1. Introduction

Nanostructures made of ZnO have attracted significant attention owing to their proposed applications in low-voltage and short-wavelength electro-optical devices, transparent ultraviolet protection films, and spintronic devices [1, 2]. A considerable attention has recently been devoted to high temperature ferromagnetism observed in transition metal doped oxides. Particularly ZnO has been identified as a promising host semiconductor material, exhibiting ferromagnetism when doped with most of the transition metals — V, Cr, Fe, Co, Ni [3]. However, the origin of ferromagnetic behavior is not very well known in these compounds. Recently, it was shown that the ferromagnetism in these materials can be induced by inclusions of nanoscale oxides of transition metals [4] and/or nanoparticles containing a large concentration of magnetic ions [5]. Novel methods enabling a control of nanoassembling of magnetic nanocrystals in nonconducting matrices as well as functionalities specific to such systems were described [5].

The samples were synthesized by use of the wet chemical method. First sample is assigned as (ZnO) where crystallite of FeO is identified [6]. Mean crystallite size is a = 24 nm. No other crystal phases are observed in these samples. In this work we present investigation of two samples. First sample is assigned as (ZnO)0.95(Fe2O3)0.05 (sample contains 5 wt.% of Fe2O3), where crystalline phase of ZnFe2O4 is identified. Mean crystallite size is a = 10 nm. Second sample is assigned as D590Fe10Zn (sample contains 90 wt.% of Fe2O3) where crystallite of Fe2O3 is identified with mean crystallite size a = 24 nm. No other crystal phases are observed in these samples.

XRD measurements did not reveal presence of ZnO phase in these samples. It is interesting that for the samples with lower concentration of Fe2O3 (up to 20 wt.% of Fe2O3) excitonic lines from ZnO are observed. In some samples, for instance sample containing 40 wt.% of Fe2O3, crystallites of ZnO and ZnFe2O4 are identified [6].

2. Results and discussion

The Raman spectra were excited by the 514.5 nm line of an Ar laser (the average power was about 120 mW) in the backscattering geometry. We used Jobin Yvon model U-1000 monochromator, with a conventional phototocounting system. In order to make low-frequency Raman modes visible we subtracted the intensity of the elastic scattering background by A/ωn approximation. Re-
resulting Raman spectra are presented in Fig. 1. The observed modes are deconvoluted using the Lorentzian line profile technique. For almost all samples, low-frequency Raman modes were identified.

Low-frequency modes are analyzed as confined acoustic vibrations of nanoparticles. The frequencies of acoustic vibrational modes can be calculated in the elastic continuum approximation. Parameters of the model are stiffness constants and mass density of the particle material. In doped samples ZnFe$_2$O$_4$ and Fe$_3$O$_4$ structures are identified. As the dimension of the particles is already determined and having in mind specific frequency to diameter dependence, we established material parameters and analyzed behavior of nanoparticles.

Transverse ($v_T$) and longitudinal ($v_L$) sound velocity are parameters of equation of motion of the three-dimensional elastic body. Transverse and longitudinal sound velocity are directly connected to stiffness constants and the mass density. If we assume that nanoparticles are small spheres, equation of motion must be solved in spherical coordinate. It is useful to introduce dimensionless variables $\eta = \omega R/v_T = \omega d/2v_T$ and $\xi = \omega R/v_L = \omega d/2v_L$, where $R$ is radius of the particle ($d$ is diameter). Boundary conditions definitely determine the solutions [7–11].

If one assumes that there is no displacement at the particle surface, it is so-called rigid boundary conditions. If one assumes that there is no force on the surface, i.e. radial components of the stress tensor at the surface are zero, it is so-called free-surface boundary conditions. We assumed the stress-free boundary conditions [10]. We believe that this model is adequate to describe behavior of nanoparticles in our samples, as there is no compact matrix surrounding them.

In spherical case, each value of angular momentum quantum number $l$ ($l = 0, 1, 2, \ldots$) gives a series of solutions. We numerate these solutions $n$ ($n = 0, 1, 2, \ldots$). So, eigensolutions are labeled as $\eta^{nl}$ ($\xi^{nl}$), and eigenstates are labeled as $(n, l)$. Two types of vibrational modes are obtained: spheroidal and torsional modes. As $\omega^{nl} = 2\eta^{nl}v_T/d$, i.e. $\omega^{nl} = 2\xi^{nl}v_L/d$, each solution gives one linear dependence $\omega^{nl} = f(1/d)$.

Dimensionless solutions of equation for spheroidal modes strongly depend on the material through ratio $v_L/v_T$. Solutions for torsional modes do not depend on material. According to the group theory analysis the spheroidal and $l = 0$ and $l = 2$ modes are Raman active [12]. Theory implies [13] that the spheroidal mode $(0, 0)$ is the most intensive in $l = 0$ series, and is the most intensive of all Raman active modes. In a lot of experimental spectra only this mode was detected. The first quadrupolar mode is the most intensive in $l = 2$ series. The frequency of $(0, 2)$ mode is almost always lower than the $(0, 0)$ mode frequency.

Structure of ZnFe$_2$O$_4$ is similar to Fe$_3$O$_4$. In our analysis we started from Fe$_3$O$_4$ acoustic properties. For Fe$_3$O$_4$ of spinel (cubic) structure we used following parameters: mass density 5240 kg/m$^3$ and stiffness constants $C_{11} = 2.17 \times 10^{11}$ N/m$^2$, $C_{12} = 1.21 \times 10^{11}$ N/m$^2$, $C_{44} = 0.46 \times 10^{11}$ N/m$^2$ [14]. Longitudinal and transverse sound velocities in a case of cubic crystal are: $v_L = (C_{11}/\rho)^{1/2} = 6400$ m/s and $v_T = (C_{44}/\rho)^{1/2} = 2960$ m/s. Solutions for Fe$_3$O$_4$, in case of stress-free boundary conditions, for the $l = 0$, $n = 0, 1, 2$ and $l = 2$, $n = 0, 1, 2, 3, 4$ are presented in Fig. 2a. We marked (solid cycles) positions of frequencies that are a result of deconvolution of ZnFe$_2$O$_4$ particles experimental spectra. First two frequencies, that are the best defined structures in spectra, are located very close to Fe$_3$O$_4$ (0, 0) and (0, 2) solutions, Fig. 2a. Also the mode at $\approx 24$ cm$^{-1}$ is more intensive than the mode at $\approx 12.6$ cm$^{-1}$.

We tentatively attributed mode at 24 cm$^{-1}$ to be $\omega^{00}$ (0, 0) and mode at 12.6 cm$^{-1}$ to be $\omega^{02}$ (0, 2). As $\omega^{00} = 2\xi^{00}v_L/d$ and $\omega^{02} = 2\xi^{02}v_T/d = 2\xi^{02}v_L/d$ follows that $\omega^{00}/\omega^{02} = \xi^{00}/\xi^{02} = 1.9$. From curves $\xi^{00}(v_L/v_T)$ and $\xi^{02}(v_L/v_T)$ function $g(v_L/v_T) = \xi^{00}(v_L/v_T)/\xi^{02}(v_L/v_T)$ can be established. As $\omega^{00}/\omega^{02} = 1.9$, from $g(v_L/v_T)$ follows that $v_L/v_T = 1.9$ and $\xi^{00}(1.9) = 2.68$. From $\omega^{00} = 24$ cm$^{-1}$, $d = 10$ nm follows: $v_L = 8355$ m/s and $v_T = v_L/1.9 = 4397$ m/s. These are new parameters necessary for further calculations.
Low-Frequency Raman Scattering from ZnO(Fe) Nanoparticles

Fig. 2. (a) Dependence of eigensolutions, for spheroidal modes in the surface stress-free approximation, on Fe$_3$O$_4$ nanoparticles inverse diameter: $v_L = 6400$ m/s and $v_T = 2960$ m/s. Plotted lines represent eigensolutions. Solid and open circles are experimental results of ZnFe$_2$O$_4$ and Fe$_2$O$_3$, respectively.

(b) Dependence of eigensolutions on nanoparticles inverse diameter: $v_L = 8355$ m/s and $v_T = 4397$ m/s. Solid circles are experimental results of ZnFe$_2$O$_4$.

that can be prescribed to ZnFe$_2$O$_4$. We solved complete problem with these new parameters. New solutions are presented in Fig. 2b).

Basic assumption was that $\omega_{00} = 24$ cm$^{-1}$ and $\omega_{02} = 12.6$ cm$^{-1}$. As we see $\omega_{12} \approx \omega_{00}$ and cannot be separated and detected in experimental spectra. Band at $\approx 40$ cm$^{-1}$ is identified as (2, 2) and band at $\approx 54$ cm$^{-1}$ as (1, 0) mode. Very good agreement between experimental and calculated results imply that our assumptions were correct.

In Fig. 2a we marked (open cycles) frequency positions that are a result of experimental Fe$_3$O$_4$ particles spectra deconvolution ($d = 24$ nm). As expected experimental frequencies are far away from calculated Fe$_3$O$_4$

values. For cubic system it is reasonable to use effective i.e. averaged parameters, as we did for Fe$_3$O$_4$ and ZnFe$_2$O$_4$. α-Fe$_2$O$_3$ crystallize in rhombohedral (trigonal) system, conventionally viewed as hexagonal. Stiffness constants, and consequently sound velocities, differ very much for different crystallographic axes in α-Fe$_2$O$_3$ and from Fe$_3$O$_4$ values. It was not reasonable to follow the procedure with averaged parameters as in ZnFe$_2$O$_4$. For investigation of low-frequency Raman spectra of Fe$_2$O$_3$ more detailed analysis is needed.

3. Conclusion

In this work we present low-frequency Raman spectra of ZnFe$_2$O$_4$ nanoparticles. We found that the observed peaks agree well with the calculated frequencies of acoustic phonons. As a result we identified (0, 2), (0, 0), (2, 2) and (1, 0) modes.

Acknowledgments

This work was supported under the Agreement of Scientific Collaboration between Polish Academy of Sciences and Serbian Academy of Sciences and Arts. The work in Serbia was supported by Serbian Ministry of Science (projects No. 141028 and No. 141047) and OPSA-026283 project within the EC FP6 programme.

References