

Student(s)

Berk Emre Aydemir
İrem Gürbüz
Selin Öykü Gündoğdu
Türker Türk

Faculty Member(s)

Assoc. Prof. Dr. Emre Erdem

PURE
PROGRAM FOR UNDERGRADUATE RESEARCH

Introduction

Electron Paramagnetic Resonance (EPR) is a spectroscopic technique that detects species that have unpaired electrons. Measuring the transitions of unpaired electrons in an applied magnetic field are detected with EPR. It deals with magnetic moments arising from electrons. Each electron possesses an intrinsic magnetic-dipole moment that arises from its spin. [1]

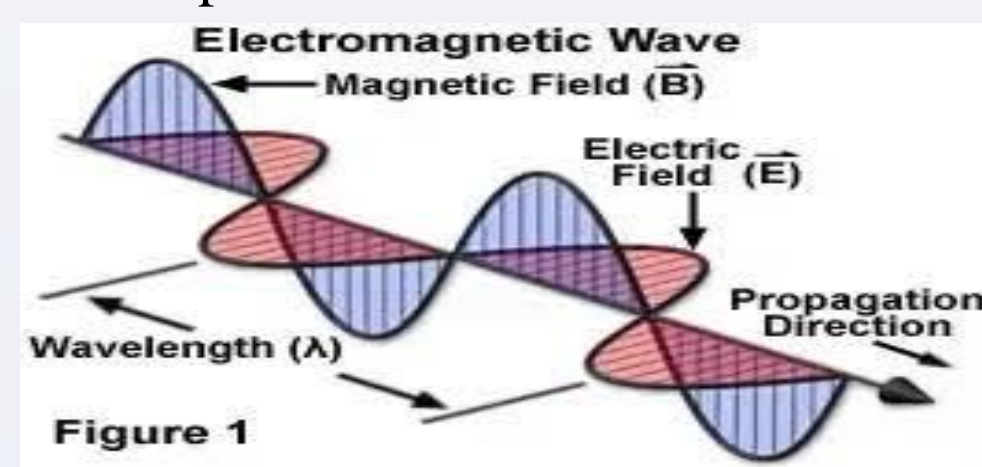


Figure 1: Wave like behaviour of electron

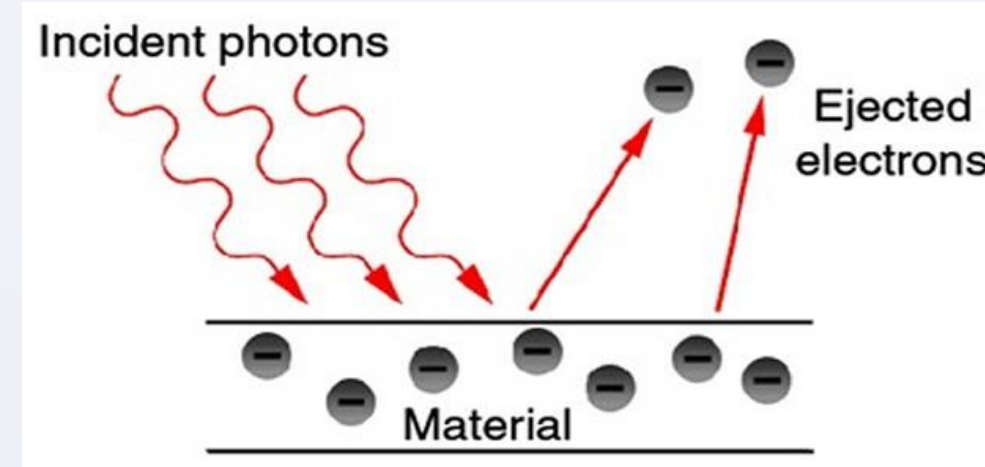


Figure 2: Particle like behavior of electron

EPR instrument constitutes of source, resonator, magnetic field and detector (Fig.3). In EPR, required microwave energy is around 9.5 GHz. Microwave source in EPR is mostly a klystron which is a vacuum tube. In resonator, incoming microwaves go through iris, which tunes the frequency of waves to be equal to the appropriate resonance frequency of the cavity. The magnetic field in EPR must be static and this static field must be very well controlled and stable. Lastly, detectors are mostly solid state diodes, which are sensitive to microwaves and they detect via absorption. When absorption occurs, detector current changes and with this change detection of microwaves with energy is justified.

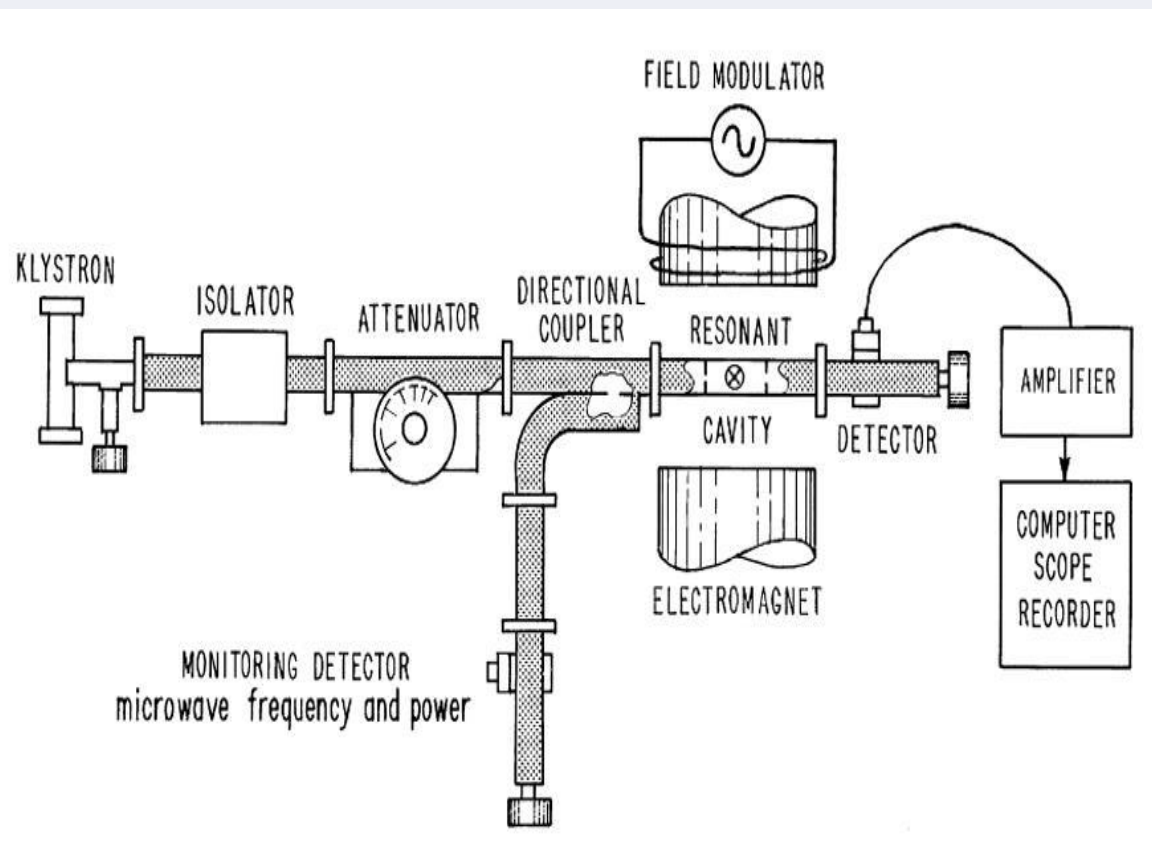


Figure 3: Diagram of a basic EPR spectrometer

ZnO is wide band gap semiconductor material and intensively used in energy storage and harvesting devices. In this work, the defect structure of zinc oxide (ZnO) nano-particles was investigated mainly by the aid of EPR spectroscopy. The main focus was given to identifying and controlling the defect centers. The results showed that the defects in pure and Mn²⁺ doped ZnO material can be controlled by annealing temperature. Moreover by reducing the particle size of ZnO to nano-dimensions (< 20 nm) strong nano-size effects, e.g. surface effects, were observed.

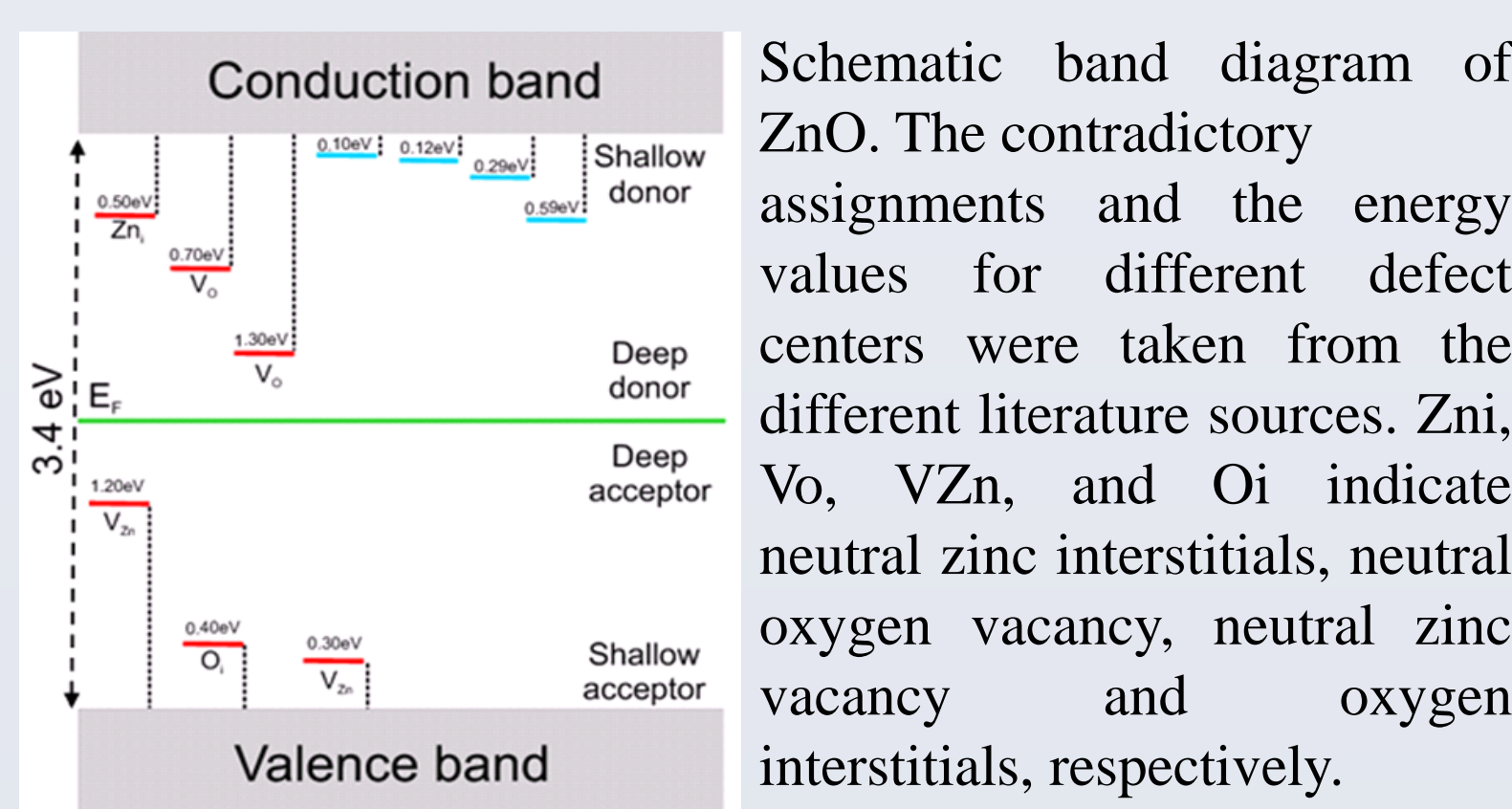


Figure 4: Energy band diagram of undoped ZnO

To simulate EPR spectra of pure (undoped) zinc oxide (ZnO) and Mn-doped ZnO which was sintered at various temperatures, samples and experimental data were gathered by the supervisor, Emre Erdem, at the University of Freiburg by the aid of Bruker EMX EPR Spectrometer. Samples were prepared as follows, ZnO (≥ 99 % purity, Merck) and MnO (99 % purity, Sigma Aldrich) were used to prepare the compositions by the conventional ceramic processing techniques. The powders of ZnO and MnO were weighed according to the molar ratios of the following compositions; 1) undoped ZnO and 2) 99.5 mol % ZnO + 0.5 mol % MnO. The calculated amounts of metal oxides for the indicated compositions were ball-milled at 125 rpm for 6 hours in nylon jars using zirconia balls and high-purity water as the milling media. The mixtures were dried at 110 °C by stirring frequently and were then granulated through a 0.5 mm sieve. Granules were die-pressed into discs of 22 mm in diameter and 3-4 mm in thickness under a pressure of 100 MPa. The samples were sintered in air at 1200 °C for 1 h employing a 360 °C/h heating rate then cooled naturally in the furnace. The bulk density of sintered samples was calculated from their weights and dimensions.

Simulations were done by using the toolbox called *EasySpin* in Matlab program. Then several modifications were done on the Matlab code to achieve the best spectral fittings.

Objectives

Aim of this project is to simulate EPR spectra of undoped and Mn²⁺ doped zinc oxide (ZnO) which were sintered at different temperatures. Obtained simulation and experimental data had outstanding overlap, which enables us to extract the accurate spin Hamiltonian parameters such as g factor, zero field splitting (ZFS) parameter D and hyperfine constant (A).

Simulation Results& Discussion

The EPR spectra of undoped and Mn²⁺ doped zinc oxide can be described by two different spin Hamiltonian respectively.

$$\text{For undoped: } H = gB\beta Sz \quad (1)$$

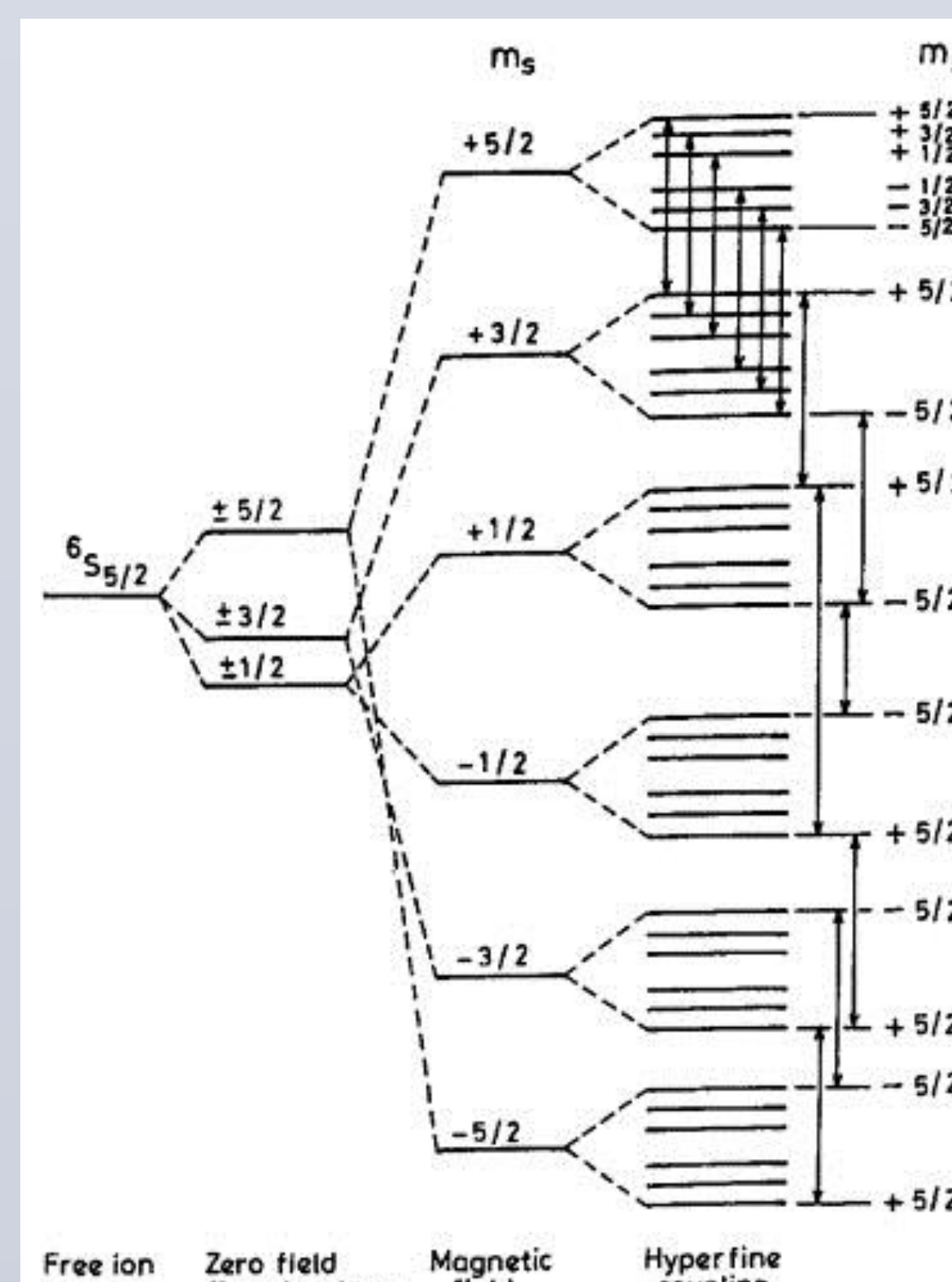
$$\text{For Mn}^{2+} \text{ doped ZnO: } H = gB\beta Sz + S \cdot D \cdot S + S \cdot A \cdot I \quad (2)$$

where; B: external Magnetic Field, g: g factor, β: Bohr magneton [9.27x10⁻²⁴ Ampere-square meter], S: electron spin number (S=1/2 for undoped, S=5/2 for Mn²⁺ doped case), I: nuclear spin number (I=0 for undoped, I=5/2 for Mn²⁺ doped), A: Hyperfine constant, D: Zero field splitting parameter

In the presence of an external magnetic field, spins get to be split apart (Figure 5). In zero field, spins with the only the same number (with different signs) get to be split with different distances apart.

Under a constant magnetic field, spins with the same numbers but with different signs also gets split. The transition between split spins are also available but up to a point since due to selective rule, allowed transition has to follow the rule, ΔMs = ±1. This rule also applied to well-known physical phenomenon, nuclear magnetic resonance (NMR), with ΔMs = 0. In EPR spectra, one can observe allowed transitions between spins.

Figure 5: Energy diagram of spins under zero field, magnetic field and hyperfine coupling for the case of S=5/2 and I=5/2 where S is electron spin number and I is the nuclear spin number. Such a case exists in Mn²⁺ ions.



Simulation Results& Discussion

Experimental and Simulated EPR spectra of undoped and pure ZnO particles

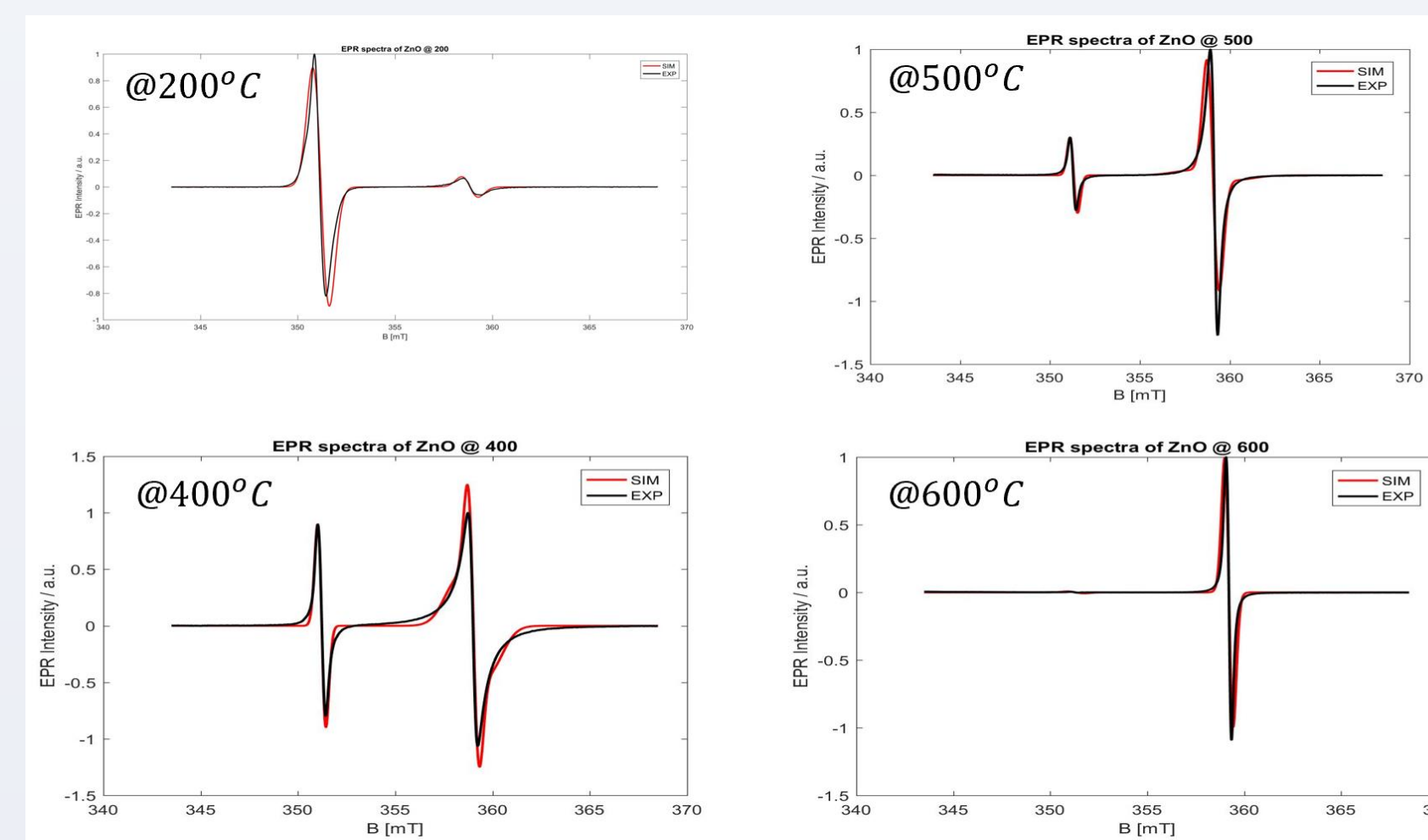


Figure 6: Experimental and Simulated EPR spectra of undoped ZnO particles for 200 °C up to 600 °C

Temperature	g _{core}	g _{surface}	lw _{core}	lw _{surface}	Intensity (core/surface)
200 °C	1.961	2.004	0.85	0.82	0.66
400 °C	1.959	2.0025	0.8	0.55	1.114
500 °C	1.9585	2.0023	0.6	0.45	3.336
600 °C	1.96	2.0045	0.4	0.5	294.117

Table 1: EPR parameters for simulation of ZnO spectra for the samples annealed at different temperatures from 200 °C up to 600 °C.

Experimental and simulated EPR spectra for Mn²⁺ doped ZnO nanoparticles

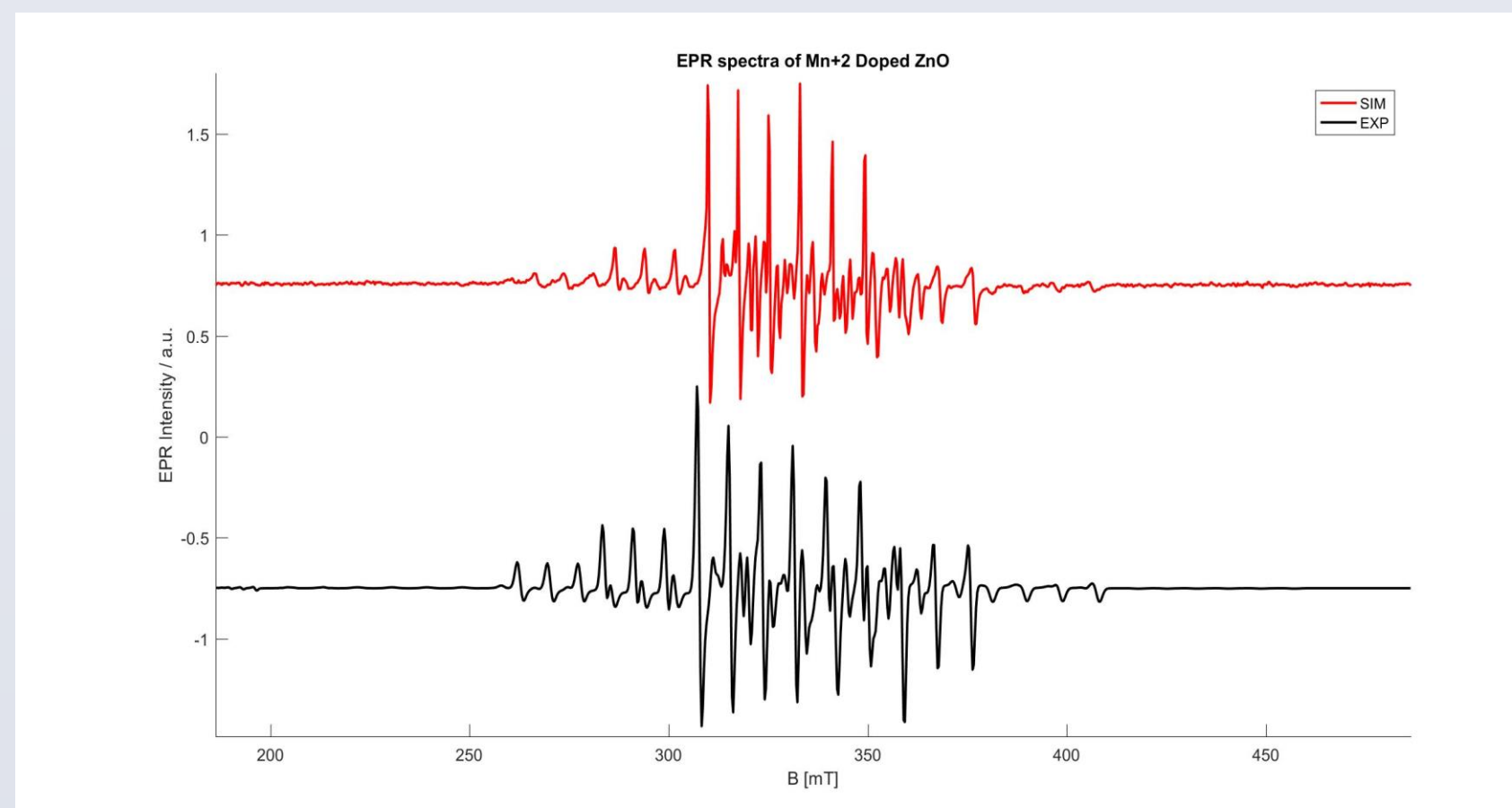


Figure 7: Experimental and simulated EPR spectra for Mn²⁺ doped ZnO nanoparticles by EasySpin

D [MHz]	E [MHz]	ZFS	A [MHz]
740	0xD	[-D/3+E -D/3-E 2*D/3]	230

g	lw [mT]	Strain in linewidth HS	Strain in ZFS DS
2.001	0.8	20	[20 0]

Table 2: EPR parameters for Mn²⁺ doped ZnO

Following Matlab code is used for simulating EPR spectra of undoped ZnO at 500 °C :

```
cd C:\Users
g1=[2.002 2.002 2.002];
g2=[1.95873 1.95873 1.95873];
g3=[1.95873 1.95873 1.95873];
lw1=0.5; %linewidth
lw2=0.8;
lw3=3;
Sys1=struct('S', 1/2,'g',g1,'lw',lw1); %structuring
the system
Sys2=struct('S', 1/2,'g',g2,'lw',lw2);
Sys3=struct('S', 1/2,'g',g3,'lw',lw3);
%experiment @ T=300K, and between 335.4mT-375.4mT
and V= 9.8622 GHz
Exp=struct('Range',[343.5 368.5],'mwFreq',9.8440,
'Temperature',300);
Opt=struct('nKnots',40,'Verbosity',1,'Intensity','
on'); %DON'T CHANGE IT IS SOME OPTIONAL FUNCS
%calculation, you need a function, called pepper,
for powder we need this
[Bsim1,Isim1]=pepper(Sys1,Exp,Opt); %calculation
of the EPR spectra
Isim1=Isim1/max(Isim1); %normalization
[Bsim2,Isim2]=pepper(Sys2,Exp,Opt);
Isim2=Isim2/max(Isim2);
[Bsim3,Isim3]=pepper(Sys3,Exp,Opt);
Isim3=Isim3/max(Isim3);
load zn500.txt
B=zn500(:,2);
I=zn500(:,3);
I=I/max(I);
B=B/10; %conversion of magnetic field unit 10
Gauss = 1 mT (mT: milli tesla)
figure(1)
clf %clear figure
hold on;
plot(B,I,'b','LineWidth',1.5)
xlabel('B [mT]')
ylabel('EPR Intensity / a.u.')
title('EPR spectra of ZnO')
%stringler ' ile zaz
plot(Bsim1,Isim1,'r','LineWidth',1.5)
plot(Bsim2,Isim2,'k','LineWidth',1.5)
figure(2)
clf
IsimS=0.3*Isim1+0.9*Isim2+0.038*Isim3;
plot(Bsim1,IsimS,'r','LineWidth',1.5)
hold on;
plot(B,I,'k','LineWidth',1.5)
xlabel('B [mT]')
ylabel('EPR Intensity / a.u.')
title('EPR spectra of ZnO @ 500')
%stringler '
ile zaz
legend('SIM','EXP')
```

Following Matlab code was used for simulating the EPR spectra of Mn²⁺ doped ZnO in this project

```
cd C:\Users
clear all
D=740; % 0 field splitting parameter [in mHz]
(energy unit)
E=0*D; % E is also 0 field splitting parameter,
according to crystallography D/E =3
ZFS=[-D/3+E -D/3-E 2*D/3];
% max value of E is 0.33*D, which gives you
max. rhombicity.
%When E is 0 that means crystal is in axial
symmetric.
A=[230 230 230];
g=[2.001 2.001 2.001];
lw=0.8;
%S=[20 20 20];
%DS=[25 25 25]; %strain in hyperfine param
DS=[20 0]; %strain in D param
Sys=struct('S',
5/2,'D',ZFS,'Nucs','55Mn','A',A,'g',g,'DStrain',
DS,'HStrain',HS,'lw',lw);
Exp=struct('Range',[186.3
486.3],'mwFreq',9.3056,'Harmonic',1);
Opt=struct('Intensity','on');
[B,Spec]=pepper(Sys,Exp,Opt);
Spec=Spec/max(Spec);
load MN3.txt
spec=MN3(:,3);
spec=spec-spec(1);
spec=spec/max(spec);
b=MN3(:,2);
b=b/10;
figure(1)
clf
hold on
plot(b,spec+0.75,'r','LineWidth',1.5);
figure(1)
plot(B,Spec-0.75,'k','LineWidth',1.5);
axis([min(B) max(B) min(Spec)-0.8
max(Spec)+0.8])
xlabel('B [mT]')
ylabel('EPR Intensity / a.u.')
title('EPR spectra of Mn2 Doped ZnO')
%stringler ' ile zaz
AX=legend('SIM','EXP');
LEG = findobj(AX,'type','text');
LEG.FontSize = 10;
```

Conclusions

In this research project, our aim was to understand the local configuration of the defects centers in the crystal of ZnO material. Here we have investigated three different systems: Undoped bulk ZnO, undoped nano ZnO and Mn doped ZnO. All of this ZnO materials can be used as energy applications for harvesting and storage.

In this comparative study defect centers were investigated by EPR spectroscopy at room temperature. By simulating the EPR spectra we understand the ratio between the concentration of core and surface defects for the undoped samples. We found that by going to nanoscale samples, surface defects increase dramatically. This means surface to volume ratio is changing which also affect the number of surface atoms thus surface defects. Actually, this can be explained by a kind of semi-empirical model which can be named as core-shell model. On the other hand, we investigated intensively Mn²⁺ doped ZnO material. This kind of material system has promising applications in spintronics which are related to quantum computer technology. Because in spintronics one may need a source of spins. In our case, Mn supplies lots of spins to semiconductor system which can be used as field effect transistor (FET). As a matter of fact, to understanding the competing effects between intrinsic and extrinsic defects is an ultimate goal of this work while it is totally debating issue to understand the effect of Mn doping on the intrinsic defect center.

Finally for us, we both had experience on EPR spectroscopy and Matlab simulations. Also get more insight on quantum mechanics approach on spins and their effect that we can observe on our daily life, like NMR and magnetic resonance imaging (MRI).

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