Journal of Magnetism and Magnetic Materials 394 (2015) 138–142

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

An X-band Co^{2+} EPR study of $Zn_{1-x}Co_xO$ ($x=0.005$–0.1) nanoparticles prepared by chemical hydrolysis methods using diethylene glycol and denaturated alcohol at 5 K

Sushil K. Misra [a,*], S.I. Andronenko [b], S. Srinivasa Rao [c], Jordan Chess [c], A. Punnoose [c]

[a] Physics Department, Concordia University, Montreal, QC, Canada H3G 1M8
[b] Physics Institute, Kazan Federal University, Kazan 420008, Russian Federation
[c] Department of Physics, Boise State University, Boise, ID 83725-1570, USA

ARTICLE INFO

Article history:
Received 9 January 2015
Received in revised form
22 June 2015
Accepted 23 June 2015
Available online 25 June 2015

Keywords:
EPR
Nanoparticle
ZnO
Dilute magnetic semiconductor
Co^{2+} ion

ABSTRACT

EPR investigations on two types of dilute magnetic semiconductor (DMS) ZnO nanoparticles doped with 0.5–10% Co^{2+} ions, prepared by two chemical hydrolysis methods, using: (i) diethylene glycol ($(CH_2CH_2OH)_2O$) (NC-rod-like samples), and (ii) denatured ethanol (CH_3CH_2OH) solutions (QC-spherical samples), were carried out at X-band (9.5 GHz) at 5 K. The analysis of EPR data for NC samples revealed the presence of several types of EPR lines: (i) two types, intense and weak, of high-spin Co^{2+} ions in the samples with Co concentration $>0.5\%$; (ii) surface oxygen vacancies, and (iii) a ferromagnetic resonance (FMR) line. QC samples exhibit an intense FMR line and an EPR line due to high-spin Co^{2+} ions. FMR line is more intense, than the corresponding line exhibited by NC samples. These EPR spectra varied for sample with different doping concentrations. The magnetic states of these samples as revealed by EPR spectra, as well as the origin of ferromagnetism DMS samples are discussed.

1. Introduction

Dilute magnetic semiconductors (DMS), lightly doped with transition-metal (TM) ions, exhibit novel magnetic and electrical properties. They possess room-temperature ferromagnetism and characterized by a rather high conductivity, rendering them potential spintronic devices. Co^{2+} -doped ZnO nanoparticles are prospective DMS candidates, and have been investigated extensively [1–25]. EPR studies of the Co^{2+} ion in magnetic semiconductors, such as SnO_2 [26], provide information on the magnetic state of this compound, and its behavior under different synthesis conditions [1,16–25]. The main conclusions of these investigations are: (i) there are present both localized Co^{2+} ions and ferromagnetically coupled Co^{2+} ions in the host material; (ii) The spin-Hamiltonian (SH) parameters for the Co^{2+} ion are very close to those for Co^{2+}-substituted ZnO crystal, characterized by high-spin Co^{2+} ions; (iii) there is exhibited an electron paramagnetic resonance (EPR) signal due to Co^{2+} ions, situated in distorted local environment, characterized by high-spin Co^{2+} ions.

ZnO is a semiconductor with the energy gap of 3.3 eV, which can be increased by introducing different impurities up to 4 eV [27]. Magnetic properties, X-ray photoelectron spectroscopy, EPR, and photoluminescence study of ZnO nanoparticles, doped with Co ions, prepared using the acetate method, were recently reported [1]. It is the purpose of the present paper to report detailed X-band (9.5 GHz) EPR investigations at 5 K on two types of ZnO nanoparticles, NC and QC, doped with 0.5%, 2.5%, 5%, 10% Co^{2+} ions, prepared from two different solutions. The present study is aimed to estimate the spin-Hamiltonian parameters of the Co^{2+} ions in NC and QC samples, and to find the reasons for different magnetization observed in NC and QC samples, and the origin of ferromagnetism in these samples.

2. Sample preparation and structure

NC and QC samples of $Zn_{1-x}Co_xO$ nanoparticles, doped with Co^{2+} ions, with $x=0.005$, 0.025, 0.05, 010, were prepared using chemical hydrolysis methods [1] using: (i) diethylene glycol ($(CH_2CH_2OH)_2O$) (NC-rod-like samples [28], referred to as NC hereafter), and (ii) denatured ethanol (CH_3CH_2OH) solutions (QC-spherical samples [29], referred to as QC hereafter).

X-ray diffraction (XRD) was employed to investigate the structural properties and crystal size, as well as to rule out the presence of undesired impurity phases. The structure and purity of NC samples has been discussed in detail in [1]. The average size of

* Corresponding author.
E-mail address: skmisra@alcor.concordia.ca (S.K. Misra).

http://dx.doi.org/10.1016/j.jmmm.2015.06.063
0304-8853/