Magnetic and Transport Properties Based on Transition-Metal Compounds

Guest Editors: Ran Ang, Hechang Lei, Shoubao Zhang, and Xuan Luo
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Editorial

Magnetic and Transport Properties Based on Transition-Metal Compounds

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So far, transition-metal compounds have triggered a tremendous wave of excitement in the scientific community due to their rich physical properties. It is extremely important to understand and realize the \(d\)-orbital state to tune the fundamental physical properties (i.e., magnetic properties and electrical and thermal transport) of transition-metal compounds as well as their applications. The selected topics and papers include the typical magnetism and transport properties; thus it is worth sharing with many readers. This special issue contains seven papers. The detailed information is as follows.

In the paper “Tuning of transport and magnetic properties in epitaxial \(\text{LaMnO}_3+\delta\) thin films,” J. Chen et al. present the effect of compressive strain induced by substrate on the transport and magnetic properties of \(\text{LaMnO}_3+\delta\) thin films. It is found that the insulator-metal transition, charge/orbital ordering transition, and paramagnetic-ferromagnetic transition are suppressed by the compressive strain. In particular, the electronic and magnetic transition temperatures decrease with increasing the compressive strain. The present results reveal that the lattice degree of freedom plays a key role to control the transport and magnetic properties of the strongly correlated \(\text{LaMnO}_3+\delta\) thin films.

In the paper entitled “Aging effect on electrical conductivity of pure and Al-doped \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) single crystals with a given topology of planar defects,” R. V. Vovk et al. present the study of the conducting properties in the basal ab plane of pure and Al-doped \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) single crystals before and after long-time exposure in air atmosphere. It is shown that prolonged aging leads to an increase of the density of effective scattering centers for the normal carriers. The aluminum doping has been revealed to partially slow down the degradation of the conducting properties in process of aging. The excess conductivity, \(\Delta\sigma(T)\), has been found to obey exponential dependence in the broad temperature range \(T_c < T < T^*\). In the pseudogap regime, the mean-field transition temperature \(T^*\) and the 3D-2D crossover point in the excess conductivity have been quantified. Near the critical temperature, \(\Delta\sigma(T)\) is described well within the Aslamazov-Larkin theoretical model. Herewith, both aluminum doping and prolonged aging have been found to essentially expand the temperature interval of implementation of the pseudogap state, thus narrowing the linear section in the dependence \(\rho_{ab}(T)\).

In the paper “Magnetism and microstructure characterization of phase transitions in a steel,” M. Güler presents the study of phase transitions in a low carbon steel according to the existing phases and their magnetism. Scanning electron microscope examinations showed that pure state of the steel was fully in the ferrite phase with equiaxed grains. Moreover, subsequent heat treatments on the studied steel also ensured the formation of austenite and followed pearlite.
phases. Mössbauer spectroscopy of these phases appeared as a paramagnetic single-line absorption peak for the austenite phase and ferromagnetic six-line spectra for both ferrite and pearlite phases. From Mössbauer data the determined the internal magnetic fields of ferrite and pearlite phases were as 32.2 Tesla and 31.3 Tesla, respectively.

In the paper “Defects induced room temperature ferromagnetism in ZnO thin films,” X. Zhang et al. prepared polycrystalline ZnO thin films by the cosputtering method under different oxygen partial pressures. They found that the films deposited in pure argon gas exhibited ferromagnetism, whereas other films deposited under different oxygen partial pressures were diamagnetism. The study indicated that Zn interstitial may play an important role in triggering magnetic order in the ZnO thin films by inducing an alteration of electronic configuration.

In the paper “Transport, magnetic, and thermal properties of La$_{0.7}$Ca$_{0.24}$Sr$_{0.06}$MnO$_3$ single crystal,” T. M. Tan et al. present the transport, magnetic, and thermal properties of La$_{0.7}$Ca$_{0.24}$Sr$_{0.06}$MnO$_3$ single crystal. They found that the floating zone (FZ) method was most suitable for the growth of CMR manganite. This study reveals that the magnetic transition temperature increased substantially to 277 K which indicates the onset of long range ordering and large TCR values are a highly desirable goal in the context of the development of highly responsive bolometer device.

In the paper entitled “Oxygen defects mediated magnetism of Ni doped ZnO,” W. J. Liu et al. synthesize Ni doped ZnO nanoparticles by a solution route and they are annealed in O$_2$, air, and Ar gas flow. Annealed ZnO samples show ferromagnetism. They discussed the origin of ferromagnetism based on magnetization and photoluminescences spectroscopy.

In another paper, J. Yun et al. present “Magnetic properties of well-aligned ZnO nanorod arrays grown by a simple hydrothermal reaction.” Well-aligned ZnO nanorod arrays with room temperature ferromagnetism were prepared by hydrothermal method. The ZnO nanorods show (002) direction with c-axis perpendicular to the substrate surface. They discussed the nature of the ferromagnetism on the term of photoluminescence spectrum and the first-principles calculations.

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Ran Ang  
Hechang Lei  
Shoubao Zhang  
Xuan Luo
Research Article

Magnetic Properties of Well-Aligned ZnO Nanorod Arrays Grown by a Simple Hydrothermal Reaction

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Well-aligned ZnO nanorod arrays with room temperature ferromagnetism were prepared on glass substrate through hydrothermal method. The as-prepared nanorod arrays were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), photoluminescence (PL) spectrum, and magnetization measurements. The XRD and SEM results indicated that the ZnO nanorods are with the wurtzite structure and exhibit preferential (002) orientation with $c$-axis perpendicular to the substrate surface. The PL results suggested that the possible defect in the as-prepared ZnO nanorod arrays might be $V_{Zn}$ or $O_{Zn}$. The first-principles calculations reveal that the room temperature ferromagnetism may result from the $V_{Zn}$ defects present in the ZnO nanorod and the hybridization of the Zn 3d states with O 2p states is responsible for the half-metallic ferromagnetism in ZnO nanorod.

1. Introduction

Recently, one-dimensional (1D) ZnO nanorods have attracted great interest due to their tunable magnetic and optoelectronic properties [1–8]. Particularly, for the potential applications in the spin electronics, the investigation to grow well-aligned ZnO nanorod arrays with room temperature ferromagnetism has been an urgent task because it is a key process toward realizing nanoscale devices [9–11]. Synthesis methods, such as physical vapor deposition [12], chemical vapor deposition [13], and pulsed laser deposition [14], have been extensively used to obtain 1D well-aligned ZnO nanorod arrays. However, these vapor-phase processes fabrication techniques need vacuum condition, high energy consumption, sophisticated equipment, and rigid experimental conditions. Compared with the vapor-phase processes, the hydrothermal process is a low cost and environmentally friendly method, which is highly welcomed by numerous researchers [15–18].

In this study, well-aligned, single crystalline ZnO nanorod arrays with room temperature ferromagnetism and high packing density were achieved via a simple hydrothermal process. A possible origin of the ferromagnetism in the prepared ZnO nanorod arrays related to the intrinsic defect is proposed.

2. Experimental Details

The procedure of the ZnO nanorod arrays prepared under hydrothermal condition consists of two steps: (a) preparation of ZnO seed-layer and (b) growth of ZnO nanorod arrays. In the first step, a layer of ZnO seed crystal was deposited on the glass substrate via sol-gel method. In detail, equal molar Zn $(\text{CH}_3\text{COO})_2\cdot2\text{H}_2\text{O}$ and glycolic amide (0.35 mol/L) were solved in ethanol with stirring at 60°C for 12 h to yield a homogeneous solution. Subsequently, the precursor solution was dropped on the glass substrate, spinning at 3000 r/min for 30 s. Then the substrate was preheated in air at 80°C for 10 min. After that, the substrates were annealed at 500°C for 90 min in air to obtain a dense and transparent ZnO seed layer on the glass substrate by using an electronic furnace. In the second step, the glass substrate with a layer of ZnO seed crystal was placed into one autoclave filled with the precursor solutions of Zn $(\text{CH}_3\text{COO})_2\cdot2\text{H}_2\text{O}$ (0.04 M) and
The obtained products are characterized by using X-ray diffraction (XRD, D/Max2550VB+/PC, Rigaku, Japan), scanning electron microscope (SEM, JSM-6390A, JEOL, Japan), photoluminescence spectrum (PL, FluoroMax-4p, HORIBA Jobin Yvon, USA), and a superconducting quantum interference device (MPMS-XL-7, Quantum Design, USA).

### 3. Results and Discussion

Figure 1 shows XRD pattern of the as-prepared sample. It is observed that all of the diffraction peaks can be well indexed to a wurtzite structure of ZnO. The strong and narrow diffraction peaks indicate that the material has a good crystallinity. In particular, the as-prepared sample exhibits preferential (0 0 2) orientation with c-axis perpendicular to the substrate surface.

Figures 2(a) and 2(b) depict the SEM images of the prepared ZnO nanorod arrays. The low-magnification SEM image in Figure 2(a) demonstrates that the nanorod array is uniform and densely packed. From the high-magnification image in Figure 2(b), it can be seen that the prepared ZnO nanorod array exhibits typical wurtzite structure and preferential (0 0 2) orientation with c-axis perpendicular to the substrate surface, which is reflected by the XRD pattern shown in Figure 1. Furthermore, energy dispersive spectroscopy (EDS) result indicates that the as-prepared ZnO nanorod array is only composed of Zn and O, and the atomic ratio of Zn and O is about 48.24 : 51.76. This suggests that the as-prepared nanorod arrays are nonstoichiometric and some defects may exist in the as-prepared nanorod arrays.

Figure 3 shows the room temperature PL spectra of the as-prepared ZnO nanorod arrays. A strong UV emission peak at 373 nm and three relatively weak and broad visible emissions centered at 425, 511, and 590 nm, respectively, can be observed. The UV emission band is usually attributed to the near-band edge emission of the wide band gap of ZnO due to the annihilation of excitons [8, 19–21]. The visible emission is the most commonly observed and is often attributed to the defect emission [22–27]. It is known that different defects may cause different electronic structures, which will be reflected on the corresponding optical properties observed in experiments. On the other hand, the electronic structure
of the defects can be predicted unambiguously from density functional calculations. Hence, combining the experimental observations with theoretical results may identify different defects such as oxygen vacancy ($V_O$), antisite oxygen ($O_{Zn}$), zinc vacancy ($V_{Zn}$), zinc interstitial ($Zn_i$), and oxygen interstitial ($O_i$) in ZnO. Theoretically, Xu et al. and Sun et al. [26, 27] calculated the electronic structure of native point defects in ZnO. Based on their results, the energy interval between the bottom of the conduction band (CB) and $V_{Zn}$ level (3.06 eV) is approximately consistent with the energy of the blue-purple emission (425 nm, 2.92 eV) observed in our experiment. The energy interval between the bottom of the CB and $O_i$ level (2.28 eV) approximately conforms to the yellow emission (590 nm, 2.10 eV). By analysis of the experimental phenomena and the calculation of the defect levels in ZnO, we suggest that the blue emission centered at 425 nm is attributed to $V_{Zn}$ [26, 27], the green emission centered at 511 nm originates from $O_{Zn}$ [26, 27], and the yellow emission centered at 590 nm is related to $O_i$ [26]. Therefore the PL results reveal that the possible defect in the as-prepared ZnO nanorod arrays might be $V_{Zn}$, $O_i$, or $O_{Zn}$.

Figure 4 shows the magnetization as a function of the applied field at 300 K for the as-prepared ZnO nanorod arrays. The diamagnetic contribution from the glass substrate has been subtracted from the raw data. It is interesting that the ZnO nanorod arrays exhibit room temperature ferromagnetism. The saturation magnetization $M_s$ and remanent magnetization $M_r$ are about $1.7 \times 10^{-3}$ and $4.33 \times 10^{-7}$ emu/g, respectively. The coercivity $H_c$ is about 60 Oe. As we know, neither doping nor evidence of secondary phase exit in the as-prepared ZnO nanorod arrays; the observed room temperature ferromagnetism in the as-prepared ZnO nanorod arrays probably results from the intrinsic defect.

In order to provide more insight into this issue, we employed first-principles calculation [28] on the electronic structure and magnetic properties for the ZnO nanorod. Since the PL study results reveal that the possible defect in the as-prepared ZnO nanorod arrays might be $V_{Zn}$, $O_i$, or $O_{Zn}$, thus, in the present calculations, the ZnO nanorods with $V_{Zn}$, $O_i$, or $O_{Zn}$ defect are investigated. The wurtzite supercell containing 96 atoms is used for calculation. For the ZnO nanorod with $V_{Zn}$ or $O_{Zn}$ defect, there are three inequivalent defect positions, which are denoted as $V_{Zn1}$–$V_{Zn3}$ and $O_{Zn1}$–$O_{Zn3}$, as shown in Figures 5(a) and 5(b). However, there are two inequivalent $O_i$ defect positions, which are denoted as $O_{i1}$ and $O_{i2}$, as shown in Figure 5(c). The formation energy of $V_{Zn}$ at $V_{Zn2}$ site is about 0.12 and 0.38 eV smaller than that at the $V_{Zn1}$ and $V_{Zn3}$ sites, respectively, and, thus, $V_{Zn2}$ is the most stable site for $V_{Zn}$ defect. Similar to $V_{Zn}$, $O_{Zn}$ also prefers at the $O_{Zn2}$ site. While for the $O_i$ defect, it prefers at the $O_{i1}$ site. Therefore, the magnetic properties of ZnO nanorod with $V_{Zn}$, $O_{Zn}$, and $O_i$ are calculated based on the $V_{Zn2}$, $O_{Zn2}$, and $O_{i1}$ geometries, respectively.

The calculated densities of states (DOSs) for the ZnO nanorod with $V_{Zn}$, $O_i$, or $O_{Zn}$ defect are shown in Figure 6. It is clear that the spin-up and spin-down DOSs of pure ZnO nanorod are completely symmetrical, indicating that the pure ZnO nanorod is nonmagnetic. Similarly, the ZnO nanorod with $O_i$ or $O_{Zn}$ defect also exhibits nonmagnetic properties. As for the ZnO nanorod with $V_{Zn}$ defect, however, a strong spin splitting phenomenon is observed. The Fermi level passes through the band gap in the spin-down DOS and an energy gap of about 1.47 eV exists in the spin-up DOS. This demonstrates that the ZnO nanorod with $V_{Zn}$ behaves as half-metallic.

By analysis of the partial densities of states (PDOSs) in Figure 7, it can be found that the metallic spin-down DOS near the Fermi level is mainly composed of Zn 3d and O 2p states. In particular, O 2p states make significant contribution to the magnetic moment. This suggests that the appearance of the half-metallic ferromagnetism in ZnO nanorod with $V_{Zn}$ originates from the hybridization of Zn 3d states with O 2p states.

4. Conclusions

In conclusion, ZnO nanorod arrays with room temperature ferromagnetism were prepared on glass substrate through hydrothermal method. The as-prepared sample shows preferential (0 0 2) orientation with c-axis perpendicular to the substrate surface. The room temperature PL measurements exhibit a prominent UV peak at about 373 nm which is attributed to the annihilation of excitons. Three relatively weak and broad visible emissions resulting from the defects can also be observed in the PL spectrum. By analysis of the calculated electronic structure of the ZnO nanorod with defects, we can get the conclusion that the $V_{Zn}$ defects present in the ZnO nanorods are responsible for the room temperature ferromagnetism.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.
Figure 5: The structure of ZnO nanorods (a) with V_{Zn}, (b) with O_i, and (c) with O_{Zn} defect.

Figure 6: Calculated DOSs for ZnO nanorod. The Fermi level is set to zero on the energy scale, which will be adopted below unless otherwise stated.
Acknowledgments

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References


Magnetism and Microstructure Characterization of Phase Transitions in a Steel

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1. Introduction

Because of their significant usage in technology and industry, detailed examinations on the solid-state phase transformations in steel drew a remarkable attention through the last century [1–3]. Applicable findings of these previous studies make steel more able to adapt quickly changing demands on daily life. Therefore, steel is the most handy and inexpensive of all materials with more than a billion tons of yearly consumption.

Steels are mainly divided into three essential categories according to their carbon content. The first category represents low carbon steel and contains maximum 0.2% C. Second category covers the medium carbon steel with 0.2% C–0.5% C. The third category represents the high carbon steel and includes more than 0.5% C or higher carbon content [4]. It should be emphasized here that low carbon steel accommodates the highest tonnage of all steel in a given year. Structural steel for buildings and bridges, line pipes, and automotive sheet applications; those are just a few major applications for low carbon steel. Also, the characteristics of all steel types depend on their chemical compositions, preparation history, applied heat treatment behaviors, and following quenching media. All of these facts on steel cause formation of various product phases such as pearlite, bainite, and martensite [3, 5–10]. For instance, when low carbon steel cools from the austenitic region after appropriate heat treatment temperature, different percentages of austenite phase transform into a new phase including lamellar plates of ferrite and cementite (Fe₃C). On the one hand, Bain introduced this newly existing phase as “pearlite.” On the other hand, according to their formation temperatures, pearlite phase occurs between 550°C and 720°C in steel, whereas austenitic region lies between 910°C and 1535°C for ferrous alloys and steel [11].

From a physical outlook, the magnetic properties of steel are ultimately linked with their own microstructure, chemical atomic composition, and alloying conditions. When compared with each other, austenite phase is nonmagnetic while ferrite, pearlite, and bainite phases are magnetic. Noteworthy to mention here, Mössbauer spectroscopy is an accurate spectroscopic technique, which clarifies the internal magnetism (B_{int}) and volume fractions of distinct phases in steel and alloys [12–14].

Investigations on the parent austenite decomposition into product phases such as pearlite, bainite, and martensite play a particular key role during the ferrous alloy and steel production. So, the physical properties, such as transformation
Table 1: Applied heat treatments and following quench cases.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Applied heat treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>As in received pure state</td>
</tr>
<tr>
<td>B</td>
<td>1100°C → 1h → water quenching</td>
</tr>
<tr>
<td>C</td>
<td>1100°C → 1h → air cooling</td>
</tr>
</tbody>
</table>

kinetics, morphology, and crystallography of both ferrous alloys and steel, need extensive examinations. Interpreting of these objectives allows improving the quality and applicability of steel for many industry fields.

Literature up to date especially deals with many studies about the mechanical properties of low carbon steel. However, there is still some scarcity especially on the microstructure-magnetism relation in low carbon steel. Therefore, the focus of the current study was to examine and clarify the microstructure-magnetism relation of the different phase formations in low carbon steel after various heat treatment conditions.

2. Experimental

AISI (American Iron and Steel Institute) 1117 type commercial low carbon steel was examined in the present study. The chemical composition of this steel was as Fe-0.11% Cr-0.19% C-1.14% Mn-0.19% Si-0.02% P-0.01% Ni (wt%). The bulk sample of the steel was in the form of the cylindrical bar with 10 cm in length and 1 cm in diameter.

To reveal the microstructural details, three slabs were cut mechanically from the bulk cylindrical sample of the steel. They then were thinned to 150 μm thickness. We selected a pure slab of the steel (specimen A) to discover the microstructural details without any treatment. Afterwards, second slab (specimen B) was homogenized at 1100°C for 1h in a quartz tube. This tube subsequently quenched into water at room temperature by cracking the quartz tube. The new third slab was homogenized at 1100°C for 1h in a quartz tube and finally cooled in air at room temperature (specimen C) to compare the quenching media influence on specimen B. Moreover, Table 1 lists the applied heat treatments of studied specimens.

Following the applied heat treatments and quenching procedure, specimens A, B, and C were mechanically thinned to 50 μm with abrasive SiC papers. After grinding, all specimens were polished with a 3μ diamond paste through a conventional procedure and these thin foil samples were finally etched in 3% Nital for SEM observations. A JEOL JSM 5600 type electron microscope was employed to research for the microstructural examinations under 20 kV operating voltage.

Specimens examined by SEM were used for Mössbauer spectroscopy measurements. During magnetic analysis, a Mössbauer spectrometer was performed at room temperature with a 50mCi $^{57}$Co radioactive source spread in Rh. Mössbauer spectra of all measured specimens were calibrated with respect to α-Fe and isomer shift values were given to the center of the α-Fe.

3. Results and Discussion

Figure 1 is a SEM micrograph taken from the specimen A. As it is obvious in Figure 1, the surface details of specimen exhibits a typical ferrite phase with the specific equiaxed grains for the pure (received) state of the steel. This phase describes the magnetic solid solution of carbon and consists of the most common microconstituent in steel. This magnetic phase appears after casting of steel, which have carbon contents lower than 0.8% [15].

Figure 2 corresponds to the SEM micrograph of B specimen. Fast cooling by water quenching caused austenite phase formation in this specimen. Further, the microstructure in Figure 2 displays the austenite phase of studied steel with typical austenite grains and grain boundaries. As well, the austenite phase forms the nonmagnetic carbon solid solution of iron. In addition, austenitic microstructures in steel are preferable because of their wide applications and uses in cutlery, hospital, and food service equipment and in tableware.

Figure 3 stands for the SEM micrograph of specimen C. Slow cooling in air at room temperature caused to coarse pearlite phase formation in C specimen with a lamellar morphology. Pearlite phase in steel forms with two prominent morphologies, namely, as coarse pearlite and fine pearlite. At low temperatures, nucleation step of phase transformation rapidly occurs and depresses the grain growth. Decreasing in the grain growth leads to fine-grained microstructure as fine pearlite. On the other hand, at higher temperatures, diffusion of the alloying ingredients allows the larger grain growth and leads to form coarse-grained microstructure as coarse...
Table 2: Determined Mössbauer parameters of specimens A, B, and C.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Observed phase</th>
<th>Volume fraction (%)</th>
<th>Isomer shift (mm/s)</th>
<th>( B_{int} ) (Tesla)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Ferrite</td>
<td>100</td>
<td>0.22</td>
<td>32.2</td>
</tr>
<tr>
<td>B</td>
<td>Austenite</td>
<td>100</td>
<td>0.19</td>
<td>—</td>
</tr>
<tr>
<td>C</td>
<td>Austenite + Pearlite</td>
<td>12 + 88</td>
<td>0.18</td>
<td>31.3</td>
</tr>
</tbody>
</table>

From a magnetic perspective, despite the paramagnetic ordering of the parent austenite phase, product phases such as bainite, pearlite, and martensite can exhibit ferromagnetic ordering [19]. In Mössbauer spectroscopy, a single-line accompanies the paramagnetic austenite phase, whereas the product ferromagnetic phases appear with typical sextet in the spectra [8]. Figures 4, 5, and 6 show the Mössbauer spectra with the count rates versus relative velocity plots of specimens A, B, and C, respectively. Detected ferrite phase in A specimen appears with a ferromagnetic sextet in the Mössbauer spectrum as in Figure 4. Also, Figure 5 shows a paramagnetic austenite phase singlet for specimen B. Conversely, the peaks in Figure 6 indicate both paramagnetic singlet for retained austenite phase and a ferromagnetic sextet belonging to pearlite phase in specimen C. In addition, Table 2 shows some important Mössbauer data collected from all studied specimens. The volume % transformations, internal magnetic field values, and isomer shifts of each specimen can be easily seen in Table 2.

4. Conclusions

From the determined results of present experiments, we deduced and outlined the following findings.

(i) Present low carbon steel showed a ferritic microstructure (Figure 1) as in the received pure state. Further, different quenching media at constant homogenization temperature caused various phases in the studied steel. Rapid water quenching of the studied steel caused the austenite phase formation in specimen B (Figure 2), whereas slow air-cooling at room temperature caused coarse pearlite phase (Figure 3) formation in the specimen C.

(ii) Depending mainly on the steel composition and applied prior heat treatment, pearlite phase displays two common morphologies in steel as fine pearlite and coarse pearlite. We observed the coarse pearlite formation (Figure 3) in the studied steel for the present composition and heat treatment.

(iii) Determined magnetism of ferrite (Figure 4) and pearlite phases (Figure 6) explain the internal magnetic field of ferrite phase is 32.2 Tesla, and it is higher than the magnetism of pearlite phase, which has the value of 31.3 Tesla.
Arbitrary counts (a.u.)

Figure 6: Mössbauer spectra of specimen C.

Conflict of Interests
The author declares that there is no conflict of interests regarding the publication of this paper.

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Tuning of Transport and Magnetic Properties in Epitaxial LaMnO$_{3+\delta}$ Thin Films


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The effect of compressive strain on the transport and magnetic properties of epitaxial LaMnO$_{3+\delta}$ thin films has been investigated. It is found that the transport and magnetic properties of the LaMnO$_{3+\delta}$ thin films grown on the LaAlO$_3$ substrates can be tuned by the compressive strain through varying film thickness. And the insulator-metal transition, charge/orbital ordering transition, and paramagnetic-ferromagnetic transition are suppressed by the compressive strain. Consequently, the related electronic and magnetic transition temperatures decrease with an increase in the compressive strain. The present results can be explained by the strain-controlled lattice deformation and the consequent orbital occupation. It indicates that the lattice degree of freedom is crucial for understanding the transport and magnetic properties of the strongly correlated LaMnO$_{3+\delta}$.

1. Introduction

Perovskite manganese oxides La$_{1-x}$A$_x$MnO$_3$ (A = alkaline earth) have attracted a great deal of attention due to their interesting properties such as colossal magnetoresistance (CMR), charge/orbital ordering (COO), and insulator-metal transition (IMT) [1–3]. The interesting properties originate from the strong correlation of charge, orbital, spin, and lattice degrees of freedom. In this family, the substitution of divalent A for La introduces hole carriers in the Mn 3D band and oxidizes Mn$^{3+}$ to Mn$^{4+}$, which results in the ferromagnetic metal (FMM) state in terms of double exchange (DE) interaction [4]. In particular, even if without chemical substitution, the LaMnO$_3$ compound also exhibits a wide range of oxygen nonstoichiometry, which involves the oxidation of some Mn$^{3+}$ to Mn$^{4+}$ in samples of global composition LaMnO$_{3+\delta}$. However, the insertion of excess oxygen is impossible in the perovskite structure as there is no straightforward way of accommodating any extra oxygen in the close-packed structure. The oxygen nonstoichiometry in LaMnO$_{3+\delta}$ is incorporated via cation vacancies on both A and B sites [5]. Therefore, the actual crystallographic formula of such compositions should be written as La$_{1-x}$Mn$_{1-x}$O$_3$, with $x = \delta/(3 + \delta)$ [6].

The structure, transport, and magnetic properties of LaMnO$_{3+\delta}$ highly depend on the value of $\delta$ [7–9]. As $0 \leq \delta \leq 0.04$, the crystallographic structure of LaMnO$_{3+\delta}$ is orthorhombic structure (Pbnm, $c/\sqrt{2} < a < b$) and is strongly Jahn-Teller (JT) distorted; with the $\delta$ increasing, the structure changes to the slightly JT distorted orthorhombic structure (Pbnm, $a < c/\sqrt{2} < b$); when the $\delta > 0.1$, it falls into the rhombohedral structure. Ritter et al. reported that a small fraction of FMM phase appears in LaMnO$_{3.07}$ due to the local Mn$^{3+}$–O–Mn$^{4+}$ DE interaction [10]. Furthermore, the COO phase emerges at low temperatures below $\sim$110 K, which is far below the FM transition temperature ($\sim$150 K) for the $\delta = 0.07$ and 0.1 samples. The magnetization measurement results of the samples (0.085 $\leq \delta \leq 0.125$) show a step-like jump at $T_C$ and $T_{COO}$ [11]. Meanwhile Choi et al. reported that a giant softening by 30 cm$^{-1}$ of the 490 and 620 cm$^{-1}$ JT and breathing optical phonon modes had been observed by Raman spectroscopy below $T_C$ in the LaMnO$_{3+\delta}$ (0.085 $\leq \delta \leq 0.125$) compounds [12]. The results indicate the importance of the electron-phonon coupling in the appearance of COO.
phase. For these LaMnO$_{3+\delta}$ (0.085 ≤ $\delta$ ≤ 0.125) compounds, with decreasing temperature these samples exhibit transition from a paramagnetic insulator (PMI) to FMM at $T_C$, where the resistivity starts to decrease. At low temperatures, the samples undergo transition from FMM state to COO state at $T_{COO}$, while the resistivity shows an upturn. This COO phase coexists with the isotropic three-dimensional FM state in spite of the insulating behavior. The overall behaviors of LaMnO$_{3+\delta}$ (0.085 ≤ $\delta$ ≤ 0.125) compounds are quite similar to those of the lightly doped La$_{1-x}$Sr$_x$MnO$_3$ (0.11 < $x$ < 0.15) [13, 14].

The study on the lightly doped La$_{1-x}$Sr$_x$MnO$_3$, the counterpart of the LaMnO$_{3+\delta}$, has verified the essential role of lattice deformation in the formation of COO phase. Chen et al. succeeded in realizing the COO phase in the La$_{7/8}$Sr$_{1/8}$MnO$_3$ thin films induced by the anisotropic strains on (001) SrTiO$_3$ substrates [15]. Wang et al. uncovered that the in-plane tensile strain in the La$_{7/8}$Sr$_{1/8}$MnO$_3$ thin film grown on the 0.7Pb (Mg$_{1/3}$Nb$_{2/3}$)O$_3$–0.3PbTiO$_3$ substrate can induce COO [16]. However, few works have been reported on the strain effect on the properties of nonstoichiometric LaMnO$_{3+\delta}$ thin films. Zheng et al. found that the JT distortion of MnO$_6$ reduces the charge coupling of the LaMnO$_{3+\delta}$ thin film under an in-plane tensile strain on 0.7Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–0.3PbTiO$_3$ substrate [17, 18]. In this letter, the epitaxial LaMnO$_{3+\delta}$ thin films have been fabricated on (001)-oriented LaAlO$_3$ substrate, and in-plane compressive strains have been modified by varying the thickness of thin film. The effect of compressive strain on COO transition and FM transition of the films has been systematically investigated.

2. Experimental

The LaMnO$_{3+\delta}$ thin films were grown on single crystal substrates by dc magnetron sputtering. We chose (001)-oriented LaAlO$_3$ (LAO) and (001)-oriented SrTiO$_3$ (STO) as substrates, and the lattice parameters of the substrates are $a_{LAO} = 3.792$ Å and $a_{STO} = 3.905$ Å. The deposition temperature is 700°C and there are 10 Pa oxygen-argon mixed gases flowing during deposition. After deposition, the films were in situ cooled to room temperature in the deposition atmosphere. The thickness of the films was controlled by the deposition time. The degree of orientation and crystallographic characterization of the LaMnO$_{3+\delta}$ thin films were measured on X-Pert-PRO system using Cu Kα radiation. The superconducting quantum interference device (SQUID) magnetometer was used to measure the magnetic properties of the LaMnO$_{3+\delta}$ thin films and electrical properties were performed by four-electrode method in a physical property measurement (PPMS) system.

3. Results and Discussion

Figure 1(a) shows the XRD $\theta$–$2\theta$ scan for the LaMnO$_{3+\delta}$/LAO thin film of thickness ∼50 nm. The LaMnO$_{3+\delta}$ thin films are $c$-axis oriented and there are no secondary phases. The inset shows the XRD $\phi$ scans on the LaMnO$_{3+\delta}$ (011) and LaAlO$_3$ (001) reflections. Fourfold symmetry is clearly seen for both LaMnO$_{3+\delta}$ thin film and LAO substrate, which is an indication of cubic-on-cubic epitaxial growth of the LaMnO$_{3+\delta}$ thin films on the LAO substrates. The out-of-plane lattice parameter $c$ of 50 nm LaMnO$_{3+\delta}$/LAO was calculated to be 3.9445 Å. As mentioned above, the lattice constants of the LaMnO$_{3+\delta}$ bulk materials vary with $\delta$. By comparing the $T_C$ and $T_{COO}$ of the LaMnO$_{3+\delta}$ thin films with those of LaMnO$_{3+\delta}$ bulk materials, it is estimated that the $\delta$ of the LaMnO$_{3+\delta}$ thin films is ∼0.09. For $\delta$ ∼0.09, the lattice constant of the LaMnO$_{3+\delta}$ bulk materials is ∼3.903 Å [10, 12]. This value is smaller than that of the 50 nm LaMnO$_{3+\delta}$/LAO, indicating that the films are subjected to in-plane compressive and out-of-plane tensile strain. Figure 1(b) shows the out-of-plane lattice parameters of the LaMnO$_{3+\delta}$/LAO depending on the film thickness. Clearly, for the 30 nm LaMnO$_{3+\delta}$/LAO thin film, the out-of-plane lattice parameter is larger than that of the bulk material, which indicates that there exists in-plane compressive strain in the LaMnO$_{3+\delta}$/LAO thin film. With the increasing of film thickness, the out-of-plane lattice parameter decreases and approaches the value of the bulk material. The results show that the in-plane compressive strain of the LaMnO$_{3+\delta}$/LAO exhibits a relaxation with the increase of film thickness.

Figure 2(a) shows the temperature-dependent resistivity of the LaMnO$_{3+\delta}$/LAO. The LaMnO$_{3+\delta}$/LAO presents a large variation of electrical transport properties with the
increase of film thickness. For the 30 nm LaMnO$_{3+\delta}$/LAO, it exhibits insulating behavior in the whole temperature range. For the 50 nm, 75 nm, and 100 nm LaMnO$_{3+\delta}$/LAO, with lowering temperature these films exhibit IMT at $T_{\text{IMT}}$, where the resistivity starts to decrease. The FMM state undergoes a transition to COO state at $T_{\text{COO}}$, while the resistivity shows an upturn. The $T_{\text{IMT}}(T_{\text{COO}})$ of the 50 nm, 75 nm, and 100 nm LaMnO$_{3+\delta}$/LAO are 182 (94) K, 186 (139) K, and 194 (141) K, respectively. Furthermore, both transition temperatures $T_{\text{IMT}}$ and $T_{\text{COO}}$ of the LaMnO$_{3+\delta}$/LAO can be enhanced by an external magnetic field. As shown by the dashed line in Figure 2(a), the magnetic field of 5 T increases the $T_{\text{IMT}}$ and $T_{\text{COO}}$ of 50 nm LaMnO$_{3+\delta}$/LAO to 208 K and 110 K, respectively. The results indicate that the magnetic field could stabilize the COO phase in LaMnO$_{3+\delta}$ thin films, which is similar to the reported in the lightly doped La$_{1-x}$Sr$_x$MnO$_3$ ($0.11 < x < 0.15$) [19]. Figure 2(b) presents the temperature dependence of resistivity of the LaMnO$_{3+\delta}$/STO thin film. The electrical transport properties of LaMnO$_{3+\delta}$/STO are almost independent of the film thickness, in contrast to those of LaMnO$_{3+\delta}$/LAO. The 30 and 100 nm LaMnO$_{3+\delta}$/STO exhibit two successive transitions upon cooling: high-temperature PMI phase to intermediate FMM phase and then to low-temperature COO phase at $T_{\text{COO}}$. The $T_{\text{IMT}}(T_{\text{COO}})$ of the 30 nm and 100 nm LaMnO$_{3+\delta}$/LAO are 125 (206) K and 134 (205) K, respectively.

Figure 3 shows the temperature dependence of the field-cooled (FC) magnetization under a field of 0.1 T for the LaMnO$_{3+\delta}$/LAO. The FM transition temperature $T_C$ is defined as the inflection point in the $M$–$T$ curves. Similar to the transport properties, the magnetic properties of LaMnO$_{3+\delta}$/LAO are strongly dependent on the film thickness as well. The 30, 50, 75, and 100 nm LaMnO$_{3+\delta}$/LAO exhibit the $T_C$ of 203, 205, 210, and 220 K. The $T_C$ values of the LaMnO$_{3+\delta}$/LAO increase with the increase of the film thickness.

The variation of the transport and magnetic properties of the LaMnO$_{3+\delta}$/LAO with the film thickness suggests the essential role of the lattice degree of freedom. In LaMnO$_{3+\delta}$/LAO under large compressive strain, the MnO$_6$ octahedra are stretched at the out-of-plane direction and compressed in the in-plane. The lattice distortion can make electrons tend to occupy the $d_{3z^2-r^2}$ orbital and the in-plane transfer integral for the FM-DE decreases, leading to a lower $T_C$ and the insulating transport behavior [20]. With the decrease of the compressive strain, the $d_{3z^2-r^2}$ orbital occupation is weakened and the $T_C$ is increased with the film thickness. Another important feature is the evolution of the COO transition of LaMnO$_{3+\delta}$/LAO with the compressive strain. For the 30 nm LaMnO$_{3+\delta}$/LAO, the COO transition is quenched and the film exhibits insulating behavior in the whole temperature range. Furthermore, the $T_{\text{COO}}$ increases with the decrease (increase) of in-plane compressive strain (film thickness). It is well known that the occurrence of COO transition in bulk material of LaMnO$_{3+\delta}$ is intimately correlated with structural anomalies that c-axis increases and $a$, $b$-axes decrease [10]. The lattice deformation associated with the structural anomalies would prefer an occupation of special orbital arrangements that are characteristic of COO.

![Figure 2](image-url)
transport and magnetic properties of LaMnO$_{3+\delta}$ thin films has been investigated. It was found that the COO transitions are independent of the film thickness, as shown in Figure 2(b). These results verify that the transport and magnetic properties of the LaMnO$_{3+\delta}$ thin film can be tuned by the epitaxial compressive strain and confirm the importance of the lattice degree of freedom in the LaMnO$_{3+\delta}$ compound.

4. Conclusion

In summary, the effect of compressive strain induced by substrate on the transport and magnetic properties of LaMnO$_{3+\delta}$/STO films with different thickness show bulk-like behavior and the COO transitions are independent of the film thickness, as shown in Figure 2(b). These results verify that the transport and magnetic properties of the LaMnO$_{3+\delta}$ thin film can be tuned by the epitaxial compressive strain and confirm the importance of the lattice degree of freedom in the LaMnO$_{3+\delta}$ compound.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Defects Induced Room Temperature Ferromagnetism in ZnO Thin Films

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Polycrystalline ZnO thin films are prepared by the co-sputtering method under different oxygen partial pressures. Films deposited in pure argon gas exhibit ferromagnetism, whereas other films deposited under different oxygen partial pressures are diamagnetism. XPS results show the presence of Zn interstitial and oxygen vacancy in all of samples. Further analysis indicates that Zn interstitial may play an important role in triggering magnetic order on the undoped ZnO thin films by inducing an alteration of electronic configuration.

1. Introduction

ZnO-based dilute magnetic semiconductors (DMSs) have attracted intense interests due to their potential applications in spintronic devices [1]. Room temperature (RT) ferromagnetism (FM) has been reported theoretically and experimentally in magnetic transition metal doped ZnO nanoparticles and thin films [2–7]. However, several works pointed out that the transition metal dopants are not essential in the observed ferromagnetism. For instance, the results of X-ray magnetic circular dichroism spectra showed that the magnetism in Mn doped ZnO nanoparticle and thin films is critically sensitive to defects other than the transition metal dopants themselves [8] and bulk ZnO doped with Co, Mn, or Cr shows paramagnetism [6, 9, 10]. Meanwhile, RT FM was observed in nonmagnetic ion doped ZnO thin films and nanoparticles [11–13] and even undoped ZnO films [14–17], nanoparticles [18, 19], or partially oxidized Zn nanowires [20, 21], which indicates that the RT FM observed in ZnO matrix may be intrinsic. It is restricted to some defect-rich regions, such as the surface, interface, and grain boundary, not uniform throughout the samples [22]. On the other hand, the indirect exchange interaction models such as Zener/Ruderman-Kittel-Kasuya-Yosida (RKKY)-type exchange, double- and super-exchange, F-center-mediated bound magnetic polaron models, are hard to explain the observed RT FM induced by only few percent of magnetic ions. Thus, the intrinsic defects should be important on the FM order in ZnO-based DMSs. However, which kinds of defects play an important role, how the defects facilitate the magnetic coupling, and how to control these defects are still under intensive debate. Some reports demonstrated that RT FM could stem from the lattice defects such as oxygen vacancy (V_O) or Zn interstitial (Zn_i) in pure ZnO thin films, nanoparticles, and nanowires [17, 23–26]. Straumal et al. [27] demonstrated that FM only appears if the ratio of grain-boundary area to grain volume exceeds a certain threshold value. Sanchez et al. [28] predicted that varying the hydrogen density on the ZnO (0001) surface can achieve reversible switch of surface FM. More interestingly, even absorbing certain organic molecules can induce ferromagnetic-like behavior in undoped ZnO nanoparticles [29]. These results challenge the understanding of the origin and mechanism of FM.

So far, although lots of works have been carried out to explore the origin of RT FM in undoped ZnO, the results are far from convincing and even some of the results are inconsistent, partly because ZnO is a semiconducting material with many species of native defects with quite a few of them behaving as shallow donors. Now, it is known that the native defects depend strongly on preparation methods and conditions. ZnO materials prepared by various methods from different
groups generally show significant differences in physical properties including native defect/impurity species and density, mobility, and crystallinity. When these ZnO materials are employed for DMSs study, it is not a surprise that distinct results were reported even with similar conditions. Therefore, it is the most important to elucidate the effect of specific film-growth conditions. In this study, polycrystalline ZnO films were fabricated under different oxygen partial pressure \( (P_{O_2}) \). The experimental results show that the only RT FM observed in ZnO film deposited under pure Ar and saturated magnetization is 0.89 emu/cc, while other samples deposited under Ar and \( O_2 \) mixture are diamagnetism. After depositing a single Zn layer on the magnetic film and annealing the sample at high temperature, the saturated magnetization significantly increased to 1.62 emu/cc. These results suggest that the Zn interstitial may be a response to the origin of FM order in pure ZnO thin films.

2. Experiments

A series of polycrystalline ZnO films were fabricated by RF-sputtering ZnO (99.99%) targets in Ar (99.999%) and \( O_2 \) (99.999%) mixture at room temperature. The base pressure of the chamber was better than \( 1 \times 10^{-5} \) Pa before deposition and the total pressure for sputtering was kept at 2.0 Pa. The RF-sputtering power of ZnO target was kept at 260 W. The films were deposited on glass and kapton substrates for the measurements of structural and transport properties, respectively. To eliminate the spurious magnetic data, the samples and polymer tweezers were cleaned with acetone prior to measurement. The films thickness was kept at 200 nm. The microstructure of the films was characterized by X-ray diffraction pattern (XRD) with Cu K\( _{α} \) radiation (\( λ = 0.15418 \) nm) using X’Pert PRO machine. The composition and chemical states of ZnO thin films were examined by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) using Physical Electronic Spectrometry machine. The DC electrical resistivity measurements were measured using a conventional four-probe method performed in a Quantum Design PPMS. The magnetization measurements were carried out using a Quantum Design vibrating sample magnetometry.

3. Results and Discussion

Figure 1(a) shows the XRD pattern of the ZnO polycrystalline samples fabricated under different oxygen partial pressure \( (P_{O_2}) \). The results indicate that all samples have highly (00l)-preferred orientation in contrast to the standard diffraction pattern of wurtzite ZnO. The particle size can be derived from the Scherrer formula [30]:

\[
D_{hkl} = \frac{0.9λ}{β \cosθ}
\]

where \( D_{hkl} \) is the particle size along (hkl) direction, \( β \) is the full width at half maximum (FWHM) of the XRD peak, \( λ = 0.154058 \) nm is the wavelength of Cu K\( _{α} \) radiation, and \( θ \) is the Bragg angle. Figure 1(b) shows the relation between obtained particle size using the FWHM of (002) peaks and \( P_{O_2} \). It can be seen that there is not monotonic dependence of particle size on the \( P_{O_2} \). At low \( P_{O_2} \), the particle size increases with increasing \( P_{O_2} \), reaches the maximum value at \( P_{O_2} = 1 \) Pa, and then decreases to 42.7(9) at \( P_{O_2} = 1.5 \) Pa. With the \( P_{O_2} \) increasing, the particle size of the ZnO thin films tends to be a constant.

The composition and chemical states of the ZnO thin films deposited under \( P_{O_2} = 0 \) Pa and \( P_{O_2} = 2 \) Pa are further investigated by XPS analysis. Samples were etched by Ar\( ^+ \) bombardment (\( 5 \times 10^{-2} \) Torr) for 5 min to examine the intrinsic chemical state of each element in the films. A broad scan survey spectrum indicates that only Zn, O, and C elements exist and no other detectable contaminated element above 0.1% exists in the ZnO samples. As shown in Figure 2(a) the peak positions of Zn 2\( p_{3/2} \) and Zn 2\( p_{1/2} \) are similar in both samples. Comparing the XPS standard spectra of Zn 2\( p \) [30], it is concluded that the valence state of Zn element is +2. On the other hand, the peaks of Zn 2\( p_{3/2} \) in both samples exhibit slight asymmetry. Islam group has analyzed the Zn 2\( p_{3/2} \) peak of ZnO thin film systematically and attributed this kind of asymmetry of Zn 2\( p_{3/2} \) peak to the existence of excess zinc in the films [31]. No such asymmetry is observed for hydrogen-annealed pure ZnO films. But the exact nature of the distribution of Zn in the ZnO matrix remains under investigation. In order to confirm the existence of zinc in the films, AES measurements were carried out. Figure 2(b) presents a Zn(L\( _{3/2} \)M\( _{45} \)M\( _{45} \)) AES signal of the ZnO samples deposited under \( P_{O_2} = 0 \) Pa and \( P_{O_2} = 2 \) Pa. The major peaks at 264.2 eV are considered to be associated with Zn\( ^{2+} \) in ZnO matrix. The minor one at 261.2 eV is due to Zn of metallic Zn or Zn\( _i \) in ZnO matrix lattice. It can be seen that the peak intensity at 261.2 eV for the sample deposited under \( P_{O_2} = 0 \) Pa is significantly larger than that for sample prepared under \( P_{O_2} = 2 \) Pa. It implies that more metallic Zn or Zn\( _i \) can be generated under oxygen-deficient atmosphere.

Deeper insight into the chemical states of oxygen is achieved through the analysis of the O 1s peaks of ZnO polycrystalline samples deposited under \( P_{O_2} = 0 \) Pa and \( P_{O_2} = 2 \) Pa, as shown in Figure 3. The broad and asymmetric O 1s peaks could be consistently fitted by a Gaussian function to separate the multicomponent oxygen species, which centered at \( 530.0 \pm 0.1 \) eV, 531.5 \( \pm 0.1 \) eV, and 532.3 \( \pm 0.1 \) eV, respectively. The component on the low binding energy side of the O 1s at \( 530.0 \pm 0.1 \) eV is attributed to O\( ^{2-} \) ions in wurtzite structure of hexagonal Zn\( ^{2+} \) ion array, surrounded by Zn atoms with their full complement of the nearest neighboring O\( ^{2-} \) ions [32]. In other words, the intensity of this component is the indicator of the amount of oxygen atoms in a fully oxidized, stoichiometric surrounding. The medium binding energy component at 531.5 \( \pm 0.1 \) eV may partially be associated with O\( ^{2-} \) ions that are in oxygen-deficient regions within the matrix. Thus, the variation of the relative intensity ratio of medium component to total O 1s may be connected in part to the variations in the concentration of oxygen vacancies. It can be seen that this ratio for the sample prepared without \( O_2 \) is remarkably larger than the sample deposited under \( P_{O_2} = 2 \) Pa. It is consistent with AES results of Zn; that is,
without $O_2$, more $Zn_i$ and $V_O$ appear when compared to the sample deposited under $O_2$. Finally, the appearance of the high binding energy component at $532.3 \pm 0.1$ eV indicates the presence of loosely bound oxygen in the ZnO films belonging to specific species, such as adsorbed $H_2O$ or adsorbed $O_2$, which is difficult to remove by just increasing $P_{O_2}$ during deposition process.

Figure 4 shows magnetization loops of ZnO films deposited under different $P_{O_2}$. The applied magnetic field was parallel to the surface of the sample. The data in the main figure is $M-H$ curves before the subtraction of the diamagnetic signal of samples, which indicates the sample prepared under $P_{O_2} = 0$ Pa shows RT FM. Upper inset of Figure 3 obtained from subtracting the saturated linear parts of the measured signal shows typical hysteresis behaviors and the saturated magnetization is $0.89$ emu/cc. However, other samples deposited under different oxygen partial pressure are diamagnetic, confirming that no FM impurities were introduced during the preparation of the films. It should be noted that FM behavior and average grains diameters upon different oxygen partial pressure have different trends. It implies that the average grains sizes are indirectly related
Indeed, the origin of RT FM in undoped ZnO is still a controversial issue. Many hypotheses have been presented to give a reasonable interpretation for the origin of the RT FM in pure ZnO. Since the sample deposited under $P_{O_2} = 0$ Pa is insulators, the carrier-mediated RKKY-type model seems not to be applicable. According to previous work [23–26], the origin of the room temperature FM of undoped ZnO is due to the introduction of Zn$_i$ and/or V$_O$ defects rather than Zn vacancies ($V_{Zn}$), because formation energy of $V_{Zn}$ is so high that it could not preferably form in ZnO. The chemical states of Zn and O ions in ZnO samples deposited under different $P_{O_2}$ show that Zn$_i$ and V$_O$ coexist in the as-deposited samples. As $P_{O_2}$ increases, both of the Zn$_i$ and V$_O$ are decreasing meanwhile the FM disappears at higher $P_{O_2}$. Thus, the Zn$_i$ and/or V$_O$ should contribute to the origin of FM in pure ZnO thin films. To further confirm which kind of defect plays a more important role in the origin of FM in the sample, a layer of pure Zn with thickness of about 70 nm was deposited on the ZnO film deposited under $P_{O_2} = 0$ Pa. Then, the sample was heated in high vacuum at 300°C for 10 min. Because the diffusion of Zn is easier than that of oxygen [33] and there are not enough oxygen atoms from the air which can diffuse in the lattice to oxidize the diffused Zn, Zn$_i$ will generate and be trapped in the lattice, which leads to the increase in defect density of Zn$_i$. On the other hand, magnetic measurement indicates that the saturated magnetization of annealed sample increases to 1.62 emu/cc. Thus, Zn$_i$ not V$_O$ should be responsible for the observed weak RT FM in as-deposited sample and the significant increase of $M_s$ in the annealed sample.

Figure 3: XPS data of O 1s and its Gaussian-resolved component for the sample deposited under (a) $P_{O_2} = 0$ Pa and (b) $P_{O_2} = 2$ Pa, respectively.

Figure 4: $M$-$H$ curves for ZnO thin films deposited under different oxygen partial pressure at 300 K. Upper inset: $M$-$H$ curves of ZnO as-deposited and annealed films deposited under $P_{O_2} = 0$ Pa at 300 K after the subtraction of the diamagnetic signal.

to the FM in undoped ZnO films. On the other hand, the measured resistivity of the samples deposited under $P_{O_2} = 0$ Pa is $6.5(2) \times 10^4 \text{\text{\Omega \text{cm}}}$ at RT.
Theoretical calculation indicated that the level of Zn lies close to the bottom of the conduction band (shallow donors), which will induce strong interaction between the localized interstitial Zn 4s level and the conduction band [5]. This interaction alternates the electronic structure, leading to ferromagnetic-like behavior. It should be noted that this modification of the semiconductor electronic structure can be realized in the absence of the magnetic ions. More generally, other methods inducing such kind of shallow donors will also alternate the electronic structure and result in the RT FM, such as fabricating ZnO low dimensional nanoparticles with more intrinsic defects, capping with organic molecules into ZnO nanoparticle [29] and producing more defects by mechanical milling in ZnO nanoparticles [23].

4. Conclusions

In summary, RT FM is observed in undoped ZnO thin films deposited without oxygen, while other samples deposited under different $P_{O_2}$ are all diamagnetism. After depositing a single Zn layer on the magnetic ZnO thin films and annealing the sample at high temperature, the saturated magnetization significantly increased. All results indicate that the origin of FM order in pure ZnO films should be related to the Zn$_2$ defects. The shallow donor caused by Zn$_2$ defects might modify the electronic structure of undoped ZnO thin films, leading to the RT FM. Our result will help to get further insight into the ferromagnetic origin in undoped ZnO systems.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References


Research Article

Aging Effect on Electrical Conductivity of Pure and Al-Doped YBa$_2$Cu$_3$O$_{7-\delta}$ Single Crystals with a Given Topology of Planar Defects

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1. Introduction

Despite the fact that almost three decades have passed since the discovery of high-temperature superconductivity (HTSC) [1], the microscopic nature of this phenomenon remains definitively unexplained so far. In accordance with the contemporary views, it is assumed that the key for understanding the nature of HTSC can be in scrutinizing the physical phenomena observed in these compounds in the normal state at temperatures at and above the critical temperature $T_c$. The transitions to the fluctuation and the pseudogap regimes are exemplary for those phenomena. Whereas thousands of papers are devoted to the treatment of physics of the pseudogap state and the fluctuation conductivity in HTSC compounds (see, e.g., [2–6] for reviews), both the nature of the pseudogap state to appear and its role in the formation of the superconducting state still remain unclear.

Along with this, in the recent years there is a tendency to expand the field of studies regarding the technological use of high-temperature superconductors (HTSCs) [7]. This is mostly associated with a more intensive use of these compounds in contemporary microelectronics, telecommunication systems, and so forth. In this respect, compounds from the system YBa$_2$Cu$_3$O$_{7-\delta}$ (1-2-3) are most promising. This is due to several factors as follows. (i) These superconductors have a high critical temperature $T_c$, above the boiling point of liquid nitrogen. (ii) One can relatively easy alter their structure and conductive properties by varying the oxygen content [8] and by substituting the constituent elements with respective isoelectronic analogues [9]. It should be noted that, in 1-2-3 compounds, there practically always exist planar defects, such as twin boundaries (TBs) that can significantly extend the range of possible research [10]. At the same time, all the aforementioned characteristics are raising new questions and challenges. For example, the presence of labile oxygen in YBa$_2$Cu$_3$O$_{7-\delta}$ often leads to a nonequilibrium state in the system, which can be induced by temperature [8, 9] or by high pressure [10–12]. In general, these effects are observed in nonstoichiometric samples in respect of the oxygen content and are absent in samples with low oxygen...
deficiency $\delta \leq 0.15$ [13]. At the same time, in the literature, there are a number of works [14–16] which note the possibility of changing the superconducting and electrotransport properties of 1-2-3 samples in the course of prolonged aging in air atmosphere. Therein, the published data are often contradictory. For instance, a significant improvement of the electrotransport and an increase of the critical current in process of long-term annealing are reported in [17]. At the same time, a pronounced degradation of these properties before long-term exposure in ambient air is noted in [14–16]. Altering the composition of 1-2-3 superconductors is also an important instrument to find empirical ways for improving their critical parameters and for extending their technological applications. It is known that a complete or partial substitution of yttrium with rare earth elements, with the exception of praseodymium (the praseodymium anomaly) which suppresses the superconducting parameters of the compound [18], slightly affects their physical characteristics in the normal and the superconducting state [9, 10, 19]. By contrast, an important role is played by the partial replacement of copper by elements such as gold, silver, and aluminum [20–24]. Gold and silver, in small concentrations of these compounds, improve conductivity and prevent degradation of the superconducting properties in the aging process [20, 21]. The published data regarding the impact of aluminum on the electrotransport properties of the compound $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ still remain unclear and are in essence contradictory. For example, a slight rise in the resistivity $\rho_{ab}$ in the basal $ab$ plane of $\text{YBa}_2\text{Cu}_{3-\gamma}\text{Al}_\gamma\text{O}_{7-\delta}$ crystals at $\gamma \leq 0.1$ was observed in [22]. At the same time, a twofold increase of $\rho_{ab}$ at the same concentration of aluminum is reported in [23]. The reason for this discrepancy is most likely a nonhomogeneous distribution of aluminum over the crystal volume, as during the crystal growth in alundum crucibles the introduction of aluminum occurs in an uncontrolled way. In particular, the nonhomogeneous distribution of aluminum results in broader transitions into the superconducting state ($\Delta T_c \geq 2$ K) and their stepwise form [22, 23]. There is also substantial variation in the superconducting parameters of the samples. It should be noted that aluminum doping facilitates a severalfold reduction of the period of the twin superstructure [24] and, at high concentrations, the formation of intersecting "tweed"-type twin domains [25]. On the one hand, TBs, which are extended planar defects, promote strengthening of the pinning processes [26], thus extending the range of the use of HTSCs in obtaining high magnetic fields. On the other hand, the presence of TBs often complicates the investigation of the resistive characteristics, due to the difficulty of defining their contribution to the electrical conductivity in HTSCs [24]. Thereby, the influence of aluminum doping on aging of 1-2-3 compounds has remained an open question so far.

Taking the above under consideration, the objective of this study is to investigate, in the different conductivity regimes, the effect of prolonged aging in ambient air on the electrotransport properties of pure and Al-doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals. The samples have a high critical temperature $T_c$ and contain a system of unidirectional TBs. The measurements are carried out with the transport current directed parallel to TBs, that is, when the influence of the TBs on the charge carrier scattering is minimal.

2. Sample Preparation

The $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals were grown in a gold crucible by the solution-melting method, under small temperature gradient along the crucible [24]. As source components we used powder compounds of $\text{Y}_2\text{O}_3$, $\text{BaCO}_3$ and $\text{Cu}$. To obtain Al-doped single crystals, 0.2 at.% $\text{Al}_2\text{O}_3$ was added. After the growth, all the crystals were annealed at 420°C in air atmosphere in order to obtain the optimal oxygen concentration and a high $T_c$. In all the samples the axis $c$ was oriented along the smallest dimension. For the resistivity measurements, the following single crystals were selected: crystal K1 ($\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$) with dimensions of $2 \times 0.3 \times 0.02$ mm$^3$ and crystal K2 ($\text{YBa}_2\text{Cu}_{3-\gamma}\text{Al}_\gamma\text{O}_{7-\delta}$) with dimensions of $2.3 \times 0.75 \times 0.03$ mm$^3$. Both single crystals contained areas with unidirectional TBs, with dimensions of $0.5 \times 0.5$ mm$^2$. The geometry was selected in such a way that we could cut out bridges with parallel TBs (see also Figure 1(a)), with a width of 0.2 mm and a distance between the voltage contacts of 0.3 mm. The standard four-contact scheme was used to form electric contacts, whose arrangement is shown in the inset of Figure 1(b). In these, gold connectors (0.05 mm in diameter) were attached to the sample surface with silver paste. To make the electrical contacts easier, both wired samples were therupon annealed in ambient air for several hours. This method provided a contact transient resistance of less than 1 Ω and made it possible to measure the resistivity at transport currents up to 10 mA in the $ab$ plane. The temperature was measured with a copper-constantan thermocouple. The first measurements of the electrical resistivity in the basal $ab$ plane were made immediately after removal of the crystals from the melt and saturating them with oxygen to the optimum value ($\delta \leq 0.1$). After these measurements, the crystals were stored in a glass container until the remeasurements, which have been done 6 years later.

We performed an inspection of the elemental composition in the as-grown crystals using energy-dispersive X-ray spectroscopy (EDX). The EDX parameters were 10 kV/2.4 nA and the probed areas were $2 \times 2 \mu$m$^2$. Here the beam energy determines the effective thickness of the layer being analyzed, which is approximately 0.7 μm. The penetration of the electrons into the crystal was calculated by the simulation program Casino available at http://www.gel.usherbrooke.ca/casino/index.html. The material composition was calculated taking into account ZAF (atomic number, absorption, and fluorescence) and background corrections. The software we used was EDAX’s Genesis Spectrum v. 5.10. The statistical error in the elemental composition is 1%. The EDX spectrum for the pure crystal K1 is shown in Figure 1(b). It shows four peaks corresponding to 7.7 at.% of Y, 16.2 at.% of Ba, 23.1 at.% of Cu, and 53 at.% of O. Other elements have not been detected in the as-grown pure crystal K1.

A photograph of the surface of the Al-doped crystal K2, with a characteristic pattern of TBs, is shown in Figure 1(a). As is known, substitutions of 3-valent ions are centers for
the defect formation [24, 25]. As their concentration increases, the period of the domain structure decreases. As a consequence of this, neighboring microtwins overlap and a tweed-like structure results [25]. As it is evident from Figure 1(a), such a tweed-like structure is absent in the investigated crystal of YBa$_2$Cu$_{3-x}$Al$_x$O$_{7-δ}$. This must be attributed to the low concentration of Al. We also note that the twin-to-twin distance in the Al-doped crystal K2 is a factor of 2-3 smaller than that in the pure crystal K1.

3. Results and Discussion

The temperature dependences of the electrical resistivity in the $ab$ plane $\rho_{ab}(T)$ of crystals K1 and K2, measured before and after prolonged aging in air atmosphere, are shown in Figures 2(a) and 2(b), respectively. The superconducting transitions for the same samples are shown in $\rho_{ab}(T)$ and $d\rho_{ab}/dT-T$ coordinates in the respective insets. One can see that in all the cases the dependences are quasimetallic. However, the ratio $\rho_{ab}(300 \text{ K})/\rho_{ab}(0 \text{ K})$ measured for the as-grown and aged samples has diminished from 64 to 39 and from 12 to 8 for crystals K1 and K2, respectively. Here, the value of $\rho_{ab}(0 \text{ K})$ was determined by extrapolating the linear section in $\rho_{ab}(T)$, as shown by the dashed lines in Figure 2. At the same time, the resistivity $\rho_{ab}(300 \text{ K})$ of crystals K1 and K2 has risen from 151 to 196 and from 421 to 453 $\mu\Omega \text{cm}$, accordingly. This has been accompanied by the respective reduction of their critical temperature from 91.75 to 90.83 and from 92.05 to 90.85 K. In our measurements, the critical temperature $T_c$ was determined as that corresponding to the maximum in the dependence $d\rho_{ab}(T)/dT$. For both aged samples, the width of the superconducting transition, $\Delta T_c$, has noticeably increased (from 0.3 and 0.5 to $\approx$1 K for crystals K1 and K2, resp.), and the transition of crystal K2 has gained a stepwise shape. The measured and calculated parameters of the investigated samples are compiled in Table 1. Using the literature data for the dependence of $T_c$ on the oxygen concentration [27], one can arrive at the conclusion that in both aged crystals its content has insufficiently (by 1-2%) decreased and is within $\delta \leq 0.15$ [27]. The broadening of the resistive transitions for both crystals reflects a decrease in homogeneity of the investigated samples [9, 10, 12, 13], whereas the stepwise shape of the transition in the remeasurements on crystal K2 testifies that the phase segregation appeared in its volume [10, 12]. The latter assumption is supported by the presence of a series of peaks in the dependence $d\rho_{ab}(T)/dT$ of crystal K2. According to [9], such peaks correspond to $T_c$ of different phases in the crystal volume. The absence of peaks for crystal K1 suggests that percolation pathways are likely to ensue for the current flow through the phase with a higher $T_c$ [28].

As it follows from Figure 2 and Table 1, the relative change in the resistive parameters during the aging process is more pronounced for the pure crystal K1 than for the Al-doped K2. As the current $I$ is applied parallel to TBs in all the samples, this difference cannot be caused by the enhanced density of TBs in crystal K2 exhibiting a smaller twin-to-twin distance. The observed increase of $\rho_{ab}$ for the aged samples must be caused by a decrease of the density of the charge carriers or the appearance of effective scattering centers. This is also supported by the reduction of the ratio $\rho_{ab}(300 \text{ K})/\rho_{ab}(0 \text{ K})$. The role of such scattering centers may be played by an increasing number of vacancies that appeared in the aged samples and by a rise in nonstoichiometry of the compound, most likely owing to losses of oxygen. Along with increasing $\rho_{ab}$, as already mentioned above, a series of peaks have appeared in $d\rho_{ab}/dT$ of sample K2. This must assert the risen number of different phase inclusions [28] in the crystal volume. As is known [24], impurities of the 3-valent Al have a significantly smaller radius than the one that Cu has, thereby providing the centers for the defects formation. In these, aluminum atoms can form a specific octahedral environment of oxygen atoms [24] that, in turn, can facilitate the segregation of the conducting subsystem into several phases with different $T_c$. The presence of such...
phases can become apparent via a stepwise shape of the superconducting transition (and the respective peaks in \(d\rho_{ab}/dT\cdot T\) coordinates) [9, 10, 12, 13], as well as a change in the mechanism of diffusion processes and, thus, a reduction of the intensity of deoxygenation of the sample volume.

As it is seen in Figure 2, with a decrease of the temperature below the characteristic value \(T^*\), the dependence \(\rho_{ab}(T)\) starts to deviate from the straight line. This fact proves the appearance of some excess conductivity which, according to the contemporary views, is stipulated by the transition into the pseudogap state (PG) [29–31]. At present, two main scenarios for the PG anomaly to appear in HTSC systems are discussed in the literature. In accordance with the first one, the appearance of the PG is connected with the short-range fluctuations of the "dielectric" type occurring in underdoped compounds [29]. Another scenario assumes the formation of Cooper pairs already at temperatures substantially higher than the critical temperature \(T^* > T_c\), where \(T^*\) is the onset temperature of the PG state. This is followed by the establishment of the phase coherence at \(T < T_c\) [30, 31]. As it is seen from Table 1 and Figure 2, prolonged aging leads to a pronounced narrowing of the linear section in \(\rho_{ab}(T)\) for both crystals as compared to the respective as-grown samples. Along with this, the temperature \(T^*\) starts to shift towards higher temperatures by 29 K for both crystals K1 and K2. This results in an expansion of the temperature range for the excess conductivity to become apparent.

We turn now to a quantitative analysis of the observed changes in the excess conductivity. The temperature dependence \(\Delta\sigma(T)\) is defined by the following relation:

\[
\Delta\sigma(T) = \sigma(T) - \sigma_0,
\]

where \(\sigma_0 = \rho_0^{-1}\) is the conductivity determined by extrapolating the linear section down to the zero-temperature value, and \(\sigma(T) = \rho^{-1}(T) = (A + BT)^{-1}\) is the experimentally measured conductivity value in the normal state. The thus calculated dependences \(\Delta\sigma(T)\) are presented in \(\ln \Delta\sigma - 1/T\) coordinates in the main panels of Figures 3(a) and 3(b). It is seen in Figure 3 that the curves \(\Delta\sigma(T)\) demonstrate linear behavior in a quite broad temperature range. This corresponds to their description by an exponential dependence of the following form:

\[
\Delta\sigma(T) \propto \exp \left(\frac{\Delta^*_{ab}}{T}\right),
\]

where \(\Delta^*_{ab}\) determines some thermally activated process over the energy gap called "pseudogap". An exponential dependence \(\Delta\sigma(T)\) was previously observed in YBaCuO.

**Figure 2:** The temperature dependence \(\rho_{ab}(T)\) of the single crystals (a) YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) and (b) YBa\(_2\)Cu\(_{1+y}\)Al\(_{y}\)O\(_{7-\delta}\) before and after long aging in ambient air, curves 1 and 2, respectively. The arrows show the mean-field transition temperature \(T^*\) to the pseudogap regime. The extrapolated values of \(\rho_{ab}(0 \text{ K})\) are traced by the dashed straight lines. The insets show the superconducting transitions in \(\rho_{ab}-T\) and \(d\rho_{ab}/dT\cdot T\) coordinates for the same samples. The numbering of the curves in the insets corresponds to that in the main panels.

**Table 1:** Resistivity parameters of the as-grown and aged samples.

<table>
<thead>
<tr>
<th>No</th>
<th>Sample</th>
<th>(T_c), K</th>
<th>(\rho_{ab}) (300 K), (\mu\Omega\text{cm})</th>
<th>(T^*), K</th>
<th>(\Delta\rho_{ab}), meV</th>
<th>(\tan\alpha_{1D})</th>
<th>(\tan\alpha_{2D})</th>
<th>(\epsilon_0)</th>
<th>(\xi_0(0), \AA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>as-grown</td>
<td>91.75</td>
<td>151</td>
<td>138</td>
<td>88.7</td>
<td>-0.508</td>
<td>-1.084</td>
<td>0.061</td>
<td>1.45</td>
</tr>
<tr>
<td></td>
<td>aged</td>
<td>90.83</td>
<td>196</td>
<td>167</td>
<td>66.3</td>
<td>-0.503</td>
<td>-1.062</td>
<td>0.088</td>
<td>1.74</td>
</tr>
<tr>
<td>K2</td>
<td>as-grown</td>
<td>92.05</td>
<td>421</td>
<td>199</td>
<td>58.1</td>
<td>-0.506</td>
<td>-0.990</td>
<td>0.157</td>
<td>2.32</td>
</tr>
<tr>
<td></td>
<td>aged</td>
<td>90.85</td>
<td>453</td>
<td>228</td>
<td>45.5</td>
<td>-0.495</td>
<td>-1.017</td>
<td>0.188</td>
<td>2.54</td>
</tr>
</tbody>
</table>
samples [13]. The fitting range of the experimental data can be substantially extended by introducing the factor \((1 - T/T^*)\). In this case, the excess conductivity turns out to be proportional to the density of superconducting carriers, \(n_\lambda \propto (1 - T/T^*)\), and inversely proportional to the number of pairs \(\propto \exp(-\Delta^*_\text{ab}/kT)\) destroyed by thermal motion. Here \(T^*\) is regarded as the mean-field transition temperature to the PG regime, and the temperature range \(T_c < T < T^*\), where the PG state exists, is determined by the rigidity of the order parameter phase. The latter, in turn, depends on the oxygen deficiency and the concentration of the doping element. Other specific mechanisms of the quasiparticle interaction, such as those caused by structural or kinematic anisotropy of the system, can also be relevant [32, 33]. The values of \(\Delta^*_\text{ab}\) calculated by (2) for our samples are presented in Table I. It is evident that the prolonged aging leads to the substantial suppression of the absolute value of the PG; namely, \(\Delta^*_\text{ab1}/\Delta^*_\text{ab2} = 1.34\) and \(\Delta^*_\text{ab1}/\Delta^*_\text{ab2} = 1.28\) for crystals K1 and K2, respectively.

As it follows from the main panels of Figure 3, with approaching \(T_c\), a sharp rise in \(\Delta\sigma(T)\) ensues. From the Aslamazov-Larkin theory [34], it is known that in the vicinity of \(T_c\) the excess conductivity is stipulated by the processes of fluctuational pairing of the charge carriers. The excess conductivity at \(T > T_c\) for the two- (2D) and three-dimensional (3D) cases is determined by the following power-law dependences:

\[
\Delta\sigma_{2D} = \frac{e^2}{16\hbar d} \varepsilon^{-1},
\]

\[
\Delta\sigma_{3D} = \frac{e^2}{32\hbar^2 \xi_c(0)} \varepsilon^{-1/2},
\]

where \(\varepsilon = (T - T_c)/T_c\) is the reduced temperature, \(\varepsilon\) is the electron charge, \(\xi_c(0)\) is the coherence length along the axis \(c\) at \(T \to 0\), and \(d\) is the characteristic dimension of the 2D layer.

To deduce the exponents determining the prevailing regime, the temperature dependences \(\Delta\sigma(T)\) are plotted in \(\ln \Delta\sigma - \ln \varepsilon\) coordinates in the insets of Figure 3. From these plots, it is seen that, in the vicinity of \(T_c\), both dependences can be fitted well by straight lines with a tilt angle \(\tan \alpha_{3D} \approx -0.5\) corresponding to the exponent \(-1/2\) in (4). This evidently asserts the 3D character of the fluctuational superconductivity in this temperature range. With a further increase of the temperature, the decrease of \(\Delta\sigma\) speeds up essentially \((\tan \alpha_{2D} \approx -1)\). This, in turn, can be treated as an indication of the dimensionality change in the fluctuation conductivity. As it follows from (3) and (4), in the 3D-2D crossover point,

\[
\xi_c(0) \varepsilon^{-1/2} = \frac{d}{2}. \tag{5}
\]

In this case, having deduced the value of \(\xi_0\) and using the literature data on the dependence of the lattice parameter on \(\delta\) [35] (\(d = 11.7\) Å), one can calculate \(\xi_c(0)\). Such calculations show that after prolonged exposure the coherence length \(\xi_c(0)\) has increased from 1.49 to 1.74 and from 2.32 to 2.54 Å for crystals K1 and K2, respectively. This is accompanied by a shift of the 3D-2D crossover temperature, \(T_{3D-2D}\), towards higher temperatures; see also Table I and Figure 3.

As a generalization of the obtained results, the observed changes in the three determinative temperatures are presented in the form of a chart in Figure 4. This sketch allows one to grasp the impact of aluminum doping and prolonged aging on the implementation of the different conductivity
regimes in the investigated samples, in the entire temperature range. The three characteristic temperatures are the superconducting transition temperature $T_c$, the mean-field transition temperature to the pseudogap regime $T^*$, and the crossover temperature $T_{3D-2D}$ for the dimensionality change in the power-law dependence of the excess conductivity. We leave more subtle subregions, such as those corresponding to the critical fluctuations and noninteger dimensionality, as they are beyond the scope of this work. From Figure 4 it follows that both the 6-year aging and aluminum doping in the investigated concentration suppress $T_c$ very slightly (by less than 1%). At the same time, when combining both of these treatments, the temperature range for the PG state to ensue is essentially expanded (by a factor of 2-3) towards higher temperatures. The increase of $T^*$ due to aluminum doping is accompanied by a worth noting rise in $T_{3D-2D}$ (by about 10%), whereas $T_{3D-2D}$ remains almost unchanged in process of aging for both investigated samples.

4. Conclusion

In conclusion, let us sum up the main results obtained in this work. A long exposure of the optimally doped single crystals of YBaCuO in air atmosphere has been found to lead to an incomplete degradation of their conductive properties and to the appearance of effective scattering centers for the charge carriers. The introduction of Al impurities assists a partial slowdown of the degradation of the conducting properties in process of aging of the samples. The excess conductivity $\Delta \sigma(T)$ of the pure and Al-doped single crystals of YBaCuO obeys the exponential dependence in the broad temperature range $T_c < T < T^*$ and, in the case of approaching $T_c$, can be described well within the Aslamazov-Larkin theoretical model. The prolonged exposure of the samples leads to an essential broadening of the temperature range for the pseudogap state in the $ab$ plane to ensue, thus narrowing the linear section in the dependence $\rho_{ab}(T)$. Along with this, indications of the phase segregation in the volume of the Al-doped sample have been observed. These become apparent via the presence of additional peaks in $d\rho_{ab}(T)/dT$ at temperatures close to the superconducting transition temperature.

Conflict of Interests

The authors declare that there is no conflict of interests.

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Research Article

Oxygen Defects Mediated Magnetism of Ni Doped ZnO

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Ni doped ZnO nanoparticles were synthesized by a solution route and annealed in O\textsubscript{2}, air, and Ar, respectively. X-ray diffraction and X-ray photoelectron spectroscopy measurements show that the samples possess typical wurtzite structure and have no other impurity phases. Magnetization loops for ZnO samples were measured and clearly show typical ferromagnetic saturation behavior. With the defect analysis based on photoluminescence spectroscopy, the effect of defects on the nature and origin of ferromagnetism was investigated. The results suggest that oxygen vacancies, especially single ionized oxygen vacancies, play a crucial role in mediating ferromagnetism in the Ni doped ZnO.

1. Introduction

Diluted magnetic oxide semiconductors (DMOSs) have gained much attention recently due to the possibility to control spin and charge simultaneously for future spintronics [1, 2]. These oxide semiconductors with a wide band gap are optically transparent in visible region and important for the development of spin related optoelectronic devices. After the theoretical prediction by Dietl et al. suggesting the existence of room temperature ferromagnetism (FM) in doped ZnO, the system has been extensively studied [3, 4]. Remarkable progress has been made in the realization of transition metal (TM) doped ZnO with Curie temperature \(T_C\) at or above room temperature (RT). It was also reported that even doping “nonmagnetic” atoms such as Cu or Bi leads to RT FM in ZnO [5, 6]. More recently, FM had been observed in undoped ZnO, which opened an extensive debate on the origin of FM [7, 8]. Therefore, some researches suggested that induced FM is due to oxygen defects in ZnO, not TM ions or secondary phases. Although the origin of FM in TM doped and undoped ZnO has not been fully understood so far, oxygen (or Zn) defects are broadly recognized as an important reason for the FM behavior of doped and undoped ZnO, which is also consistent with our previous work on FM of undoped ZnO [9].

In the present work, we have focused our attention on further research of the role of oxygen (or Zn) defects by investigating the effect of different annealing atmospheres on the FM properties of Ni doped ZnO nanoparticles based on an analysis of photoluminescence (PL) spectroscopy.

2. Experimental

2.1. Preparation of Ni Doped ZnO Nanoparticles. Ni doped ZnO nanoparticles were prepared by a solution method. A total of 0.01 mol of zinc acetate \((Zn(AC)_2 \cdot 2H_2O)\) and Nickel acetate \((Ni(AC)_2 \cdot 4H_2O)\) in the chosen atomic rations were dissolved in 200 ml deionized water as the precursor together with 0.01 mol methenamine \((C_6H_{12}N_4, HMT)\). Then they were mixed under vigorous stirring for 30 min in a glass beaker. Before growth, a glass substrate was cleaned carefully and put into the glass beaker. The growth time and temperature were 24 h and 95°C, respectively. After growth, the substrate was taken out the solution, thoroughly rinsed with deionized water, treated in an ultrasonic water bath for 10 min, and dried in air at room temperature. To investigate the influence of defects on the inducing magnetic moment, the resulting sample was divided into three parts for the followed anneal at 800°C for 30 min in Ar, air, and O\textsubscript{2}, respectively.

2.2. Characterization. The structure of Ni doped ZnO nanoparticles was determined by X-ray diffraction (XRD) with Cu Ka radiation \((\lambda = 0.1542\ nm)\) at RT. The effective concentration and binding state of the ions in the
energy is due to the substitution of parts of the lattice Zn to the Zn$_{2p3}$ of Ni doped ZnO. This increase of binding at 1020.93 eV corresponds to the binding energies of Zn$_{2p3}$ at 1020.93 and 1022.42 eV (see Figure 2(b)). The peak centered at 380–400 nm. Here, we only report data for visible emission, which is referred to as deep-level emission and attributed to recombination of electrons deeply trapped in oxygen/Zn vacancies and interstitials, with photo-generated holes.

3. Results and Discussion

3.1. Microstructure. The structure of Ni doped ZnO particles was characterized by XRD at RT, as shown in Figure 1. No other diffraction peaks besides those of wurtzite ZnO can be observed. Thus, it was demonstrated that the samples possess the typical wurtzite structure and no impurity phases are present.

3.2. XPS Analysis. X-ray photoelectron spectroscopy is the most useful tool to analyze the surface valence states of the elements in a material. To further investigate the composition and structure of the prepared particles, XPS spectra of Ni doped ZnO sample were measured and are shown in Figure 2.

3.3. Photoluminescence Properties. To investigate the presence of defects, the RT PL spectra of Ni doped ZnO as grown and annealed at three different atmospheres are shown in Figure 3(a). Each spectrum displays ultraviolet (UV) near band-edge (NBE) emission. It is well known that, at RT, ZnO typically exhibits UV band-edge emission and broad visible emissions at green, orange, yellow, and red spectral bands. The UV band-edge emission is attributed to free excitonic emission. It is reasonable to assume that this PL mechanism is the same for all our investigated Ni doped ZnO samples. We observed the UV near-band-edge emission peak at 380–400 nm. Here, we only report data for visible emission, which is referred to as deep-level emission and attributed to recombination of electrons deeply trapped in oxygen/Zn vacancies and interstitials, with photo-generated holes.

Many reports have focused on the origin of the PL in doped and undoped ZnO. There are three peaks in the visible band, 527 nm, 575 nm, and 657 nm. The green emission (527 nm) is generally attributed to the recombination of electrons trapped in single ionized oxygen vacancies (V$_{O}^{+}$) with photo generated holes [13, 14]. The green emission (575 nm) is related to the doubly ionized oxygen vacancy (V$_{O}^{++}$) [15–17]. The red emission around 657 nm originates from the intrinsic defects of oxygen interstitials) (O$_{i}$) [18–20], which act as traps for photo-generated holes.
Gaussian fitting is performed on each spectrum to investigate the distributing of the above three defects, which is shown in Figure 3(b). Figure 4 displays the contents of oxygen related defects in Ni doped ZnO samples as grown and postannealed in different atmospheres (O\textsubscript{2}, air, and Ar).

During the annealing process in Ar and air, oxygen easily escapes from the ZnO particles, the concentration of oxygen vacancies (V\textsubscript{O}\textsuperscript{+} and V\textsubscript{O}\textsuperscript{+ +}) increases, and the concentration of O\textsubscript{2} decreases. After annealed in O\textsubscript{2}, the oxygen vacancies in the sample are filled to a large extent and the concentration of oxygen interstitials have increased. At the same time, the relative contents of V\textsubscript{O}\textsuperscript{+ +} increases due to the fact that part of V\textsubscript{O}\textsuperscript{+ +} have been transformed into V\textsubscript{O}\textsuperscript{+} during the annealing process.

3.4. Magnetic Properties. Magnetization loops for the samples in capsules were measured at 300 K using a VSM magnetometer and the M-H curves are shown in Figure 5. The actual magnetization of the samples was determined by subtracting the diamagnetic contribution of the capsule and substrate from the raw data. Our experimental results presented indeed show that all the samples are ferromagnetic at RT. The M-H curves clearly show that the typical ferromagnetic saturation behavior. Particularly, it is observed that the post-annealing in different atmospheres does not change the essential FM of the samples but does change significantly the saturated magnetic moments (M\textsubscript{s}) of the samples.

3.5. Discussion. The mechanism of intrinsic FM in TM doped oxides still remains controversial, whether it is an intrinsic or extrinsic property of these materials. A diversity of theories has been proposed. For instance, the magnetism of the TM doped ZnO has been attributed to ferromagnetic coupling of the local moment of TM dopants through the carrier-mediated Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction [21], indirect double-exchange [22, 23] or super-exchange [24], and so forth. There are even proposals that the observed FM originate from the local magnetic moment of defects such as the Zn vacancies [25] or O vacancies [26–29].
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Figure 3: RT photoluminescence spectra of Ni doped ZnO samples as grown and annealed in different atmosphere (a) and Gaussian fit of each PL spectrum (b) (The gray lines are the experimental results and the black solid curves are Gaussian fits).

Figure 4: The contents of oxygen related defects \( V_o^+, V_o^{++} \) and \( O_i \) in as grown Ni doped ZnO nanoparticles, and samples with thermal annealing in O\(_2\), air, and Ar, respectively.

In the present work, XRD and XPS results clearly demonstrate that the samples have a single wurtzite phase and there is no indication of additional phases, such as the Ni magnetic precipitation. So, we expect that FM is from an intrinsic exchange interaction of magnetic moments in Ni doped ZnO. Although the exact mechanism of intrinsic FM in Ni doped oxides is still under debate, defects have greatly been suggested to play an important role in the magnetic origin in the Ni doped ZnO system. As the postannealing is expected to have remarked effects on the defects rather than on the TM dopants, the combination of the present defects analyses based on the PL and the magnetic measurements provides a good opportunity to clarify the physical nature of the local magnetic moment.

In the PL results, Zn vacancies and interstitials were not observed in the prepared Ni doped ZnO system. So the contributions of the observed oxygen defects on FM will be discussed below.

From Figure 5 it is observed that the saturated magnetic moment increases after annealing in Ar and air but decreases after annealing in O\(_2\). We compared the saturated magnetic moments with the optical spectroscopic intensities originated from the oxygen vacancies in two charge states and oxygen interstitials (Figure 4). A definitely positive correlation between the \( M_s \) and the intensity of \( V_o^+ \) (\( V_o^+ \) and \( V_o^{++} \)) is observed, while a pronounced negative correlation between the \( M_s \) and the intensity of \( O_i \) can be seen. These results indicate that the observed three different defects may make different contributions to FM and that oxygen vacancies and
its related defect complexes play an essential role in the Ni doped ZnO system. As the annealing in different atmospheres does not change the concentration of the Ni dopants, it is expected that the dominant differences of FM introduced by annealing among the samples are either the concentrations or the charge states of the oxygen related defects, such as oxygen vacancies ($V_o$) and $V_{o^+}$-Ni complexes.

Theoretical and experimental studies have later confirmed that ferromagnetism in transition metal doped ZnO system, especially in ZnO thin film, is genuine and commonly believed to be due to an exchange interaction between magnetic moments localized at the TM sites mediated by free charge carriers. And, the magnetic moment can actually be mediated by tuning the concentration of lattice defects, as well as that of the dopants [30]. In the present ZnO: Ni samples, there may coexist two different mechanisms in response to the observed magnetism. There is an indirect RKKY interaction among the magnetic dopants/defects, which is always ferromagnetic in the short-range regime. In addition, there is the antiferromagnetic superexchange interaction via the O anions. The observed magnetism depends on the competition of these two mechanisms. With increasing the oxygen vacancies, the antiferromagnetic superexchange is suppressed so that the positive correlation between the $M_s$ and the intensity of oxygen vacancy is observed. In any sense, based on the present results, we suggest that in addition to the magnetic doping effect, oxygen vacancies, especially $V_{o^+}$, play an essential role in the magnetic origin for Ni doped ZnO. The role of oxygen defects in mediating the FM in TM doped ZnO still needs further theoretical and experimental research.

4. Conclusion

In summary, Ni doped ZnO nanoparticles have been prepared with a solution method. The structure and the surface valence states of the elements in the samples were studied in detail. To investigate the influence of the defects on the inducing magnetic, the particles are annealed in O$_2$, air, and Ar, respectively. RT PL spectra were measured to facilitate an investigation of the defects. Magnetization loops for the samples were measured at 300 K and clearly show typical ferromagnetic saturation behavior. A combination of results from the defects analyzes based on the PL and the magnetic measurements suggest that oxygen vacancies, especially singly ionized oxygen vacancies, play a crucial role in mediating ferromagnetism in the Ni doped ZnO system.

Conflict of Interests

All the authors declare that they do not have any conflict of interests.

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Research Article

Transport, Magnetic, and Thermal Properties of La$_{0.7}$Ca$_{0.24}$Sr$_{0.06}$MnO$_3$ Single Crystal

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We report the transport, magnetic, and thermal properties of La$_{0.7}$Ca$_{0.24}$Sr$_{0.06}$MnO$_3$ single crystal. It was prepared using floating zone technique used under oxygen pressure of 1 bar with a typical growth rate of 1 mm/hr. The resistivity data shows the metal to insulator transition (M-I) occurring at $T_{MI} = 290$ K along the $c$-axis and at $T_{MI} = 280$ K along the $ab$-plane. It is observed that the $T_{MI}$ is higher along the $c$-axis as compared to that in the $ab$-plane, thus indicating that more favorable hoping of electrons is along the $c$-axis. From bolometric application point of view, the temperature coefficient of resistance (TCR) is found to be $\sim 28\% K^{-1}$. The $ac$-susceptibility measurement shows that this material exhibits ferromagnetic to paramagnetic transition temperature ($T_C$) 277 K. Sharp peak around this temperature in heat capacity data indicates the onset of long-range ordering. The entropy change associated with this transition is found to be 2.3 J/mol K.

1. Introduction

The colossal magnetoresistance (CMR) of hole doped manganites RE$_{1-x}$A$_x$MnO$_3$, with RE = La, Nd, and Pr and A = Ba, Sr, Ca, and Pb, is promising magnetoresistance materials in which the change of resistivity by applying magnetic field is so large that this effect is described as colossal. They were studied very intensively in the last few years due to the effect of CMR [1–4]. They exhibit ferromagnetic to paramagnetic (FM-PM) transition as well as metal to insulator (M-I) transition. The perovskite structure of ABO$_3$ with A = La, Pr, and Nd and B = Mn, is paramagnetic insulator at all temperatures. When these are doped with divalent ion, their resistivity decreases with formation of Mn$^{2+}$, which decreases the Jahn-Teller distortion, creates double exchange interactions, and hence plays a crucial role in the electrical transport and magnetic properties of these oxides [1]. La$_{1-x}$A$_x$MnO$_3$ perovskite systems have been studied extensively for their remarkable CMR properties that have technological applications [5]. The CMR behavior occurs near the ferromagnetic (FM) transition temperature, and this remarkable phenomenon is attributed to the magnetic coupling between Mn$^{3+}$ and Mn$^{4+}$ ions as well as to the strong electron-phonon coupling arising due to Jahn-Teller splitting of Mn 3d levels. It has also been found that the bond angle and bond length of Mn$^{3+}$–O$^{2-}$–Mn$^{4+}$ play a crucial role in controlling the CMR properties of these manganites as the geometric quantity and the tolerance factor are modified when suitable ions are substituted for La to fill the 3d network of MnO$_6$ octahedra [6]. The problem, however, is that samples used for such studies (typically ceramic, thin films, or single crystal) represent properties of samples but not the compound as such. It concerns especially magnetic and electrical characteristics because they are extremely sensitive to the defect structure of samples. In the case of ceramic and thin film samples, these properties are determined mostly by grain boundaries and the substrate-thin film interface, respectively. The single crystals are more preferable for the right investigations, but manganite crystals of the nominal composition demonstrate significantly different magnetic and electric characteristics.
depending on their mosaicity and/or point defect structure. So, preparation of high-quality single crystals of manganite is more important. We have chosen La$_{0.7}$Ca$_{0.24}$Sr$_{0.06}$MnO$_3$ single crystal as La$_{0.7}$Ca$_{0.3}$MnO$_3$ [7] and La$_{0.7}$Sr$_{0.3}$MnO$_3$ [8], which exhibit a Curie transition below and above room temperature, respectively. Therefore it is expected that the solid solution between end members, that is, the compounds with $0 < x < 0.33$, might have the Curie temperature in between (i.e., around room temperature), leading to magnetocaloric and magnetoresistive temperature working range relevant to device designed at ambient condition. Earlier, no such efforts have been made, so the present results could not be compared with earlier work.

Among other methods, the floating zone (FZ) method is most suitable for the growth of CMR manganite. In this paper, the transport, magnetic, and thermal properties of La$_{0.7}$Ca$_{0.24}$Sr$_{0.06}$MnO$_3$ single crystal have been studied.

2. Experimental

The single crystal of La$_{0.7}$Ca$_{0.24}$Sr$_{0.06}$MnO$_3$ was prepared by using floating zone technique with radioactive heating under oxygen pressure of 1 bar with a typical growth rate of 1 mm/hour. The size of crystal was 4.76 mm in diameter and 3.2 mm in length. Temperature dependence of electrical resistivity was measured using standard four-probe method along $ab$-plane and $c$-axis in temperature range 77 K to 300 K. The $ac$-susceptibility was measured using susceptometer as a function of temperature at 3.87 Oe magnetic field and an exciting frequency of 131.11 Hz. The specific heat was measured by the semiadiabatic heat pulse method. The temperature was varied by using a commercial liquid nitrogen closed cycle cryostate equipped with a temperature controller. All measurements were carried out in the temperature range 80–300 K [9].

3. Results and Discussion

Typical plot of resistivity versus temperature for La$_{0.7}$Ca$_{0.24}$Sr$_{0.06}$MnO$_3$ single crystal along $ab$-plane and $c$-axis is shown in Figure 1. Such a study was undertaken so as to estimate the direction dependence of charge flow. It is seen from Figure 1 that along $ab$-plane there is a large increase in resistivity (of about five times) as compared to that along $c$-axis. Such an evolution is a characteristic of an insulator to metal (I-M) transition with decreasing temperature coinciding with an abrupt change of the magnetic state. Here the resistivity shows a peak at 280 K, which separates the high temperature paramagnetic insulating phase from the low temperature ferromagnetic metallic phase. It is noted that the M-I transition temperature is higher and its magnitude is less than that of $ab$-plane. This is expected, as the Mn–O–Mn bond along $c$-axis is linear (i.e., 180°), while the same along $ab$-plane is nonlinear. Thus the hoping of electron is favorable along the $c$-axis and not in the $ab$-plane. This can be understood from metal to insulator (M-I) transition at $T_{MI} = 290$ K along $c$-axis. The magnitude of resistance along the $c$-axis is small (of the order of 1 Ω).

To evaluate the possibility of this single crystal for sensor application point of view, we have calculated the temperature and the field sensitivity of resistivity. This parameter is quantified in terms of temperature coefficient of resistance (TCR) and is shown in Figure 2.

Consider the following:

$$\text{TCR} = \left(\frac{1}{R}\right) \times \left(\frac{dR}{dT}\right) \times 100\% .$$  \hspace{1cm} (1)

It seems that the maximum TCR value we got along $c$-axis is 28.6% K$^{-1}$ whereas along $ab$-plane value of TCR is 21% K$^{-1}$. This is expected, as the Mn–O–Mn bond along $c$-axis is linear (i.e., 180°). Such large TCR values are a highly desirable goal in the context of the development of highly responsive bolometer.

Figure 1: Resistivity versus temperature plot for the single crystal of La$_{0.7}$Ca$_{0.24}$Sr$_{0.06}$MnO$_3$.

Figure 2: TCR versus temperature plot for the single crystal of La$_{0.7}$Ca$_{0.24}$Sr$_{0.06}$MnO$_3$, along $ab$-plane and along $c$-axis.
The temperature dependence of the real part of \( \chi_{ac} \)-susceptibility has been measured at fixed applied field of 3.87 Oe and an exciting frequency of 131.11 Hz. This result is shown in Figure 3. The \( La_{0.7}Ca_{0.24}Sr_{0.06}MnO_3 \) single crystal undergoes a phase transition from paramagnetic to a ferromagnetic state at the Curie temperature \( T_C = 277 \) K. Therefore, the magnetic measurement is in good agreement with the resistivity results. Plot shown in the inset is the evidence for short-range ferromagnetic correlations that emerge from the susceptibility measurements. The Curie-Weiss behavior is followed above 1.0 \( T_C \), but below this temperature the behavior clearly indicates the presence of short-range ferromagnetic correlations which is in good agreement with the resistivity and specific heat results.

The temperature dependence of specific heat of \( La_{0.7}Ca_{0.24}Sr_{0.06}MnO_3 \) single crystal is shown in Figure 4. It shows a deviation from the onset ferromagnetic ordering around 276 K, which is close to the transition temperature obtained from the \( \chi_{ac} \)-susceptibility and resistivity measurements. A comparison of these data with that of LCMO single crystal [7] shows that by codoping of Sr, we have achieved a larger transition temperature (near the room temperature) which can be useful for device application. This change in the heat capacity data indicates the onset of long-range ordering. To estimate the entropy change associated with the transition, we subtracted the background, which is obtained by fitting the measured heat capacity data excluding peak region with a polynomial. The entropy change associated with this transition is found to be 2.3 J/mol K.

4. Conclusion

All these measurements are consistent with each other to reveal the electronic and magnetic phase transition in CMR single crystal investigated by doping small amount of Sr (0.06%). This study reveals that the magnetic transition temperature increases substantially to 277 K and also matches with heat capacity data which indicates the onset of long-range ordering around 276 K around room temperature, and large TCR values are a highly desirable goal in the context of the development of highly responsive bolometer device application.

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