe^{2+} intensity. The Fe $3d$ partial density of states and the host valence-band emission near valence-band maximum increased with Li content, consistent with the increase of electrical conductivity. Based on these findings, percolation of bound magnetic polarons is proposed as an origin of the ferromagnetic behavior.

Photoemission and x-ray absorption studies of $In_{2-x}V_xO_3$

Recently, In_2O_3 -based DMS's have attracted much attention because of the reports of room temperature ferromagnetism and of the potential of the host material In_2O_3 for applications. We have performed PES and XAS measurements on $In_{2-x}V_xO_3$ thin films, which show ferromagnetism at room temperature, in order to obtain a fundamental understanding of the electronic structure. From comparison with previous reports, the V $3d$ ions are expected to be trivalent, implying that the V ion

substitutes for the In site. The V 3d PDOS in the valence band has been observed using RPES

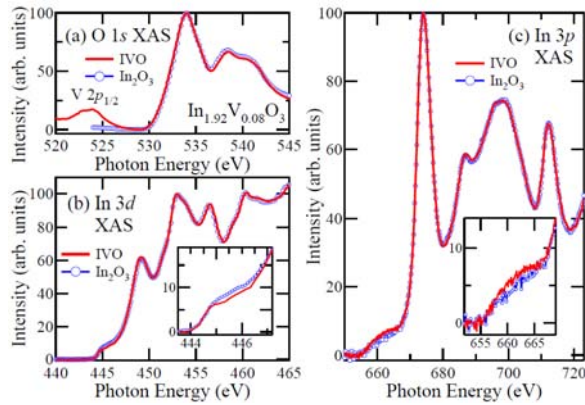


Fig.3 X-ray absorption spectra of $\text{In}_{2-x}\text{V}_x\text{O}_3$ (IVO) measured at In and O absorption edges. (a) O K XAS spectra. (b), (c) In 3d and 3p XAS spectra, respectively.

technique and shows a sharp peak within the band gap of In_2O_3 , implying the localized nature of the V 3d orbitals in the valence band. There are differences of XAS spectra measured at the In 3p and 3d edges although the O K XAS spectrum is independent of V doping, as shown in Fig.3. Based on the findings, it is likely that the *s-d* exchange interaction is dominant for the ferromagnetism in $\text{In}_{2-x}\text{V}_x\text{O}_3$.

Soft x-ray angle-resolved photoemission study of ZnO

ZnO is one of the most promising oxide semiconductors for applications to semiconductor electronics, especially for optical devices. Their inexpensiveness and environmental safety are also advantages for practical applications. We have performed an SX-ARPES study on a ZnO thin film in order to probe the bulk electronic properties. As shown in Fig.4, we have succeeded to observe clear band dispersions of ZnO. Figure 4 also shows the valence-band spectra of ZnO and the Co 3d PDOS of $\text{Zn}_{1-x}\text{Co}_x\text{O}$. Comparison of the band dispersion of ZnO with the Co 3d PDOS of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ suggests that the Co 3d orbitals well hybridize with the O 2p bands.

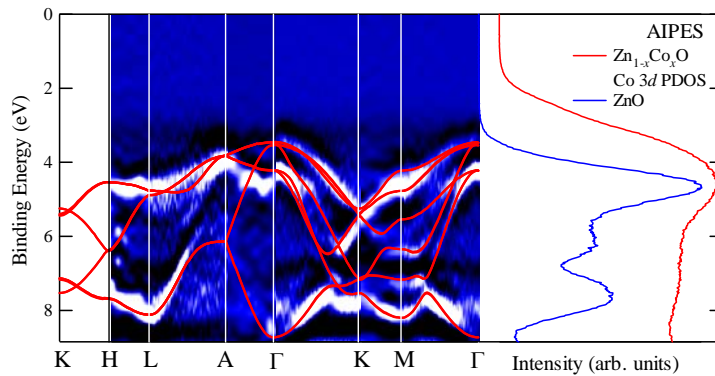


Fig.4 Band dispersion along the high symmetry edges of ZnO compared with the Co 3d partial density of states (PDOS) of $\text{Zn}_{1-x}\text{Co}_x\text{O}$. Red curves are theoretical band structure calculated by first principle calculation. The Co 3d PDOS have been obtained by Co 2p-3d resonant photoemission technique.

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