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Magnetic circular dichroism of ferromagnetic Co²⁺-doped ZnO

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Cobalt-doped ZnO (Co²⁺:ZnO) films were studied by magnetic circular dichroism (MCD) spectroscopy. A broad 300 K ferromagnetic MCD signal was observed between 1.4 and 4.0 eV after exposure of paramagnetic Co²⁺:ZnO films to zinc metal vapor, attributed to low-energy photoionization transitions originating from a spin-split donor impurity band in ferromagnetic *n*-type Co²⁺:ZnO. © 2006 American Institute of Physics. [DOI: 10.1063/1.2221871]

Diluted magnetic semiconductors¹ (DMSs) have attracted recent attention due to their potential application in semiconductor spintronic devices. For practical applications, ferromagnetic DMSs with Curie temperatures (T_C) well above room temperature are desired. Important advances have been made by several laboratories toward understanding the high- T_C ferromagnetism observed in oxide DMSs.² In some cases, dopant clustering was observed and the ferromagnetism evidently had extrinsic origins. In other cases, evidence points toward intrinsic ferromagnetism that relies on the presence of *n*- or *p*-type lattice defects. Co²⁺:ZnO grown without deliberate incorporation of such defects has been studied extensively and exhibits only paramagnetism (with weak local antiferromagnetic super-exchange),^{3,4} but weak ferromagnetism can be induced by vacuum annealing⁴ and stronger ferromagnetism can be achieved by growth under lower O₂ partial pressures,⁵ both linked to introduction of shallow donor defects. Quantitatively reversible 300 K ferromagnetic ordering in Co²⁺:ZnO was demonstrated⁶ by Zn vapor diffusion (“on”) and subsequent aerobic reoxidation (“off”), attributed to introduction and removal of the native shallow donor, interstitial zinc (Zn_i).

Magnetic circular dichroism (MCD) spectroscopy provides a sensitive tool for exploring the magnetic and electronic structural properties of DMSs. MCD measurements at the band edge of paramagnetic Co²⁺:ZnO have verified the existence of a giant excitonic Zeeman effect,^{7–9} the analysis of which yielded total *s*,*p*-*d* exchange energies ranging from $N_0(\alpha-\beta) \approx 0.8$ to 2.5 eV.^{8,9} To date, however, the MCD spectroscopy of ferromagnetic ZnO DMSs has received relatively little attention.¹⁰ In these studies, very broad MCD features were observed that generally bore little resemblance to those of the parent paramagnetic DMSs. In particular, the absence of structure at 2.0 eV was invoked to suggest extrinsic ferromagnetism in Co²⁺:ZnO.¹⁰ In Co²⁺:TiO₂, however, similar broad MCD spectra were interpreted as arising from intrinsic DMS ferromagnetism,¹¹ but the electronic structural origins of the sub-bandgap MCD intensities were not addressed. In this letter we examine the broad sub-bandgap MCD intensity observed in ferromagnetic Co²⁺:ZnO films exposed to Zn metal vapor and propose assignment of this intensity to photoionization transitions involving a spin-split cobalt/Zn_i donor impurity band.

Figure 1(a) shows 300 K absorption spectra of a ~50 nm thick 4.2% Co²⁺:ZnO polycrystalline film before

and after exposure to Zn vapor at 450 °C for 1 h.¹² The absorption spectrum of the as-prepared film is the same as those of paramagnetic Co²⁺:ZnO single crystals, showing the characteristic spin-orbit split ⁴A₂→⁴T₁(P) ligand-field transition of substitutional Co²⁺ at ~2.0 eV [Fig. 1(b)] (Ref. 13) and the first excitonic absorption maximum of ZnO at ~3.5 eV. Upon exposure to Zn vapor, the ZnO absorption edge shifted slightly to higher energy and a broad, weak absorption tail was observed throughout the visible energy range. A new absorption band can also be detected at ~0.4 eV, as described previously.⁶ These spectroscopic changes were also observed in undoped ZnO exposed to Zn vapor and are characteristic of the introduction of shallow donors, in this case likely Zn_i.^{6,14,15}

Figure 1(c) shows MCD spectra of the same Co²⁺:ZnO film before and after exposure to Zn vapor. Before Zn exposure [dotted line in Fig. 1(c)], only very weak MCD intensity was observed at 300 K. Magnification of this spectrum [Fig. 1(b)] reveals the Co²⁺ ⁴A₂→⁴T₁(P) band. Variable-temperature, variable-field MCD spectroscopy and superconducting quantum interference device (SQUID) magnetometry confirmed that these Co²⁺:ZnO films were paramag-

FIG. 1. (Color online) Spectroscopic data for a 4.2% Co²⁺:ZnO polycrystalline film before (dotted) and after (solid) exposure to Zn vapor at 450 °C for 1 h in vacuum. (a) 300 K absorption. (b) Magnified 300 K absorption and MCD spectra in the ⁴A₂→⁴T₁(P) ligand-field region prior to Zn exposure. (c) 300 and 10 K, 0.5 T MCD spectra. (d) EPR spectra at 300 K (before exposure) and between 160 and 300 K (after Zn exposure).

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FIG. 2. (a) 300 and (b) 10 K magnetic hysteresis loops measured for the $\text{Zn}_{1-x}\text{Co}^{2+}_x\text{ZnO}$ film from Fig. 1. SQUID magnetization data (open circles) are superimposed on the MCD data (solid line). 300 and 10 K MCD coercivities were 71 and 188 Oe, respectively.

netic, with strongly temperature-dependent MCD intensities growing in at low temperatures consistent with previous measurements.^{3,4,8,9} Upon exposure of the paramagnetic $\text{Co}^{2+}:\text{ZnO}$ films to Zn vapor, the 300 K MCD intensity was strongly enhanced and its band shape changed [Fig. 1(c), solid line]. The $^4A_2 \rightarrow ^4T_1(P)$ transition was still weakly evident, superimposed upon a new MCD feature spanning the entire visible range. In contrast with the MCD intensities of paramagnetic $\text{Co}^{2+}:\text{ZnO}$, which are strongly temperature dependent, this new MCD signal is nearly temperature independent [Fig. 1(c), solid and dashed lines]. There was no detectable MCD intensity in undoped ZnO films with or without exposure to Zn vapor.

The magnetic field dependence of the 300 and 10 K MCD intensities at different photon energies was measured for several $\text{Co}^{2+}:\text{ZnO}$ films before and after exposure to Zn vapor (Fig. 2). Before exposure to Zn vapor, the 300 K MCD intensities increased linearly with increasing magnetic field (data not shown), consistent with paramagnetism. In contrast, the magnetic field dependence of the MCD spectrum measured after Zn vapor diffusion revealed magnetic ordering at 300 K. Hystereses measured by MCD at 300 and 10 K for the film from Fig. 1 are shown in Fig. 2. For comparison, 300 and 10 K magnetization data measured for the same film using a SQUID magnetometer are also included in Fig. 2. The SQUID and MCD hystereses are in excellent agreement. Observation of the same hystereses and temperature dependence over the entire spectral range suggests that the broad MCD signal in Fig. 1(c) all comes from a single chromophore, which we propose to be the ferromagnetic DMS $\text{Zn}_{1-x}\text{Co}^{2+}_x\text{ZnO}$.

Figure 3 plots the deconvoluted ferromagnetic and para-

FIG. 3. Dependence of the deconvoluted ferromagnetic (closed diamonds) and paramagnetic (open circles) MCD intensities of a $\text{Co}^{2+}:\text{ZnO}$ film on Zn vapor anneal temperature, T_A . MCD intensities were measured at 300 K and 0.6 T. The dashed line shows the vapor pressure of Zn metal in the same temperature range.

magnetic $\text{Co}^{2+}:\text{ZnO}$ MCD intensities versus Zn vapor annealing temperature (T_A). At $T_A \leq 375^\circ\text{C}$, vacuum annealing with Zn metal had no effect on $\text{Co}^{2+}:\text{ZnO}$ magnetism or MCD. Increasing T_A just slightly from 375 to 400°C had a dramatic effect on both. The sharp increase in MCD intensity with such a small change in T_A reveals a discrete thermal activation barrier. This barrier is undoubtedly associated with the vaporization of Zn metal. The vapor pressure of Zn metal over this same temperature range¹⁶ is included in Fig. 3 and correlates very well with the activation of ferromagnetism in the $\text{Co}^{2+}:\text{ZnO}$ films. Rather surprisingly the ferromagnetic MCD intensity reached a maximum at $T_A \approx 425^\circ\text{C}$ and actually decreased substantially at higher T_A . Although the decrease in ferromagnetic MCD intensity with greater T_A at first suggested film decomposition, the MCD spectra of these samples still clearly showed the signature $^4A_2 \rightarrow ^4T_1(P)$ ligand-field feature of substitutional Co^{2+} in ZnO, indicating that the DMS did not decompose under these conditions. Indeed, careful examination of the paramagnetic Co^{2+} ligand-field MCD intensity shows a dependence on T_A that is inversely related to the ferromagnetic MCD signal intensity, having a minimum precisely where ferromagnetism is maximized and returning again at higher T_A (Fig. 3). These data demonstrate conclusively that cobalt segregation out of the ZnO lattice is not the cause of the diminished ferromagnetism at $T_A \geq 500^\circ\text{C}$ and is not the source of the ferromagnetism at $T_A < 500^\circ\text{C}$. These conclusions are supported by several control experiments described previously,⁶ in which it was demonstrated, for example, that these films show no detectable cobalt migration even after 15 h of vacuum annealing at 500°C , that films annealed in Zn vapor at 600°C for 2 h are returned quantitatively to their original paramagnetic phase with brief, aerobic annealing (e.g., ~ 1 min at 500°C), and that very similar results are obtained with epitaxial films grown by metal-organic chemical vapor deposition (MOCVD) that have orders-of-magnitude smaller surface areas, all inconsistent with phase segregation. The cause of the maximum in ferromagnetism at $T_A \approx 425^\circ\text{C}$ remains unknown, but these data clearly support the assignment of the broad MCD signal in Fig. 1(c) to ferromagnetic $\text{Zn}_{1-x}\text{Co}^{2+}_x\text{ZnO}$.

Similar broad sub-band-gap ferromagnetic MCD features have been reported previously for $\text{Co}^{2+}:\text{ZnO}$ ¹⁰ and $\text{Co}^{2+}:\text{TiO}_2$.¹¹ Since the ferromagnetic MCD signal of $\text{Co}^{2+}:\text{ZnO}$ did not resemble that of paramagnetic $\text{Co}^{2+}:\text{ZnO}$ and specifically lacked the $^4A_2 \rightarrow ^4T_1(P)$ ligand-field feature of substitutional Co^{2+} in ZnO, there was speculation that it should be attributed to phase-segregated precipitates.¹⁰ Broad sub-band-gap ferromagnetic MCD features have also been observed in $\text{Mn}:\text{GaAs}$,¹⁷ $\text{Cr}:\text{ZnTe}$,¹⁸ and $\text{Mn}:\text{InAs}$,¹⁹ however, materials for which the intrinsic origins of ferromagnetism are less controversial. We propose that the ferromagnetic MCD signal in Fig. 1(c) is indeed intrinsic in origin and that it differs from the MCD of paramagnetic $\text{Co}^{2+}:\text{ZnO}$ ($S=3/2$) because the transitions originate from a fundamentally different (ferromagnetic) electronic ground state.

In models of donor-mediated ferromagnetism in $\text{Co}^{2+}:\text{ZnO}$,²⁰ shallow donors hybridize with the dopant 3d orbitals to yield a spin-split impurity band near the Fermi level, just below the conduction band.^{6,21} We propose that the broad MCD signal in Fig. 1(c) arises from low-energy donor-type photoionization processes originating from the spin-

FIG. 4. (Color online) Schematic illustration of the spin-dependent density of states of (a) paramagnetic $\text{Co}^{2+}:\text{ZnO}$ and (b) ferromagnetic $\text{Zn}_i:\text{Co}^{2+}:\text{ZnO}$. Scheme format adapted from Ref. 20.

split cobalt/ Zn_i donor impurity band. The decrease in photoionization threshold upon conversion from paramagnetic $\text{Co}^{2+}:\text{ZnO}$ (1.73 eV, Ref. 22) to ferromagnetic $\text{Zn}_i:\text{Co}^{2+}:\text{ZnO}$ (<1.5 eV) is consistent with the formation of a shallow donor impurity band, as summarized schematically in Fig. 4. In this assignment, the breadth of the ferromagnetic MCD signal in Fig. 1(c) reflects the multitude of excited states accessed at similar relatively low photon energies above the donor impurity band [Fig. 4(b)].

There is extensive literature precedence for the appearance of new transitions in the optical spectroscopies of inorganic materials upon formation of new magnetic ground states due to magnetic exchange coupling. For example, analogous broad near infrared (NIR) transitions are observed in the absorption spectra of manganites below but not above T_C .²³ Another relevant example is found in the spectroscopy of the well-defined molecular species $[\text{Fe}_2(\text{OH})_3(\text{tmtacn})_2]^{2+}$ (tmtacn=trimethyltriazocyclononane), in which two Fe^{3+} ions are coupled together ferromagnetically by an additional itinerant electron via Zener's double exchange mechanism.²⁴ The spectroscopy of this dimer bears little resemblance to those of analogous Fe^{2+} or Fe^{3+} complexes, or of analogous antiferromagnetically coupled iron dimers. Specifically, an intense new absorption and MCD band dominates the spectra of $[\text{Fe}_2(\text{OH})_3(\text{tmtacn})_2]^{2+}$ that has no analog in comparable Fe^{2+} or Fe^{3+} complexes. The observation of an MCD spectrum dominated by new transitions in ferromagnetic $\text{Zn}_i:\text{Co}^{2+}:\text{ZnO}$ is thus consistent with the formation of a new magnetic ground state via magnetic exchange coupling.

The paramagnetic-to-ferromagnetic phase transition should not only alter the optical spectra of a DMS, but should generally affect the results of every experiment that selectively probes the valence electrons [e.g., magnetism, optical MCD, absorption, and electron paramagnetic resonance (EPR)]. EPR spectra of the $\text{Co}^{2+}:\text{ZnO}$ films collected before and after exposure to Zn metal vapor support this assertion [Fig. 1(d)]. The EPR spectrum of paramagnetic $\text{Co}^{2+}:\text{ZnO}$ is featureless at 300 K due to rapid relaxation within the 4A_2 ground state, but shows the well-known $g=2.25$ and 4.55 resonances²⁵ at cryogenic temperatures (data not shown). In contrast, the EPR spectrum of $\text{Zn}_i:\text{Co}^{2+}:\text{ZnO}$ shows new ferromagnetic resonance intensity at 300 K, the breadth of which reflects the high density of Zeeman sublevels within the Zeeman-split ferromagnetic ground state. The absence of signatures of the paramagnetic ground state in valence electronic spectroscopies therefore cannot be used to evaluate the integrity of a ferromagnetic phase of the same DMS. For this purpose, core-level spectroscopies are more appropriate.²⁶

In summary, 300 K ferromagnetism was detected by MCD spectroscopy in polycrystalline $\text{Co}^{2+}:\text{ZnO}$ films ex-

posed to Zn vapor. The broad sub-band-gap MCD signal of the ferromagnetic phase is attributed to low-energy donor-type photoionization transitions originating from a shallow spin-split $\text{Co}^{2+}/\text{Zn}_i$ donor impurity band. A similar interpretation is proposed for the sub-band-gap MCD intensities of ferromagnetic $\text{Co}^{2+}:\text{TiO}_2$ and related oxide DMSs.

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¹²Polycrystalline films (0.05–3.00 μm thick) of $\text{Co}^{2+}:\text{ZnO}$ were prepared on quartz substrates and characterized as described previously.⁶ Exposure to Zn vapor was achieved by sealing the films and Zn powder in glass tubes under vacuum ($\sim 10^{-3}$ Torr) and annealing for 1 h at temperatures between 350 and 550 °C. MCD, electronic absorption, and magnetic susceptibility data were collected as described previously.^{6,9}

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