

Optical evidence of strong coupling between valence-band holes and d -localized spins in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$

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We report on optical-absorption study of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x=0-0.06$) films on fused silica substrates taking special attention to the spectral range of the fundamental absorption edge (3.1–4 eV). Well-pronounced excitonic lines observed in the region 3.40–3.45 eV were found to shift to higher energies with increasing Mn concentration. The optical band-gap energy increases with x too, reliably evidencing strong coupling between oxygen holes and localized spins of manganese ions. In the 3.1–3.3 eV region the optical-absorption curve in the manganese-contained films was found to shift to lower energies with respect to that for undoped ZnO. The additional absorption observed in this range is interpreted as a result of splitting of a localized Zhang-Rice-type state into the band gap.

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I. INTRODUCTION

Dilute magnetic semiconductor $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ is one of the most promising materials for the development of optoelectronic and spin electronic devices with ferromagnetism retained at practical temperatures (i.e., >300 K). However, researchers are confronted with many complex problems. Ferromagnetic ordering does not always appear and the nature of its instability is a subject of controversy. In addition, optical properties of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ appreciably differ from those in $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ and $\text{Zn}_{1-x}\text{Mn}_x\text{S}$ related compounds, where the intracenter optical transitions of Mn^{2+} ions are conventionally observed in the optical-absorption and photoluminescence spectra.^{1,2} In contrast, a very intense absorption in the 2.2–3.0 eV region was reported in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ without any manifestations of intracenter transitions,^{3–5} and photoluminescence due to ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ optical transition of Mn^{2+} is absent as well. Interpretation of this absorption band as a charge transfer^{3,5} is complicated by the fact that Mn^{2+} forms neither d^5/d^4 donor nor d^5/d^6 acceptor levels in the forbidden gap of ZnO.^{6,7}

To resolve this contradiction, Dietl⁸ put forward the concept that the oxides and nitrides belong to the little studied family of dilute magnetic semiconductors with strong correlations. Characteristic features of such compounds are an increase in the band gap with the concentration of magnetic ions and emergence of a Zhang-Rice (Z-R)-type state in the forbidden gap⁹ arising as a result of strong exchange coupling of $3d$ -localized spin of the impurity centers and valence-band holes. According to Ref. 8, fulfillment of strong hybridization condition depends on the ratio of the impurity-center potential U to a critical value U_c ; a coupled hybrid state can be formed when $U/U_c > 1$. Existence of such electronic state has been verified by *ab initio* theoretical treatment of electron correlations using the local spin-density approximation (LSDA+ U model) and calculation of the exchange coupling values.¹⁰ In $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ the hole can originate by electron transfer from the Mn^{2+} adjacent oxygen to the conduction band. The resulting hole localizes as the Z-R

state leading to appearance of additional broad, intense absorption band. In this way the study of optical-absorption spectra can be used as a probe to identify the Z-R states.

It is known that the optical band-edge absorption spectrum of Mn-doped ZnO is characterized by the onset of a strong rise of the absorption coefficient in the ~ 3.1 eV spectral region.¹¹ In Refs. 11 and 12, this absorption in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films was treated as a product of direct interband optical transitions using conventional formula $\alpha^2 \sim (\hbar\omega - E_g)$. The resulting magnitudes of band gap for composition with $x=0.05$ have been estimated as $E_g=3.10$ eV (Ref. 11) and 3.25 eV,¹² which is appreciably less than $E_g=3.37$ eV in ZnO.¹³ Such “redshift” of the band gap was considered in Ref. 12 as a result of p - d exchange interaction, in analogy to the shift of the excitonic lines in reflectivity and luminescence spectra observed in Ref. 14 for $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$. At the same time theory predicts an increase in $E_g(x)$ with x for $\text{Zn}_{1-x}\text{Mn}_x\text{O}$.⁸ Also excitonic absorption spectrum in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ nanopowders,¹⁵ appeared to be located at energies higher than that in ZnO nanopowders, that does not confirm the shift of E_g to lower energies for $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films.

In this work we report on the optical-absorption spectra studies in thin $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films deposited on fused silica substrates. Using such films we succeed to detect the absorption spectra of excitons and to determine reliably the width of the optical gap E_g . This allowed us to elucidate the nature of the additional absorption band appearing at $\hbar\omega < E_g$ near the fundamental absorption edge as a result of splitting of one more Z-R-type state due to strong hybridization and exchange coupling of $3d$ -localized spin of the manganese and valence-band oxygen hole.

II. EXPERIMENTAL

Thin $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films with $x=0-0.06$, 120–130, and 200–250 nm of thicknesses were deposited on fused silica substrates by the atmospheric barrier-torch discharge technique, as it was described in Refs. 16 and 17. The substrate

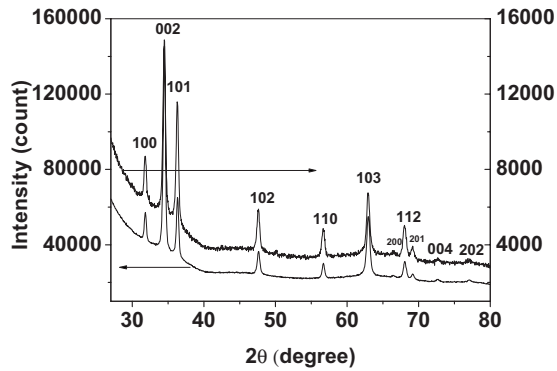


FIG. 1. XRD pattern of ZnO (left scale) and $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ (right scale) films.

temperature during deposition was kept at $\sim 200^\circ\text{C}$. Mn content was controlled by measurements of Mn and Zn emission ($\lambda_{\text{em}}=4031\text{ \AA}$ and 4810 \AA , respectively) of plasma during deposition and crosschecked by the postgrown EPMA (JEOL JXA-733 device with Kevex Delta Class V microanalyser) analysis with accuracy $\pm 0.3\%$. X-ray diffraction (XRD) studies were performed with a Panalytical X'PertMRD Pro diffractometer with Eulerian cradle using $\text{Cu } K\alpha$ radiation ($\lambda_{\text{em}}=1.5405\text{ \AA}$) in the parallel beam geometry. XRD profiles were fitted with the Pearson VII function by the DIFFPATAN code.¹⁸ Correction for instrumental broadening was performed using NIST LaB6 standard and Voigt function method.¹⁹

Optical absorption within the 1.2–6.5 eV spectral region was measured in unpolarized light at room temperature using a Shimadzu UV-2401 PC spectrophotometer. The bare silica substrate and $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ film on silica substrate were mounted into the reference and test channel, respectively. The optical density αd (product of optical-absorption coefficient and film thickness) was calculated without taking into account multiple reflections as $\alpha d = \ln(I_0/I)$, where I_0 and I are intensities of light passed through bare substrate and film/substrate structure.

III. RESULTS AND DISCUSSION

Figure 1 presents XRD pattern for ZnO and $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ films, as an example. All obtained films revealed crystalline block structure with dominant (002) orientation of blocks' optical C -axes aligned normal to substrate.

Observed reflexes correspond to wurtzite structure evidencing absence of extraneous phases. Both pure and Mn-doped ZnO films appeared to be compressively strained with 0.2% of strain, $s=(a_0-a_s)/a_0$, where a_0 and a_s are the lattice parameters of nonstrained and strained films. The analysis reveals that the value of compressive strain is controlled predominantly by stresses, but not by presence of Mn (at least for Mn concentrations used).

Figure 2 presents the optical-absorption spectra for $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films. A wide absorption line is seen in the region of the band edge (Fig. 2), whose energy appears to be shifted by about 100 meV to higher energies in comparison with the excitonic line in ZnO [$\sim 3.31\text{ eV}$ at $T=300\text{ K}$ (Ref.

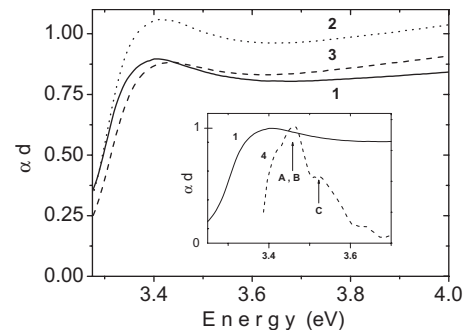


FIG. 2. Exciton absorption spectra of compressed $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films: 1— $x=0\%$, 2— $x=1.8\%$, and 3— $x=5\%$; film thickness: $d=(120-130)\text{ nm}$; and $T=300\text{ K}$. Inset shows excitonic absorption lines for compressed ZnO: 1— $T=300\text{ K}$ and 4— $T=77.3\text{ K}$.

13]). The line shift is very likely connected with the compressive strain of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films mentioned above. The wide and shifted line has been observed earlier in ZnO film on sapphire substrate^{20,21} and was identified as a shift of the excitonic line due to compressive strain of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films.²¹ The inset represents spectra of this line obtained in ZnO at $T=300\text{ K}$ and 77.3 K . It is seen that the excitonic line is narrowed, split into two components and shifted to higher energies on lowering the temperature, clearly evidencing its excitonic nature. The first line is a sum of A and B excitons, the second one is the C exciton appearing due to disorientation of blocks forming the film.¹⁶ Analogous temperature evolutions have been reported for a wide excitonic line in ZnO nanocrystals.¹⁵

As the concentration of Mn impurity increases, the excitonic line additionally broadens and shifts to higher energies. Figure 3 shows the actual Mn concentration shift of the excitonic line energy $\hbar\omega_{\text{exc}}$. It is seen that the increase in Mn concentration leads to not only changes in the excitonic spectrum but also exhibits enhancement of the band-gap energy in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films (band-gap magnitude can be estimated as $E_g = \hbar\omega_{\text{exc}} + E_{\text{exc}}$, where $E_{\text{exc}}=60\text{ meV}$ is the excitonic binding energy¹³). It is known that the band-gap magnitude in ZnO-MnO system varies from 3.37 eV in ZnO up to 3.8 eV in MnO.²² According to the theoretical analysis⁸ performed taking into account inversion of Γ_7 and Γ_9 valence subbands in ZnO,^{23,24} strong coupling of manganese spin and p states of valence band leads to appearance of a positive

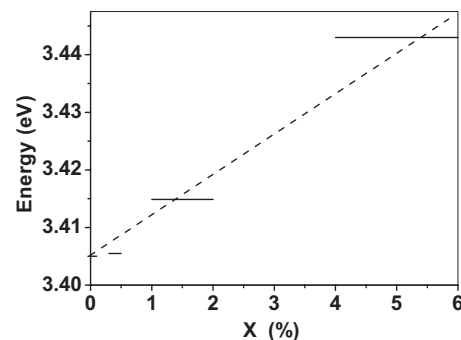


FIG. 3. Mn-concentration dependence of the excitonic line energies for $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films.

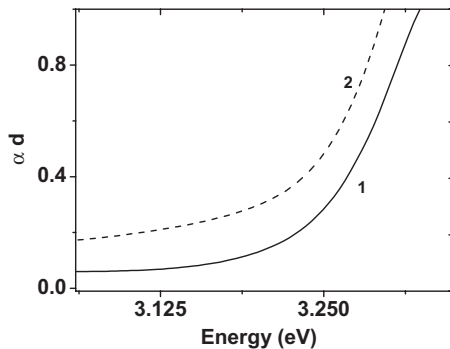


FIG. 4. Spectral dependence of the optical density αd in the 3.1–3.3 eV spectral region for $\text{Zn}_{1-x}\text{Mn}_x\text{O}$, 1— ZnO ; 2— $x=0.3\text{--}0.5\%$; film thickness 200–250 nm; and $T=300$ K.

additive in optical absorption of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ at small x values. The sum of two contributions at sufficiently small x results in an increase in E_g magnitude. The rise of the band-gap magnitude with the admixture of the second component $E_g(x)$ has been observed in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ (Ref. 25) for excitonic lines registered in the reflection spectra at 1.6 K. The shift of the excitonic line to higher energies was observed in $\text{Zn}_{0.99}\text{Fe}_{0.01}\text{O}$, too.²⁰ In the case of weak d - p coupling the additive into the band gap change appeared to be negative.⁸ In this case the band-gap value E_g decreases with x for $x \leq 0.1$, as it was found for $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ (Fig. 6 in Ref. 14) and for $\text{Cd}_{1-x}\text{Mn}_x\text{S}$.²⁶ Therefore, the observed rise of the $E_g(x)$ value with Mn addition provides the reliable experimental proof that the strong hybridization condition $U/U_c > 1$ in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ is fulfilled. Figure 4 presents optical absorption in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films recorded in the spectral region 3.1–3.3 eV.

It is seen that the onset of optical absorption in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films emerges at lower energies than that for ZnO ones. Analogous shift had been observed earlier in the spectrum of the photoluminescence excitation over deep impurity centers in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ for Ref. 15.

Unlike authors of Refs. 11 and 12, we assume that additional absorption of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ (in comparison with ZnO) in the 3.1–3.3 eV range is a result of pushing the Z-R-type states out of valence band to the forbidden gap.⁹

The essence of this state consists of localization of the valence-band hole within the first coordination sphere on the oxygen ions as a result of strong exchange interaction of manganese and hole spins. Such electronic state is similar to the Z-R-type state originally considered for La_2CuO_4 oxide

superconductor.⁹ This state is a singlet one, because in La_2CuO_4 the spins of d^9 configuration of Cu^{2+} ion and oxygen holes are equal but of opposite direction. The situation is more complex in the case of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ since the top of valence band is formed by three close subbands: Γ_7 , Γ_9 , and Γ_7 .^{23,24} In such case we have serious reasons to assume that not only the presence of one deep Z-R-type state is responsible for optical absorption in the 2.2–3.0 eV spectral region. We assume the presence of another, relatively shallow Z-R-type state too, which has been split off into the gap providing additional absorption in the 3.1–3.3 eV region of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$. Tentatively, using results^{11,12,15} we estimate the splitting of the second Z-R level from the valence band as 0.12–0.27 eV. More reliable determination of the split energy can be performed using more sensitive methods of absorption spectra, e.g., modulation methods, which are in progress.

IV. CONCLUSION

Thin $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films ($x=0\text{--}0.06$) have been sintered and their optical-absorption spectra were investigated. The well-pronounced excitonic absorption lines in the fundamental absorption spectral regions were observed. Position of excitonic absorption lines in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films shifts to higher energies with increasing Mn content. This evidences an increase in the E_g magnitude with x for small values x and reliably corroborates fulfillment of the strong coupling criterion ($U/U_c > 1$) in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$. The last effect leads to emergence of an intense optical-absorption band in the 2.2–3.0 eV region due to the presence of the band-gap Z-R-type state. The additional absorption observed in the range of 3.1–3.3 eV is interpreted as a result of splitting of one more Z-R-type states into the band gap.

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¹D. W. Langer and H. J. Richter, *Phys. Rev.* **146**, 554 (1966).

²T. Hoshina and H. Kawai, *Jpn. J. Appl. Phys.* **19**, 267 (1980).

³F. W. Kleinlein and R. Helbig, *Z. Phys.* **266**, 201 (1974).

⁴R. Beaulac, P. I. Archer, and D. R. Gamelin, *J. Solid State Chem.* **181**, 1582 (2008).

⁵T. Fukumura, Z. Jin, A. Ohtomo, H. Koinuma, and M. Kawasaki, *Appl. Phys. Lett.* **75**, 3366 (1999).

⁶K. A. Kikoin and V. N. Fleurov, *Transition Metal Impurities in*

Semiconductors: Electronic Structure and Physical Properties (World Scientific, Singapore, 1994), p. 349.

⁷T. Dietl, *J. Magn. Mater.* **272-276**, 1969 (2004).

⁸T. Dietl, *Phys. Rev. B* **77**, 085208 (2008).

⁹F. C. Zhang and T. M. Rice, *Phys. Rev. B* **37**, 3759 (1988).

¹⁰T. Chanier, F. Viot, and R. Hayn, *Phys. Rev. B* **79**, 205204 (2009).

¹¹V. Shinde, T. Gujar, C. Lokhande, R. Mane, and S.-H. Han,

- Mater. Chem. Phys.* **96**, 326 (2006).
- ¹²Y. Guo, X. Cao, X. Lan, C. Zhao, X. Hue, and Y. Song, *J. Phys. Chem. C* **112**, 8832 (2008).
- ¹³Zh. L. Wang, *J. Phys.: Condens. Matter* **16**, R829 (2004).
- ¹⁴R. B. Bylisma, W. M. Becker, J. Kossut, U. Debska, and D. Yoder-Short, *Phys. Rev. B* **33**, 8207 (1986).
- ¹⁵V. I. Sokolov, A. Ye. Yermakov, M. A. Uimin, A. A. Mysik, V. A. Pustovarov, M. V. Chukichev, and N. B. Gruzdev, *J. Lumin.* **129**, 1771 (2009).
- ¹⁶M. Chichina, Z. Hubicka, O. Churpita, and M. Tichy, *Plasma Processes Polym.* **2**, 501 (2005).
- ¹⁷Z. Hubicka, M. Cada, M. Sicha, A. Churpita, P. Pokorny, L. Soukup, and L. Jastrabík, *Plasma Sources Sci. Technol.* **11**, 195 (2002).
- ¹⁸<http://www.xray.cz/priv/kuzel/dofplatan/>
- ¹⁹R. Kuzel, Jr., R. Cerny, V. Valvoda, and M. Blomberg, *Thin Solid Films* **247**, 64 (1994).
- ²⁰Z. Jin, T. Fukumura, M. Kaasaki, K. Ando, H. Saito, T. Skiguchi, Y. Z. Yoo, M. Murakami, Y. Matsumoto, T. Hasegawa, and H. Koinuma, *Appl. Phys. Lett.* **78**, 3824 (2001).
- ²¹J.-M. Chauveau, J. Vives, J. Zuniga-Perez, M. Lüigt, M. Teisseire, C. Deparis, C. Morhain, and B. Vinter, *Appl. Phys. Lett.* **93**, 231911 (2008).
- ²²R. J. Lad and V. E. Henrich, *Phys. Rev. B* **38**, 10860 (1988).
- ²³K. Shindo, A. Morita, and H. Kamimura, *J. Phys. Soc. Jpn.* **20**, 2054 (1965).
- ²⁴W. Y. Liang and A. D. Yoffe, *Phys. Rev. Lett.* **20**, 59 (1968).
- ²⁵W. Pacuski, D. Ferrand, J. Gibert, C. Deparis, J. A. Gaj, P. Kossacki, and C. Morhain, *Phys. Rev. B* **73**, 035214 (2006).
- ²⁶M. Ikeda, K. Itoh, and H. Sato, *J. Phys. Soc. Jpn.* **25**, 455 (1968).