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Magnetic Properties of $Zn_{1-x}Mn_xTe_{1-y}O_y$ Alloys

A. Avdonin, W. Knoff and R.R. Gałązka

Institute of Physics, Polish Academy of Sciences, al. Lotników 32/46, 02-668 Warsaw, Poland

The results of the magnetization and photoluminescence measurements of the $Zn_{1-x}Mn_xTe_{1-y}O_y$ are presented. Under field cooling conditions a phase transition is observed. The dependence of the temperature of transition on oxygen concentration is analyzed. A model is proposed.

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1. Introduction

$Zn_{1-x}Mn_xTe_{1-y}O_y$ (ZMTO) is a derivative of a typical semimagnetic semiconductor $Zn_{1-x}Mn_xTe$ (ZMT) which is famous for inherent strong interaction between manganese ions and free carriers (*sp–d* interaction). Oxygen doping greatly changes the band structure of ZMT, and hence it is expected to influence *sp–d* interaction. Such changes are expected for both holes and electrons. Indeed, the oxygen substituting tellurium atoms in the lattice should change the valence band states since the valence band in ZMT is formed mostly of *p*-orbitals of Te anions. On the other hand, it was reported that a large enough amount of oxygen in ZMT produces a splitting of the conduction band due to the "band anticrossing effect" [1].

2. Experimental

The samples were synthesized by fast crystallization of the melted mixture of ZnTe, MnTe and ZnO. The detailed description of the procedure is presented in [2]. The composition of the samples was investigated by X-ray diffraction, secondary ion mass spectroscopy (SIMS), microprobe and bulk energy dispersive X-ray (EDX) analysis. Microprobe investigation showed that the crystal grains are composed of $Zn_{1-x}Mn_xTe$ with small amount of oxygen. Between the grains there are precipitations rich in Mn, Zn and O and poor in Te. Although the size of precipitations is typically 10 μm, usually no additional peaks are visible on the X-ray diffraction diagram.

In studied samples Mn content (x) varied between 0.015 and 0.185. The EDX measurement of oxygen content provided inconsistent results. Thus the oxygen concentration in the samples was estimated by the X-ray diffraction measurements, considering the dependence of the lattice constant on oxygen concentration and assuming that the Vegard's rule applies in this case [2]. The fact that the lattice constant of the alloy is sensitive only to oxygen dissolved in the $Zn_{1-x}Mn_xTe$ lattice and is not sensitive to precipitations, speaks in favor of this method. The oxygen content (y) varies between 0.0008 and 0.0056 and it is proportional to the concentration of manganese.

The magnetization measurements were performed on a SQUID magnetometer in the range between 5 K and 100 K. On zero field cooling (ZFC) conditions all samples are paramagnetic with the Curie–Weiss ($T_{\rm CW}$) temperature between -0.3 K and -1.9 K. The absolute value of $T_{\rm CW}$ increases with increasing manganese content according to $T_{\rm CW} = -72x$. Such trend indicates on the increase of the antiferromagnetic interaction with the decreasing average distance between manganese ions. The precipitations are usually seen as a weak ferromagnetic background with susceptibility of order 10^{-6}–10^{-7} emu/g.

3. Results

There is a difference between ZFC and field cooling (FC) magnetization. An example of ZFC and FC magnetization is presented in Fig. 1 together with the difference between those two curves. Typically upon FC measurement an additional magnetization appears below a certain transition temperature. The fact that it does not appear on ZFC conditions means that the magnetic moments are frozen below that temperature. The magnetic moments producing this additional magnetization are frozen in a such way that below the transition temperature the field as much as 1000 Oe does not influence their orientation. For example, dependence $M(H)$ measured below the transition temperature will be shifted by an amount equal to additional magnetization.

It is tempting to explain such behavior by the presence of manganese oxide precipitations, which indeed were observed between crystallites. There are reports on ferrimagnetic phase transitions in Mn_3O_4 and Mn_2O_3 with transition temperatures 41–43 K [3] and 39 K [4], respectively. However those values, although close, are different from presented here. Besides, presented transition temperatures depend on sample composition (Fig. 2); they were found to be proportional to diluted oxygen concentration, estimated from the X-ray diffraction data. One expects that gradual increasing of oxygen content

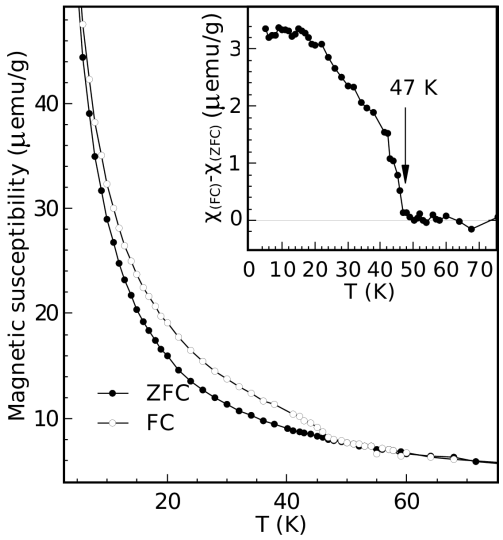

Fig. 1. FC (open circles) and ZFC (filled circles) magnetic susceptibility as a function of temperature measured at 200 Oe. In the inset: difference between FC and ZFC magnetic susceptibility as a function of temperature.

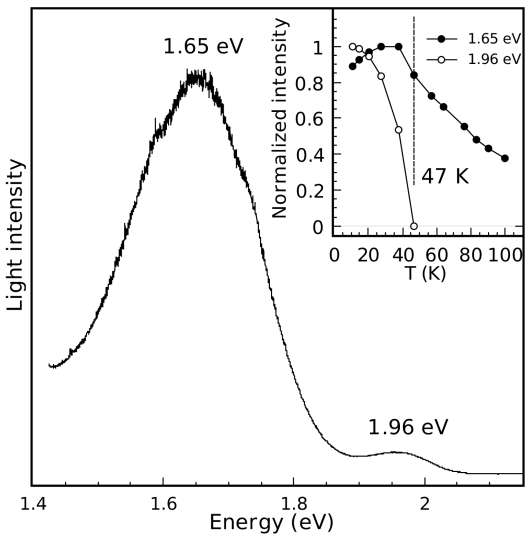

Fig. 3. PL spectra of the ZMTO sample at 11 K. In the inset: normalized intensity of the PL bands at 1.65 eV (filled circles) and 1.96 eV (open circles) as a function of temperature. Vertical dashed line indicates the temperature of magnetic transition for this sample.

would increase gradually the magnitude of the effect (the number of precipitations) but not the transition temperature. Thus the transition might not be related with macroscopic precipitations. The dependence of the transition temperature on concentration suggests that magnetic moments producing the effect are scattered.

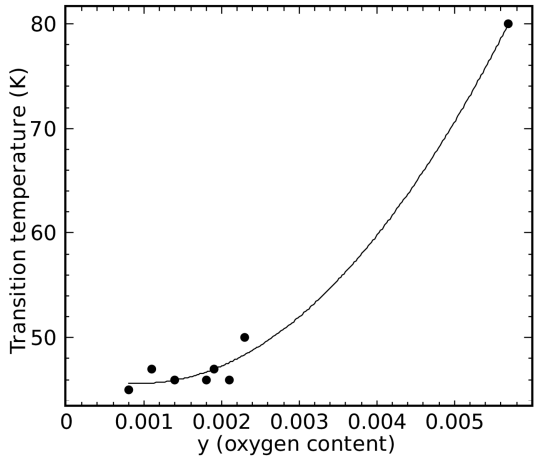

Fig. 2. Transition temperature as a function of oxygen content.

The structure and nature of the mentioned above "scattered" components is unknown. Possibly they are some complex defects composed of oxygen and manganese impurity. This hypothesis is supported by the fact that distribution of the diluted oxygen is non-statistical, i.e. in $Zn_{1-x}Mn_xTe_{1-y}O_y$ the oxygen atom is always placed near at least one manganese atom [2]. In fact this is why the oxygen solubility in ZnTe increases in the presence of manganese impurity. There is a correlation between magnetization and photoluminescence (PL) data. For illustration the PL spectrum of one of $Zn_{1-x}Mn_xTe_{1-y}O_y$ samples is presented in Fig. 3. The band at 1.96 eV is identified as internal transitions of Mn^{2+} ions. Another band, at 1.65 eV was only observed in samples simultaneously doped with manganese and oxygen and is attributed to some complex (MnO) defects [2]. The correlation is manifested in the temperature dependence of the intensities of those bands (Fig. 3, inset). The Mn^{2+} band (1.96 eV) decreases and disappears at 47 K at the same temperature where the step appears on the FC magnetization curve. The band related with (MnO) complexes first increases and then passes through a maximum slightly below that temperature. Authors think that such dependence is related with variation of free carrier concentration with temperature. If so, it is possible that magnetic transition temperature is also related with the concentration of free carriers.

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